Department of Energy
Washington, DC 20585

DEC 01 2005

The Honorable A.J. Eggenberger
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, NW, Suite 700
Washington, DC 20004-2901

Dear Mr. Chairman:

This letter provides you with new information on Hanford Tank AN-107 chemistry concerns and the Department of Energy's (DOE) planned actions. Since our meeting in September 2005, the Chemistry Optimization Expert Panel, Oversight Committee (hereinafter called the Committee), has provided an assessment of Tank AN-107 corrosion properties of the interstitial liquid in the solids layer. This assessment (Enclosure 1) and CH2M Hill's assessment (Enclosure 2) conclude that Tank AN-107 waste chemistry is benign from a stress corrosion cracking perspective, and will remain protected during the minimal chemistry changes projected over the next decade or more. The Committee recently released additional supplemental assessments (Enclosures 3 and 4) noting that Tank AN-107 chemistry should not appreciably increase general or pitting corrosion during this same extended time period. This information has led DOE to conclude that Tank AN-107 is safe and will remain so for the foreseeable future.

DOE is changing the Tank AN-107 chemistry limits for interstitial liquid in the solids layer to allow for a hydroxide concentration roughly equivalent to pH 10 or greater in accordance with the Committee's assessment. This change will be implemented by modifying the existing chemistry control table (Table 5.16-1) in Administrative Control 5.16 of the Tank Farms Technical Safety Requirements (TSR) (HNF-SD-WM-TSR-006) for Tank AN-107 interstitial liquid. In accordance with these changes, a mixer pump is not required and is no longer planned for installation.

As a defense-in-depth, and in accordance with the Committee recommendations, an in-tank multi-function corrosion and corrosion potential monitoring probe is being procured and will be installed in Tank AN-107. TSR controls recognizing the corrosion probe as a key element in the corrosion protection program will be implemented with the chemistry limit change. As noted previously to the Defense Nuclear Facilities Safety Board, the tank surface ultrasonic testing area has already been doubled and test frequency has been increased in accordance with earlier Committee recommendations.

The existing Tank AN-107 chemistry technical safety requirement recovery plan will be revised accordingly. We will continue to keep your staff informed on this new path forward.

If you have any questions, please call me at (202) 586-0738 or Dae Y. Chung, Acting Deputy Assistant Secretary for Integrated Safety Management and Operations Oversight, at (202) 586-5151.

Sincerely,

Inés Triay

Dr. Inés R. Triay
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Enclosures

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MICHAEL T. TERRY, P.E.

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October 8, 2005

Mr. Robert Popielarczyk
CH2M HILL, Hanford Group Inc.
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SUBJECT: ASSESSMENT OF THE 241-AN-107 STRESS CORROSION CRACKING EXPERIMENTAL PROGRAM BY THE EXPERT PANEL FOR HANFORD SITE DOUBLE-SHELL TANK WASTE CHEMISTRY OPTIMIZATION, OVERSIGHT COMMITTEE

Dear Mr. Popielarczyk,

Members of the Corrosion Optimization Expert Panel have been overseeing the experimental program for the implementation of Recommendation III of our final report, *Expert Panel Workshop for Hanford Site Double-Shell Tank Waste Chemistry Optimization*, RPP-RPT-22126. Recommendation III provided specific requirements necessary for Panel approval of a proposal to revise the conservative chemistry control limits based on information available at the time of the workshops, including successful performance of an accelerated stress corrosion cracking experimental program. The Department of Energy, Office of River Protection, and CH2M HILL Hanford Group, Inc. (CH2M HILL) chose a simulant based on waste tank chemistry composition found in DST 241-AN-107 (AN-107) to use as a pilot case for conducting this work. The report of interim findings from the experimental program has recently been released for review.[1] This letter presents our assessment of the new results and prior findings regarding the propensity for stress corrosion cracking (SCC) in waste tank AN-107.

