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**Part IV: WRPS Internal Review**

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<td>12-12-2013</td>
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<tr>
<td>Responsible Manager</td>
<td>K. D. Boomer</td>
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**Part V: IRM Clearance Services Review**

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When IRM Clearance Review is Complete – Return to WRPS Originator for Final Signature Routing (Part VI)
# INFORMATION CLEARANCE REVIEW AND RELEASE APPROVAL

## Part VI: Final Review and Approvals

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Comments:

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**APPROVED**

By Janis D. Aardal at 2:01 pm, Jan 07, 2014

Approved for Public Release; Further Dissemination Unlimited

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### Information Release Station

Was/is Information Product Approved for Release?  ☒ Yes  ☐ No

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Page 2 of 2
Rob,
I have reviewed the photos contained in the document “Tank 241-AY-102 Liner Evaluation”, as requested from an industrial safety point of view. Based on that review the photos are approved for use. Any question or comment, please ask.

Hugh Lawrence
WRPS Safety Programs
cell (208) 547-7334

Hugh,
Please provide a review and email concurrence, if applicable, of the photos in this document being cleared for public release.
Thanks,

Rob Roxburgh
WRPS External Affairs
(509) 376-5188
WashingtonRiverProtectionSolutions
Contractor to the U.S. Department of Energy
www.wrpsloc.com
Tank 241-AY-102 Secondary Liner Corrosion Evaluation

Waste Management 2014 - 14191

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-08RV14800

P.O. Box 850
Richland, Washington 99352
Tank 241-AY-102 Secondary Liner Corrosion Evaluation

Waste Management 2014 - 14191

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Abstract

In October 2012, Washington River Protection Solutions, LLC (WRPS) determined that the primary tank of 241-AY-102 (AY-102) was leaking. A number of evaluations were performed after discovery of the leak which identified corrosion from storage of waste at the high waste temperatures as one of the major contributing factors in the failure of the tank. The propensity for corrosion of the waste on the annulus floor will be investigated to determine if it is corrosive and must be promptly removed or if it is benign and may remain in the annulus.

The chemical composition of waste, the temperature and the character of the steel are important factors in assessing the propensity for corrosion. Unfortunately, the temperatures of the wastes in contact with the secondary steel liner are not known; they are estimated to range from 45°C to 60°C. It is also notable that most corrosion tests have been carried out with un-welded, stress-relieved steels, but the secondary liner in tank AY-102 was not stress-relieved. In addition, the cold weather fabrication and welding led to many problems, which required repeated softening of the metal to flatten secondary bottom during its construction. This flame treatment may have altered the microstructure of the steel.

1.0 INTRODUCTION

Routine visual inspections in August 2012 discovered small amounts of foreign material on the floor of the annulus space in Tank 241-AY-102 (Tank AY-102). Further examination of the tank annulus found material near Riser 83. Materials identified near Riser 83 and Riser 90 was determined to be leaked waste from the primary tank (RPP-ASMT-53793, Tank 241-AY-102 Leak Assessment). Corrosion of the primary tank may have contributed to its failure. Thus, corrosion of the secondary liner could provide a path for the waste to breach the secondary containment. The corrosive properties of the leaked wastes are examined in this report.

2.0 BACKGROUND

As part of the investigation of the leak from AY-102, one sample of the actual leaked waste in contact with the secondary liner has been collected and partially characterized. The analytical results suggest that the solid was formed by the evaporation of water from an approximately equal mixture of the waste supernatant and interstitial liquids that had reacted with carbon dioxide as it dried. Comparison of the composition of this waste with the chemistry control limits implies that it would not cause stress corrosion cracking or pitting of stress-relieved steels at 50°C because of the high hydroxide ion content and the favorable nitrite ion/nitrate ion concentration ratio.

In brief, undiluted interstitial liquid and undiluted supernatant liquid do not cause cracking or pitting of stress-relieved steel at 77°C in corrosion tests. All of the waste leaked may not have the same proportions of the two waste
liquids and may have formed liquids of still different compositions as they reacted with carbon dioxide and water evaporated. Some waste may have reacted with the refractory separating the primary tank from the secondary liner as it seeped through it to the top of the secondary liner. The propensities for corrosion of a range of other liquids were examined. Mixtures of the interstitial liquid and the supernatant liquid that contain from 10% to 90% interstitial liquid have compositions that are within the chemistry limits for the minimization of stress corrosion cracking at 50°C. However, the chemistry limits for the control of pitting from the Savannah River Site imply that several of these mixtures have insufficient hydroxide ion or nitrite ion for the control of pitting.

The hydroxide ion content of the leaked liquid will be reduced by the reaction with carbon dioxide in air as water evaporates. The behavior of a solution with 50% of the supernatant liquid and 50% of the interstitial liquid was explored. Since the rate of evaporation is more rapid than the rate of incorporation of carbon dioxide, it is unlikely that the neutralization reaction will proceed to completion. The composition of the waste would remain within the chemistry control limits for stress corrosion cracking at 50°C. However, the propensity for pitting increases as the pH is reduced and pitting may occur in these circumstances.

3.0 CHARACTERISTICS OF THE WASTE IN THE TANK AY-102 ANNULUS

The available analytical work suggests that one of the dried solid wastes originally consisted of approximately equal volumes of the supernatant liquid and the interstitial liquid (ISL) from the solid layer. However, the chemical compositions of the other leaked materials in the refractory and the annular spaces of the tank have not been characterized. Consequently, this corrosion assessment considers the properties of the liquids that might leak from the tank and the liquids that would be formed in the subsequent chemical reactions of these leaked substances. Specifically, the supernatant liquid, the ISL, simple mixtures of these two liquids from 10% to 90% supernatant material, a liquid with 50% ISL and 50% supernatant liquid that has absorbed carbon dioxide (CO₂) from the air. In addition, a liquid of the same composition that has reacted with the refractory, and liquids from which different amounts of water have evaporated are considered.

Samples of the three different materials were collected in September and October 2012. The brown mound, which was composed of rust, mill scale, sand and soil, did not originate from tank waste. However, the white crystalline deposits near Riser 83 and Riser 90 proved to be leaked tank waste (RPP-ASMT-53793).

