**RAI: Volume 3, Chapter 2.2.1.3.1, Number 1:**

1. Describe the pretest specimen preparation procedure and the polished condition of the starting surfaces of the 2.5-year titanium Grade 7 and 42-day titanium Grades 7 and 29 test coupons.

2. Assess how the posttest specimen cleaning operations used in the 2.5-year and 42-day weight-loss experiments comply with the cleaning procedures given in ASTM G1-90, specifically with regard to the use of uncorroded control specimens and the uncertainly in the weight-loss data resulting from repetitive cleaning cycles as a function of the number of equal cleaning cycles. Provide the weight-loss data sets (e.g., DTN: LL030410012251.056 and MO0705SCCIGM06.000) used to calculate the corrosion rates for the general corrosion model.

3. Explain the effect of posttest sample cleaning uncertainty of the 2.5-year titanium Grade 7 coupons (uncertainty made evident by negative corrosion rates) on the positive titanium corrosion rate values used in the performance assessment. Justify the exclusion of negative corrosion rate values and the associated uncertainty of the 2.5-year titanium Grade 7 general corrosion rate values.

4. Verify that the experimental uncertainty in the 42-day data is less than the measured variability in the corrosion rates. Assess the need to propagate experimental uncertainty into the titanium Grade 29 to Grade 7 corrosion rate ratios.

***Basis:*** DOE relies on corrosion rates for titanium Grades 7 and 29 that are derived from weight-loss measurements based on analyses conducted in accordance with ASTM G1-90 (ASTM International, 1999; BSC, 2007a, Section 6.5.3). DOE has not adequately described experimental details that could lead to uncertainties in these rates; particularly, pretest sample preparation and posttest sample cleaning. DOE did not describe the pretest sample preparation procedure and the as-polished starting surface condition of the 2.5-year titanium Grade 7 crevice and weight-loss coupons - only the posttest sample cleaning operation. For posttest sample cleaning, BSC (2007a, Addendum, p. 6-7, 1st paragraph) states that the observed zero and negative corrosion rates for titanium Grade 7 are physically impossible and were probably caused by incomplete removal of the oxide films on the sample coupon surface during the posttest sample cleaning operations. However, BSC (2007a, Addendum, p. 1-1, 2nd paragraph) indicates more complete cleaning procedures were used for the 2.5-year titanium Grade 7 test coupons than for the 1-year titanium Grade 16 test coupons.

In constructing the titanium Grade 7 general corrosion rate distributions, DOE ignored the negative corrosion rate values. However, DOE did not explain how the posttest sample cleaning uncertainty associated with the 2.5-year titanium

Grade 7 coupons, indicated by weight gain reported in some samples, would affect corrosion rate estimates for other samples (not only those exhibiting weight gain). A technical basis is needed to explain why correcting the corrosion rate distribution was not considered for treating data indicating weight gains.

SAR Section 2.3.6.8 and BSC (2007a, Section 5.1.2) state that the general corrosion rates of titanium Grade 29 are estimated as the product of the general corrosion rate distribution of titanium Grade 7 for aggressive conditions and a multiplier distribution. This multiplier distribution function was derived from general corrosion rate ratios of titanium Grade 29 to Grade 7 from 42-day weight-loss data (BSC, 2007a, Section 6.2[a]). For the 42-day weight-loss tests of titanium Grades 7 and 29, DOE did not detail the pretest sample preparation and the posttest sample cleaning steps. In addition, DOE did not assess the experimental uncertainty from 42-day weight-loss measurements and its effects on the ratio estimates and corrosion rate.

The information above is needed to assess whether these data suitably demonstrate compliance with 10 CFR 63.21(c)(15) and 63.114(b).

# 1. RESPONSE

This RAI response is organized in direct relation to the four questions posed in the RAI.

## 1.1 PRE-TEST SPECIMEN PREPARATION METHODOLOGY FOR TITANIUM GRADE 7 AND 29 COUPONS

### 1.1.1 2.5-Year Exposure

The 2.5-year experiments were performed in the Long Term Corrosion Test Facility (LTCTF), which was located at Lawrence Livermore National Laboratory. Coupons were procured in the as-polished state from Metal Samples Corporation. The surface finish was specified to be equivalent to a 32 microinch (0.8 micron) surface finish (arithmetical mean roughness, Ra). Once machined, specimens were cleaned via a suitable solvent, and then placed in individual bags by the supplying vendor. Care was taken to prevent surface contamination due to handling once they had been cleaned. Coupons were stored in their individual bags until the time of use, when they were removed and placed on specimen racks. Inspection of the coupons upon removal from the LTCTF revealed that they have a unidirectional surface finish approximately equal to a 600-grit wet finish.

### 1.1.2 42-Day Exposure

The 42-day experiments were performed at GE Corporate Research and Development Lab. Prior to the start of each experiment, the coupons were mechanically polished to a 600-grit finish (polishing was performed wet). Once polished, coupons were cleaned ultrasonically in acetone, followed by ultrasonic cleaning in high purity water. The cleaned coupons were then placed into desiccators until the start of the experiment.

## 1.2 POST-TEST CLEANING/DESCALING METHODOLOGY FOR TITANIUM GRADES 7 AND 29 COUPONS

### 1.2.1 2.5-Year Exposure

Specimens taken from the LTCTF were cleaned using the same cleaning procedure established for Alloy 22 coupons. Specimens were cleaned a total of either 1 or 2 cycles. At that point, scanning electron microscopy (SEM) evaluation of the test coupons revealed no foreign deposits, and as such, the specimens were considered to be clean. The specifications in ASTM G1-90, *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*, do not provide any recommended cleaning solutions or procedures for titanium alloys. Given the corrosion resistance of Titanium Grade 7, it is unlikely that the cleaning solutions would result in readily measurable material removal. This and other technical concerns relative to the chemical descaling procedures used for the corrosion test coupons taken from the LTCTF are being evaluated within the corrective action program.

Recent experiments were performed to view the oxide layer present on the titanium surfaces in cross section. While the oxide on a portion of the coupons evaluated in this way was comparable to that observed on an unexposed control coupon, a thicker oxide was observed on others. Considering the oxide layer present, the corrosion rate presented in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007) may have underestimated the actual corrosion rate as the coupons may not have been completely descaled. A series of calculations were performed to estimate the oxide thickness if the corrosion rates presented in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007) were greater by a factor of 2, 3, or 4. The residual oxide thickness corresponding to each increased corrosion rate was calculated by using the maximum corrosion rate observed under aggressive conditions (from SNL 2007) and converting that depth of attack to an oxide thickness using a Pilling-Bedworth ratio of 1.73 for titanium. Based upon those calculations, if the corrosion rate were a factor of two greater, the oxide remaining on the coupon surface should be 200-nm thick, if it were a factor of three greater, 400-nm thick, and for a factor of four greater, 600 nm. Based upon the cross-sectional analyses, the vast majority of the thicker oxide regions were less than or equal to 200 nm, thus indicating that the corrosion rate was understated by at most a factor of two. An uncertainty analysis was performed to establish the implications of higher general corrosion rates on the functional performance of the drip shields, as well as the impact on the expected annual dose in the seismic ground motion modeling case. That analysis, presented in its entirety in the response to RAI 3.2.2.1.3.1-005, demonstrated that an increase in the general corrosion rate of Titanium Grade 7 by as much as a factor of four would not significantly affect the long term performance of the repository.

### 1.2.2 42-Day Exposure

Once the specimens were removed from the test solution, they were cleaned ultrasonically in acetone for 5 minutes, then ultrasonically in high purity water for 5 minutes. The two steps were repeated a total of three times. At the completion of the cleaning process, the coupons were evaluated via a combination of light microscopy and transmission electron microscopy (TEM) to verify that the surfaces were devoid of any oxide particles or other contamination. Once visually

verified to be clean, each coupon was weighed, and the value recorded. As no chemical cleaning steps were involved, the recommended practices in ASTM G1-90 do not apply.

### 1.2.3 Disposition of Requested Data

The two DTNs that were requested – LL030410012251.056 and MO0705SCCIGM06.000 – will be provided as enclosures along with this response. It should be noted that, as a result of the concerns regarding the validity of these data, the use of both files has been restricted to limit any analyses performed utilizing them.

## 1.3 EVALUATION OF CLEANING UNCERTAINTY FOR 2.5-YEAR TITANIUM GRADE 7 COUPONS

As discussed in Section 6.1.3[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007), following the cleaning of the 2.5-year Titanium Grade 7 coupons from the LTCTF, all of the data from coupons that had a net weight gain (which would translate into a negative corrosion rate) were removed from further use in the analysis. The rationale behind the rejection of these data was that non-positive corrosion rates were not physically meaningful. There are several possible explanations for these results. First, it could be that the specimens were insufficiently cleaned, and that corrosion product was still present on the specimen surface. If the corrosion product was not sufficiently removed, then the resulting corrosion rates would underestimate the true corrosion rate.

A second potential explanation is that the technique utilized to weigh the coupons introduced significant uncertainty into the measurements. Looking at the data, the coupons that underwent a weight increase had values ranging from 100 to 300 micrograms for the weight loss coupons, and 100 to 700 micrograms for the crevice coupons (DTN: LL030410012251.056). As the balance used to make these measurements was a four place balance, they represent values in the lowest readable digit on the balance. Furthermore, these measurements were not made using a single substitution method, or other technique designed to address changes in environmental conditions and laboratory balance drift. If experimental uncertainty were proven to be the source of the error, then there would be a probability that weights were over-estimated as well, complicating interpretation of the data.

Because determination of the actual cause or causes of the negative corrosion rates is not readily achievable, more detailed analysis of the coupons was performed. As discussed in Section 1.2.1 of this response, analyses were performed to view and measure the oxide layer present on the titanium surfaces in cross section that indicate a maximum understatement of approximately two, and a sensitivity analysis, presented in its entirety in the response to RAI 3.2.2.1.3.1-005, demonstrated that an increase in the general corrosion rate of Titanium Grade 7 by as much as a factor of four would not significantly affect the long term performance of the repository.

## 1.4 EVALUATION OF EXPERIMENTAL UNCERTAINTY FOR 42-DAY TITANIUM GRADES 7 AND 29 COUPONS AND THE ASSOCIATED CORROSION RATE RATIO

In Section 6.2.2[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007), the method used to estimate the general corrosion rate of Titanium Grade 29 from the corrosion rate of Titanium Grade 7 is presented. However, recent re-evaluation of the titanium corrosion rate data used to develop these conversion factors has shown that the variations in the data are dominated by experimental uncertainty, and as such, cannot be used to derive a conversion factor between Titanium Grades 7 and 29. This issue is currently being evaluated within the corrective action program.

The basis for the factor used to convert the corrosion rate is a series of 42-day corrosion experiments for Titanium Grades 7 and 29 (see Table 13 in Andresen and Kim 2006). In these experiments, the corrosion rates were calculated based upon the weight change for each coupon. The measured weight changes used in these calculations ranged from 10 to 80 micrograms. The mass change measurements were all made using a 5-place balance with a manufacturer stated repeatability of 20 micrograms (1 standard deviation) and a linearity of 30 micrograms. Based upon these values, it is likely that measurements made with this balance have an uncertainty larger than the majority of the weight change values. Inspection of the data reveals no clear trends between the two materials in any of the environments. As such, it appears that the response observed in the 42-day weight-loss testing is due entirely to uncertainty. Thus, it must be concluded that either the weight change signal is below the noise level of the instrument, and/or the test is unable to distinguish between the two materials.