Although a few additional confirmatory tests are necessary to eliminate the remaining ambiguities, we consider the present and projected tank saltcake chemical composition to be benign from an SCC perspective. These conclusions are based on the available information concerning the present condition of the tank wall, the present and future chemical compositions of the supernatant and solid layers (i.e. condensed solids plus interstitial liquid), the corrosion potentials measured in the new study and those measured in the tank, the waste temperature, and

[1] *Investigation of Chemistry Factors Influencing Stress Corrosion Cracking Susceptibility of High-Level Waste in Double Shell Tank 241-AN-107*, Draft Interim Report, CC Technologies Laboratories, Inc. Report 80 5062 01.

calculated stress levels for the wall. The above noted factors, and the combination of recent testing results, all indicate a minimal likelihood of SCC growth in the present saltcake region of the tank, and that this condition will not be adversely affected by the anticipated chemistry changes over time.

We reviewed the present and projected chemical composition of tank AN-107 waste to provide a basis for the preparation of simulants.[2, 3] The primary constituents of concern for SCC are nitrate and nitrite ion, hydroxide ion and total organic carbon (TOC). Nitrate ion causes SCC, while SCC may be inhibited by hydroxide and nitrite ions and some organic complexants. The concentrations of these substances were analytically determined in 2003 after sodium hydroxide had been added to the supernatant layer of this tank. Their future concentrations were calculated on the basis of their known rates of disappearance during the first 18 years of storage.[4] A study of the thermodynamic equilibrium by Felmy shows the hydroxide ion concentration in this waste is buffered and the eventual pH will be about 10.1.[5] The current and estimated future concentrations are summarized in the following table.

Estimated Future Concentrations of TOC, Nitrate, Nitrite and Hydroxide Ions

	Unmixed Supernatant Layer			Unmixed Solid Layer			Mixed
Constituent	2003	2008	2023	2003	2008	2023	2023
TOC, g/L	37	34	24	35-47	32-44	22-34	24-25
$NO_3^{(-1)}$, M	3.5	3.3	2.9	3.0	2.8	2.4	2.8
$NO_2^{(-1)}$, M	1.2	1.4	2.1	1.4	1.6	2.3	2.1
pH	>13.5	>12.7	>10.9	11.3	>10.7	10.1	—

The addition of sodium hydroxide to the supernatant layer in 2002 did not materially alter the composition of the solid layer, and the lower pH in the solid layer is therefore of most concern because it covers the lower knuckle area, the area of highest stress, and therefore most susceptible to SCC. The results show that the TOC and nitrate ion concentrations slowly decrease as the nitrite ion concentration slowly increases. The hydroxide ion concentration of the waste changes more rapidly. The analysis implies the pH of the solid layer will decrease from 11.3 in 2003 to between 10.7 and 11.1 in 2008. If no operations are carried out, the kinetic and thermodynamic information imply the pH will reach its limiting value, 10.1, between 2008 and 2023.

If a pump were installed in the waste in 2008 to promote the mixing of the two layers, then the composition of the liquid in contact with the walls in the lower knuckle area would change as the chemically more basic supernatant liquid became mixed with the interstitial liquid of the lower layer. Inasmuch as the concentrations of the nitrate and nitrite ion and TOC concentrations in the

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[2] *Tank 241-AN-107 Fiscal Year 2003 Core Sample Analytical Results for the Final Report*, H. L. Baker, FH 0303673, Fluor Hanford, 2003.

[3] *Updated Tank 241-AN-107 Fiscal Year 2003 Core Sample Analytical Results for the Final Report*, H. L. Baker, 7S120-HLB-03-001, CH2M HILL Hanford Group, Inc., 2003.

[4] *Caustic Dynamic Mixing Analysis for Tanks 241-AY-101, 241-AY-102, 241-AZ-102, 241-AN-102, and 241-AN-107*, RPP-12387, CH2M HILL Hanford Group, Inc., Ogden, D. M., and M. J. Thurgood, K. G. Carothers, and G. P. Duncan, 2005, and private communication.