The deposit near Riser 83 was a green liquid with white crystalline nodules as shown in Figure 1. Two materials were observed near Riser 90. One was a white crystalline solid that appeared to have flowed out of a refractory slot into the annulus as shown in Figure 2A. The second material near Riser 90 was a mound of brown solids as shown in Figure 2B.
Riser 90 Crystalline Material

Only a small sample of the solid near Riser 90 could be collected for characterization, and only very limited analytical work could be performed. X-ray work showed that anhydrous sodium carbonate was a major component with minor amounts of sodium nitrite, sodium oxalate, and possibly a phosphate. The concentrations of nitrate, nitrite, and hydroxide ion were not determined. Measurements of its sodium and potassium content and its radioactivity showed conclusively that the white solid was formed from tank waste. However, these limited measurements are insufficient to determine whether the leaked material originated from the solid or the supernatant layer of the tank or to define its corrosive properties.

Riser 83 Crystalline Material

Much more information about the character of the waste that leaked from the tank and eventually solidified on the floor of the secondary liner was obtained by the analysis of the solid that was collected near Riser 83. The major solid phases were identified by X-ray analysis as sodium nitrate and sodium carbonate monohydrate. There were smaller amounts of sodium nitrite and potassium nitrate and trace amounts of sodium fluoride sulfate and sodium oxalate.

The sample was too small to enable the determination of the customary suite of analytes and neither the water content nor the concentrations of hydroxide, chloride and sulfate ions were determined. The other analytical information and the analyte/sodium molar ratios for the solid material are summarized in Table 1.

The pH was not measured in the customary manner, but other tests implied that the pH of a dilute solution of the solid was over 11. This observation is consistent with the high total inorganic carbon (TIC) content (see Table 1) and the X-ray work that found sodium carbonate was a major constituent of the solid. It is pertinent that the TIC content of the solid is greater than expected on the basis of the concentration of carbonate ion in the supernatant and interstitial liquids.
3.1 EVAPORATION OF WATER AND ABSORPTION OF CARBON DIOXIDE

The analytical observations for the white solid near Riser 83 are compatible with the viewpoint that liquid waste leaked from the tank and then absorbed CO₂ from the air as water evaporated from the liquid to form the essentially dry solid.

The primary tank is cooled by a ventilation stream originating underneath the center of the primary tank flowing into the annulus through the refractory slots. Carbon dioxide would react with the alkaline liquid wastes in the slots and on the annulus floor as water evaporated from them. The rates of evaporation and of depletion of the hydroxide ion concentration by the absorption of CO₂ are both dependent upon the liquid surface area and the ventilation flow rate. The high surface area and the high ventilation rate of approximately 850 cfm accelerate both these processes. The rate of consumption of CO₂ is also dependent on the hydroxide ion concentration and its rate of absorption slows as the neutralization reaction proceeds.

Laboratory work implies that the rate of evaporation of water is often faster than the rate of absorption of CO₂. This factor and the possibility that a solid crust may form on the surface of the liquid may prevent the attainment of equilibrium between CO₂ and bicarbonate and carbonate ion in the solution and CO₂ in the air to form solutions that retain low concentrations of hydroxide ion. This condition may have been realized with the Riser 83 solid which appears to have a relatively high pH and became moist during laboratory operations, possibly because it retained small amounts of deliquescent material.

Table 2 provides an estimate of the original composition of the liquid that leaked from the tank and is compatible with the analyte/sodium ion ratios for the unreactive analytes (nitrate ion, nitrite ion, potassium, and total organic carbon [TOC]) on the basis of the assumption that 1.25 L of supernatant was diluted with 1 L of ISL. The relationship between the composition of the white solid and the compositions of the liquids in the supernatant and solid layers of the tank can be conveniently assessed by comparison of several analyte/sodium ratios. The nitrate ion/sodium ion ratio of 0.24 for the solid is incompatible with the lower value (0.002) for the interstitial liquid or the higher value (0.33) for the supernatant liquid. The same situation obtains for the potassium ion/sodium ion.

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<th>Analyte/Na Ratio</th>
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Source: RPF-ASMT-53793
relationship. These findings suggest that the leaking liquid was formed by the combination of the supernatant and interstitial liquids.

The notion that CO₂ absorbed into the leaked liquid is consistent with the estimated pH value (11) and with the fact that the carbonate ion/sodium ion ratio for the deposited solid is significantly larger than the carbonate ion/sodium ion ratios for the supernatant and ISL. The hydroxide ion and carbonate ion contents that would be realized by the complete neutralization of hydroxide ion by CO₂ are shown in the center column of Table 2. The general agreement between the calculated analyte/sodium ion ratios for the neutralized liquid with the observed analyte/sodium ion ratios for the solid deposit is shown in the two right hand columns.

The decrease in temperature and the time dependent evaporation of water from the leaked liquid result in the deposition of solids from the leaked liquid. The changing liquid compositions that occurred during the drying of several wastes were studied in the laboratory and thermodynamically modeled (PNNL-19767, Chemical Species in the Vapor Phase of Hanford Double-Shell Tanks: Potential Impacts on Waste Tank Corrosion Processes).

The PNNL study evaluated the changes in pH and the changes in the compositions of the liquids and solids during evaporation. The pH never fell below 10 in any of the solutions that were investigated. It was also noted in the experimental work that one simulant, which had high concentrations of carbonate, nitrate and nitrite ions, did not reach thermodynamic equilibrium with atmospheric CO₂, resulting in a higher pH than predicted by the thermodynamic model. This state occurred because water loss was faster than the CO₂ incorporation from the atmosphere. The more rapid loss of water relative to the uptake of CO₂ means that the final pH of the evaporating solution will be higher than predicted by the thermodynamic model.

### 3.2 CHARACTERISTICS OF THE LEAKED WASTE THAT AFFECT CORROSION

As discussed in Section 3.1, the properties of the steel, temperature, pH, the nitrite ion content and the concentrations of aggressive ions (nitrate, carbonate, chloride and sulfate) are important factors in assessing the propensity for corrosion of the estimated leaked liquid and the liquids that are produced during the evaporation of water.