The corrosion rates for Titanium Grades 7 and 29 at 42 days were also determined via electrochemical impedance spectroscopy and linear polarization resistance (Andresen and Kim 2006, Table 13). The results of both electrochemical tests were nominally identical for the two materials, suggesting that the experiments were not able to distinguish between the corrosion rates of the two materials. These results support the conclusion that under the conditions in which the two materials were evaluated, their corrosion behavior is the same and, as such, no conversion factor is necessary or justified – in other words, under the conditions evaluated here, the corrosion rate of Titanium Grade 7 is essentially identical to that of Titanium Grade 29. Such a conclusion is also supported by results presented in the literature (Schutz 2005; replotted as Figure 6-22[a] in SNL 2007), which illustrates that while Titanium Grades 7 and 29 differ in performance in highly acidic chloride solutions (pH < 1), as the conditions become more benign, the corrosion rates observed for the various titanium alloys become indistinguishable from one another.

Based upon the above analysis, two statements can be made: first, the 42-day titanium corrosion rate data presented in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007) are dominated by experimental uncertainty and, as such, cannot be used to derive a conversion factor between Titanium Grades 7 and 29; and second, that for conditions of relevance to the repository, based upon the results from electrochemical techniques, the corrosion behavior of the aforementioned titanium alloys is nominally identical (i.e., no conversion factor is needed). As such, the ratio of the general corrosion rates of Titanium

Grade 29 to Titanium Grade 7 is effectively 1 to 1. A discussion of the impact of this change is presented in the response to RAI 3.2.2.1.3.1-002 and will not be repeated here.

## 2. COMMITMENTS TO NRC

The DOE will revise Sections 6.1[a] and 8.1[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007), as well as SAR Sections 2.3.6.8.1.3 and 2.3.6.8.1.5, Figures 2.3.6-44, 2.3.6-45, 2.3.6-46, 2.3.6-48, and 2.3.6-49, and Tables 2.3.6-24 and 2.3.6-25, to reflect the uncertainty of Titanium Grade 7 cleaning and remaining oxides. DOE will document in these revisions that this change does not significantly affect the estimated repository performance. The change to be made to the license application will be included in a future license application update.

## 3. DESCRIPTION OF PROPOSED LA CHANGE

Discussion of the uncertainty associated with Titanium Grade 7 corrosion rates will be revised in SAR Sections 2.3.6.8.1.3 and 2.3.6.8.1.5, Figures 2.3.6-44, 2.3.6-45, 2.3.6-46, 2.3.6-48, and 2.3.6-49, and Table 2.3.6-24 and 2.3.6-25 in a future update to the license application.

## 4. REFERENCES

Andresen, P.L. and Kim, Y.J. 2006. *Stress Corrosion Crack Initiation & Growth Measurements in Environments Relevant to High Level Nuclear Waste Packages.* Report Number: GE-GRC-Bechtel-2006-2. Niskayuna, New York: General Electric Global Research Center. ACC: MOL.20061109.0070; MOL.20061108.0004. (Included in Enclosure 6.)

ASTM G1-81. 1987. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.* Philadelphia, Pennsylvania: American Society for Testing and Materials.

LL030410012251.056. LTCTF Corrosion Rate Calculations for 2 1/2 - Year Exposed Titanium Alloy GR7 Specimens Cleaned Under TIP-CM-51. Submittal date: 07/16/2003. (Provided as Enclosure 7.)

MO0705SCCIGM06.000. Final Report for FY06: Stress Corrosion Crack Initiation & Growth Measurements in Environments Relevant to High Level Nuclear Waste Packages. Submittal date: 05/14/2007. (Provided as Enclosure 6.)

Schutz, R.W. 2005. *Corrosion of Titanium and Titanium Alloys*. ASM Handbook Vol. 13B Corrosion: Materials. Materials Park, Ohio: ASM International.

SNL (Sandia National Laboratories) 2007. *General Corrosion and Localized Corrosion of the Drip Shield*. ANL–EBS–MD–000004 REV 02 AD 01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20060427.0002; DOC.20070807.0004; DOC.20071003.0019; LLR.20080423.0006.

**RAI: Volume 3, Chapter 2.2.1.3.1, Number 2:**

*Part 1:* Provide a technical basis to support the extrapolation of general corrosion rate ratios (developed from 42-day weight-loss test data) of titanium Grade 29 to Grade 7 to the repository performance period, given the metallurgical differences between the two metals.

*Part 2:* Explain how uncertainty resulting from different metallurgical compositions in titanium Grades 7 and 29 is propagated through the performance assessment.

***Basis***: DOE modeled the corrosion behavior of titanium Grade 29 in terms of the comparative behavior of titanium Grade 29 vs. Grade 7 (SNL, 2007, Section 6.2[a]). This approach assumes the passive film characteristics of these materials remain unchanged with time and are independent of the allotropic content of the parent metal. However, titanium Grade 7 is a palladium-containing single α-phase material and titanium Grade 29 is an aluminum-, vanadium-, ruthenium-containing α+β phase material. DOE did not provide a technical basis to determine whether these differences in chemical composition and phase structure could result in long-term changes in passive film characteristics; these changes could affect the general corrosion rate ratio of titanium Grade 29 to Grade 7 over long periods of time (i.e., representative of the repository performance period). This information is needed to assess whether titanium Grade 29 general corrosion rate data, derived from 42-day experiments and used in the performance assessment, suitably demonstrate compliance with 10 CFR 63.21(c)(15) and 63.114(b).

## 1. RESPONSE

In Section 6.2.2[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a), the method used to estimate the general corrosion rate of Titanium Grade 29 from the corrosion rate of Titanium Grade 7 is presented. However, recent re-evaluation of the titanium corrosion rate data used to develop these conversion factors has shown that the variations in the data are dominated by experimental uncertainty, and as such, cannot be used to derive a conversion factor between Titanium Grade 7 and Titanium Grade 29. The issue is being addressed through the corrective action program. As demonstrated in this response, modeling Titanium Grades 7 and 29 general corrosion rates as equal (rather than as related by the rate ratio) does not affect the results of the performance assessment.

The DOE commits to updating SAR Sections 2.3.6.8.1.3 and 2.3.6.8.1.5 and Figure 2.3.6-48, to remove the general corrosion rate ratio between Titanium Grades 7 and 29. Appropriate revisions will be made to rewrite/update Sections 6.2[a] and 8.1[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a).

## 1.1 USE AND ADEQUACY OF CORROSION RATE CONVERSION RATIOS

The basis for the factor used to convert the corrosion rate is a series of 42-day corrosion experiments for Titanium Grades 7 and 29. In these experiments, the corrosion rates were calculated based upon the weight change for each coupon. The measured weight changes used in these calculations ranged from 10 to 80 micrograms. The mass change measurements were all made using a 5-place balance with a manufacturer stated repeatability of 20 micrograms (1 standard deviation) and a linearity of 30 micrograms. Based upon these values, it is likely that measurements made with this balance have an uncertainty larger than the majority of the weight change values. Inspection of the data reveals no clear trends between the two materials in any of the environments. As such, it appears that the response observed in the 42-day weight loss testing is due entirely to uncertainty. Thus, it must be concluded that either the weight change signal is below the precision and accuracy (e.g., noise level) of the instrument, and/or the test is unable to distinguish between the two materials.

The corrosion rates for Titanium Grades 7 and 29 at 42 days were also determined via electrochemical impedance spectroscopy and linear polarization resistance. The results of the both electrochemical tests were nominally identical for the two materials, suggesting that the experiments were not able to distinguish between the corrosion rates of the two materials. One conclusion which could be drawn from these results is that under the conditions in which the two materials were evaluated, their corrosion behavior is the same and, as such, no conversion factor is necessary or justified – in other words, under the conditions evaluated here, the corrosion rate of Titanium Grade 7 is essentially identical to that of Titanium Grade 29. This conclusion is also supported by results presented in the literature (Figure 20 in Schutz 2005; Figure 6-22[a] in SNL 2007a), which illustrates that while Titanium Grades 7 and 29 differ in performance in highly acidic chloride solutions (pH <1), as the conditions become more benign, the corrosion rates observed for the various titanium alloys become indistinguishable from one another.

Based upon the above analysis, two statements can be made: first, the 42-day titanium corrosion rate data presented in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a) are dominated by experimental uncertainty and, as such, cannot be used to derive a conversion factor between Titanium Grade 7 and 29; and second, that for conditions of relevance to the repository, based upon the results from electrochemical techniques, the corrosion behavior of the aforementioned titanium alloys is nominally identical (i.e., no conversion factor is needed). As such, the ratio of the general corrosion rates of Titanium Grade 29 to Titanium Grade 7 is effectively 1 to 1, rather than up to approximately 7 to 1 as presented in SAR Figure 2.3.6-48. The impact of this change is discussed in Section 1.3.

## 1.2 IMPACT OF VARYING ALLOY COMPOSITION ON LONG TERM PROPERTIES

While the general corrosion rate of various titanium alloys has been observed to be a function of material composition in aggressive environments, such as low pH, high chloride conditions, it becomes increasingly difficult to resolve a difference between the materials for more benign conditions. This is clearly demonstrated by Schutz (2005, Figure 20) in boiling, aerated hydrochloric acid solutions of varying concentration. In that study, it is demonstrated that it is

not possible to distinguish between Titanium Grades 7, 28, or 29 at a concentration of ~0.5 wt % HCl (corresponding to a pH value slightly below 1) (SNL 2007a). As such, the treatment of general corrosion by the Project can be concluded to effectively capture the impact that material composition or microstructure might have.

As has been demonstrated for many passive materials, including titanium, the general corrosion rate decreases with time. However, the models for general corrosion use constant rates of general corrosion that are based on the weight loss observed over the first 2.5 years of exposure, rather than time-varying corrosion rates. Effectively, the models assume that the passive film breaks down or spalls off completely and a new material surface is introduced every 2.5 years. Thus, the models do not take credit for the fact that the general corrosion rate will decrease with time over the entire repository performance period, but rather, offer a highly conservative constant value for the corrosion rate based on short-term, 2.5-year test duration data.

## 1.3 EFFECT OF UNCERTAINTY IN THE RATIO OF GENERAL CORROSION RATES ON PERFORMANCE ASSESSMENT

In the performance assessment conducted for the license application, the ratio of general corrosion rates between Titanium Grades 29 and 7 was treated as uncertain and was modeled by the discrete distribution described in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a, Table 6-8[a]), ranging between ratios of 1 to 6.6786. As discussed in Section 1.1, it would be more appropriate to model general corrosion rates as equal for both grades of titanium. As demonstrated by analyses presented here, modeling corrosion of Titanium Grade 29 as equal to corrosion of Titanium Grade 7 (rather than potentially faster than corrosion of Titanium Grade 7) has a negligible effect on the results of the performance assessment for the license application.

