

7. WASTE PACKAGE AND DRIP SHIELD DEGRADATION

This section documents analyses conducted to quantify conservatism and unquantified uncertainties in the corrosion models and parameters that were incorporated in the waste package and drip shield degradation analysis for the *Total System Performance Assessment for the Site Recommendation* (TSPA-SR) (CRWMS M&O 2000 [DIRS 153246]). This section also documents new data and analyses that were developed to model degradation of the waste package and drip shield materials since the completion of the TSPA-SR analysis. Most of the new analyses documented relate to the degradation of the Alloy 22 outer barrier of the waste package. Those updated corrosion models and parameters (with quantified uncertainties) and their abstracted models were input into the integrated waste package degradation model (i.e., the WAPDEG V4.0 model) (CRWMS M&O 2000 [DIRS 151566]) to evaluate the effects of the quantified uncertainties and conservatism on waste package (and, for a few cases in Section 7.4, drip shield) degradation. Where necessary, sensitivity analyses are also conducted for the evaluation. A waste disposal container becomes a waste package when it is loaded with waste (such as commercial spent nuclear fuel [CSNF], U.S. Department of Energy (DOE) spent nuclear fuel, and DOE high-level radioactive waste) and sealed (CRWMS M&O 2000 [DIRS 152104], Section 1.0).

7.1 INTRODUCTION

The lifetimes of the waste package and drip shield will depend on the environmental conditions to which they are exposed and the degradation processes that occur in those environments. Environmental conditions within the emplacement drifts that influence the degradation of the waste package and drip shield are closely coupled to the thermal-hydrologic and geochemical processes occurring within the emplacement drifts. These processes involve the evaporation and condensation of water under changing thermal conditions, the redistribution and precipitation of dissolved salts, and the effects of gaseous species on solution chemistry. Also included in the conceptualization are the contributions of construction material degradation processes (i.e., ground structural support materials) and the effects of microbial action.

Once the exposure environments have been established, the most important and relevant degradation processes can be identified, which can be used for confirming the selection of materials for the drip shield and the waste package. Corrosion has been judged the most relevant and important degradation process in the selection of the materials for the waste package and drip shield. A number of corrosion processes have been investigated in detail and the results used to support the selection of materials and the design of these components.

Waste Package and Drip Shield Materials—Degradation modes for the waste package and drip shield depend on the materials used to make these components and, as mentioned earlier, on the environment in which they perform. Figure 7.1-1 provides a visual perspective to illustrate the physical arrangement of the waste packages and drip shield in the drift and shows schematically the arrangement of different types of waste packages and the drip shield. Figure 7.1-2 shows a schematic sketch of a typical waste package designed for 21 pressurized water reactor fuel assemblies, along with the materials used for the various components. Titanium (Grade 7 was selected for construction of the drip shield because of its high resistance to corrosion (CRWMS M&O 2000 [DIRS 153802], Section 3.1.1.1). This corrosion resistance results from the

formation of a passive oxide film that is stable over a relatively wide range of exposure environments.

Alloy 22 was selected for construction of the waste package outer barrier (CRWMS M&O 2000 [DIRS 153802], Section 3.1.1.2). The main alloying elements in this material are nickel, chromium, molybdenum, iron, tungsten, and cobalt. Alloy 22 is less susceptible to localized corrosion in environments that contain chloride ions than Alloys 825 and 625, materials of choice in earlier waste package designs (CRWMS M&O 2000 [DIRS 153802], Section 3.1.1.2). Alloy 22 was developed for application in a wide variety of chemical environments with highly corrosive conditions (Gdowski 1991 [DIRS 100859], pp. 1 to 8). This material is one of the most corrosion-resistant nickel alloys for the expected range of repository environments (Gdowski 1991 [DIRS 100859], pp. 1 to 8). Alloy 22 and its predecessor alloys have been used for the past 50 years in a variety of environments and have performed extremely well. For example, test coupons made from Alloy C, which is a predecessor of Alloy 22, continue to maintain a mirror-like finish after almost 50 years of exposure to a marine environment (McCright 1998 [DIRS 100289], Figure ES-1). In comparison to Alloy C, Alloy 22 has greater corrosion resistance. This is based on the fact that Alloy C and Alloy C-276 have a comparable corrosion resistance (Gdowski 1991 [DIRS 100859], Section 1.2) and the resistance of Alloy 22 to crevice corrosion is greater than that of Alloy C-276 (Gdowski 1991 [DIRS 100859], Tables 22 and 25).