[5] *Thermodynamic Modeling of Hanford Waste Tank 241-AN-107*, Letter Report, A. R. Felmy, 2005.

two layers are similar, their concentrations in the mixed liquid could be estimated on the basis of the idea that they would change at about the same rates as in the unmixed waste. Unfortunately, it is not possible to predict the pH of this liquid in 2023 with confidence because the differences in pH of the two layers are large and because operational factors regarding the pump will have a major influence the outcome. If mixing were complete and hydroxide ion were consumed at the same rate as in the past, then the pH in the liquid in 2023 would be >10.9, significantly larger than the Felmy equilibrium value, 10.1.

Accordingly, the electrochemical studies that are presented in the Draft Interim Report used tank AN-107 simulants in which the pH was varied from 7 to 12, but focused on tests at pH 10 and 11.

While the severity of SCC increased somewhat with decreasing pH of the waste simulant, the electrochemical conditions required to produce SCC in the laboratory were generally much more severe than those anticipated to be present in the waste tanks. In the slow strain rate (SSR) tests, SCC was not observed at the free corrosion potential (anodic polarization was required) and the measured potentials in actual waste (from as recent as 2002) are well outside the cracking potential range in the pH range studied (9-11). Furthermore, at these pH conditions, it was necessary to strain the specimens well above yield to produce SCC in the SSR tests performed at polarized potentials within the cracking range.

A striking finding of the recent work is the sharp potential threshold for the onset of SCC, and its independence of pH. Such a strong dependence on potential offers an opportunity for accurate and sensitive monitoring of SCC susceptibility.

Corrosion potential was measured in a variety of ways during the CCT experiments in both deaerated and air-exposed solutions over the range of pH studied. However, except for one measurement at pH 7, all values were below the lowest potential at which SCC was observed (-50 mV versus a Saturated Calomel Electrode or SCE). With decreasing pH, the corrosion potential tended to become less negative and thus the difference between E_{corr} and the critical potential for SCC decreased.

CCT measured corrosion potential after relatively short exposure of fresh samples to a simulant solution. Reports provided to the Committee offer some insight on real tank potentials, which could be different. The potentials of the AN107 tank and a test probe during the month of December 1987 were reported to be -340 and -450 mV SCE, respectively.[6] It was later reported that these values were stable and almost unchanged over a 3-year period of measurement.[7] The pH during this time varied from about 12.5 to 12.[8] Hot cell experiments at CH2M HILL were performed with a test probe on a core sample segment of actual AN-107 saltcake from the year 2002 and corrosion potentials of -370 and -281 mV SCE, were measured at 25 and 36°C, respectively.[9] The pH of the interstitial liquid from nearby segments was in the range of 11-11.5. From these data, the actual potential of the tank is probably more negative than the critical potential for SCC by at least 200 mV. This could change with time as the tank pH decreases.

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[6] *Corrosion Monitoring in 241-AN107 – Progress Report for December 1987*, Battelle PNL memo from N.J. Olson to D.A. Reynolds, January 8, 1988.

[7] *Summary of Corrosion Studies for Tank AN-107*, Westinghouse Hanford Company Internal Memo from Reynolds to J.P. Harris III, January 4, 1991.

[8] K.G. Carothers, personal communication, 2005.

[9] *Electrochemical Corrosion Testing of A537 Class 1 Carbon Steel in 241-AN-107 Sludge*, Fluor Hanford memo from J.B. Duncan to K.G. Carothers, January 20, 2003.

The pH difference between the saltcake and supernate forms a concentration cell that likely results in a difference in potential and galvanic coupling between tank regions exposed to these two layers. This interaction polarizes the knuckle region to more negative potentials, which is beneficial for its SCC resistance, and mixing would eliminate this protection. The magnitude of this protective interaction could be assessed by further analysis, but is presently outside the scope of the program.