Uncertainty in the general corrosion rate of Titanium Grade 29 only affects the outcome of the seismic ground motion modeling case for 1,000,000 years postclosure in the total system performance assessment. In all other modeling cases, the drip shield diverts seepage until failure of the Titanium Grade 7 components occurs via general corrosion (i.e., in the waste package early failure modeling cases), or until the occurrence of an event which compromises the drip shield (i.e., an early drip shield failure, an igneous intrusion, or a seismic fault displacement). In the seismic ground motion modeling case, drip shield framework failure is not considered for the first 10,000 years post-closure, as justified in *Total System Performance Assessment Model/Analysis for the License Application* (SNL 2008, Section 7.3.2.6.1.3.3). The justification for not considering drip shield framework failure in the 10,000-year analysis does not depend on the rates of general corrosion of drip shield materials, and thus not considering such failure is still justified when the ratio of the general corrosion rates of Titanium Grade 29 to Titanium Grade 7 is effectively 1 to 1, rather than up to ~7 to 1. Thus, uncertainty in the general corrosion rate of Titanium Grade 29 only affects the outcome of the seismic ground motion modeling case for 1,000,000 years postclosure.

Sensitivity analyses performed with the results of the seismic ground motion modeling case for 1,000,000 years postclosure indicate the effect of uncertainty in the general corrosion rate of Titanium Grade 29. In these analyses, regressions were performed between uncertainty in

expected annual dose to the RMEI (where the expectation averages over uncertainty in the occurrence and extent of seismic events) and uncertainty in model parameters (including the ratio of general corrosion rates for Titanium Grade 29 to Grade 7) to determine the relative influence of uncertain parameters on uncertainty in the model results. The sensitivity analyses are reported in *Total System Performance Assessment Model/Analysis for the License Application* (SNL 2008, Section K7.7.2[a]). In particular, a stepwise regression analysis performed at 200,000 years indicated a negative correlation between *EXPDOSE* (expected annual dose to the RMEI) and *WDDSGC29* (the ratio of general corrosion rates between Titanium Grade 29 to Grade 7), although the correlation is not strong (standardized rank regression coefficient (SRRC) = –0.18) and is eclipsed by a relatively strong correlation between *EXPDOSE* and *SCCTHRP* (uncertainty in stress corrosion cracking threshold for Alloy 22; SRRC = –0.72). Stepwise regression results performed at additional times are reported in Table 1; descriptions of the relevant independent variables are given in Table 2. Between 80,000 and 300,000 years postclosure, the relatively weak, negative correlation between *EXPDOSE* and *WDDSGC29* indicates that decreasing the ratio of general corrosion rate for Titanium Grade 29 relative to Grade 7 would result in an increase in the expected annual dose to the RMEI, although the increase is small (as demonstrated by the impact assessment presented below). Before 80,000 and after 300,000 years, *WDDSGC29* does not appear in the stepwise regressions for *EXPDOSE*.

Table 1. Stepwise Rank Regressions for *EXPDOSE* at Various Times

| | 80,000 years | | | 120,000 years | | | 160,000 years | | |
|---|---|---|---|---|---|---|---|---|---|
| **Step [a]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** |
| 1 | SCCTHRP | 0.66 | –0.81 | SCCTHRP | 0.60 | –0.77 | SCCTHRP | 0.60 | –0.75 |
| 2 | WDDSGC29 | 0.68 | –0.11 | WDDSGC29 | 0.64 | –0.19 | WDDSGC29 | 0.64 | –0.23 |
| 3 | EP1LOWPU | 0.70 | 0.12 | MICTC99 | 0.67 | 0.12 | SZGWSPDM | 0.65 | 0.10 |
| 4 | DSNFMASS | 0.72 | 0.12 | EP1LOWPU | 0.68 | 0.11 | EP1NPO2 | 0.66 | 0.09 |
| 5 | SZKDSEVO | 0.73 | –0.09 | DSNFMASS | 0.69 | 0.10 | RHI85 | 0.66 | –0.10 |
| 6 | MICTC99 | 0.73 | 0.10 | HLWDRACD | 0.69 | 0.10 | CSNFMASS | 0.67 | 0.10 |
| 7 | HLWDRACD | 0.74 | 0.10 | EP1NPO2 | 0.70 | 0.10 | | | |
| 8 | SZLODISP | 0.74 | –0.10 | MICSE79 | 0.70 | 0.10 | | | |
| | **200,000 years** | | | **240,000 years** | | | **300,000 years** | | |
| **Step [a]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** | **Variable [b]** | **$R^2$ [c]** | **SRRC [d]** |
| 1 | SCCTHRP | 0.54 | –0.72 | SCCTHRP | 0.42 | –0.60 | SCCTHRP | 0.35 | –0.57 |
| 2 | WDDSGC29 | 0.58 | –0.18 | WDGCA22 | 0.49 | –0.25 | WDGCA22 | 0.49 | –0.37 |
| 3 | WDGCA22 | 0.60 | –0.14 | WDDSGC29 | 0.51 | –0.18 | WDDSGC29 | 0.51 | –0.13 |
| 4 | DSNFMASS | 0.61 | –0.11 | CSWFA4AC | 0.52 | –0.12 | CPUPERWF | 0.52 | 0.11 |
| 5 | CSNFMASS | 0.62 | –0.10 | COLU | 0.53 | 0.11 | | | |
| 6 | | | | FHHISKCP | 0.54 | –0.10 | | | |

[a] Steps in stepwise rank regression analysis.
[b] Variables listed in order of selection in stepwise regression.
[c] Cumulative $R^2$ value with entry of each variable into regression model.
[d] Standardized rank regression coefficients (SRRCs) in final regression model.

The negative correlation between *EXPDOSE* and *WDDSGC29* results from the abstractions for waste package damage from seismic events, which in turn depend on the state of the drip shield framework. As summarized in *Total System Performance Assessment Model/Analysis for the License Application* (SNL 2008, Section 7.3.2.6.1.3.3), the probability of damage to codisposal waste packages from a seismic event decreases significantly after failure of the drip shield framework. After the drip shield framework buckles or collapses, the drip shield may be resting on top of the waste packages. In the models for estimating damage to waste packages from seismic ground motion, after drip shield framework failure the drip shield acts to constrain movement of the waste packages (SNL 2007b, Section 6.8.4), thereby significantly reducing the occurrence of damage to co-disposal waste packages. After drip shield framework failure, the probability of damage to commercial SNF waste packages increases moderately but remains quite low. Additional information about these probabilities of damage is provided in the DOE response to RAI 3.2.2.1.3.1-5. The net effect of more rapid corrosion of Titanium Grade 29 (higher values of *WDDSGC29*) is earlier failure of the drip shield framework, which in turn reduces the likelihood of seismic damage to codisposal waste packages, which decreases the expected annual dose to the RMEI (lower values of *EXPDOSE*).

## 1.4 IMPACT ASSESSMENT FOR EQUAL RATES OF GENERAL CORROSION RATES

Section 1.1 concludes that it would be more appropriate to model general corrosion rates as equal for both grades of titanium. Based on the sensitivity analyses presented above, modeling corrosion rates as equal may result in an increase in expected annual dose in the seismic ground motion modeling case between about 80,000 and 300,000 years postclosure, as indicated by the sensitivity analysis results. To quantify the potential increase in the expected annual dose that results from modeling titanium corrosion rates as equal for both grades, an impact assessment was performed with the TSPA-LA model. In the impact assessment, the general corrosion rate of Titanium Grade 29 was set equal to that of Titanium Grade 7. No other change to the TSPA-LA model or its input data was made for the impact assessment.

Figure 1 compares the distribution of the time of drip shield framework failure between the TSPA-LA base case and the alternate case in which the general corrosion rate of Titanium Grade 29 was set equal to that of Titanium Grade 7. Figure 1 shows that framework failure occurs later in the alternate case due to the slower rate of general corrosion. Figure 2 compares the distribution of expected annual dose for the seismic ground motion modeling case for the two cases. Despite the change in time of drip shield framework failure, the timing and magnitude of expected annual dose for each realization, and the range of uncertainty among realizations, are similar for both cases. Figure 3 compares statistics for the distribution of expected annual dose between the two cases. Except for slight increases between 80,000 and 160,000 years postclosure, the mean annual dose is essentially unchanged between the base case and the alternate case. Between about 80,000 and 300,000 years postclosure, the median annual dose is roughly 25% greater in the alternate case than in the base case; slight increases are also observed in the 5th percentile. These increases are due to the increased likelihood of seismic damage to waste packages, as described above. However, the relatively small contribution of the seismic ground motion modeling case to total mean annual dose during these time periods (SAR Figure 2.4-18b) confirms that modeling titanium corrosion rates as equal for

both grades has a negligible effect on the results of the performance assessment for the license application.

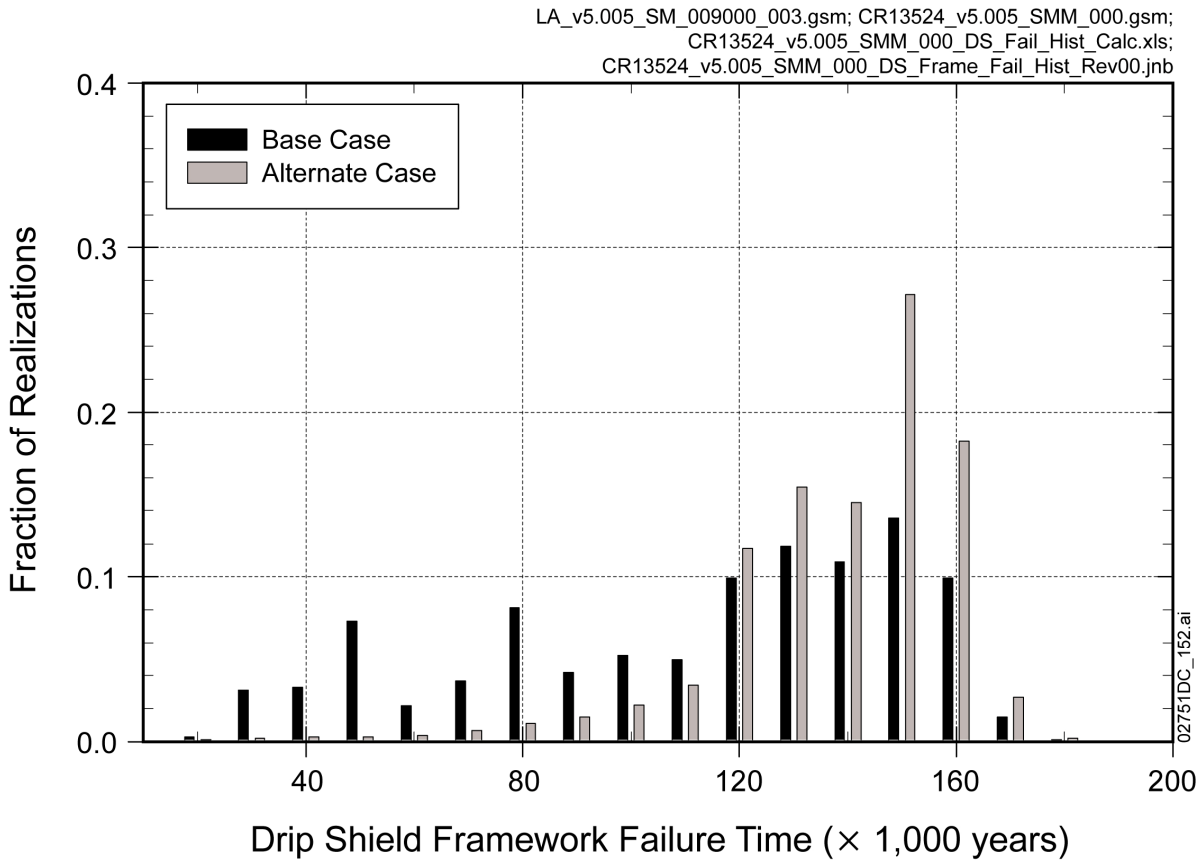


Figure 1. Drip Shield Framework Failure Times for the TSPA-LA Base Case and the Alternate Case

