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DESCRIPTION OF DST SELECTION CRITERIA FOR
INSPECTION

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Description of Double-Shell Tank Selection Criteria For Inspection

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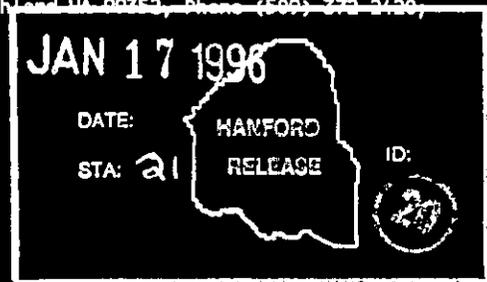
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Abstract: Technical criteria for selecting DSTs for inspection are presented. Inspection of DSTs is planned to non-destructively determine the general condition of their inner wall and bottom knuckle. Inspection of representative tanks will provide a basis for evaluating the integrity of all the DSTs and provide a basis for estimating remaining life. The selection criteria recommended are tank age based on date-of-first fluid entry, waste temperature, corrosion inhibitor levels, deviations from normal behavior - involving sludge levels, hydrogen release and waste transfers - least waste depth fluctuation, tank steel type, other chemical species that could activate stress-corrosion cracking, and waste types.

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DESCRIPTION OF DOUBLE-SHELL TANK SELECTION CRITERIA FOR INSPECTION

1.0 INTRODUCTION

The purpose of performing an ultrasonic examination of the double-shell tanks (DSTs) is to determine the general condition of the their tank walls and, with periodic examination, estimate their remaining service life.

Inspecting representative tanks provides a basis for evaluating the integrity of all the DSTs. The key is to identify which tanks provide a reliable indication of the condition of the other tanks. To ensure representative tanks are identified, criteria for their selection are presented in this report. The criteria are based primarily on factors that may enhance corrosion degradation mechanisms.

Four distinct forms of corrosion attack may be observed in systems such as waste tanks:

- General or uniform corrosion, where the surface is attacked uniformly resulting in a gradual thinning of the structure.
- Pitting, wherein the surface is attacked at very localized sites forming relatively deep pits or crevices. Pitting may cause very rapid penetration of the structure after an incubation time has been exceeded.
- Beachline (waterline) attack where the metal is attacked more rapidly at the liquid-air interface.
- Stress-corrosion cracking (SCC); under the influence of a tensile stress, a slightly corrosive environment, and an incubation time, the metal cracks at a stress much less than its tensile strength, and often less than the design stress.

2.0 APPROACH

The inspection criteria are based on the four corrosion degradation mechanisms noted in the Introduction.

The following criteria were established as bases for the selection of a representative sample of DSTs. The criteria are consistent with Tank Structural Integrity Panel (TSIP) guidelines (Bandyopadhyay 1994) and previous WHC selection criteria (Pfluger 1994). Some criteria are weighted as being more important than others and will be described later. The criteria are:

- Age of the DSTs
- Waste Temperature
- Corrosion Inhibitor Levels

- Deviation from the Norm in Tank Wastes:
 - Sludge Levels above a Certain Depth
 - Hydrogen Release
 - Higher Level of Waste Transfer to and From Tanks
- Least Waste Depth Fluctuation
- Tank Steel
- Other Chemical Species that can Activate Stress-Corrosion Cracking
- Spectrum of Waste Types

Several of the above criteria are expanded upon in Appendix A (Effect of Inhibitor Chemicals on Corrosion Rates in DST Steels) and Appendix B (Effect of Different Waste Tank Alloys on Stress-Corrosion Cracking). In addition, some miscellaneous effects or factors on SCC are noted in Appendix C; these particular factors may have made some DSTs more sensitive to SCC than others.

3.0 DESCRIPTION OF SPECIFIC TANK SELECTION CRITERIA

3.1 FLUID AGE OF DSTs

Because time is a major ally of fluid-based corrosion, the age of a given tank, as a selection criterion, is based on the date of first-fluid entry. A difference in age of 5-years is considered significant.

Additional age categories considered were date-of-construction and date-of-first waste. Selection of the first was inadequate because for one tank (AY-101), the first fluid entry was seven years after construction. The date-of-first waste was not selected because water was often the first fluid into a given tank and water may be more corrosive than treated waste.

3.2 WASTE TEMPERATURE

Corrosion damage processes almost always increase in severity with increasing temperature. Waste temperature, past or current, greater than 200°F is considered significant. Except for the distinction between tanks with temperatures < 200°F and the tanks with temperatures > 200°F, no further distinction is justified by the data. Some comments follow on the temperature nature of corrosion test data and possible concerns for future in-tank processing.