The temperature of the waste in the bottom of Tank AY-102 is currently around 60 °C. Thermocouples in the outer radius of the refractory concrete indicate lower temperatures of approximately 45 °C. The annulus ventilation originates at the center of the primary tank, thus the outer radius of the refractory experiences higher temperatures. Recent ventilation outage events have caused the temperature in the primary tank to increase by approximately 20 °C.

The pH of the liquid in the solid layer of Tank AY-102 is between 11 and 12 and the pH of the liquid in the supernatant layer is more than 14. If the liquid that leaked from the tank was formed from approximately equal volumes of these two liquids, the pH would be more than 14. The absorption of CO₂ apparently reduced the concentration of hydroxide ion significantly in the solid material near Riser 83 sample, and its pH was estimated to be 11. The pH of the evaporating liquid presumably ranged between these two values during the solidification process.

The ISL can be accurately described as a ‘carbonate ion waste’, but any mixture of supernatant and ISL would be described as a ‘nitrate ion waste.’ The high concentrations of the nitrate ion, nitrite ion and hydroxide ions in the supernatant dominate any mixture of the two waste types. The complete range of concentrations that would be realized by mixtures of the supernatant and ISL indicate a pH above 12 and nitrite ion/nitrate ion concentration ratios above 0.50. It should be noted that the ISL and supernatant compositions used in the best-basis inventory (BBI) are derived from sampling. If the sampler didn’t reach the bottom of the tank, any un-sampled bottom ISL layer would not be included in the estimated compositions.
Table 2. Calculated Concentrations and Concentration Ratios for Leaking Liquid and Solid Deposit near Riser 83

<table>
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<tr>
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<th>Estimated Current Composition(after CO₂ Reaction) (M)</th>
<th>Estimated Current Composition Analyte/Na Ratio</th>
<th>Riser 83 Sample Analyte/Na Ratio</th>
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*Estimated leaked material based on 1.25 L supernatant and 1 L ISL mixture using BBI (2012) estimates

ND = not determined

The average nitrite ion concentrations of the ISL and the supernatant liquid are about 0.10 M and 0.90 M, respectively. If the liquid that leaked from the tank was formed from approximately equal volumes of these two liquids the concentration of nitrite ion in the leaking liquid would be about 0.60 M. A mixture of 90% by volume...
ISL and 10% by volume supernatant would result in a nitrite ion and nitrate ion concentrations of 0.18 M and 0.23 M, respectively. The evaporation of water would increase their concentrations.

The nitrite ion/nitrate ion concentration ratio of the ISL in the solid layer is very large because the concentration of nitrate ion is very small. The nitrite ion/nitrate ion concentration ratio of the liquid in the supernatant layer is about 0.50. The nitrite ion/nitrate ion ratio for a liquid formed from approximately equal volumes of these two liquid would be about 0.56. This ratio would not change appreciably during the first stages of the evaporation of water because sodium nitrate and sodium nitrate are both very soluble in water. The ratio would increase when the solutions became very concentrated because sodium nitrite is somewhat more soluble than sodium nitrate in concentrated salt solutions. The chloride ion also increased during the phases of evaporation and has the potential for becoming the aggressive ion for pitting corrosion. The sulfate ion concentrations are too low in the waste to be a corrosion concern.

3.3 REACTIONS OF THE LEAKED WASTE WITH THE REFRACTORY

Visual observations show that the waste flowed through the refractory slots underneath the primary tank to reach the annulus. The waste has the opportunity to react with the refractory prior to reaching the annulus and the waste could flow downwards through the refractory to the bottom of the secondary liner. The analysis of the waste near Riser 83 does not show signs of significant reactions with the refractory.

The leaked waste may chemically react with the constituents in the refractory that is made of Kaolite 2200-LI that rests on the top of the secondary liner beneath the bottom of the primary tank. The principal constituents of the refractory other than oxygen are silicon, aluminum, and calcium with small amounts of iron, magnesium, sodium and titanium (RPP-ASMT-53793).

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<th>Element</th>
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<td>Aluminum</td>
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</table>

Testing of Kaolite 2200-LI with simulated waste showed it was susceptible to alkaline hydrolysis (RPP-ASMT-53793). This observation is consistent with the known chemistry of the oxides of calcium, aluminum and silicon and the behavior of calcium silicates and calcium aluminate as well as aluminosilicate clays (Zhao et al., 2004). The reaction of the liquid waste with the refractory occurs in competition with the evaporation of water and the neutralization of the hydroxide ion in the liquid by reaction with CO₂ in air.

It is pertinent that the observed carbonate ion content of the solid near Riser 83 is significantly higher than implied by its concentration in the supernatant and ISL, and that the analyte/sodium ion ratios for aluminum, calcium and silicon in the solid near Riser 83 are not significantly different that the values of these ratios for the estimated supernatant and interstitial liquids². These two observations suggest that the liquid that reached the vicinity of Riser 83 did not react in a significant way with the refractory. The lack of reactivity of the refractory may be a consequence of a short residence time for the flowing liquid or of the fact that the surface layers of the slots, which have been exposed to CO₂ for many years, have been thoroughly carbonated as discussed in RPP-ASMT-53793. In contrast, the slot in the refractory near Riser 90 is blocked with solid waste. Liquids that leak into this slot may remain liquid for longer times because they are not be subject to the same rapid air flows and the alkaline waste will be in contact with the solid refractory for longer times.

In summary, the rates of the reactions between the leaked waste and the refractory are difficult to predict because unknown physical factors such as the blockage of air passages are difficult to assess, but any reactions of the alkaline leaked waste with the refractory that do occur will degrade the refractory and consume hydroxide ion to reduce the hydroxide ion content of the leaking liquid waste and increase the concentrations of soluble aluminate and silicate ions in the liquid as it passes through the refractory. New solid aluminosilicates that are formed in the process will deposit in the refractory together with solid calcium carbonate. Waste liquids that pass through the

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1 Kaolite is a registered trademark of Babcock & Wilcox Company
2 The increase in calcium is equivalent to no more than a 0.03 M decrease in hydroxide ion.
refractory and deposit on the top of the secondary steel liner will probably be less alkaline and will probably contain less carbonate ion than the estimated leaked waste.