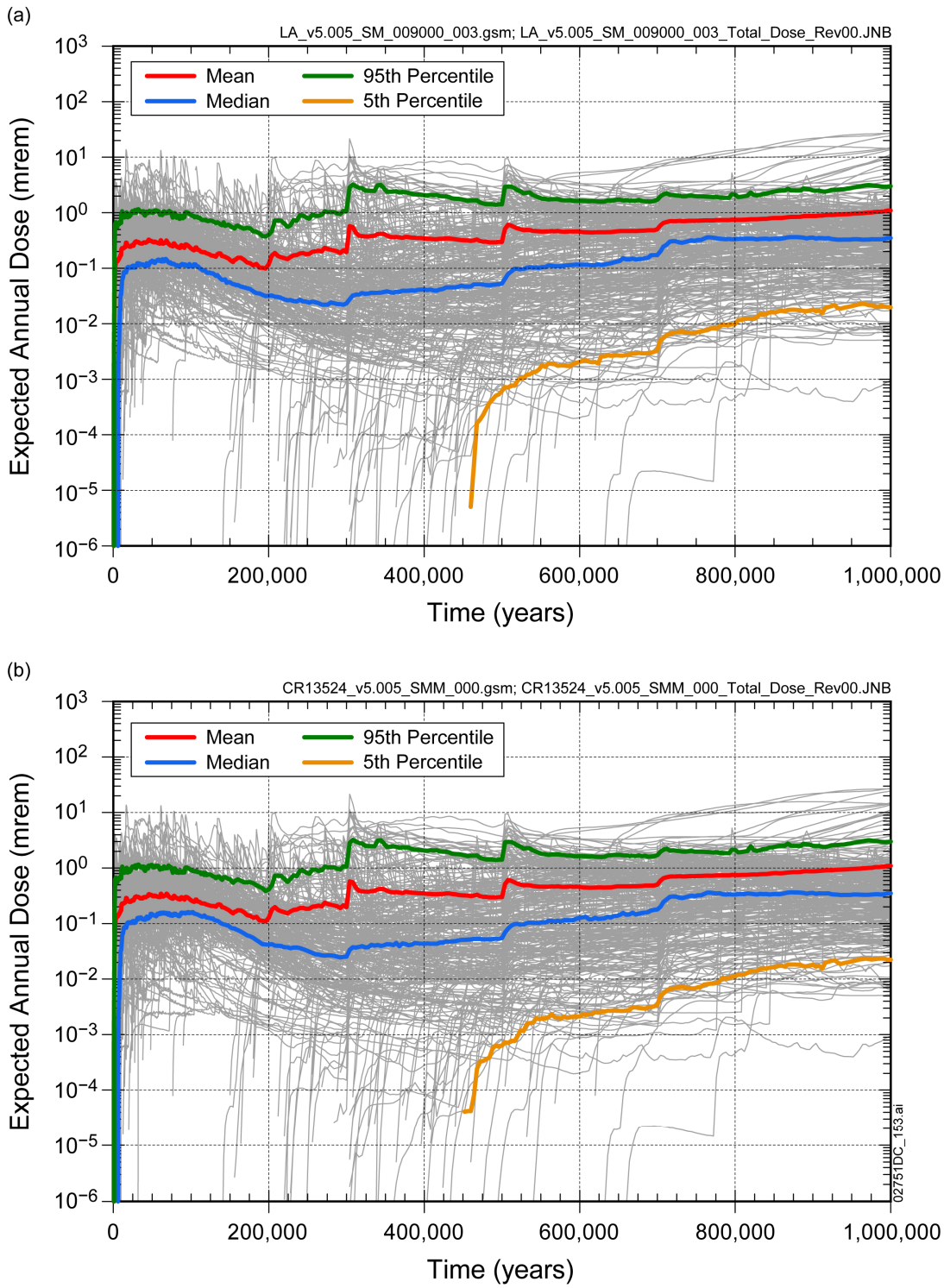


Figure 2. Distribution of Expected Annual Dose in the Seismic Ground Motion Modeling Case for (a) TSPA-LA Base Case and (b) Alternate Case

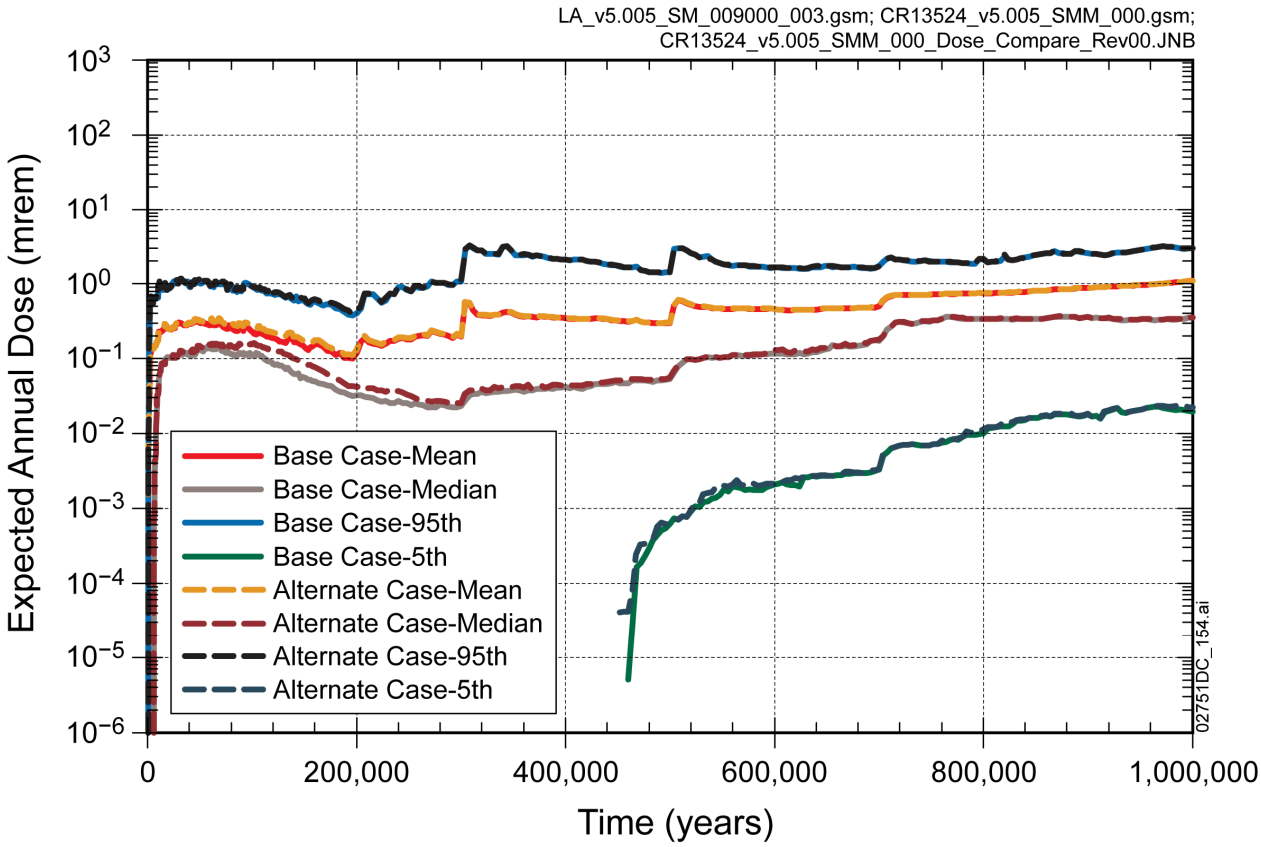


Figure 3. Comparison of Statistics for the Distribution of Expected Annual Dose in the Seismic Ground Motion Modeling Case for the TSPA-LA Base Case and the Alternate Case

Table 2. Independent Variables Identified in Stepwise Rank Regressions for Expected Dose (*EXPDOSE*)

| Variable | Description |
|---|---|
| COLU | Concentration of uranophane colloids when colloids are stable (mg/L) |
| CPUPERWF | Concentration of irreversibly attached plutonium on glass/waste form colloids when colloids are stable (mol/L) |
| CSNFMASS | Scale factor used to characterize uncertainty in radionuclide content of CSNF (dimensionless) |
| CSWFA4AC | Correlated coefficient a4 in the abstracted rate model for CSNF degradation under acid conditions (dimensionless) |
| DSNFMASS | Scale factor used to characterize uncertainty in radionuclide content of DSNF (dimensionless) |
| EP1LOWPU | Logarithm of the scale factor used to characterize uncertainty in plutonium solubility at an ionic strength below 1 molal (dimensionless) |
| EP1NPO2 | Logarithm of the scale factor used to characterize uncertainty in $NpO_2$ solubility at an ionic strength below 1 molal (dimensionless) |
| FHHISKCP | Frenkel Halsey Hill water vapor adsorption isotherm parameter, *k*, for corrosion products (dimensionless) |
| HLWDRACD | Effective rate coefficient (affinity term) for the dissolution of HLW glass in CDSP waste packages under low pH conditions ($g/(m^2d)$) |
| MICSE79 | Groundwater BDCF for $^{79}Se$ in modern interglacial climate ($(Sv/yr)/(Bq/m^3)$) |
| MICTC99 | Groundwater BDCF for $^{99}Tc$ in modern interglacial climate ($(Sv/yr)/(Bq/m^3)$) |
| RHI85 | Uncertainty factor in the IDPS process model for the logarithm of the ionic strength of the in-drift waters at high relative humidity (≥85%) (log molal) |
| SCCTHRP | Residual stress threshold for SCC nucleation of Alloy 22 (as a percentage of yield strength in MPa) (dimensionless) |
| SZGWSPDM | Logarithm of the scale factor used to characterize uncertainty in groundwater specific discharge (dimensionless) |
| SZKDSEVO | Selenium sorption coefficient in volcanic units (mL/g) |
| SZLODISP | Logarithm of longitudinal dispersivity (m) in the saturated zone |
| WDDSGC29 | General corrosion rate ratio for drip shield support material (ratio of Titanium Grade 29 to Titanium Grade 7) |
| WDGCA22 | Temperature dependent slope term of Alloy 22 general corrosion rate (K) |

NOTE: BDCF = Biosphere Dose Conversion Factor; CDSP = co-disposal; CSNF = commercial spent nuclear fuel; DSNF = DOE spent nuclear fuel; HLW = high-level (radioactive) waste; IDPS = in-drift precipitates/salts; SCC = stress corrosion cracking.