3.2.1 Corrosion Test Data

Hanford corrosion test data (Divine et al., 1983, 1984a, 1984b, 1984c and 1985), show that the effect of temperature on uniform corrosion and pitting corrosion is generally

insignificant;¹ the effect of temperature on SCC growth-rate is not known because almost all of the solutions were not corrosive enough to initiate cracks within the testing time period.

Uniform and pitting corrosion tests on the two major tank steel categories (ASTM A515/516 and ASTM A537) were based on about 3,000 specimens, six temperature levels (40, 60, 80, 100, 140 and 180°C), more than 80 waste compositions, and generally three test time periods (4-, 8-, and 12-months). Average corrosion rates for the longest exposure tests slowly increased with temperature; the average rates went from less than 0.1 mil per year (mpy) at 40°C to as much as about 0.8 mpy at 180°C. Only several test solutions produced significant pitting or uniform attack. Those particular solutions are restricted from occurring based on the waste composition limits (Kirch 1984) developed from these data.

Based on the above average corrosion rate data, estimates can be made of the amount of uniform corrosion within a given DST. DST average, maximum, and minimum temperatures (Brevick 1995) generally cover the last 10-years, more-or-less.

Limitation of known maximum temperature levels of the DSTs to only the last 10-years is not restrictive. For example, based on the highest known waste temperature level of 128°C (or 263°F) for DST AZ-101, its highest corrosion rate would be < 0.2 mpy; combining the oldest known tank (DST AY-102, at about 25-fluid-years of age) with the highest temperature tank, the total corrosion after about 25-years would be less than 5-mils. Thus the effect of temperature on uniform corrosion (and pitting) is insignificant.

3.2.2 Stress-Corrosion Test Data

The approximately 1,200 smooth (unnotched) SCC specimens (Divine et al., 1983, 1984a, 1984b and 1984c) provided an adequate measure of steel SCC-sensitivity for more aggressive test solutions (like those containing 10 M OH⁻) but probably not for the less aggressive ones. This is so because SCC is composed of an initiation phase and a propagation phase, both of which can be impacted by the solution chemistry. Either, or both can be shortened. However, because the majority of the test solutions were less aggressive (they contained nitrites and lower OH⁻ concentrations), this meant that the crack initiation time could have exceeded the time of test. Because crack-like defects did not form during the time of test of the less aggressive solutions, it was not possible to assess the effects of temperature (if any) on the subsequent SCC growth-rate.

3.2.3 Future In-Tank Processing

In-tank chemical processing may occur in the future and could pose some further upper limit on waste temperature. For example, Westinghouse

¹ Several test solutions produced a slowly increasing corrosion rate with time based on 8- and 12-month data. By extrapolation, the data indicates that longer-term corrosion rates of 2-3 mpy could occur; see Appendix A, below.

Savannah River Site's new 1990 Tank Waste Composition Limits document (DPSTS 1990), places a limit of 60°C (140°F) mainly for tank pitting corrosion control, when in-tank sludge processing is to take place. In contrast, Hanford still allows temperatures > 100°C (212°F) for control of all three primary modes of corrosion (uniform corrosion, pitting corrosion, and SCC - (Kirch 1984).

In the future, those Hanford DSTs that are to be used for in-tank processing should be considered as a separate category and inspections targeted at the waterline to detect possible pitting (see also Item 3.6, below relating to waterline pitting and Item 3.8, "Other Chemical Species that Can Activate SCC").

3.4 LOW INHIBITOR LEVELS

Corrosion inhibitor levels either too low or too high in concentration can enhance corrosion. Several DSTs are reported to have low levels of the caustic inhibitor chemical, OH⁻. Thus, DST waste compositions that do not meet chemical corrosion control requirements for OH⁻, and the additional inhibitor chemical nitrite (NO₂⁻) will be selected for inspection if those inhibitor levels have been out-of-specification (Kirch 1984) for more than 3-years.

Through experience and testing (and because no corrosion equations-of-state exist), corrosion technologists have found that the presence of certain chemicals, usually in small amounts, can be used to inhibit corrosion. Inhibit here means to slow, as in a chemical reaction, not to eliminate. Details concerning corrosion inhibition by OH⁻ and NO₂⁻ in Hanford DST wastes, including some solution compositions that could slightly increase corrosion rates, are discussed in Appendix A.

3.5 DEVIATIONS FROM NORMAL OPERATION IN WASTE TANKS

Deviations from "normal" operation or behavior were selected as a criterion because some changes in waste behavior, or in waste tank operation, may act to accelerate or aggravate corrosion.

3.5.1 Sludge Levels

A tank sludge level greater than 12-in. in depth is considered important as a selection criterion.