Stainless Steel Type 316NG will be used for construction of the structural support shell inside the waste package outer barrier to increase the overall strength of the waste package. Because the stainless steel inner shell is used primarily for structural support for the outer barrier, the potential performance credit of the shell as a corrosion barrier to the ingress of water into the waste package is not considered in waste package performance and total system performance assessment (TSPA) analysis. The key factor in placing the structural material on the inside is that its strength does not begin to degrade until the outer shell is breached by corrosion or other degradation modes.

As discussed in Section 7.2, degradation processes evaluated for the drip shield and waste package for the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) include general and localized corrosion under humid-air and aqueous conditions, stress corrosion cracking, and hydrogen induced cracking. Also considered in the TSPA-SR analysis were the effects of microbiologically influenced corrosion (MIC), aging of the waste package outer barrier, and manufacturing flaws on stress corrosion cracking of the waste package outer barrier. The WAPDEG model was used to evaluate the combined effects of the various degradation modes and to estimate the range of lifetimes of the drip shields and the waste packages, including an evaluation of uncertainties.

Since the completion of the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) analysis, the models and parameters of the degradation processes included in the waste package and drip shield degradation analysis were reevaluated to further quantify associated uncertainties and to reduce conservatism that was introduced to bound the degradation processes. The degradation processes, models, and parameters that were reevaluated are documented in Sections 7.3.1 through 7.3.7. The updated corrosion models and parameters, along with their quantified uncertainties and their abstracted models, were input to the WAPDEG model to evaluate the

effects of the quantified uncertainties and conservatism on the waste package and drip shield degradation, which is documented in Section 7.4.

Table 7-1 shows the correlation between the supplemental analyses that have been produced for waste package and drip shield degradation, the rationale for obtaining that supplemental information (i.e., unquantified uncertainties, new science, or lower-temperature operating mode analyses), and the subsection in this section where the work is documented. Details of the goals and scope are discussed in Section 1.2 of this volume.

7.2 OVERVIEW OF TOTAL SYSTEM PERFORMANCE ASSESSMENT-SITE RECOMMENDATION REV 00 TREATMENT

This section provides an overview of the treatment used to address and quantify the uncertainties in the various corrosion models and their parameters that have been incorporated into the waste package and drip shield degradation analysis for the TSPA-SR model (CRWMS M&O 2000 [DIRS 148384]). In general, the approach used in the TSPA-SR in dealing with the uncertainties in each of the process models (and the abstraction models used in the TSPA) is to employ conservative assumptions and bound the models. The conservatism and uncertainties in each of the process models discussed in this section were captured in their respective abstraction models and incorporated into the WAPDEG model, the integrated waste package degradation model (CRWMS M&O 2000 [DIRS 151560]).

Of the degradation processes (and their associated uncertainties) discussed in this section, the uncertainties of the models and parameters of key degradation processes are re-evaluated, updated and further quantified. Details of the analyses for the uncertainty update and quantification are discussed in Section 7.3. These key degradation processes are:

- Chemical environment on waste package and drip shield surfaces (Section 7.3.1)
- Thermal aging and phase stability of Alloy 22 outer barrier (Section 7.3.2)
- Stress corrosion cracking (Section 7.3.3)
- Passive film stability of Alloy 22 outer barrier (Section 7.3.4)
- Temperature-dependent general corrosion, especially temperature dependency, of Alloy 22 outer barrier (Section 7.3.5)
- Early waste package failure by improper heat treatment (Section 7.3.6).