## 2. COMMITMENTS TO NRC

The DOE commits to rewrite/update Sections 6.2[a] and 8.1[a] of *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a), as well as all impacted SAR Sections including 2.3.6.2.3, 2.3.6.8.1.3, 2.3.6.8.1.5, and 2.4.2.3.2.1.5 and all impacted tables and figures, including Table 2.3.6-2 and Figure 2.3.6-48, to reflect removal of the rate ratio between Titanium Grades 7 and 29. The DOE will document that this change does not impact the estimated repository performance. The changes to the license application will be made in a future license application update.

## 3. DESCRIPTION OF PROPOSED LA CHANGE

Discussion of the rate ratio between Titanium Grades 7 and 29 will be removed from all impacted SAR Sections including 2.3.6.2.3, 2.3.6.8.1.3, 2.3.6.8.1.5, and 2.4.2.3.2.1.5 and all impacted tables and figures, including Table 2.3.6-2 and Figure 2.3.6-48. A discussion will be added to illustrate that the general corrosion rate for these two materials is nominally identical under repository relevant environmental conditions.

## 4. REFERENCES

SNL (Sandia National Laboratories) 2007a. *General Corrosion and Localized Corrosion of the Drip Shield*. ANL–EBS–MD–000004 REV 02 AD 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20060427.0002; DOC.20070807.0004; DOC.20071003.0019; LLR.20080423.0006.

SNL 2007b. *Seismic Consequence Abstraction*. MDL-WIS-PA-000003 REV 03. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070928.0011; LLR.20080414.0012.

SNL 2008. *Total System Performance Assessment Model/Analysis for the License Application*. MDL–WIS-PA–000005 REV 00 AD01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20080312.0001; LLR.20080414.0037; LLR.20080507.0002; LLR.20080522.0113.

Schutz, R.W. 2005. "Corrosion of Titanium and Titanium Alloys." *ASM Handbook* Vol. 13B, Corrosion: Materials. Materials Park, Ohio: ASM International.

**RAI: Volume 3, Chapter 2.2.1.3.1, Number 3:**

Assess the significance of available information that indicates a potential temperature dependence of general corrosion rates for titanium Grades 7 and 29, including welds.

**Basis**: The drip shield general corrosion rate, as described in SAR Section 2.3.6.8, is assumed to be independent of temperature. However, Hua and Gordon (2004) indicated that, between 50 and 110 °C, the general corrosion rate for titanium Grade 7 was a function of temperature and the general corrosion rate increased faster at temperatures greater than 80 °C. Hua and Gordon (2004) also found that the oxide films formed around 80 °C are different from the oxide films formed at lower and higher temperatures. He, et al. (2007) showed that for temperatures greater than 70 °C, titanium oxide film fracture and repair events could be relatively frequent for titanium Grade 7, which would lead to corrosion at the grain boundaries of the alloy. Zhu, et al. (2007) demonstrated that thermal effects on titanium corrosion processes are associated with the formation of iron-stabilized phases in the grain boundaries of the alloy. Information in these investigations appears to contradict the DOE modeling assumption of temperature independence for titanium corrosion rates. Potential temperature effects on titanium corrosion must be resolved to support the performance assessment used to demonstrate compliance with 10 CFR 63.114(f).

## 1. RESPONSE

While a temperature dependence of the general corrosion rate is observed for very short exposure periods, such as the results presented by Hua and Gordon (2004), this variation decreases in magnitude with time, effectively vanishing for extended time periods. As such, when evaluating the corrosion behavior of a structure during the postclosure period of performance, it is appropriate to consider the general corrosion rate to be temperature independent for titanium.

The drip shield will be fabricated from Titanium Grade 7 plates, Titanium Grade 29 structural supports, and Alloy 22 base plates. Welds will be made between adjacent Titanium Grade 7 plates, between the Titanium Grade 7 plates and Titanium Grade 29 structural supports, and between adjacent Titanium Grade 29 structural support members. The weld between Titanium Grade 29 and Titanium Grade 7, will be Titanium Grade 28 (SAR Table 1.9-9). Titanium Grade 28 is essentially Titanium Grade 9 (Ti – 3Al – 2.5V) with the addition of ruthenium. The other weldments are of a nominally identical composition.

In the study by He et al. (2007), the open circuit potential of Titanium Grade 7 coupons exposed to an 0.27 M NaCl solution at temperatures from 25°C to 150°C was monitored. In that study, it was found that increases in temperature brought about a series of transients in the open circuit potential whose number and magnitude increased with increasing temperature. However, the study also demonstrated that these transients were short lived, and that the material repassivated and/or stabilized with time. It was speculated that the transients were related to dissolution events which may have taken place in iron rich beta-phase regions or on $Ti_xFe$ precipitates in the

material. The assertion that the metastable events likely took place at such iron rich regions was reinforced by the results for Titanium Grade 2 (Titanium Grade 7 is essentially Titanium Grade 2 plus palladium, the addition of which renders it far more corrosion resistant) presented by Zhu et al. (2007). In that study, scanning electrochemical microscopy (SECM) was used to identify the location of the active regions, and the authors proposed that their results indicated iron rich regions on the grain boundaries. It should be noted that Zhu et al. (2007) did not explore the effect of temperature.

In the study by Hua and Gordon (2004), Titanium Grade 7 coupons were exposed to basic saturated water (BSW) for time periods of 4 and 8 weeks. The general corrosion rates, as well as the oxide thicknesses, were observed to generally increase with increasing temperature. However, when comparing the results from the 4 and 8 week exposures, the magnitude of the increase with temperature (i.e., the sensitivity of the general corrosion rate to temperature), as well as the overall corrosion rate, decreased. While only two time periods were presented in this paper, they do illustrate the decrease in temperature dependence with time.

The most definitive evidence that any difference in corrosion rate due to variations in temperature will be short lived is presented by Smailos et al. (see Figure 1 in Smailos et al. 1987). In that study, a material compositionally identical to Titanium Grade 7 was evaluated in Q brine (a pH 4.9 chloride-sulfate brine) at temperatures ranging from 90°C to 200°C for a period of over 1,200 days. Initially, the observed general corrosion rate was impacted by temperature. However, after less than 3 years, the rates observed from 90°C to 200°C were significantly lower in magnitude than at the start of the experiment, and more importantly, were indistinguishable from one another.

While the general corrosion rate of various titanium alloys has been observed to be a function of material composition in aggressive environments, such as low pH, high chloride conditions, it becomes increasingly difficult to resolve a difference between the materials for more benign conditions. This is clearly demonstrated by Schutz (see Figure 20 in Schutz 2005) in boiling, aerated hydrochloric acid solutions of varying concentration. In that study, the corrosion rates were indistinguishable between Titanium Grades 7, 28, or 29 at a concentration of 0.5 wt % HCl (corresponding to a pH of slightly below 1). As such, for the environments of relevance to the drip shields during the postclosure period of performance (pH range from approximately 4 to approximately 11.5; SNL 2007, Figures 6.13-5 through 6.13-8), it is reasonable to conclude that the general corrosion rate of Titanium Grade 7 is nominally identical to that of Titanium Grade 29 or of the dissimilar metal weldments made between the two, which will be nominally Titanium Grade 28.

To summarize, while the general corrosion rate does appear to have a temperature dependence for short exposure times (e.g., results in Hua and Gordon 2004), at longer times no such dependence can be distinguished (e.g., results in Smailos et al. 1987). Thus, in assessing the general corrosion rate of the drip shields (including the weldments) during the postclosure period of performance, it is appropriate to treat the general corrosion rate as being temperature independent, and any variation caused by temperature changes is bounded by the conservative general corrosion rate applied to drip shields in the TSPA model.

## 2. COMMITMENTS TO NRC

None.

## 3. DESCRIPTION OF PROPOSED LA CHANGE

None.

## 4. REFERENCES

He, X.; Noël, J.J.; and Shoesmith, D.W. 2007. "Temperature Effects on Oxide Film Properties of Grade-7 Titanium." *Corrosion, 63,* (8), 781-792. Houston, Texas: NACE International.

Hua, F. and Gordon, G. 2004. "Corrosion Behavior of Alloy 22 and Ti Grade 7 in a Nuclear Waste Repository Environment." *Corrosion, 60,* (8), 764-777. Houston, Texas: NACE International.

Schutz, R.W. 2005. "Corrosion of Titanium and Titanium Alloys." *ASM Handbook*, Vol. 13B, Corrosion: Materials. Materials Park, Ohio: ASM International.

Smailos, E. and Köster, R. 1987. "Corrosion Studies on Selected Packaging Materials for Disposal of High Level Wastes." *Materials Reliability in the Back End of the Nuclear Fuel Cycle, Proceedings of a Technical Committee Meeting, Vienna, 2-5 September 1986*. IAEA TECHDOC-421, 7-24. Vienna, Austria: International Atomic Energy Agency.

SNL (Sandia National Laboratories) 2007. *Engineered Barrier System: Physical and Chemical Environment*. ANL-EBS-MD-000033 REV 06. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070907.0003; LLR.20080328.0031.

Zhu, R.; Nowierski, C.; Ding, Z.; Noël, J.J.; and Shoesmith, D.W. 2007. "Insights into Grain Structure and Their Reactivity on Grade-2 Ti Alloy Surfaces by Scanning Electrochemical Microscopy." *Chemistry of Materials*, *19*, 2533-2543. Washington, D.C.: American Chemical Society.

**RAI: Volume 3, Chapter 2.2.1.3.1, Number 4:**

Provide a technical basis to assess the passivity behavior and the subsequent effect on general corrosion rates of titanium Grades 7 and 29 and the weldments during the performance assessment period for the following potential repository environmental conditions:

1. Dust deliquescence brines

2. Seepage water dripping vs. immersion condition

**Basis**: SAR Section 2.3.6.8 and BSC (2007a) state that the general corrosion rate of titanium Grade 7 is based on immersion tests at 60 °C and 90 °C. DOE modeled the corrosion behavior of titanium Grade 29 in terms of the comparative behavior of titanium Grade 29 vs. Grade 7 (BSC, 2007a, Section 6.2[a]). The rates in the general corrosion model abstraction are constant with time, implying that the drip shield material maintains passivity over the repository period. However, at some point under the potential repository conditions, the drip shield likely will be exposed to environmental conditions that are more aggressive than those used in the immersion experiments. Solutions with more aggressive compositions than simulated concentrated water such as dust deliquescence brines also appear credible for the range of potential repository conditions (BSC, 2007b). Drip shields also could be exposed to dripping seepage water (SAR Section 2.1.2.24, p. 2.1-66), which can lead to different corrosion processes than those that occur during constant immersion (He, et al., 2007; Lee and Solomon, 2006). DOE has not assessed the potential effects of these environmental conditions on the passivity, nor has DOE provided a technical basis to demonstrate that these effects would not significantly affect general corrosion rates of titanium Grades 7 and 29 and their weldments during the performance assessment period. This information is needed to assess assumptions in the drip shield general corrosion model for titanium Grades 7 and 29 used to demonstrate compliance with 10 CFR 63.114(f).