Bottom-lying deposits could aggravate so-called under-deposit corrosion (also called crevice² corrosion). If sludges or corrosion products form as solids on the bottom of a tank, they could act as semi-impervious to impervious shields to the surrounding fluid. This may cause significant local variations in waste composition and concentration from the adjacent bulk fluid (Fontana 1978). In turn, this effect may accelerate corrosion in the

² Crevice corrosion is, in essence, an advanced form of pitting corrosion.

shielded areas. The metal from the bottom of the tank to the top of the lower knuckle would be exposed to the sludge.

Sludge layers greater than 12-in. would mean that all highly-stressed bottom knuckles, which are inspectable, could also suffer such attack and thus be a forerunner of the behavior of the virtually uninspectable lower-stressed tank bottom.

3.5.2 Hydrogen Release

Some DSTs periodically release large amounts of hydrogen. Tanks under flammable gas controls are selected as a criterion.

The release of hydrogen is a measure of some waste thermal and chemical activity. Both radiolysis (breakdown of water into hydrogen and oxygen) and chemical reactions that produce hydrogen, may be locally altering waste chemistry. Corrosion reactions can also produce hydrogen but only in small amounts, relative to radiolysis, as uniform corrosion is not likely to be significant, see Section 3.2.1.

3.5.3 Higher Levels of Waste Transfers To and From Tanks

The number of significant waste height fluctuations has been selected as a criterion. Any DST having had 200 (or more) fill and empty cycles > 200-in. in extent, would be selected.

The effects on low-cycle fatigue and corrosion-fatigue due to waste height fluctuations, are insignificant. For example, a low-cycle, reversed (tension-compression) plastic strain of 1% generally requires about 1,000 reversals to produce failure (Tetleman et al. 1967). In a highly aggressive (non-inhibited) chemical environment this might be reduced to 200 or so, reversals. The typical corrosion-inhibited environment of the DST wastes are not expected to have any significant effect on the low-cycle or corrosion-fatigue life of any DST.

Maximum stress levels in bottom knuckles could be in the neighborhood of a tank material's yield stress (Shurrab et al., 1991). Furthermore, the largest number of waste tank filling and emptying cycles, > 200-in., have not exceeded 23 (Brevick et al., 1995, DST AY-102, p. 168). Thus low-cycle fatigue, and corrosion-fatigue for the same reasons, are not significant damage-producing phenomena.

Some exacerbation of stress-corrosion cracking in the knuckle by stress-cycling could occur. This is the primary reason for retaining waste height variation as a selection criterion.

3.6 LEAST WASTE DEPTH FLUCTUATION

DSTs with the least variation in waste height has been selected as a criterion because of possible long-term, stationary waterline corrosion effects. A virtually constant waste level for a period of 5-years is considered significant.

Corrosion, in the region where vapor meets liquid, has been observed in other environments. Airborne, acid-forming carbon dioxide may decrease the OH^- concentration in the meniscus region of the sidewall fluid (Zapp and Hobbs 1992); this has the effect of producing a highly localized decrease in the concentration of the corrosion-inhibiting OH^- chemical in the vapor-liquid interface. This local decrease in OH^- is independent of the bulk OH^- level, although a decreased bulk OH^- concentration would further decrease the meniscus concentration.

Waterline tests were not conducted in previous corrosion test programs (Divine et al., 1983, 1984a, 1984b and 1984c) and thus there are no laboratory-based data for comparison. In addition, crustal deposits on the wet side of the tank wall can cause local chemistry variations in trapped liquid waste. Consequently, tanks that have shown the least variation in waste height may have undergone a more intense local corrosion, or local crustal buildup, in contrast to a waterline that has varied in position over time.

3.7 WASTE TANK STEEL

With DST steels a decreasing strength and an increasing alloy sulfur content both increase susceptibility to SCC. Thus, the lowest strength steel and a tank steel sulfur content exceeding 0.02% (by weight) are selected as a dual criterion.

ASTM A516 (ASTM 1986a) steel has a lower yield strength (and lower ultimate strength) than ASTM A537 (ASTM 1986b) steel. Alloy sulfur levels greater than 0.02% are considered important but until actual DST construction steel chemical analyses are obtained, selection by sulfur level cannot be done. See Appendix B for a more detailed description of the effect of alloy strength and sulfur level on SCC.

3.8 OTHER CHEMICAL SPECIES THAT CAN ACTIVATE STRESS-CORROSION CRACKING

In addition to nitrates, Hanford's DSTs could be susceptible to SCC from caustics, phosphates and carbonates. Most DST wastes also contain these three species but in amounts that are not expected to exacerbate SCC under present conditions. These species may become important after in-tank processing begins. Such processing could require general changes in waste chemistry levels including these three species, and others, that may or may not have an inhibitory influence. Since no in-tank processing has yet occurred, selection of a given tank for inspection, based on caustic, phosphate, and carbonate levels is not planned at this time.