3.4 CHARACTERISTICS OF THE SECONDARY LINER

Tank AY-102, which was constructed in 1968, was the first DST to be constructed on the Hanford Site. The secondary liner bottom plates and bottom knuckle are made of ¼ in. thick carbon steel. The secondary liner bottom was sized to make the bottom section an 80-ft diameter secondary liner around the 75-ft diameter primary tank. As summarized in RPP-ASMT-53793, many difficulties were experienced during the construction of the secondary liner.

The secondary liner bottom knuckles were fabricated offsite at the Pittsburgh-Des Moines Steel Company in Provo, Utah, prior to being shipped to the worksite for welding to join the knuckles with the adjacent plates. Difficulties in welding of the secondary liner occurred during fabrication and at the Hanford site with reports of repaired welds that were increased from the original nominal ½ in. to a dimension of 1 ¾ in. wide and more buckling of the material during preheating in cold weather. Once all welds were complete, flame shrinking was used to reduce the wrinkles, but was unsuccessful.

The flatness of the liner was examined in February 1969 upon completion of welding. Of the 33 shots of the bottom plates, five were near the 2 in. maximum convexity. Of the 23 on the knuckles, 12 were between 2 in. and 3 in., with one slightly more than 3 in. Due to the continued issues, the construction specifications for 241-AY Farm were changed from what was original specified to allow the slope of “bubbles” or ripples in tank bottom to be 1 in. per foot rather than ⅜ in./ft. per specification.

4.0 CORROSION EVALUATION

The propensity for corrosion of the secondary steel liner is addressed in this section by consideration of previous evaluations and by new evaluations of the corrosive properties of wastes formed from different amounts of the interstitial and supernatant liquids. Changes that occurred in the composition of these leaked liquids as they evaporated and reacted with the CO₂ and the refractory are also addressed.

4.1 CORROSION MECHANISMS AND SPECIFICATIONS

The types of corrosion that may occur in the Tank AY-102 annulus include pitting corrosion and SCC. For nitrate ion concentrations of >1 M, the main corrosion concern is SCC, and for nitrate ion concentrations of < 1 M, pitting is the main corrosion concern. The results of corrosion testing programs provide a technical basis for assessing the propensity of the different waste compositions for pitting corrosion and for the initiation of SCC with stress-relieved steels. This approach has been used in the preliminary assessment of the corrosion threat even though the secondary liner has not been stress-relieved. Tests with steel that is representative of the secondary liner are subsequently recommended in Section 4.0.

Due to the lack of temperature data in the annulus, three possible temperature scenarios are used for the corrosion evaluation. First, is the conservative assumption that the annulus experiences temperatures similar to the temperatures at the bottom of the primary tank, which are generally around 60 °C. Second, is to assume that the annulus floor experiences similar temperatures as the outside radius of the refractory concrete underneath the primary tank, which are an average of approximately 45 °C. The third scenario includes the outer radial refractory temperatures experienced during a ventilation outage. Assuming that the waste has been in the annulus since approximately 2006, the highest temperature recorded in the outer refractory since that time is approximately 57 °C. The annulus floor temperature is expected to be lower than the measured temperatures in the tank and the refractory; however, these measured temperatures provide a conservative temperature range of 45 °C to 60 °C for corrosion analysis.

4.1.1 Stress Corrosion Cracking

<table>
<thead>
<tr>
<th>DST Specification Criteria</th>
<th>Limit</th>
</tr>
</thead>
</table>

Table 3. Proposed Specifications for the Control of Stress Corrosion Cracking in Nitrate Ion Wastes in Double-Shell Tanks with Temperatures Less than 50°C
Stress-corrosion cracking can occur in solutions with high nitrate ion or high bicarbonate ion concentrations. The ISL of Tank AY-102 is characterized as a carbonate waste and the supernatant is characterized as a nitrate waste. The specifications that were recommended by the Expert Panel Oversight Committee (EPOC) for the minimization of the SCC for DST wastes are shown in Table 3 (RPP-RPT-47337).

4.1.2 Pitting Corrosion

The Savannah River Site (SRS) has produced multiple studies on pitting corrosion in dilute wastes, as preparation for feed to their vitrification facility required washing and storing sludge slurries. While waste compositions at the SRS site vary from the Hanford Site, the work on pitting corrosion provides further insight on dilute nitrate solutions.

Nitrate ion was determined to be the usual controlling aggressive species for pitting corrosion when its concentrations ranged between 0.01 M and 1 M (WSRC-TR-90-512, Effect of Temperature on the Nitrite Requirement to Inhibit Washed Sludge). Other pitting corrosion studies determined that chloride ion becomes the controlling corrosive ion if its concentration is greater than 3 percent of the nitrate ion concentration, while sulfate ion becomes controlling if its concentration is greater than 30 percent of the nitrate ion concentration (WSRC-TR-94-0250, Recommended Nitrite Limits for Chloride and Sulfate in ESP Slurries and SRNL-STI-2011-00479, Effect of Chloride and Sulfate Concentration on Probability Based Corrosion Control for Liquid Waste Tanks – Part IV). The limits shown in Table 4 were developed to establish the nitrite ion inhibitor concentrations when the hydroxide ion concentration was less than 1 M in dilute nitrate ion solutions. These chemistry limits have been adopted at the SRS Site (WSRC-TR-2002-00327).

Testing showed that a minimum nitrite ion concentration of 0.033 M at 40 °C and pH 10.3 would prevent pitting in the presence of any of these aggressive ions. However, more stringent restrictions are recommended on the basis of the concentration of each particular aggressive ion. This approach provides a conservative specification as the observations imply that pitting can be avoided when the nitrite ion concentration is 0.01 M at very low nitrate ion concentrations (< 0.01M), as experienced in the Tank AY-102 ISL (WSRC-TR-94-0250 and SRNL-STI-201-00479).