# 1. RESPONSE

As discussed in SAR Section 2.3.6.8.1, general corrosion of the drip shield is modeled to occur regardless of the environment.

## 1.1 BEHAVIOR OF TITANIUM GRADES 7 AND 29 UNDER DELIQUESCENT CONDITIONS

Due to the environmental conditions present for the dust deliquescence scenario, general corrosion is very unlikely to take place on either the Titanium Grade 7 plates, Titanium Grade 29 structural supports, or the weldments joining the various components due primarily to the lack of an aqueous environment. This is supported by:

*(1)* *Nature of Dust on the Drip Shield*: Atmospheric dust will be deposited on the surfaces of drip shields primarily during their emplacement. Unlike the waste packages, which will see atmospheric dust accumulation throughout the pre-closure ventilation period, the drip shields will not be subject to such an extended accumulation period, as they are emplaced near the end of the pre-closure period. As such, the quantity of atmospheric dust deposited on the surface of the drip shields will be lower than that on the waste package surface. In addition, the dust which is deposited on the surface of the drip shield during the postclosure period will be composed predominantly of tunnel dust, rather than atmospheric aerosols. Tunnel dust is composed primarily of powdered rock and contains a much lower soluble salt concentration (<<1%) than atmospheric aerosols (10% to 20%) (SNL 2007a, Section 6.1). As a result, the volume of brine produced by such dusts will be lower on a per mass basis than that present in the dust layer that will reside on the surface of the waste packages following the ventilation period.

(2) *Solution Volume*: The maximum brine quantity on the waste package surface due to the deliquescence of salts in the dust layer has been calculated to be 1.8 $\mu l/cm^2$ at 120°C (SNL 2007a, Section 6.4.1.3). The quantity on the surface of the drip shields will be much lower due to the lower concentration of soluble salts in the dust on the surface of the drip shields combined with the much lower absolute quantity of dust present per unit area of drip shield. In the case where brine quantity is limited, only a limited quantity of reactant is present on the surface. Further, in a bulk solution, the anode and cathode may be separated spatially, such that reactions occurring at the cathode do not act to alter the chemistry of the bulk electrolyte. As the volume of solution becomes vanishingly small, so does the potential distance between the anodic and cathodic regions of the surface. Cathodic reactions will act to increase the pH of the limited volume of solution, further reducing the current-delivering capacity of the cathode and significantly reducing the corrosiveness of any brine which does form.

(3) *Solution Chemistry*: As discussed in *Analysis of Dust Deliquescence for FEP Screening* (SNL 2007a, Sections 6.3 and 6.3[a]), the brine chemistries expected to persist on a dust coated surface are anticipated to predominantly have a high nitrate to chloride ratio and as such be benign.

Thus, in addition to a very small portion of the drip shield surface being in contact with the brine, any brine which does form will either be, or in short order become, benign. As such, localized corrosion will not occur and other than benign humid air corrosion, it is unreasonable to consider that general corrosion will take place on either the Titanium Grade 7 plates or Titanium Grade 29 structural supports during the time the in-drift temperature and relative humidity supports the formation of local environments due to dust deliquescence (i.e., during the thermal pulse following the closure of the repository).

## 1.2 IMPACT OF DRIPPING CONDITIONS VS. IMMERSION CONDITIONS

As presented in SAR Section 2.3.6.4.4.1, seepage will not occur until the drift wall temperature is below 100°C, at which point the waste package surface temperature will be approximately 120°C. The temperature of the drip shield will be somewhere between those two temperatures. In the study by Lee and Solomon (2006), an experiment was run where the metal surface was held at a temperature of 200°C, and a liquid phase was formed on the surface (which was unstable, and rapidly dried out) while continuously dripping water onto the surface. The metastable solution, or "salt puddle," formed in the Lee and Solomon (2006) drip test experiment is not well-characterized. Lee and Solomon (2006, p. 122) concluded that "with well controlled situation the solution was stable at about 140°C for a few hours at the most." Moreover, the brine formed in the Lee and Solomon (2006) experiments requires temperatures greater than 120°C, yet seepage will not occur with the drift walls above 100°C, which is the condition that would result in waste package temperatures above 120°C (SAR Section 2.3.6.4.4.1). Therefore, seepage conditions are not conducive to the formation of this brine on the drip shield.

The solution chemistries that are expected to form due to evaporative concentration of seepage water have been accounted for by the experiments performed to date (SNL 2007b, Sections 6.2 and 6.5.1; SNL 2007c, Section 6.4.3.1.3). As such, the solution which might form on the drip shield surface due to dripping of seepage water has been accounted for. Furthermore, as the current implementation of the general corrosion model applies to the entire surface area of the drip shield, rather than just local regions where seepage water may have dripped, it is a far more conservative representation of the impact which general corrosion will have on the drip shield surface.

## 1.3 THE RELATIVE BEHAVIOR OF TITANIUM GRADE 7, GRADE 29, AND ASSOCIATED WELDMENTS

The drip shield will be fabricated from Titanium Grade 7 plates, Titanium Grade 29 structural supports, and Alloy 22 base plates. Welds will be made between adjacent Titanium Grade 7 plates, between the Titanium Grade 7 plates and Titanium Grade 29 structural supports, and between adjacent Titanium Grade 29 structural support members. The composition of the dissimilar metal weld between Titanium Grade 7 and Grade 29 will be largely defined by the filler metal which is used, in this case, Titanium Grade 28 (SAR Table 1.9-9). Titanium Grade 28 is essentially Titanium Grade 9 (Ti – 3Al – 2.5V) with the addition of ruthenium. The other weldments are of a nominally identical composition.

While the general corrosion rate of various titanium alloys has been observed to be a function of material composition in aggressive environments, such as low pH, high chloride conditions, it becomes increasingly difficult to resolve a difference between the materials for more benign conditions. This is clearly demonstrated by Schutz (see Figure 20 in Schutz 2005) in boiling, aerated hydrochloric acid solutions of varying concentration. In that study, the corrosion rates were indistinguishable between Titanium Grades 7, 28, or 29 at a concentration of 0.5 wt % (corresponding to a pH of slightly below 1). The conservative treatment of general corrosion utilized in the SAR (i.e., that general corrosion of the drip shield always occurs, irrespective of the environmental conditions) effectively captures the impact which material composition or microstructure might have. Therefore, the passivity of the material will not be disrupted by the environmental conditions to which the drip shield will be exposed during the postclosure period of performance.

## 2. COMMITMENTS TO NRC

None.

## 3. DESCRIPTION OF PROPOSED LA CHANGE

None.

## 4. REFERENCES

Lee, S.G. and Solomon, A.A. 2006. "Localized Corrosion of Alloy C22 Nuclear Waste Canister Material Under Limiting Conditions." *Materials Science and Engineering*, *A 434*, 114–123. New York, New York: Elsevier.

Schutz, R.W. 2005. "Corrosion of Titanium and Titanium Alloys." *ASM Handbook*, Vol. 13B, Corrosion: Materials. Materials Park, Ohio: ASM International.

SNL (Sandia National Laboratories) 2007a. *Analysis of Dust Deliquescence for FEP Screening*. ANL–EBS–MD–000074 REV 01 AD 01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070911.0004; DOC.20070824.0001; DOC.20080109.0005.

SNL 2007b. *General Corrosion and Localized Corrosion of the Drip Shield*. ANL-EBS-MD-000004 REV 02 AD 01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20060427.0002; DOC.20070807.0004; DOC.20071003.0019; LLR.20080423.0006.

SNL 2007c. *General Corrosion and Localized Corrosion of Waste Package Outer Barrier*. ANL-EBS-MD-000003 REV 03. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070730.0003; DOC.20070807.0007; LLR.20080414.0018.

**RAI: Volume 3, Chapter 2.2.1.3.1, Number 5:**

Demonstrate that using conservative assumptions for assessing drip shield corrosion performance in the nominal scenario does not underestimate the effects of drip shield stability on enhancing waste package damage in the seismic scenario.

**Basis:** SAR Section 2.3.6.8 and BSC (2007a) state that the drip shield outer surface general corrosion rate is modeled based on test data from simulated concentrated water at 90 °C. DOE states that it is conservative to use the most aggressive solution of the three test solutions to model outer surface corrosion rates, which leads to higher corrosion rates and earlier drip shield failure times. However, drip shield failure at earlier times might not be a conservative assumption with respect to the seismic scenario. In the seismic scenario, waste packages fail because of free motion impacts during the earthquake; these impacts result in stress corrosion cracking. Drip shield failure at earlier times will allow rock rubble to restrict waste package movement in a seismic event, thus reducing the potential for stress corrosion cracking and subsequent radionuclide release. A technical basis is needed to determine whether introducing conservatism in titanium general corrosion rates leads to nonconservative conditions for the seismic scenario. This information is needed to support the models used to demonstrate compliance with 10 CFR 63.114(g).

# 1. RESPONSE

This response first summarizes the assumptions regarding drip shield corrosion that are described as conservative, and the context in which these assumptions are considered conservative in terms of assessing the general corrosion rate. Next, the response presents a sensitivity study that investigated the effect of these assumptions on the estimates of repository performance. The sensitivity study results demonstrate that the assumptions made for assessing drip shield corrosion performance have a negligible effect on the overall results of the performance assessment. When a wider range of uncertainty in titanium corrosion rates is considered, the performance assessment results (i.e., mean annual dose) are different by less than 1%.

## 1.1 CONSERVATIVE ASSUMPTIONS IN THE MODELS FOR THE GENERAL CORROSION OF TITANIUM ALLOYS

The DOE applies several assumptions in the models for corrosion of titanium materials in drip shields that are described as conservative because each leads to results that overestimate the rate and extent of general corrosion of drip shield materials:

1. Aqueous general corrosion is applied for all repository conditions even when the drip shield is dry (SAR Section 2.3.6.8.1). This is conservative with respect to the actual rate of titanium corrosion as the model does not consider whether or not the environment is sufficiently aggressive to result in measureable general corrosion – it assumes general corrosion can always take place.

2. The outer surface of the drip shield is assumed to be subjected to seepage at all times (SAR Section 2.3.6.8.1.2.1), irrespective of the drift wall temperature. This is conservative with respect to the quantity of water reaching the drip shield because the model does not wait until the drift wall is below the boiling point of water, such that seepage can take place, thus general corrosion is able to occur even under conditions where the drip shield would be dry.

3. Weight-loss samples with negative values for weight loss were omitted from the calculation of corrosion rates (SAR Section 2.3.6.8.1.3). This provides a more conservative estimate of the corrosion rate due to weight loss as negative values are removed and do not skew the distribution to lower values.

4. The distribution of general corrosion rates is constant with time (SAR Section 2.3.6.8.1.3). This is conservative with the respect to the actual rate of corrosion as general corrosion rates are observed to decrease with time, particularly for passive metal systems.