Effects of these updated and quantified uncertainties on the waste package performance are discussed in Section 7.4. Testing and analyses of all the corrosion processes considered in the TSPA-SR analysis are being continued to address and quantify their effects and associated uncertainties on waste package and drip shield degradation under expected repository exposure conditions.

Table 7-1. Summary of Supplemental Models and Analyses

Key Attributes of System	Process Model (Section of S&ER)	Topic of Supplemental Scientific Model or Analysis	Reason For Supplemental Scientific Model or Analysis			Performance Assessment Treatment of Supplemental Scientific Model or Analysis ^a		
			Unquantified Uncertainty Analysis	Update in Scientific Information	Lower-Temperature Operating Mode Analysis	Section of Volume 1	TSPA Sensitivity Analysis	Included in Supplemental TSPA Model
Long-Lived Waste Package and Drip Shield	In-Drift Moisture Distribution (4.2.5)	Environment on surface of drip shields and waste packages	X			7.3.1		
	Drip Shield Degradation and Performance (4.2.4)	Local chemical environment on surface of drip shields (including Mg, Pb) and potential for initiating localized corrosion	X			7.3.1		
	Waste Package Degradation and Performance (4.2.4)	Local chemical environment on surface of waste packages (including Mg, Pb) and potential for initiating localized corrosion	X			7.3.1		
		Aging and phase stability effects on Alloy-22	X	X		7.3.2	X	
		Uncertainty in weld stress state following mitigation	X			7.3.3	X	X
		Weld flaws	X			7.3.3	X	X
		Early failure due to improper heat treatment	X		X	7.3.6	X	X
		General corrosion rate of Alloy-22: Temperature dependency	X		X	7.3.5	X	X
		General corrosion rate of Alloy-22: Uncertainty/variability partition	X			7.3.5	X	X
		Long-term stability of passive films on Alloy-22	X			7.3.4		
		Stress threshold for initiation of stress corrosion cracking	X	X		7.3.3	X	X
		Probability of non-detection of manufacturing flaws		X		7.4.3	X	X
		Distribution of crack growth exponent (repassivation slope)	X	X		7.3.3	X	X

NOTE: S&ER = Yucca Mountain Science and Engineering Report (DOE 2001 [DIRS 153849]).

^a Performance assessment treatment of supplemental scientific model or analysis discussed in SSPA Volume 2 (McNeish 2001 [DIRS 155023]).

7.2.1 Thermal Aging

The long-term aging of Alloy 22 at elevated temperatures may cause the precipitation of intermetallic phases, affecting the corrosion resistance of the metal. Experiments to obtain the data needed to develop the model and analysis for the aging process are typically conducted at temperatures higher than those expected in the repository. This is necessary because the precipitation of intermetallic phases at expected repository temperatures would be extremely slow, and would be difficult to observe after reasonable test periods. This necessitates the extrapolation of parameters to temperatures expected in the repository environment.

The thermal aging model for Alloy 22 assumes Arrhenius-type kinetics (CRWMS M&O 2000 [DIRS 147639], Sections 6.2 and 6.5). Precipitation of intermetallic phases and long-range ordering can be accelerated by increasing the exposure temperature to levels well above those expected in the repository. The best estimate of the thermal aging model indicates that thermal aging of Alloy 22 base metal would not progress to a significant level in the first 10,000 years (CRWMS M&O 2000 [DIRS 147639], Section 6.2). However, the model estimate has large uncertainties.