Before in-tank waste processing occurs, the effect of changing levels of hydroxide, phosphate, and carbonate should be studied. Further corrosion testing may become necessary. Also, the effect of minor chemical additions to hydroxide solutions, to phosphate solutions, and to carbonate solutions on SCC are simply not known (Parkins 1973). In several cases some minor chemical impurities in NaOH have been known to produce cracking in carbon steel when relatively pure NaOH, by itself, would not (Parkins 1973). Thus, minor

impurities along with in-tank processing changes in other major chemicals in DST wastes, could be important to future DST integrity.

3.9 SPECTRUM OF WASTE TYPES RELATED TO CORROSION

Selection of tanks based on title-designated waste types is considered a secondary criterion for selection.

Generalization of waste compositions in storage tanks based on flowsheet or process analyses is not possible because wastes are intermixed, and because evaporation changes concentrations and induces insoluble precipitates. Further, radiation can induce changes in composition.

Where some significant DST waste designation remains valid, then waste type will be used as a criterion.

Some miscellaneous effects on SCC are discussed below in Appendix C.

4.0 SUMMARY

Non-destructive inspection of the inner wall and bottom knuckle of representative DSTs is expected to provide a basis for evaluating the integrity of all 28 Hanford DSTs. Such inspections will require a significant investment both in time and cost for the robotic equipment, the inspecting team(s), multiple on-tank support personnel and ancillary equipment, and engineering analysis staff.

To ensure maximum return on the investment in inspection it is important that key tanks be identified that provide a reliable indication of the condition of the other DSTs. To ensure that representative tanks are identified, technical criteria for their selection were developed. These criteria were based primarily on those factors that can effect tank steel corrosion degradation mechanisms.

The selection criteria presented were: tank age based on date-of-first fluid entry, waste temperature, corrosion inhibitor levels, deviation from normal behavior - involving sludge levels, hydrogen release and number of waste transfers- least waste depth fluctuation, tank steel type, other chemical species that could activate stress-corrosion cracking, and waste types.

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APPENDIX A

EFFECT OF INHIBITOR CHEMICAL LEVELS ON CORROSION RATE OF DST STEELS

EFFECT OF INHIBITOR CHEMICAL LEVELS ON CORROSION RATE OF DST STEELS

Inhibitor chemicals may enhance corrosion if their concentrations are too low or too high. Paradoxically, although either nitrate (NO_3^-) or OH^- can cause mild steel to crack, the presence of either can inhibit cracking by the other (Donovan 1977). Furthermore, NO_2^- acts synergistically with OH^- to inhibit NO_3^- -SCC (Ondrejcin et al., 1979).

Fortunately, the presence of the two inhibitor chemicals also acts to inhibit uniform corrosion and pitting corrosion. Thus, knowledge of the levels of both OH^- and NO_2^- levels, relative to the amount of NO_3^- , are important for estimating the potential for corrosion attack in a given DST.

Specifications that define the levels of inhibitor chemicals are taken from (Kirch 1984), and presented below. It will be shown, however, that inhibitor levels that are relatively low or high have also produced nominal increases in corrosion rate.

The inhibitor chemical controls are based on two waste temperature levels [$T \leq 100^\circ\text{C}$ (212°F) and $T > 100^\circ\text{C}$] and three ranges of NO_3^- concentrations. The individual OH^- and NO_2^- levels, sometimes combined, are regulated based on the three molarity concentration ranges of NO_3^- :

For $\text{NO}_3^- \leq 1.0 \text{ M}$:

- The OH^- shall be in the range: $0.01 \text{ M} \leq \text{OH}^- \leq 5.0 (10 \text{ M})$
- While the NO_2^- range shall be: $0.011 \text{ M} \leq \text{NO}_2^- \leq 5.5$

If the waste temperature is less than 75°C (167°F) then the upper OH^- limit may be increased to 10 M .

For NO_3^- Between 1.0 and $\leq 3.0 \text{ M}$:

- The OH^- level shall be a minimum of 0.1 times the NO_3^- (i.e., $\geq 0.1 \times \text{NO}_3^- \text{ M}$) but always $< 10 \text{ M}$.
- The combined OH^- and NO_2^- level (i.e., $\text{OH}^- + \text{NO}_2^-$) shall be ≥ 0.4 times the NO_3^- concentration (i.e., $\geq 0.4 \times \text{NO}_3^- \text{ M}$)

For NO_3^- Between $> 3.0 \text{ M}$ and 5.5 M :

- The OH^- level shall be limited to be between 0.3 M and $< 10 \text{ M}$.
- The combined $\text{OH}^- + \text{NO}_2^-$ shall be $\geq 1.2 \text{ M}$.

For Temperatures $> 100^\circ\text{C}$

- Here OH^- concentration shall always be less than 4 M ; the NO_3^- and NO_2^- levels are as defined above for $T \leq 100^\circ\text{C}$.