Fracture mechanics tests are being performed on pre-cracked specimens of the tank steel in the waste simulants at an imposed potential within the cracking range. Crack velocity as a function of the applied stress intensity factor (K_I) is being measured in order to estimate the threshold stress intensity factor for crack growth due to SCC (K_{Iscc}) and the crack velocity at stress intensity factors above K_{Iscc}. The result will be compared to the applied stress intensity factors (K_I) for AN-107, which is being calculated at PNNL. If $K_I < K_{Iscc}$, crack growth by SCC is not expected. The initial crack propagation rates of all cracks were very low, on the order of 0.03 inches per year, which is 300 times slower than rates measured at the Savannah River Site in SCC potent waste environments.[10] Furthermore, all of the cracks have exhibited declining crack growth rates with time, indicating likely crack arrest (i.e., any potentially existing tank wall flaws are not likely to propagate). The only possible exception are fracture mechanics tests performed at high stress intensity factors, which are well above any values expected within the waste tanks. The most likely explanation for the decrease in crack growth rate with time observed for the tests is related to the occurrence of creep exhaustion at the crack tip. This behavior indicates that the K_{Iscc} is relatively high in these benign environments and that the majority of the tests have been performed below this value.

Fracture mechanics analysis indicates that even at a worst-case K_{Iscc} of between 15 to 20 ksi $\sqrt{in}$ (this value could increase with longer test exposures), the minimum flaw size able to propagate through the tank lower knuckle high stress region would be on the order of 25% of the total wall thickness, ~0.220 in., an extremely large value. These observations suggest that an existing defect in the tank wall would not be expected to propagate unless it was very large.

Based on the data presented in the Draft Interim Report and the chemical composition analyses presented above, we offer these additional specific observations with respect to SCC or significant propagation of any potentially existing defects in the interstitial liquid (i.e., saltcake region).

- The testing temperature for the experimental work is 122 °F (50 °C). However, the actual AN-107 waste temperature is currently less than 95 °F (35 °C), and our understanding indicates that no historic SCC testing has ever produced SCC initiation below 50 °C in waste tank simulants.
- Specimens tested in pH 9.5 to 11 all pass the historic Ondrejcin Savannah River Site waste chemistry acceptability criteria, i.e., chemistry is acceptable if no tensile failure by 13% elongation for a sample held at constant current conditions.[11]
- Ultrasonic Testing from 1998 show no thinning, pits, or cracks in the examined areas of the primary tank lower knuckle.[12]

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[10] *Resistance to Type A-537 Class I Steel to Nitrate Stress Corrosion Cracking*, DPST-81-687, J. A. Donovan, September 18, 1981.

[11] *Prediction of Stress Corrosion of Carbon Steel by Nuclear Process Liquid Wastes*, Savannah River Laboratory, August 1978.

In conclusion, the results of the SCC laboratory testing completed to date and the analysis of the relevant information provided to the Committee support the concept of allowing the pH of the saltcake region in tank AN-107 to naturally decline with time. This approach avoids the inherent risk and costs associated with the alternative option of installing and operating a mixer pump in the tank.

The recommended path forward for AN-107 is to complete the laboratory testing in which the acceptable factor space, with respect to chemical composition, corrosion potential, and stress intensity factor, is defined. This work includes investigation of the effect of projected "end point" changes in the concentration of TOC, nitrate and nitrite ion concentrations at pH 10, as well as completion of the verification of the fracture mechanics test technique by demonstrating that the results are consistent with previous testing and field experience. Installation of the new in-tank multi-probe for both real time and frequent coupon analysis for field corrosion monitoring, is recommended to verify the corrosion potentials of the tank and to confirm the expected low corrosivity of the waste. Finally, we recommend that periodic ultrasonic testing (UT) inspection (5 – 7 year cycle) of the tank, in conjunction with statistical analysis of the UT data, be performed to verify the current and ongoing integrity of the tank and provide additional confirmation of the conclusions of the laboratory testing. Furthermore, if the installed multi-probe exhibits increased corrosion activity, CH2M HILL should consider increasing the frequency of UT examinations, and performing additional core sampling to verify sludge conditions.