The effects of intermetallic phase precipitation and long-range ordering on corrosion of Alloy 22 have been investigated with electrochemical techniques (CRWMS M&O 2000 [DIRS 144229], Section 6.7). From the corrosion tests conducted, it appears that aging of Alloy 22 results in anodic shifts in the observed corrosion potential. However, the shift is not significant enough to substantially alter passive film stability and result in significantly enhanced corrosion. The TSPA-SR (CRWMS M&O 2000 [DIRS 148384]) assumes the closure weld of the waste package outer barrier and heat-affected areas near the closure weld are subject to thermal aging, and the effect on corrosion is accounted for with a corrosion rate enhancement factor (CRWMS M&O 2000 [DIRS 151566], Sections 4.1.11 and 5.9). The enhancement factor is determined from the ratio of measured passive current densities for fully aged and unaged samples (CRWMS M&O 2000 [DIRS 144229], Section 6.7); it is based on a ratio of the nonequilibrium passive current densities for unaged metal and fully aged metal (CRWMS M&O 2000 [DIRS 144229], Section 6.7). The enhancement factor is represented with a range of values to account for uncertainty in the thermal aging process and the effects on corrosion. Based on measured data, the factor is assumed to be a uniform distribution with an upper bound of 2.5 and a lower bound of 1 (CRWMS M&O 2000 [DIRS 151566], Sections 4.1.11 and 5.9). The enhancement factor is applied only to the closure weld region of the waste package outer barrier and assumed to represent variability in the aging effect on the closure weld region. Additional data and analyses to quantify and reduce the present uncertainties are discussed in Section 7.3.2.

Thermal aging of Titanium Grade 7 under repository-relevant thermal conditions is expected to have little impact on the corrosion resistance of this material (CRWMS M&O 2000 [DIRS 144971], Section 5.9). Because no credit is claimed for the corrosion resistance of Stainless Steel Type 316NG, the TSPA calculation is insensitive to the uncertainty associated with its corrosion.

7.2.2 General Corrosion

General corrosion is the relatively uniform thinning of materials without significant localized corrosion. Conceptual models for general corrosion of the drip shield and waste package outer barrier are discussed in *General Corrosion and Localized Corrosion of the Drip Shield* (CRWMS M&O 2000 [DIRS 144971]) and *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 144229]), respectively. The mode of general corrosion differs depending on the local environment; the repository environment will result in three general corrosion modes (dry oxidation, humid-air corrosion, and aqueous-phase corrosion).

General Corrosion Initiation Threshold—Dry oxidation (dry-air corrosion) occurs at a relative humidity below the threshold for humid-air corrosion (CRWMS M&O 2000 [DIRS 144229], Sections 5.1 and 6.1). Humid-air corrosion is defined as a corrosion condition in the absence of dripping water. Aqueous-phase corrosion requires the presence of dripping water. In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), a carbonate-base water (which has characteristics of J-13 well water) was considered the most likely to contact the drip shield and waste package (CRWMS M&O 2000 [DIRS 151568], Section 6.4.2). Sodium nitrate salt is the most soluble salt formed during the evaporative concentration testing of simulated J-13 well water and has the lowest deliquescence point among salts produced from the testing (CRWMS M&O 2000 [DIRS 151568], Section 6.4.2). The threshold relative humidity for humid-air and aqueous-phase corrosion is based on the deliquescence point of sodium nitrate salt (CRWMS M&O 2000 [DIRS 151568], Section 7.0; CRWMS M&O 2000 [DIRS 144229], Section 4.1.2). Because hygroscopic salts could form from the salts entrapped in the dusts settled on the waste package and drip shield surfaces, the deliquescence point of sodium nitrate salt is conservatively assumed also for the threshold of corrosion initiation for humid-air condition. However, for humid-air corrosion and aqueous-phase corrosion conditions, the deliquescence point of the assemblage of mixed salt phases resulting from evaporation of condensed water interacting with the dusts and/or dripping water onto the waste package and drip shield surfaces could be lower than “pure” sodium nitrate salt. Additional analyses for potential development of other more hygroscopic salts (e.g., magnesium and calcium chloride salts) from drift dust containing soluble salts and from non-carbonate dominated waters contacting the waste package are discussed in Section 7.3.1.