As noted earlier, inhibitor concentration levels that are either too high or too low can enhance corrosion. Specifically, OH^- concentrations greater than 10 M are considered SCC-inducing, (Divine et al., 1984a). Even for low OH^- concentrations (i.e., $\text{pH} > 14$ or > 1 M), (Donovan 1977) indicated that general corrosion rates in excess of several mpy could occur. In addition, previous Hanford corrosion test data (Divine et al., 1984a, 1984b and 1984c) showed that several synthetic waste composition solutions displayed low, but continually increasing corrosion rates with increasing time. These latter solutions and corrosion rates are now detailed further because if certain DSTs had a combination of high waste temperatures and relatively high OH^- and relatively high and low NO_2^- levels, although still within the above (Kirch 1984) specification, they might undergo uniform corrosion rates of 2-3 mpy.

Specifically, in (Divine et al., 1984a, 1984b and 1984c), two test solutions (both at 140 and 180°C) contained relatively high levels of OH^- and NO_2^- inhibitor chemicals³ (solutions 20 and 7) while two other solutions contained high OH^- and low NO_2^- (solutions 28 and 30). When the subsequent chemical control specification (Kirch 1984) was settled on, these particular solutions were declared to be outside the specification because they had OH^- concentrations > 4.0 M, for $T > 100^\circ\text{C}$. However, these particular solutions also showed a distinctly different corrosion behavior from all the other solutions (83 total). Generally their 8- and 12-month data showed an increasing corrosion rate with time, and when extrapolated to 24-months (2-years), showed that corrosion rates could be as high as 2-3 mpy. For solution 30 the rate could be even higher yet, but this particular solution (10 M OH^- , 0.2 M NO_2^- and 1.0 M NO_3^-) is unlikely to be allowed to occur in any DST. It should be emphasized however, that all 87 corrosion test solutions that were maintained at or below 100°C, showed a desirable contrasting corrosion behavior: here the corrosion rates were low (< 1 mpy), they decreased with increasing time, and thus they extrapolated to even lower rates at a 2-years exposure.

Where these extrapolated rates may be important, is that some DSTs had recent maximum temperature levels that were greater than the 100°C corrosion test temperature, but less than the higher temperatures (140 and 180°C) that were used to obtain the extrapolated 2-3 mpy data. At least three DSTs had recent maximum temperature levels $> 110^\circ\text{C}$. They were AZ-101 (128° C), AY-101 (119°C), and AZ-102 (116°C) [Brevick et al., 1995]. Further, DST SY-101 may have OH^- and NO_2^- levels near that of solution No. 7.³ Thus it is possible that DST SY-101 may have suffered from an increased corrosion rate of 2-3 mpy for some undefined period of time. Moreover, other DSTs may have relatively high levels of those same inhibitor chemicals; Brevick's supernatant mixing model (Brevick et al., 1995), for predicting waste tank composition, indicates that DSTs SY-103, and AN-103 to 107 could have OH^- and NO_2^- levels in the ranges 4 to 7M and 2-4 M, respectively. The maximum waste temperatures for the AN tank farm, however, appear to have been no higher than 66 °C (150° F)

³ The inhibitor chemical levels were:

| Solution No. | NO_2^- (M) | OH^- (M) | Solution No. | NO_2^- | OH^- |
|--------------|---------------------|-------------------|--------------|-----------------|---------------|
| 28 | 0.6 | 7.0 | 7 | 4.1 | 4.0 |
| 20 | 4.1 | 7.0 | 30 | 0.2 | 10.0 |

[Brevick et al., 1995] and thus may not have been subject to the nominally higher corrosion rate.

It is recommended that further investigations be done to determine which DSTs may have had a combination of waste temperatures and OH^- and NO_2^- levels that could have produced a 2-3 mpy corrosion rate.

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APPENDIX B

EFFECT OF DIFFERENT WASTE TANK ALLOYS ON STRESS-CORROSION CRACKING

EFFECT OF DIFFERENT WASTE TANK ALLOYS ON STRESS-CORROSION CRACKING

For DST steels two specific factors appear to contribute to an increase in their susceptibility to nitrate-SCC: a decreasing strength and an increasing alloy sulfur content. Further complicating the issue, are the number of approaches used to assess SCC.

A measure of the complexity of SCC is that many different types of specimens are used to detect and measure it; also no single test provides enough information to satisfactorily characterize both its initiation and propagation modes. The various test specimens and methods (and the presence of the corroding media) include both static or dynamic loading of smooth specimens under a tension or a bending stress state and static or dynamic loading of notched or pre-cracked specimens including various electrochemical methods involving cyclic polarization. Smooth specimen types include tensile specimens, bent-beam specimens, C-ring, etc. Notched specimens are often characterized by the term fracture mechanics specimens and can involve an increasing or a decreasing stress intensity factor, K (Metals Handbook 1987) Chapters on Laboratory testing and Evaluation of SCC for more detail on SCC specimens and testing methods).