Once again, we are indeed pleased that CH2M HILL is taking such a responsible and thorough approach to evaluating and implementing the recommendations of the Committee. The Committee also considers that continuation of the studies for all six waste types necessary to bound all Hanford DSTs would provide a firm technical basis for assessing risk and optimizing waste chemistry.

Sincerely,

Michael T. Terry, P.E.
Chairman, Chemistry Optimization Expert Panel,
Stress Corrosion Cracking Experimental Program
Oversight Committee

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[12] *Final Results of Double-Shell Tank 241-AN-107 Ultrasonic Testing, HNF-3353.*

CH2M HILL
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CH2MHILL
Hanford Group, Inc.

October 20, 2005 CH2M-0502967 R1

Mr. R. J. Schepens, Manager
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Dear Mr. Schepens:

CONTRACT NUMBER DE-AC27-99RL14047 – STATUS OF THE CH2M HILL HANFORD GROUP, INC. DOUBLE-SHELL TANK CORROSION TESTING PROGRAM

References:

1. Letter, E. S. Aromi, CH2M HILL, to R. J. Schepens, ORP, "Contract Number DE-AC27-99RL14047 - Status of the CH2M HILL Hanford Group, Inc. Double-Shell Tank Corrosion Testing Program," CH2M-0502967, dated October 11, 2005.
2. RPP-24887, 2005, "The Long-Term Management of Hanford Tank Waste," Rev. 1, CH2M HILL Group, Inc., Richland, Washington.
3. Letter, E. S. Aromi, CH2M HILL, to R. J. Schepens, ORP, "Contract Number DE-AC27-99RL14047 - Request for Approval of Revised Recovery Plan to Restore Chemistry Control in Tank 241-AN-107," CH2M-0303535 R19, dated June 27, 2005.

This letter is an update to the U.S. Department of Energy, Office of River Protection (ORP) on the status of the CH2M HILL Hanford Group, Inc. (CH2M HILL) Double-Shell Tank Corrosion Testing Program (Reference 1). CH2M HILL has received an assessment by the Chemistry Optimization Expert Panel, Stress Corrosion Cracking Experimental Program Oversight Committee on the potential for stress corrosion cracking (SCC) in Tank 241-AN-107 (enclosed). Based on the committee's assessment and our own analysis, Tank 241-AN-107 chemistry is currently safe and will remain safe during the minimal changes expected in the interstitial liquid over the next decade.

Based on chemical testing and their observations, the committee has recommended to CH2M HILL a path forward in accordance with Specific Action Number 5 from the current technical safety requirement (TSR) recovery plan (Reference 3). This path forward does not include installation of

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a mixer pump. The committee assessment provides a compelling case that Tank 241-AN-107 interstitial liquid waste chemistry is safe in its current configuration and for the foreseeable future based on:

1) The present and projected tank saltcake (solids and interstitial liquid) chemical composition is benign from a SCC perspective.

2) There is a minimal likelihood of SCC growth in the present saltcake region of the tank, and this condition will not be adversely affected by the anticipated chemistry changes over time.

3) In the slow strain rate tests, SCC was never observed at E_{corr}, which is the free corrosion potential, even down to pH 7 for the simulants tested.

4) The temperature of the recent testing was conducted at 122°F while the tank temperature is currently below 95°F and will continue to cool with time.

5) Experimentally induced SCC from pH 9.5 to pH 11 required stress conditions far greater than those possible in Tank 241-AN-107.

In addition to these extracts from the committee's assessment, CH2M HILL noted that they also recommended not installing the mixer pump into Tank 241-AN-107 because it may increase the corrosion potential in the sludge-covered areas of the tank. The potential difference between the supernatant and interstitial liquid sets up a galvanic concentration cell that anodically protects the knuckle.