Dry Oxidation—Dry oxidation occurs at a relative humidity below the threshold for humid-air corrosion. This process results in the formation of an adherent, protective oxide film of uniform thickness. The rate of dry-air corrosion may be limited by the rate of mass transport through the growing metal oxide film. In such cases, the oxide thickness is expected to obey a parabolic growth law (film thickness proportional to the square root of time). This scenario has been adopted for Alloy 22 and Stainless Steel Type 316NG, mainly due to the availability of data at elevated temperatures to support such a model (CRWMS M&O 2000 [DIRS 144229], Section 6.1). There are sufficient data to support the application of a logarithmic law to the dry-air corrosion of titanium (CRWMS M&O 2000 [DIRS 144971], Section 6.1).

The rates of dry-air corrosion are small for Alloy 22 (CRWMS M&O 2000 [DIRS 144229], Section 6.1) and Titanium Grade 7 (CRWMS M&O 2000 [DIRS 144971], Section 6.1). Given

the extremely small magnitudes and uncertainties of these rates, dry-air corrosion is expected to have no significant impact on waste package and drip shield performance.

Humid-Air and Aqueous-Phase General Corrosion Rate—Humid-air corrosion is assumed to occur above the threshold relative humidity (provided that there are no impinging drips), and aqueous-phase corrosion is assumed to occur in the presence of dripping water (CRWMS M&O 2000 [DIRS 144229], Sections 6.2 and 6.3). The distributions of general corrosion rates for Alloy 22 and Titanium Grade 7 used in the TSPA-SR are based upon weight-loss data from the Long-Term Corrosion Test Facility (LTCTF) over a two-year period. The test program includes sample coupons exposed to a variety of test media (e.g., water chemistry, temperature) to cover a potential range of corrosion conditions in the repository. The test program is ongoing and designed to provide corrosion data for at least 60 months of exposure.

To date, corrosion data for Alloy 22 and Titanium Grade 7 indicate that the general corrosion rates for humid-air and aqueous-phase corrosion are about the same (i.e., water chemistry has no significant effect) (CRWMS M&O 2000 [DIRS 153802], Sections 3.1.5.4.2 and 3.1.5.4.3). The data also show little sensitivity to exposure temperature for the water chemistry and temperature ranges considered in the test program. Because the general corrosion rate is expected to decrease with exposure time, the current general corrosion rate models based on data from the Long-Term Corrosion Test Facility represent reasonably conservative corrosion behaviors of those highly corrosion-resistant materials under the expected repository conditions. Therefore, in the TSPA-SR, it was conservatively assumed that the rate of humid-air corrosion is represented by the same corrosion rate distribution used for aqueous-phase corrosion during the period where humid-air corrosion is operable (CRWMS M&O 2000 [DIRS 153802], Section 3.1.5.4.2). It was further assumed that the corrosion rate is constant and does not decrease with time at times greater than two years. Less conservative corrosion models assume that the rate decays with time. The calculated general corrosion rates were corrected for the effects of silica scale deposits on the sample coupons, which were estimated to increase the general corrosion rate from the weight-loss measurements by as much as 0.063 $\mu\text{m}/\text{yr}$ (CRWMS M&O 2000 [DIRS 144229], Section 6.5.5). The corrections were made by sampling the silica scale correction factor from a uniform distribution between zero and 0.063 $\mu\text{m}/\text{yr}$ and adding the sampled factor to the general corrosion rate from the weight-loss measurements (CRWMS M&O 2000 [DIRS 152542], Sections 2 and 3).

The general corrosion rate distributions for Alloy 22 and Titanium Grade 7 include substantial uncertainties. Most of the uncertainties result from insufficient resolution of the weight-loss measurements of the sample coupons due to the extremely low corrosion rates of the materials in the test media. The testing data and information are not sufficient to quantify the uncertainty fully, and the fraction of the corrosion rate distribution that is attributed to spatial variability (and conversely uncertainty) is not known. The conceptual approach in the waste package and drip shield degradation analysis in the TSPA-SR assumes that this fraction is unknown and varies uniformly, ranging from pure uncertainty to pure variability. The Gaussian variance partitioning technique was used to accomplish the separation of the uncertainty and variability from the original distribution (CRWMS M&O 2000 [DIRS 151566], Section 6.4.7). Long-term corrosion testing continues, and the results will be used to reduce uncertainties. Near-term activities that address the treatment of this uncertainty are described in Sections 7.3.4 and 7.3.5.