1.0 EFFECT OF SPECIMEN TYPE ON SCC SENSITIVITY MEASUREMENT

There are only three known SCC investigations where a fracture mechanics (FM), or notched specimen approach, was used to evaluate the effect of various caustic-nitrate wastes on SCC growth rate properties in waste tank steels (Sarafian 1975a, Donovan 1977 and WHC). These references lend credence to the low strength-increasing sulfur effect on SCC, and are briefly discussed later.

First, the FM approach, as opposed to the so-called smooth specimen approach, is more applicable to waste tank structures because it assesses the susceptibility of steel to SCC growth as opposed to initiation and growth combined. In contrast, the smooth specimen approach primarily measures the time required to both initiate a crack (by corrosion processes) and grow that crack (by SCC) to a critical size. Because the initiation phase generally takes the longest time to occur, significant variations in the growth rate, which produce significant decreases in propagation time, cannot be readily detected. The FM approach however, is important for conducting future integrity assessments of DSTs that may be found, by UT inspection, to contain flaws.

In the FM approach, SCC growth will not occur (in a through-wall cracked flat plate specimen) if the multiple of gross stress (σ) and the square root of the crack length, $(\pi a)^{0.5}$, does not exceed a material-environmental property, $K_{I_{SCC}}$. This term is called the threshold stress intensity factor for propagation of a stress-corrosion crack.

From the viewpoint of a DST, $K_{I_{SCC}}$ is the K -level below which no significant crack growth will occur from either a pre-existent flaw, or a generated-in service crack, within the tank wall. A 'high' $K_{I_{SCC}}$ value is desirable in that it means for a given tank wall stress, a larger crack must

be developed before SCC growth will occur. Correspondingly, a low K_{ISCC} value reduces the flaw depth that will initiate growth. In turn this means that a UT inspection must become more stringent in looking for, and sizing, smaller flaws.

In the main Hanford waste tank corrosion study (Divine et al., 1984a, 1984b, and 1984c), as mentioned in the body of this report, many smooth (unnotched) SCC test specimens (about 1200) were used to provide a measure of the total time required to both initiate and propagate a crack (or cracks) to failure in about 87 different test solutions. As noted above, for this type of specimen, the majority of the testing time is spent in initiating the crack, usually with a much lesser time required for propagating the crack to failure. Thus, if a given test solution caused a rapid failure, it would have been due mainly to a significant decrease in the time required to initiate a crack (usually by corrosion processes). Because the testing time is skewed more toward initiation, significant variations in the speed of crack propagation will not be seen even though they may be occurring. Thus it is possible that relatively innocuous-to-initiation test solutions could have significantly different effects on crack propagation rate, but never be noticed.

Furthermore, if flaw-initiating corrosion processes are very slow-acting, cracks large enough to begin the SCC growth process in such specimens may not occur because the time-of-test is too short. SC cracks can take longer than 1-year to develop, and most corrosion tests rarely exceed 1-year. In contrast, the FM test approach emphasizes crack propagation over initiation and allows investigators to primarily measure the K-level at which crack propagation begins and time needed to propagate⁴ a crack.

2.0 FRACTURE MECHANICS STRESS-CORROSION DATA ON WASTE TANK STEELS

Table A-1 presents a comparison of the three known FM investigations on the effect of heat treatment, and possibly sulfur, on the critical stress intensity factor (K_{ISCC}) required to cause a crack to grow by stress-corrosion.

The ASTM A285 Grade B (ASTM 1982) Savannah River tank steel noted in Table A-1, was tested by Donovan (Donovan 1977); he used a series of 95°C caustic-nitrate synthetic waste solutions, some of which contained NaNO_2 . Sarafian (Sarafian 1975a), used one heat of ASTM A516 (Ref. 9) steel initially in the hot-rolled condition, termed hot-rolled steel (HRS) and he mainly used 95°C 5 M NaNO_2 solutions, some of which contained NaOH. He conducted a number of different heat treatments on that steel, two of which (normalized and quenched and tempered) are included, along with HRS, in the Table. The third investigation (WHC), conducted at PNL for WHC, used higher strength ASTM A537 steel (ASTM 1986b) and involved 5 M NaNO_3 or 5 M NH_4NO_3 solutions, both at about 95°C. That particular steel was used to grow various size stress-corrosion cracks in

⁴ Some time is required to initiate a SC crack even from a specimen with a critical-sized flaw (or crack) but is generally less in comparison to the time needed to 'initiate' and grow a crack from a small defect to a size where SCC will finally drive its growth (i.e., where $K > K_{ISCC}$).