In their assessment, the committee reiterated the need for installation of the in-tank multi-function corrosion monitoring probe (multi-probe) and a more frequent ultrasonic test tank inspection cycle (five to seven years), all of which CH2M HILL has included in its planning (Reference 2). The committee also referred to the need for confirmatory tests to eliminate remaining ambiguities. CH2M HILL has discussed these ambiguities with the committee. They pertain to defining the numeric value of the crack stress intensity factor (K_{Iscc}) that current tests have bracketed and a more thorough exploration of the extent of the safe chemistry envelope afforded by the current test work. None of these additional tests would compromise or undermine any of the present committee conclusions or recommendations.

Based on our assessment of the committee's report, CH2M HILL concludes that Tank 241-AN-107 is safe and recommends that the ORP approve terminating procurement of the mixer pump for Tank 241-AN-107. As such, CH2M HILL will issue a revised TSR recovery plan for the ORP's approval by November 30, 2005. This plan will include a schedule for a proposed documented safety analysis amendment and specific action items for completion of chemical testing and procurement and installation of the new multi-probe in Tank 241-AN-107.

Should you have questions regarding this matter, please call Mr. S. M. Mackay at 372-3634.

Very truly yours,

Edward S. Aromi, President
and Chief Executive Officer
CH2M HILL Hanford Group, Inc.

bc

Enclosure

cc: ORP Correspondence Control
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MICHAEL T. TERRY, P.E.

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VIA E-MAIL

October 28, 2005

Mr. Robert Popielarczyk
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SUBJECT: CURRENT ASSESSMENT OF TANK 241-AN-107 PITTING BY THE EXPERT PANEL FOR HANFORD SITE DOUBLE-SHELL TANK WASTE CHEMISTRY OPTIMIZATION, OVERSIGHT COMMITTEE

Dear Mr. Popielarczyk,

Recently, the Expert Panel for Hanford Site Double-Shell Tank Waste Chemistry Optimization, Oversight Committee (EPOC), evaluated the propensity for stress-corrosion cracking (SCC) in double-shell tank (DST) 241-AN-107 (AN-107).[1] Subsequent to that letter, CH2M HILL Hanford Group, Inc. (CH2M HILL) asked the EPOC to assess the vulnerability of AN-107 to pitting corrosion.

Pitting corrosion was detected in early tests of Hanford Site waste simulants, and recent cyclic potentiostatic polarization (CPP) tests showed that pitting could occur in AN-107 waste simulants.[2] The propensity for pitting was discussed in Section 3.0 of the final report from 2004[3], and this letter considers those findings as well as new statistical work on the AN-107 ultrasonic tests (UT). In summary, we conclude that pitting occurs so slowly that it would be detected by the current and proposed monitoring systems well before it could threaten the integrity of the tank.

Unlike SCC, pitting corrosion proceeds at a slow rate that diminishes as the pit depth increases.

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[1] *Assessment Of The 241-AN-107 Stress Corrosion Cracking Experimental Program By The Expert Panel For Hanford Site Double-Shell Tank Waste Chemistry Optimization, Oversight Committee*, Letter to R. Popielarcsyk from M. Terry, October 8, 2005.
[2] *Investigation of Chemistry Factors Influencing Stress Corrosion Cracking Susceptibility of High-Level Waste in Double Shell Tank 241-AN-107*, Final Interim Report, CC Technologies Laboratories, Inc., Report 80506201, October 20, 2005.
[3] Ibid.

The maximum measured depth of pitting of the AN-107 tank wall was 0.02 inches (20 mils) in 1998. This depth is approximately 5% of the minimum nominal wall thickness of 0.375 inches.[4] The original expert panel expressed concerns in the workshop that the surface area of the tank examined was small in comparison with the total surface area of the tank and that this large difference could adversely affect estimates of the maximum possible pitting depth. Accordingly, CH2M HILL commissioned PNNL to study this uncertainty and provide a statistical basis for the evaluation of the UT observations. The statistical analysis considered the impacts of manufacturing variability (initial plate thickness), measurement variability, and the fact that the inspection of AN-107 was performed only from one riser. The statistical results indicate that the maximum pit depth expected for AN-107 in 1999 was 0.054 inches at the 95% confidence level.[5]

As already mentioned, pitting corrosion was considered in the original EPOC report. The assessment assumed the pit was formed in the thinnest plate (in AN-107) at the highest DST corrosion rate ever detected (from AY-101). It was assumed that the pit depth followed a $(\text{Time})^{1/2}$ dependence, which is commonly found in pitting kinetics. These calculations predicted that the pit would penetrate 50% of the thin plate in 31 years (2035) and that complete penetration would not be realized for 122 years (2136).