While these specifications focus on the nitrite ion concentration at a pH of 10, the additive concentration of both the nitrite ion and increased hydroxide ion concentrations in relation to the aggressive ion concentrations reduces the propensity for pitting corrosion.

4.1.3 Specifications for Chemistry Control at the Hanford Site

Table 5. Current Waste Chemistry Limits for Tanks AN-102, AN-106, AN-107, AY-101, and AY-102 Interstitial Liquid

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Variable</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: RPP-RPT-47337, Specifications for the Minimization of the Stress Corrosion Cracking Threat in Double-Shell Tank Wastes
Corrosion testing programs that have been underway for many years provide the technical basis for the current DST chemistry control limits outlined in Tables 1.5.1-1 and 1.5.1-2 in OSD-T-151-00007, Operating Specification Document for Double-Shell Tanks. Both pitting and SCC have been assessed for the various waste compositions at the Hanford Site. Table 5 and Table 6 outline the chemistry specifications for the supernatant and ISL in the Hanford Site DSTs.

### Table 6. Current Waste Chemistry Limits for All Double-Shell Tank Wastes

<table>
<thead>
<tr>
<th>For [NO₃⁻] Range</th>
<th>Variable</th>
<th>For Waste Temperature (T) Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO₃⁻] ≤ 1.0 M</td>
<td>[OH⁻]</td>
<td>≤122°F</td>
</tr>
<tr>
<td>[NO₂⁻]</td>
<td>0.010M≤[OH⁻]≤8.0 M</td>
<td>0.010 M≤[OH⁻]≤5.0 M</td>
</tr>
<tr>
<td>[NO₃⁻]/([OH⁻]+[NO₂⁻])</td>
<td>&lt;2.5</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>1.0M&lt; [NO₃⁻] ≤ 3.0 M</td>
<td>[OH⁻]</td>
<td>0.1 ([NO₃⁻]) ≤ [OH⁻] &lt; 10 M</td>
</tr>
<tr>
<td>[NO₂⁻]</td>
<td>≥0.4 ([NO₃⁻])</td>
<td>≥0.4 ([NO₃⁻])</td>
</tr>
<tr>
<td>3.0M&lt; [NO₃⁻]</td>
<td>[OH⁻]</td>
<td>0.3M≤[OH⁻]&lt;10 M</td>
</tr>
<tr>
<td>[NO₂⁻]</td>
<td>≥1.2 M</td>
<td>≥1.2 M</td>
</tr>
<tr>
<td>[NO₃⁻]/([OH⁻]+[NO₂⁻])</td>
<td>≤5.5 M</td>
<td>≤5.5 M</td>
</tr>
</tbody>
</table>
| Source: OSD-T-151-00007

### 4.2 EVALUATION OF CORROSION THREAT

The analytical information about the composition of the waste that has leaked onto the secondary liner is very limited. The uncertainty about the waste composition prompted the evaluation of the corrosive character of leaked materials with several different compositions. The propensity for the initiation of pitting and cracking corrosion for each of the following compositions is assessed in Sections 3.3.1 through 3.3.7.

- Tank AY-102 supernatant liquid
- Tank AY-102 ISL
- Mixtures of the Tank AY-102 supernatant and ISL
- A mixture of Tank AY-102 supernatant and ISL after CO₂ absorption
- A mixture of Tank AY-102 supernatant and ISL from which water has evaporated
- A mixture of Tank AY-102 waste after passage through the refractory

#### 4.2.1 Corrosion Threat of the Supernatant Liquid

Simulants of the present and aged supernatant in Tank AY-102 were studied in 2006 (RPP-RPT-33284, *Hanford Tanks AY-102 and AP101: Effect of Chemistry and Other Variable on Corrosion and Stress Corrosion Cracking*). Simulants of the current Tank AY-102 supernatant did not show cracking or pitting at pH 11 and temperatures of 50 °C or 77 °C (RPP-ASMT-35619, *Expert Panel Oversight Committee Assessment of Fiscal Year 2007 Corrosion and Stress Corrosion Cracking Simulant Testing Program and Impact on Double-Shell Tank 241-AY-102*). The testing indicated that the supernatant liquid in AY-102 has a very low propensity for pitting or cracking corrosion of stress-relieved carbon steel at temperatures below 77 °C.

#### 4.2.2 Corrosion Threat of Interstitial Liquid

The ISL in Tank AY-102 has a high carbonate ion concentration with a very low concentration of the nitrate ion (< 0.01 M). The pH is greater than 11 and the nitrite ion concentrations range from 0.33 M to 0.01M from the top to the bottom of the bulk solids layer. As discussed in Section 3.1, the propensity for pitting by dilute solutions is low if the nitrite ion concentration is greater than 0.033 M at pH 10 and at 40 °C. This value provides a conservative specification since other observations imply that pitting can be avoided when the nitrite ion concentration is 0.01 M in very dilute solutions.
Simulants of the least inhibited ISL in the lower segment of Tank AY-102 were examined at pH below the pH of the actual waste (RPP-RPT-33284). The carbonate ion rich simulants, which contained less than 0.01 M nitrate ion, were examined at pH 10, 10.5 and 11. They did not cause pitting or cracking of stress-relieved carbon steel at either 50 °C or 77 °C. The specific testing for Tank AY-102 ISL and other tests at the SRS imply that the ISL of Tank AY-102 have a low propensity for pitting and cracking corrosion of stress-relieved carbon steel at temperatures below 77 °C.

4.2.3 Corrosion Threat of Combinations of Supernatant and Interstitial Liquid

As discussed in Section 2.1 and Appendix A, the compositions of mixtures of the supernatant and ISL are dominated by the higher pH and higher nitrate ion and nitrite ion concentrations in the supernatant liquid. Table 7 shows the nitrite ion/nitrate ion concentration ratio would be above 0.5 and the pH above 12 for the range of mixtures of the supernatant and ISL.

The relatively high pH of these mixtures coupled with relatively high nitrite ion/nitrate ion concentration ratios result in a low propensity for cracking corrosion of stress-relieved carbon steel at temperatures below 77 °C. Assessing the propensity for pitting corrosion of the mixtures of the supernatant and ISL is more complicated because the pH ranges from about pH 12 for the liquid with 10 % supernatant liquid to greater than 14 for the liquids with more than 50 % supernatant liquid.