Table A-1. Effect of Yield Strength (Heat Treatment) and Alloy Sulfur Content on K_{Isc} of Three Pressure Vessel Steels in a 5M $NaNO_3$ Solution at About 95°C.

| Matl | Ht Trtmnt or Condition | Yield Stress (Ksi) | Sulfur Content Wt. % | Max Sulfur (Wt. %) | K_{Isc} (Ksi/in) |
|-------------|------------------------|--------------------|----------------------|--------------------|------------------------|
| A285 Gr. B | HRS | 27* | 0.015 | 0.04 | 28.2 ^a |
| A515 Gr. 60 | HRS | 32* | | 0.04 | No data |
| A516 Gr. 60 | HRS | 38.3 | 0.029 | 0.04 | 13.1-22.6 ^a |
| A516 Gr. 60 | Norm. | 43.0 | 0.029 | 0.04 | 32.6 ^a |
| A516 Gr. 60 | Q & T | 54.3 | 0.029 | 0.04 | 49.5 ^a |
| A537 Cl.1 | Norm. | 50.0* | 0.005 | 0.04 | > 38.5 ^b |

* Minimum Y.S. values per ASTM spec; all others actual data.

^a Data obtained from less-accurate bolt-loaded WOL specimens.

^b Actual value is greater than this level as the crack would quickly arrest in plate bending specimen each time after load was increased; arrest did not occur when the solution was changed to 5 M NH_4NO_3 .

A 285 Gr. B data were taken from Donovan, J. A., 1977, "Factors Controlling Nitrate Cracking of Mild Steel," Proc. of Conference Environmental Degradation of Engineering Materials, Coll. of Engr., Virginia, Tech, Blacksburg, Virginia.

A 516 Gr. 60 data were taken from, Sarafian, P. G., 1975, "The Influence of Microstructure on Stress-Corrosion Cracking of Mild Steel in Synthetic Caustic-Nitrate Nuclear Waste Solution," a Thesis Presented to the Faculty of the Division of Graduate Studies and Research, Georgia Institute of Technology.

A 537 Class 1 data were taken from WHC-PNL SCC Performance Demonstration Specimen Development, 1994-5, Westinghouse Hanford Company, Richland, Washington.

a series of bend-loaded plate specimens. These specimens are being used as a basis to assess a Hanford UT system for detecting and sizing stress-corrosion cracks in DST walls (Pfluger 1994).

Sarafian's data (Sarafian 1975a) is the most enlightening as it shows an uncharacteristic decrease in K_{Isc} with decreasing metal strength, either as measured by yield strength (shown in Table) or ultimate strength. While there are some K-inaccuracies associated with the bolt-loaded, wedge-opening-load (WOL) specimen used by Sarafian (and Donovan too) the trend in K_{Isc} to decrease with decreasing strength is probably valid. Whether the decrease in K_{Isc} is due to strength or microstructure is unclear. Either one could be a consequence of heat treatment, while the other, the cause. What is clear is that ASTM A515 (ASTM 1982) and A 516 hot-rolled steels that were used to

construct at least three tank farms (AY-515, AZ-515, and SY-516, See Table 2.1 (Edgemon and Anantatmula 1995) and that A515/516 alloys are probably more SCC-susceptible than the A 537 steel used to construct the remaining tank farms (AN, AW, and AP).

Comparison of Sarafian's⁵ data with Donovan⁶ (and WHC) in Table A-1, indicates that sulfur level may also be modulating the K_{Isc} values. Although Donovan's material apparently has a lower strength (27 Ksi min., per ASTM specification) it also has a much lower sulfur content (0.015 versus 0.029 %) which could counter by acting to drive up the K_{Isc} value. The combined higher strength and lower sulfur content (0.005 %) of the (WHC) study shows an even higher K_{Isc} when comparing the HRS and normalized metallurgical conditions.

Another factor that supports the increased sulfur theory on increasing SCC-susceptibility is based on the early work of Seah (and Hondros) [Seah 1975b]. While the bulk sulfur (and also phosphorous) concentration appears nominally low for both steels (A 516 Grade 60 and A 285 Grade B) both elemental species are known to be maldistributed within their bulk metal; that is, much of the S and P reside in grain boundaries, right where the intergranular nitrate-stress-corrosion crack growth process takes place. That maldistribution is also severe, but is worse for sulfur. That is, most of the S and P (in the grain boundaries) are at relative concentrations of roughly 30,000 and 300 times greater, respectively, than their average or bulk concentration values; this effect was first found by the pioneering Auger spectroscopy work noted in (Seah 1975b). Thus even a relatively small increase in a relatively low bulk concentration (viz., 0.005 % S in the A537 to 0.029 % in the A516) represents a very large increase in the amount of S in the metals stress-corrosion sensitive grain boundaries.