We have reexamined this calculation and assumed that the pit depth increases in a linear fashion, $(\text{Time})^1$. This more conservative assumption leads to an estimated time for perforation of the tank wall between 25-35 years. Although this period is much shorter than the 122 years estimated using parabolic growth kinetics, it is still sufficiently long that the planned protocols, which include UT work, corrosion coupons, and active monitoring with the required in-tank corrosion probe, should allow sufficient time to enable the Hanford Site to react to any unforeseen threat to the tank integrity from this type of corrosion.

In addition to the pitting rate argument, the following factors also apply to the adequacy of monitoring argument:

- AN-107 operated out-of-specification with current chemistry limits for over 20 years, but the UT examination performed in 1999 only discovered relatively light pitting, with no reportable depths (i.e., none at ≥25% of wall thickness). The supernatant returned to specification in 2002 with the addition of sodium hydroxide.

- AN-107 has had EN monitoring probes installed for about 8 years (including the presently operating EN probe). Forensic examination of an older EN probe that had been in the tank environment for about 4 years confirmed only slight pitting in the supernatant and saltcake regions of the tank.

- As a prudent measure, for both pitting and SCC detection, the frequency of UT inspection for AN-107 under the new chemistry requirements is being increased to every 5-7 years versus the normal 8-10 year cycle. Additionally, AN-107 will have its next UT examination performed in early FY '06, providing a good measure of condition and corrosion rates since the 1999 examination.

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[4] *Estimation of Maximum Wall Thickness Loss of Five DSTs (AN-107, AP-102, AW-101, AZ-102, and SY-101)*, Pacific Northwest National Laboratories, PNNL-15415, September 2005.
[5] Ibid.

- Finally, a condition of revising the tank chemistry specification is the installation of a corrosion multi-probe. This multi-probe will enable "real time" detection of pitting with its electro-chemical noise (EN) monitor, as well as periodic visual and quantifiable corrosion determination by the removal of corrosion coupons for forensic analysis.

Therefore, based on these arguments, the EPOC considers that the required monitoring and examination of AN-107 provide defense-in-depth to detect and respond to any integrity threat to the tank from pitting corrosion. The same measures will also provide for similar detection of unusual general corrosion rates and cracking.

Once again, we are indeed pleased that CH2M HILL is taking such a responsible and thorough approach to evaluating and implementing the recommendations of the Committee.

Sincerely,

Michael T. Terry, P.E.
Chairman, Chemistry Optimization Expert Panel,
Oversight Committee

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VIA EMAIL

November 10, 2005

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SUBJECT: CLARIFICATION OF CURRENT ASSESSMENT OF TANK 241-AN-107 PITTING BY THE EXPERT PANEL FOR HANFORD SITE DOUBLE-SHELL TANK WASTE CHEMISTRY OPTIMIZATION, OVERSIGHT COMMITTEE

Dear Mr. Popielarczyk,

Recently, the Expert Panel for Hanford Site Double-Shell Tank Waste Chemistry Optimization, Oversight Committee (EPOC), evaluated the pitting corrosion situation in double-shell tank (DST) 241-AN-107 (AN-107).[1] In summary, it was concluded that, even using very conservative assumptions, the rate of pit growth is expected to be slow enough that perforation will not occur within decades, allowing coupon, corrosion probe, and nondestructive ultrasonic testing (UT) techniques to detect it in a timely manner. Subsequent to that letter, we were informed that staff members from the Defense Nuclear Facilities Safety Board asked the EPOC to clarify their position on the effect of pH on pitting, given that the pH of AN-107 will trend to lower values around 10.