7.2.3 Localized Corrosion

The generic localized corrosion model for waste package materials assumes that localized attack occurs if the open circuit corrosion potential (E_{corr}) exceeds the threshold (critical) potential for breakdown of the passive film (E_{crit}). In some cases, the threshold potential is assumed to be the repassivation potential. The repassivation potential is the level at which a failed passive film repassivates, or heals, thereby protecting the surface. In other cases, the threshold potential is assumed to be the pit or crevice initiation potential. Therefore, initiation of localized corrosion processes can be expressed in terms of the threshold electrochemical potential. For the highly corrosion-resistant materials under consideration, the threshold potential approach is recommended because it is more solidly rooted in the theoretical concepts underlying passive film stability.

A correlation was developed to compare corrosion and threshold potentials as a function of exposure conditions and determine whether localized corrosion initiates for the waste package (Alloy 22) and drip shield (Titanium Grade 7) (CRWMS M&O 2000 [DIRS 144971], Section 6.4; CRWMS M&O 2000 [DIRS 144229], Section 6.4.3). The correlation is based upon standard cyclic polarization measurements in a variety of test solution media covering a broad range of temperatures. The uncertainty in the corrosion potential due to gamma radiolysis (i.e., a maximum positive shift of about 250 mV for Alloy 22) has been addressed (CRWMS M&O 2000 [DIRS 144971], Section 6.8; CRWMS M&O 2000 [DIRS 144229], Section 6.4.4). The current potential-based localized-corrosion initiation threshold model is considered to represent the realistic behavior of Alloy 22 and Titanium Grade 7 under the expected repository conditions. Estimates of uncertainty in the selection of corrosion and threshold potential have been made and are incorporated in WAPDEG analyses. Because the threshold potentials on the waste package and drip shield surfaces were not exceeded, both the waste package and drip shield are never subject to localized corrosion for the entire simulation period (CRWMS M&O 2000 [DIRS 151566], Sections 5.3 and 5.4).

When exposure conditions are such that the threshold potential is exceeded, localized corrosion rates are applied to simulate penetration of the waste package and drip shield by the rapid-penetrating localized corrosion. The rates of localized corrosion for Alloy 22 and Titanium Grade 7 have been bounded with the range of values found in the published literature (CRWMS M&O 2000 [DIRS 144229], Section 6.6.6; CRWMS M&O 2000 [DIRS 144971], Section 6.7). The localized corrosion rates for Alloy 22 are assumed to be log-uniformly distributed between the bounds of 0.0127 mm/yr and 1.27 mm/yr, and the distribution is assumed to represent uncertainty in the localized corrosion rate (CRWMS M&O 2000 [DIRS 144229], Section 6.6.6). The localized corrosion rates for Titanium Grade 7 are assumed to be uniformly distributed between the bounds of 0.49 mm/yr and 1.12 mm/yr, and the distribution is assumed to represent uncertainty in the localized corrosion rate (CRWMS M&O 2000 [DIRS 144971], Section 6.7).

7.2.4 Microbiologically Influenced Corrosion

It has been observed that Titanium Grade 7 and Alloy 22 are relatively resistant to MIC (CRWMS M&O 2000 [DIRS 144971], Section 6.9; CRWMS M&O 2000 [DIRS 144229], Section 6.8). Furthermore, microbial growth in the repository will be limited by the availability of nutrients. In general, the impact of MIC can be accounted for by adjusting E_{corr} , E_{crit} , pH, and

the sulfide concentration in the area affected by the microbial activity (CRWMS M&O 2000 [DIRS 144229], Section 6.8).