The adoption of the SRS approach, which is shown in Table 4 indicates the nitrite ion concentration is insufficient to prevent pitting by the aggressive chloride ion and nitrate ion at pH 10.3 and temperature of 40 °C. A pH of 14 (> 1 M OH-) is used at the SRS site for pitting prevention when the nitrite ion concentration is insufficient. The pH of the waste in Tank AY-102 is presumably higher, but the temperature is also higher and the propensity for pitting is therefore somewhat uncertain. However, the compositions that may be realized by mixing the supernatant and ISL are within the current chemistry control specifications for the DSTs as outlined in OSD-T-151-00007.

Table 7. Compositions of Combined Interstitial Liquids and Supernatant

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Combination of Interstitial Liquid to Supernatant Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100% ISL</td>
</tr>
<tr>
<td>OH (M)</td>
<td>0.032</td>
</tr>
<tr>
<td>NO₂ (M)</td>
<td>0.158</td>
</tr>
<tr>
<td>NO₃ (M)</td>
<td>0.006</td>
</tr>
<tr>
<td>Cl (M)</td>
<td>0.004</td>
</tr>
<tr>
<td>pH</td>
<td>12.5</td>
</tr>
<tr>
<td>NO₂/NO₃</td>
<td>25.25</td>
</tr>
</tbody>
</table>

Source: ISL and Supernatant Compositions from BBI, 2012

4.2.4 Corrosion Threat of Waste Reacted with Carbon Dioxide

The next waste composition to be considered is one formed from an equal mixture of the ISL and supernatant liquid that has been neutralized by the absorption of CO₂ from the atmosphere. The analytical observations for the waste near Riser 83 imply the pH of a mixture of this kind will be greater than 11. This observation is in accord with the
results of laboratory tests that imply waste may evaporate at a higher rate than the absorption of CO₂, resulting in a higher pH than would be expected if the liquid reached equilibrium with the CO₂ in air before water evaporated.

The composition of a waste of this kind is shown in Table 2. The pH and the high nitrite ion/nitrate ion concentration ratio imply the waste would not cause SCC at 50 °C, and testing of similar wastes implies that the waste would not cause SCC at 77 °C. The propensity for pitting is more difficult to determine, because the waste contains more than 1 M nitrate ion. However, the composition of the waste is within the chemistry control limits.

4.2.5 Corrosion Threat of Evaporating Waste

As discussed previously, the waste in the annulus is mostly solid material and shows evidence of solidifying liquid. While the composition of the initial leaked material remained within the boundaries of a mixed solution of the Tank AY-102 supernatant and ISL, the composition of the material has changed. The annulus material would have experienced various compositional changes during the stages of evaporation and CO₂ absorption. The hydroxide ion of the solution is reduced due to both evaporation and absorption of CO₂. The nitrate ions and nitrite ions would remain in solution initially, resulting in an increase of concentration in the solution before precipitating out. The fact that the nitrite ion is slightly more soluble than the nitrate ion is of benefit as the nitrite ion/nitrate ion concentration ratio in the liquid would increase.

The propensity for SCC would not increase importantly under these conditions because the nitrite ion concentration increases and because the nitrite ion/nitrate ion concentration ratio also increases. The propensity for pitting is more difficult to judge since the concentrations of at least two of the aggressive ions (chloride ion and nitrate ion) increase as water is evaporated. Technical work is now underway to determine the compositions of evaporating Tank AY-102 wastes to enable an assessment of these issues.

4.2.6 Corrosion Threat for Waste Reacted with the Refractory

Reactions between the leaked alkaline waste and the solid refractory would not alter the concentrations of chloride, fluoride, nitrite, nitrate, phosphate or sulfate ion significantly. However, the reactions would consume hydroxide and carbonate ion in the leaked liquid to produce soluble aluminates and silicates and insoluble calcium carbonate. The propensity for corrosion can be illustrated by considering a bounding reaction in which a leaked waste composed of 50 % by volume of the supernatant and ISL passed through the refractory and completely reacted with it before reaching the secondary steel liner. As discussed in Section 2.1, if the reaction went to completion, the hydroxide ion content (1 M) would be reduced to a negligible level and the carbonate ion would be slightly reduced as a consequence of the reactions to form a solution containing silicate and aluminate ions.

The nitrite ion/nitrate ion concentration ratio of 0.58 with a pH of at least 11 would provide for a low propensity for SCC to occur at temperatures below 77 °C for stress-relieved carbon steels, as bounded by the Tank AY-102 supernatant simulant testing. Pitting by a solution with a nitrate ion concentration of less than 1 M cannot be dismissed as the SRS standards require a higher nitrite ion concentration. The concentration of nitrite ion in the solution exceeds the OSD-T-151-00007 limits; however, the pH is less than 12 and is lower than specified for corrosion prevention.

4.3 STRESS CORROSION CRACKING IN CARBON STEEL LINERS THAT WERE NOT STRESS-RELIEVED

Corrosion propensity studies for DST waste simulants were developed upon the notion that the welds were properly made as well as on the notion that the heat treatment removed stress. Work at the SRS site, WSRC-MS-2005-00078, Stress Corrosion Cracking of Carbon Steel Weldments, determined that these two matters can increase the propensity for SCC. In a situation where the weld or heat treatments were not adequate, the thresholds for stress induced corrosion would have been lower (i.e., the concentrations of the inhibitors would have to have been higher than those discussed and temperature threshold for corrosion would be lower). Thus, it is important to evaluate the increased susceptibility to SCC for the secondary liner inasmuch as it did not receive post-weld stress-relief (stress-relief).
A structural investigation (BNWL-B-475, Computer-Based Structural Investigation of the SY-103 Waste Storage Tank which Contains an Out-of-Tolerance Bottom Bump) in 1976 of the bottom liner ‘bump’ in Tank SY-103 that exceeded the bottom liner tolerance concluded that increased local tensile stresses would exist in the bottom liner. The analysis concluded that the increased localized stresses would not increase the concern for the initiation of SCC. A recent review of this document by members of the EPOC concluded that, based on current information, the presence of bumps in the bottom liner will increase the tensile stresses and could contribute to SCC initiation, especially if the bumps occurred near a weld defect or from stress concentration at the T-joint of the weld. Therefore, the wrinkling and bulging experienced during fabrication of the liner could impose further stresses on the liner, independent of the welding stresses.