5. The distribution of corrosion rates for aggressive (i.e., topside) conditions is determined only from weight-loss data for samples in simulated concentrated water (SCW) at 90°C (SNL 2007a, Section 6.1.6.1[a]). This is conservative with respect to actual corrosion rates because lower temperatures and less concentrated waters will be present for much of the performance period.

These assumptions are described as conservative because they lead to results that overestimate the rate and extent of general corrosion of drip shield materials, which in turn increases the likelihood of drip shield failure. Only in this context, however, are the assumptions considered as conservative. As demonstrated in the next section, these assumptions collectively have a negligible effect on the results of the performance assessment, and consequently are not "conservative" in the sense of the total system.

## 1.2 EFFECT OF CONSERVATIVE ASSUMPTIONS ON REPOSITORY PERFORMANCE

The NRC observes that an assumption that is conservative with respect to estimating the time of drip shield failure may not be conservative with respect to estimating repository performance. In particular, the potential exists that later drip shield failure (from lower titanium general corrosion rates) could increase the likelihood and/or extent of seismic damage to waste packages. The DOE performed a sensitivity study whose results demonstrate that the conservative assumptions regarding drip shield corrosion do not significantly affect the results of the performance assessment. The effect of corrosion of Titanium Grades 7 and 29 on the likelihood of seismic damage is first discussed, followed by the results of the sensitivity analysis.

In the seismic scenario, the probability that a given waste package is damaged by a seismic event depends on four variables describing the state of the Engineered Barrier System (EBS):

1. Condition of the drip shield plates (represented as either intact or failed)

2. Condition of the drip shield framework (represented as either intact or failed)

3. Condition of the internal structure (e.g., inner vessel, transportation, aging, and disposal (TAD) canister, or naval canister, etc.) of the waste package (represented as intact or degraded)

4. Average thickness of the waste package outer corrosion barrier (decreases with time as general corrosion of the outer corrosion barrier progresses).

The state of the drip shield plates and framework is determined by probability models documented in *Seismic Consequence Abstraction* (SNL 2007b) for failure of these components. These models are functions of seismic event magnitude, rockfall loading, and component thinning by general corrosion. Similarly, for each type of waste package (codisposal or commercial spent nuclear fuel (SNF)) and for combinations of values for the EBS state variables, *Seismic Consequence Abstraction* (SNL 2007b) provides a model for the probability of stress-corrosion cracking damage to waste packages from seismic events. Given an average thickness of the waste package outer barrier of 23 mm, these probability models can be integrated to obtain expected values for the frequency of seismic events that result in damage to waste packages. For example, assuming that the average thickness of the waste package outer barrier is at least 23 mm, Table 1 summarizes the expected value for these frequencies for each waste package type and value for the EBS state variables. In Table 1 the expectation is over the epistemic uncertainty in the residual stress threshold for Alloy 22.

Table 1. Expected Frequencies of Seismic Events That Damage Waste Packages

| | **Expected Frequency of Seismic Events ($yr^{-1}$) That Could Cause Damage** | |
|---|---|---|
| **EBS State Variables** | **Codisposal** | **Commercial SNF** |
| Drip shield plates intact<br>Drip shield framework intact<br>Waste package internals intact | $7.48 \times 10^{-6}$ (1) | $5.25 \times 10^{-9}$ (2) |
| Drip shield plates intact<br>Drip shield framework failed<br>Waste package internals intact | $2.23 \times 10^{-8}$ (3) | $2.23 \times 10^{-8}$ (3) |
| Drip shield plates intact<br>Drip shield framework intact<br>Waste package internals degraded | $2.96 \times 10^{-5}$ (1) | $3.12 \times 10^{-5}$ (4) |
| Drip shield plates intact<br>Drip shield framework failed<br>Waste package internals degraded | $2.96 \times 10^{-5}$ (3) | $3.12 \times 10^{-5}$ (4) |
| Drip shield plates failed[a] | $2.23 \times 10^{-8}$ (3) | $2.23 \times 10^{-8}$ (3) |

Source: Files: [1]*FreqDamageCDSP_v5.xmcd* (DTN: MO0708CDSPSEIS.000); [2]*FreqDamageTAD.xmcd* (DTN: MO0708FREQCALC.000); [3]*Rubble_Damage.xmcd* (DTN: MO0708FREQCALC.000); and [4]*FreqDamageTAD deg.xmcd*.

[a] When the drip shield plates fail, it is assumed that the drip shield framework also fails. In this case the probability model for waste package damage does not depend on the state of the waste package internals, because it is also assumed that the waste package internals are degraded by the time that the drip shield plates fail.

The values in Table 1 indicate that changes in general corrosion rates of titanium (and thus the rate of drip shield thinning) may result in complex changes to the results of the performance assessment. For example, failure of the drip shield framework has different effects on the likelihood of seismic damage to codisposal and commercial SNF waste packages. For codisposal waste packages with intact internals, the likelihood of seismic damage is much greater while the drip shield framework is intact, whereas for commercial SNF waste packages with intact internals, the likelihood of seismic damage is somewhat greater after failure of the drip shield framework. For both types of waste package, once the internal structure of the waste package has degraded, failure of the drip shield framework does not change the likelihood of seismic damage.

Failure of the drip shield plates also has different effects on codisposal and commercial SNF waste packages. For codisposal waste packages, the likelihood of seismic damage is generally less after failure of the drip shield plates. However, for commercial SNF waste packages with intact internals, the likelihood of seismic damage is somewhat greater after drip shield plate failure, while for commercial SNF waste packages with degraded internals, the likelihood of seismic damage is significantly lower after drip shield plate failure.

Thus, changes in the general corrosion rate of titanium that alter the time of failure of the drip shield framework and plates may result in complex changes to the results of the performance assessment, depending on the sequence of waste package failure times and drip shield failure times. Consequently, the sensitivity study summarized in this response considered both slower and faster general corrosion rates for titanium. By considering both slower and faster corrosion rates, the sensitivity study determines the extent to which the performance assessment model could be sensitive to the assumptions made with respect to the determination of the general corrosion rate of titanium.

The analysis compares results from the TSPA-LA to those from an alternate case, in which general corrosion rates for titanium were modified. In the alternate case, corrosion rates for the topside and underside of the drip shield plates were sampled from the distributions described in *General Corrosion and Localized Corrosion of the Drip Shield* (SNL 2007a, Table 8-1[a]). The resulting total corrosion rate (i.e., the sum of the sampled rates for the inner and outer surface of the drip shield) was then multiplied by an uncertainty factor between 0.5 and 4 to introduce a wider range of uncertainty in the general corrosion rates. This uncertainty factor was represented as a piecewise uniform distribution ranging from 0.5 to 4.0, with median of 1. Consistent with the response to RAI 3.2.2.1.3.1.7-002, the ratio of general corrosion rate for Titanium Grade 29 to Titanium Grade 7 was fixed at a constant value of one in the alternate case. This approach results in general corrosion rates for the Titanium Grade 29 structural components that are nearly equal to, but are slightly higher than, the general corrosion rates applied to the topside surface of the Titanium Grade 7 plate components. The multiplier has the effect of shortening or extending the drip shield framework and plate lifetime well outside the range currently observed in model results (SAR Figure 2.4-24). Thus, if the performance assessment model were sensitive to the general corrosion rate of titanium, the expected annual dose should be higher and/or lower in the alternate case depending on the value of the uncertain multiplier.

The sensitivity of the TSPA-LA model to assumptions regarding general corrosion of titanium alloys can be determined by considering the seismic ground motion modeling case for 1,000,000 years postclosure. This modeling case accounts for the combined effects of seismic ground motion events and nominal corrosion processes, and estimates the contribution of these events and processes to the mean dose to the reasonably maximally exposed individual (RMEI). As justified in *Total System Performance Assessment Model/Analysis for the License Application* (SNL 2008, Section 7.3.2.6.1.3.3), drip shield failure (either of the framework or of the plates) does not significantly contribute to the expected annual dose in the seismic ground motion modeling case for 10,000 years postclosure, even when faster rates of general corrosion of titanium alloys are considered. In all other modeling cases, the drip shield diverts seepage until failure of the Titanium Grade 7 components occurs via general corrosion (i.e., in the nominal and waste package early failure modeling cases), or until the occurrence of an event which compromises the drip shield (i.e., an early drip shield failure, an igneous intrusion, or a seismic fault displacement). However, for these cases the occurrence of damage to waste packages is not dependent on the state of the drip shield. Consequently, the analysis considered only the seismic ground motion modeling case for 1,000,000 years postclosure.

Figure 1 compares the distributions of failure time for the drip shield plates in the TSPA-LA model and in the alternate case. The figure demonstrates that applying the uncertain multiplier to the Titanium Grade 7 corrosion rates results in both earlier and later drip shield plate failures, as evident in the bimodal appearance of the histogram in the alternate case. Figure 2 compares the distributions of expected annual dose to the RMEI (where the expectation averages over uncertainty in the occurrence and extent of seismic events) for the base and alternate cases. Despite the wider variability in the time of drip shield plate failure, the timing and magnitude of expected annual dose for each realization, and the range of uncertainty among realizations, are similar for both cases.

Figure 3 compares statistics for the distribution of expected annual dose between the two cases. The measures of central tendency (i.e., mean and median) are essentially unchanged over the 1,000,000-year period postclosure. Specifically, the maximum of the mean annual dose in the base case is 1.096 mrem at 1,000,000 years; in the alternate case, the maximum of the mean annual dose is 1.107 at 1,000,000 years, a difference of less than 1%. At 1,000,000 years, the seismic ground motion modeling case contributes approximately half of the total mean annual dose (SAR Figure 2.4-10b). Thus, if the alternate case results were added with results of other modeling cases to estimate the effect on the total mean annual dose, the effect on total mean annual dose would be negligible.

When assumptions related to titanium corrosion rates are changed, either by reducing the corrosion rate or by increasing the corrosion rate, the effect on expected dose would be most evident in the tails of the distribution, as expressed by the 5th and 95th quantiles. Although some variability in these quantiles can be observed in the results, the variations are small in magnitude. Together, the similarity in the distributions of expected annual dose (Figure 2), the similarity in the measures of central tendency of this distribution (Figure 3) and the lack of sizable variation in the tails indicate that the distribution of expected annual dose is not sensitive to the general corrosion rates of titanium. These results demonstrate that the performance

assessment is not sensitive to the conservative assumptions made with respect to the determination of the general corrosion rate of titanium.

In summary, the sensitivity study reported in this response demonstrates that the conservative assumptions made for assessing drip shield corrosion performance have a negligible effect on the overall results of the performance assessment. When a wider range of uncertainty in titanium corrosion rates is considered, the performance assessment results (i.e., mean annual dose) are different by less than 1%. In particular, the conservative assumptions made for drip shield corrosion performance do not lead to significantly nonconservative (i.e., lower) estimates of expected annual dose in the seismic scenario.