⁵ The composition of Sarafian's A 516 alloy was: C 0.21, Mn 1.09, Si 0.24, P 0.01 and S 0.029, all in weight percent.

⁶ The composition of Donovan's A 285 Grade B alloy was C 0.012, Mn 0.49, P 0.010 and S 0.015; all values in weight percent. Heat treatment conditions are not noted in the A 285 spec; most likely the material is hot-rolled.

⁷ Multiplication of 30,000 times the bulk S concentrations results in values of 150 % and 870 % which are mainly relative measures of the number of monolayers of S within a grain boundary region, not the actual concentration per se.

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APPENDIX C

MISCELLANEOUS EFFECTS ON STRESS-CORROSION CRACKING

MISCELLANEOUS EFFECTS ON STRESS-CORROSION CRACKING

Several miscellaneous effects on SCC are noted, not as selection criteria, but as factors which may have made the tanks more sensitive to in-tank SCC than were the corrosion specimens used to measure their laboratory SCC behavior. These effects deal with limitations in the scope of Hanford corrosion test programs and differences in stress-relieving.

1.0 CORROSION TESTING LIMITATIONS

First, all previous corrosion test programs did not include either weldment specimens, or vapor phase test conditions, or crack propagation specimens. Because of their exclusion from testing, it has not been possible to assess or rate the effect of weldments or waterlines on localized corrosion (pitting and cracking) behavior, nor to gage the effect of the chemically uninhibited vapor phase on the general corrosion behavior of the entire vapor phase region of the tanks. If corrosion damage occurs within a system, its worst effects will probably be biased toward weldments, waterlines, and higher stressed regions.

Because only unnotched bent-beam SCC specimens were used in one corrosion test program (Divine et al., 1984a, 1984b and 1984c), and testing was limited to a 12-month period, only gross effects of waste chemistry on SCC could be detected. This is so because bent-beam specimens, as noted above in Appendix B, essentially measure only the initiation phase of SCC. If the incubation time of cracking is longer than the testing period (which is likely the case for less-aggressive, inhibited waste test solutions, concerning both pitting and cracking), chemically sensitive crack propagation, simply would not have been allowed enough time to occur. Ondrejcin (Ondrejcin et al., 1979) indicated that he found it necessary to use a more severe stress-corrosion test specimen (slow-strain rate versus bent beam) because standard SCC specimens did not crack while Savannah River waste tanks did.

If stress-corrosion crack propagation specimens had been used, this would essentially eliminate the crack initiation phase and thus dominantly measure the K_{ISCC} -sensitivity of SCC rate to waste chemistry variations.

2.0 STRESS-RELIEVING DIFFERENCES

The two-part second limitation deals with differences in stress-relieving between DSTs and between DSTs and their corrosion test specimens; both these effects probably play a minor role in making the tanks more sensitive to SCC than the specimens used to gage SCC. These effects are in addition to the more significant limitations noted directly above.

First, some waste tanks that were stress-relieved at 1,000°F for 3-hr probably retain some slightly higher (SCC-promoting) residual stresses than tanks conditioned at 1,100°F for 1-hr. Remaining residual stress levels could be about 10 ksi instead of about 5 Ksi. The 10 Ksi value was obtained using a 1,000°F temperature at 3-hr exposure in Fig. 3.45 [Percent relief of Initial Stress versus Stress Relieving Temperature] (Stout 1987), and the observation

that most steel Y.S. values are nominally higher than the minimum specified value. A higher-than-average Y.S. simply ensures that a higher level of residual stress is left because the figure is based on the percent relief of stress.

Second, to more correctly reflect the time-of-heating and time-of-cooling during a DST stress-relief, corrosion test specimens should have been stress-relieved for about 2-hr instead of 1-hr; this was based on calculations using the Larson-Miller (LM) parameter (Stout 1987).

Relief of residual stress is a parametrically controlled (time-at-temperature) phenomenon regulated by the LM parameter where the degree of "thermal effect" (Stout 1987) is,

$$\text{Thermal Effect} = T(\log t + 20)(10^{-3})$$

where, T = absolute temperature in degrees Rankine or Celsius, and,

t = time in hr.

Temperature has a far stronger effect on stress relief than time. For example at about 1,100°F, doubling the time would be equivalent to a temperature rise of about 23°F. Even so, allowing for regulated heat-up and cool-down times during a DST stress relief (HWS-8982 1970) the corrosion test specimens would have to be stress-relieved for a total of about 1.71, or essentially 2-hr. to obtain the same "thermal effect."

This differential probably made the tank wall metallurgically more SCC-sensitive than the unnotched laboratory test specimens used to assess SCC, even though the remaining weldment residual stress is nominally lower due to an effectively longer tank stress relief time.

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