Stress corrosion cracking occurred with some early DSTs at Savannah River. These tanks were constructed of carbon steel but, unlike the Hanford tanks, were not stress-relieved to reduce welding residual stresses. The tanks with SCC were exposed to relatively high temperature wastes with adverse waste chemistries that were outside the 2005 limits imposed on both SRS and Hanford tanks. Other early Savannah River tanks (also of low carbon steels and without stress-relieving) were operated at less severe waste chemistries and temperatures without reported SCC.

The stress corrosion cracks at Savannah River were adjacent to and normal to seam welds and were in plates that made up the vertical walls of the tanks. The cracks penetrated the complete wall thickness but stopped after growing to a few inches in length; evidently, the cracks grew beyond regions of high welding residual stresses. The cracks had orientations normal to the direction of the seam welds and were near the top of the tank, evidently associated with local waste chemistries near the top surface of the stored waste (water line). In some cases, were no reported cracks in the lower regions of the tanks, including the lower knuckle of the tank that forms the joint between the vertical and bottom plates. Other tanks that had SCC did show cracks in the lower regions of the tanks.

The SRS experience demonstrates that SCC can occur if worst-case welding residual stresses, operating temperatures, and waste chemistries are present. Subsequent experience benefited from the combined effects of stress-relieving and specifications for waste composition. Although both stress-relieving of the liners and improved specifications on waste chemistries could individually have been sufficient to prevent cracking, the limited operating experience is insufficient to support such a conclusion.

Tests were performed at the Savannah River Site during the 1960s using simulated waste solutions. The welded specimens were intended to simulate tank materials and fabrication. Tests were performed for 100 to 200 days at significantly higher temperatures (32–35 °C) and far more aggressive chemistries (50 wt% NaNO3) than any conditions the current Hanford DSTs experience, even tanks such as Tank AN-107 with deviations from waste chemistry limits. Work was cited for evidence that susceptibility to SCC becomes greater with increasing temperature and nitrate concentration. The Savannah River specimens included surface conditions of mill scale and stress risers (repair welds and effects of welded attachments) that would enhance the initiation of stress corrosion cracks.

As-welded specimens during the tests cracked under conditions that caused cracking of as-welded tanks in the field. Cracking did not occur in specimens subjected to somewhat less severe conditions under which tanks in the field did not crack. It is not possible to examine failed liners of single-shell tanks, which precludes the detailed analyses needed to determine whether the failures were caused by corrosion, wall thinning, pitting, or cracking. It is likely that SCC was a factor because none of the older tanks were stress-relieved to reduce welding residual stresses. Furthermore, the past service conditions included storage of wastes at high temperatures with chemical compositions known to contribute to SCC.
5.0 CONCLUSIONS AND RECOMMENDATIONS

The propensity for corrosion was assessed by reviewing previous work directed to the assessment of the vulnerability of the secondary liner, by examining test results and by comparing plausible compositions of the leaked waste with the chemistry control limits employed at the Hanford and SRS. The temperature and stresses imposed on the steel are important factors in assessing the propensity for corrosion. None of these factors have been adequately defined for the situation in Tank AY-102.

A previous evaluation of the potential for corrosion of leaked waste the annulus identified hydroxide depletion as a possible cause of stress corrosion cracking, and thus, the recommendation of immediate removal of the waste. The Savannah River Site has also experienced waste leaks onto the annulus pan, but concluded that the potential for corrosion was minimal due to the high nitrite ion concentrations and low temperatures. These conflicting evaluations prompted the present assessment of the propensity for corrosion.

The available analytical work concerning the composition of the solid waste on the floor of the annulus provided a starting point for this assessment. However, it became evident that the results for this one sample were insufficient and it would be necessary to consider other alternative compositions for the leaked wastes. Consequently, this assessment was extended to include the known compositions of the supernatant liquid, the interstitial liquid and simple mixtures of these two liquids that contain from 10% to 90% supernatant liquid. The evaporation of water and chemical reactions with CO₂ in air and with the refractory can alter the composition of the leaked waste. Accordingly, the compositions of a liquid with 50% interstitial liquid and 50% supernatant liquid that had absorbed CO₂ from the air, a liquid of the same composition that had reacted with the refractory, and liquids from which different amounts of water have evaporated were considered. It is recommended that additional samples of the leaked waste be obtained to provide better perspective about the actual compositions of the materials in contact with the secondary steel liner.

The temperatures of the wastes in contact with the secondary liner are not known with confidence, the estimated values range from 45 °C and 60 °C. Inasmuch as the evaluation of the corrosion threat would be facilitated by more accurate temperature information; it is recommended that the annular floor and refractory temperatures be determined with greater accuracy. It is also recommended that corrosion tests be carried out if the temperature measurements indicate the leaked wastes are actually exposed to temperatures in excess of 50 °C.

The chemistry control limits were established for the minimization of the corrosion threat of stress-relieved steels. Unfortunately, the related limits for steels that have not been stress-relieved are not well defined. The stresses on the secondary liner presumably vary from locations beneath the refractory to locations in the annulus. In any case, studies at the SRS indicate that carbon steel liners that are not stress-relieved are more susceptible to SCC. The increase in the corrosion risk for the secondary liner due to the properties of the steel and the absence of stress-relieving of the welds is not well defined. It is recommended that slow strain rate tests and electrochemical polarization tests be carried out with steels that have not been stress-relieved to gain perspective on this important matter.

Testing has demonstrated that the interstitial liquid and the supernatant liquid that are now present in Tank AY-102 have low propensities for the cracking or pitting of stress-relieved steels at temperatures as high as 77 °C. The leakage of either of these two liquids onto cooler, stress-relieved steel would not be expected to cause cracking or pitting. Corrosion tests of as received steels are recommended to establish the propensity for corrosion for the secondary liner.