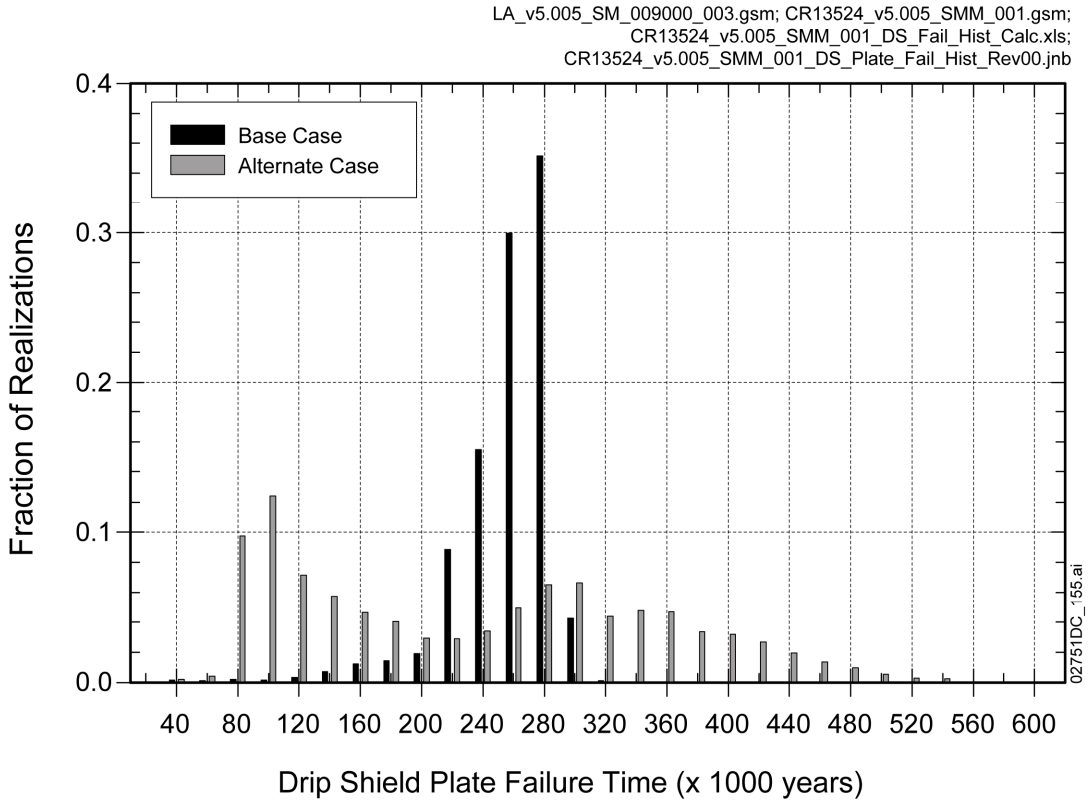


Figure 1. Comparison of Drip Shield Plate Failure Time for the Base and Alternate Cases

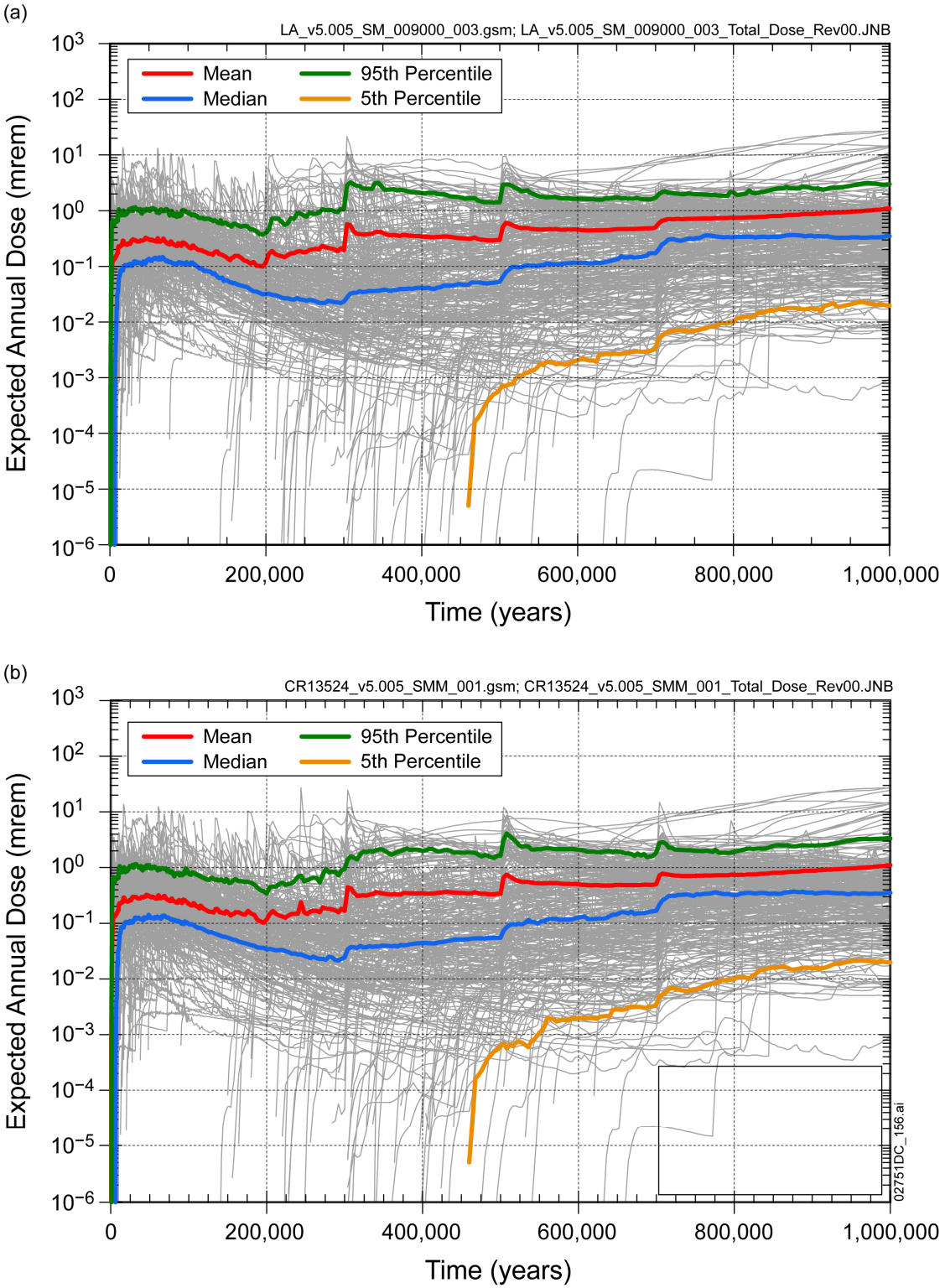


Figure 2. Distribution of Expected Annual Dose in the Seismic Ground Motion Modeling Case for (a) TSPA-LA Base Case and (b) Alternate Case

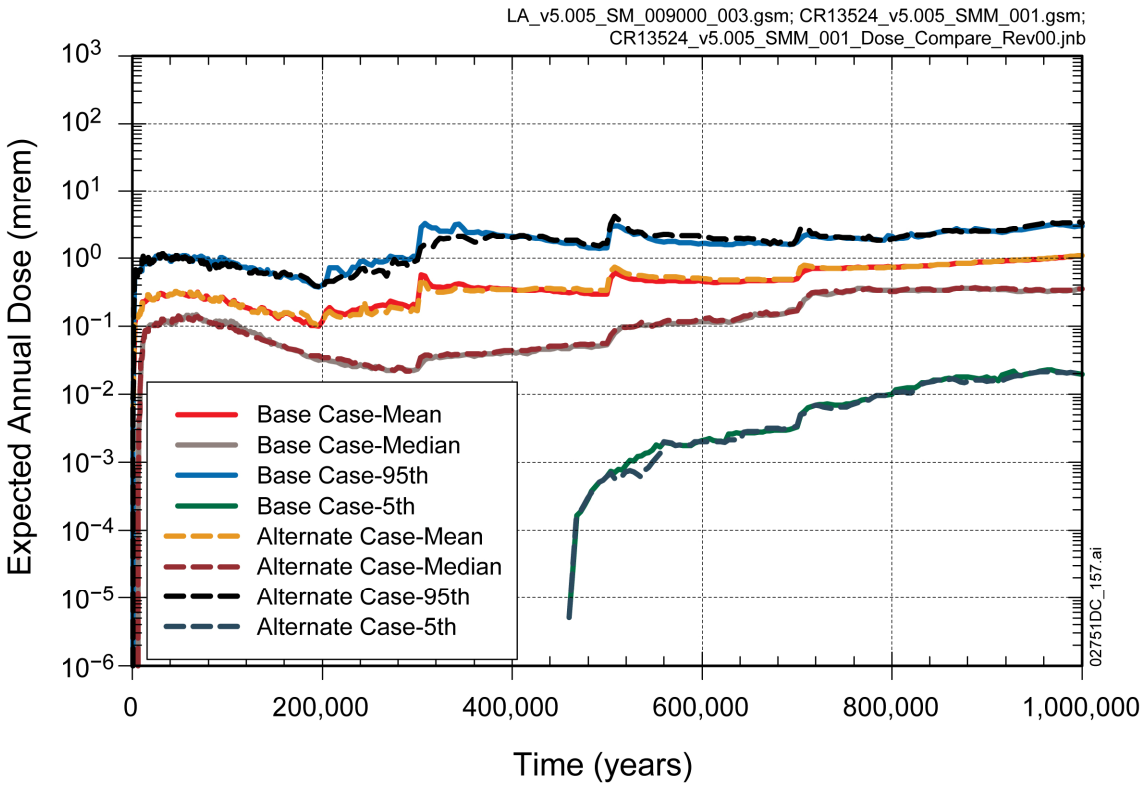


Figure 3. Comparison of Statistics for the Distribution of Expected Annual Dose in the Seismic Ground Motion Modeling Case for the TSPA-LA Base Case and the Alternate Case

## 2. COMMITMENTS TO NRC

None.

## 3. DESCRIPTION OF PROPOSED LA CHANGE

None.

## 4. REFERENCES

SNL (Sandia National Laboratories) 2007a. *General Corrosion and Localized Corrosion of the Drip Shield*. ANL–EBS–MD–000004. Rev. 02 AD 01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20060427.0002; DOC.20070807.0004; DOC.20071003.0019; LLR.20080423.0006

SNL 2007b. *Seismic Consequence Abstraction*. MDL-WIS-PA-000003 REV 03. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20070928.0011; LLR.20080414.0012.

SNL 2008. *Total System Performance Assessment Model /Analysis for the License Application.* MDL-WIS-PA-000005 REV 00 AD 01. Las Vegas, Nevada: Sandia National Laboratories. ACC: DOC.20080312.0001; LLR.20080414.0037; LLR.20080507.0002; LLR.20080522.0113; DOC.20080724.0005; DOC.20090106.0001[a].

NOTE: [a] Provided as an enclosure to letter from Williams to Sulima dtd 02/17/2009. "Yucca Mountain – Request for Additional Information Re: License Application (Safety Analysis Report Section 2.1), Safety Evaluation Report Volume 3 – Postclosure Chapters 2.2.1.1 and 2.2.1.3.7 – Submittal of Department of Energy Reference Citations"