In general, the factors that are used to evaluate pitting corrosion susceptibility, such as pitting and protection potentials, are not dependent on pH.[2] Pitting susceptibility encompasses 1) the resistance to pit initiation and 2) the stability of a growing pit. The lack of dependence of the critical potentials on pH is because the local environment within a pit is altered (acidified as a result of cation hydrolysis) to a condition that is practically independent of the external environment. On the other hand, other factors that can play a role in pitting susceptibility, such as

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[1] Letter to R. Popielarcsyk from M. Terry, *Current Assessment Of Tank 241-AN-107 Pitting By The Expert Panel For Hanford Site Double-Shell Tank Waste Chemistry Optimization, Oversight Committee*, October 28, 2005.

[2] Z. Szklarska-Smialowska, *Pitting and Crevice Corrosion*, NACE Press, 2005.

the corrosion potential, might be dependent on the external environment. Corrosion potential often increases with decreasing pH, which can result in the corrosion potential being closer to the pitting potential, indicating an increase in the material's pitting susceptibility.

The recent experimental program at CC Technologies, Inc. included cyclic potentiodynamic polarization (CPP) measurements in the AN-107 simulants adjusted to pH values from 7-11. The objective of the CPP testing was to establish possible potential ranges for SCC in the simulants. Data from CPP scans also provide some information regarding pitting susceptibility, although time to pit initiation and growth rate cannot be inferred. Nonetheless, analysis of the CC Technologies data provided no clear indication regarding the effects of pH in that range on pitting susceptibility.

Other studies on pitting initiation, which included CPP scans and coupon tests, have been performed on carbon steel in similar waste environments. The results indicated that there is not a simple direct relationship between pit initiation and pH.[3, 4, 5] Other variables, such as the temperature and concentrations of nitrate and nitrite ions, also have significant effects on pit initiation. These data indicated that pit initiation would not be expected even at a pH of 10 if there were sufficient quantities of nitrite ion or if the temperature was low. Thus, the environment of each tank would need to be evaluated separately to determine whether pitting would initiate at pH 10.

In the previous letter from the EPOC, the effects of pitting were addressed by assuming conservatively that pits had already initiated and were growing. The rate of pit growth used for AN-107 was based on UT measurements at a liquid-air interface, worst-case situation on tank AY-101, which actually was out of specification with a pH near 9.5. Pits usually grow at a rate that decreases with time; a common kinetic expression indicates pit depth increasing with time to the ½ power. However, to be more conservative, the EPOC used linear kinetics to calculate the time to perforate the thinnest AN-107 plate. As reported in the last letter, even this very conservative approach led to penetration times on the order of decades.

The fact that the pH in tank AN-107 will slowly decrease to 10 does not alter the EPOC conclusion that the rates of pit initiation and growth will be slow enough that UT examination coupon, and multi-probe monitoring techniques would detect it well before approaching any potential perforation. As an additional observation, it is expected that the rate of wall thinning from uniform corrosion would not be faster than the rate of pit growth so that the inspection and monitoring described above would most certainly detect any accelerated wall thinning well before structural or leak integrity were compromised.

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[3] R. Carranza, C.M. Giordano, E. Sáenz, *Corrosion of Steel Tanks in Liquid Nuclear Wastes*, CORROSION/2006, Paper No. 635, NACE International, 2006.
[4] J. W. Congdon, *Inhibition of Partially Washed Precipitate*, DPST-87-663, September 17, 1987.
[5] P. E. Zapp, *Effect of Temperature on the Nitrite Requirement to Inhibit Washed Sludge*, WSRC-TR-90-292, September 18, 1990.

Should you have additional questions, please feel free to contact me.

Sincerely,

Michael T. Terry, P.E.
Chairman, Chemistry Optimization Expert Panel,
Oversight Committee