The propensity for corrosion of mixtures of the interstitial liquid and the supernatant liquid that contains from 10% to 90% interstitial liquid was assessed by comparing the concentrations of the principal inhibitors, hydroxide ion and nitrite ion, and the concentrations of the aggressive substances, chloride, sulfate and nitrate ion, in the various mixtures with the chemistry control limits for cracking and pitting corrosion. The compositions of these mixtures are within the chemistry limits for the minimization of SCC. However, the chemistry limits for the control of pitting from the SRS imply that several of these mixtures have insufficient hydroxide ion or nitrite ion for the control of pitting. The evaporation of water and reactions of the leaked waste with CO₂ in air and with the refractory are complicating features.
First, water evaporates from the leaked liquid in the ventilation slots in the refractory and on the floor of the secondary liner in the annular space. Recent work with a waste simulant, which had a composition similar to the composition of the liquid with 50% of each tank liquid, indicated that the concentration of nitrate ion can become quite large (3.5 M) before sodium nitrate begins to precipitate from solution. This undesirable result is mitigated in part by the higher solubility of the two principal inhibitors, sodium nitrite and sodium hydroxide. On balance, the available information suggests that the composition of the liquid will remain within the chemistry control limits for SCC at 50 °C. However, the results also suggest that the concentration of chloride ion will increase during evaporation and that the concentrated liquid may cause pitting. It is recommended that thermodynamic calculations be carried out to determine the compositions of evaporating waste solutions to gain perspective on the corrosion threat posed by the concentrated liquid solutions that form during the evaporation of water.

Next, the hydroxide ion content of the leaked liquid will be reduced by the reaction with CO₂ in air as water evaporates from the solution. Since the rate of evaporation is more rapid than the rate of incorporation of CO₂ into the liquid, it is unlikely that the neutralization reaction will proceed to completion and that concentrated liquid will retain unreacted sodium hydroxide. The available information suggests that the composition of the liquid will remain within the chemistry control limits for SCC at 50 °C. However, the propensity for pitting increases significantly as the pH is reduced and pitting may occur in these circumstances.

Also, the carbonate and hydroxide ion concentrations may be decreased by reactions between hydroxide ion in the waste and the refractory. A significant reduction in the hydroxide ion content would increase the propensity for corrosion for wastes that seeped through the refractory and reached the secondary liner. However, the available information implies that the extent of the reaction between the refractory and the hydroxide ion in the waste diminishes as the hydroxide ion content decreases. Although the final pH of the waste liquid is very difficult to estimate from the information in the literature, it is reasonable to infer that the final pH would not be smaller than the pH dictated by the carbonate ion content, somewhat greater than 11. As in the other cases, the composition of liquid that reached the floor of the secondary liner under the refractory would remain within the chemistry control limits for SCC at 50 °C largely because the nitrite ion content would not be decreased as the waste passed through the refractory. However, as noted previously, the reduction in the hydroxide ion content may initiate pitting. It is recommended that the representative waste solutions be contacted with cast refractory to determine the pH and the composition of the solutions are produced by reactions with the refractory.

In summary, this evaluation suggests that certain leaked waste compositions may cause pitting of the secondary steel liner because of the relatively low pH that may be realized in some circumstances. The propensity for pitting would of course be greater at the higher temperature that may exist under the refractory. The evaluation also suggests that there is a lesser propensity for SCC because the pH apparently remains above 11 with a sufficient concentration of nitrite ion and a favorable nitrite ion/nitrate ion concentration ratio. However, this conclusion needs to be affirmed by tests of as-received non-stress-relieved steels, especially if the temperatures exceed 50 °C.

The following recommendations were developed in collaboration with the EPOC, who reviewed the information about the present status of Tank AY-102. It was concluded that the available analytical data and the information about the temperature of the waste in contact with the secondary liner are not sufficient to determine the corrosion threat to the secondary liner with the desired degree of confidence. Subsequently, the length of time that the waste may remain in the annulus is inclusive. The initial recommendations are that WRPS:

- Initiate efforts to obtain accurate temperature information regarding the temperature in the refractory and regarding the temperature of the wastes in the annular space in contact with the secondary liner.

- Initiate efforts to obtain analytical samples from the leaked waste sufficient to perform the conventional suite of analyses including the water content and the pH as well as the conventional group of anions and metal analytes.

- Assess the consequences of the evaporation of water from leaked waste and the introduction of CO₂ into leaked waste. Experience suggests that this information can be obtained by thermodynamic calculations for the compositions shown in Table 8.
Table 8. Suggested Compositions for Tank AY-102 Waste Calculations

<table>
<thead>
<tr>
<th>Case</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Supernatant</td>
</tr>
<tr>
<td>2</td>
<td>Interstitial Liquid</td>
</tr>
<tr>
<td>3</td>
<td>50% Supernatant + 50% Interstitial Liquid</td>
</tr>
<tr>
<td>4</td>
<td>25% Supernatant + 75% Interstitial Liquid</td>
</tr>
<tr>
<td>5</td>
<td>75% Supernatant + 25% Interstitial Liquid</td>
</tr>
</tbody>
</table>

The supernatant and ISL compositions will be derived from the 2012 Best-Basis Inventory

- Perform slow-strain rate tests to evaluate the propensity for SCC and perform cyclic-potentiodynamic polarization (CPP) tests to evaluate the propensity for pitting for selected compositions at the limiting high temperature. The tests should be carried out with as received, non-stress-relieved steels that are representative of the steel in the secondary liner of Tank AY-102.

- Investigate the chemical reactions between the waste and the refractory with special emphasis on the assessment of the concentrations of the aggressive ion and the inhibitors.

These tests will indicate whether plausible compositions of the leaked waste are a threat for the pitting or cracking of as-received, non-stress-relieved steel at the temperature of the secondary liner. If corrosion is not observed in these tests, other carefully designed tests may be necessary to determine if the same compositions pose a threat to the liner because of the difficulties, such as low quality welds, that were encountered during construction.
6.0 REFERENCES