The TSPA-SR analysis assumes that when the relative humidity at the surface of the waste package and drip shield is greater than a threshold value (i.e., 90 percent relative humidity), microbial activity becomes important enough that MIC can occur on Alloy 22 (CRWMS M&O 2000 [DIRS 151566], Section 5.8). The analysis assumes conservatively that when the relative humidity condition is met, microbial activity is at such a level that the biofilm covers the entire surface of all the waste packages and drip shields (CRWMS M&O 2000 [DIRS 151566], Section 4.1.10).

The TSPA-SR assumes that Titanium Grade 7 is not subject to MIC (CRWMS M&O 2000 [DIRS 151566], Section 5.8). The effect of MIC of Alloy 22 is modeled with a corrosion rate enhancement factor. The enhancement factor is determined from the ratio of measured corrosion current densities for abiotic and inoculated samples. Based on measurement data, the enhancement factor is assumed to be a uniform distribution with an upper bound of 2 and a lower bound of 1 (CRWMS M&O 2000 [DIRS 144229], Section 6.8). As discussed, this enhancement factor is applied to the entire surface of the waste package outer barrier and assumed to represent variability in the MIC effects on corrosion (CRWMS M&O 2000 [DIRS 151566], Sections 4.1.10 and 6.4.14).

7.2.5 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a potential degradation mode that can result in penetration of the waste package outer barrier (Alloy 22). SCC of materials may occur when an appropriate combination of material susceptibility, tensile stress, and environment is present. SCC is assumed to occur only in the regions around the closure welds of the Alloy 22 outer barrier because the residual stress in this weld cannot be relieved completely. It is assumed that residual stress in all welds used in the fabrication of the waste package outer barrier and Titanium Grade 7 drip shield are fully annealed, and thus are not subject to SCC (CRWMS M&O 2000 [DIRS 151564], Section 5.0). The effect of rockfall on the waste package outer barrier is excluded because of protection provided by the drip shield (CRWMS M&O 2000 [DIRS 153802], Section 1.0). SCC of the drip shield is possible under the applied stresses resulting from rockfall; however, it is assumed that SCC is of low consequence to drip shield performance, so it is not modeled (CRWMS M&O 2000 [DIRS 151564], Section 6.5.5).

An effective approach to eliminate the threat of SCC and the resultant through-wall cracking in the closure weld is to implement a post-weld stress mitigation process to either remove residual tensile stresses in the weld region or reduce them below threshold values for SCC initiation and growth. The closure of the waste package outer barrier is designed to include two lids (inner and outer) with two separate post-weld stress mitigation processes: laser peening of the inner lid weld and induction annealing stress relief of the outer lid weld. This two-lid design and stress mitigation strategy forms part of the conceptual model for the SCC model. The SCC model includes two alternative models, one based on the slip-dissolution mechanism at the crack tip for crack initiation and propagation, and another based on the threshold stress intensity factor at the tip of preexisting flaws. The slip dissolution model is preferred because it is the more conservative model, the U.S. Nuclear Regulatory Commission (NRC) has accepted the method,

and the model has been used for predicting the performance of boiling water reactor piping (Carpenter and Lund 1999 [DIRS 154988]; ASM International 1987 [DIRS 103753], p. 930). Additional data and analyses to quantify and reduce the present uncertainties in associated model parameters as described below are discussed in Section 7.3.3.

Slip Dissolution Model—The slip dissolution model employs a threshold stress for crack initiation (CRWMS M&O 2000 [DIRS 151564], Section 6.5.2). SCC is initiated if the threshold stress is exceeded on a smooth surface. The SCC propagation rate is calculated as a function of local environment and stress intensity factor. The time-to-failure is determined by integrating the calculated propagation rate. Thus, the residual stress and corresponding stress intensity factor are the two most important parameters in SCC analysis with the slip dissolution model.

In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), the slip dissolution model and its parameters are based primarily on published data. Limited data have been obtained under repository-relevant conditions. The parameters for the slip dissolution model are based on data for stainless steel in the boiling water reactor industry. Because stainless steels are much more prone to SCC than Alloy 22, these parameter estimates are conservative. The rate of repassivation is captured by the repassivation-slope parameter. A characteristic of the slip dissolution (or film rupture model) is that SCC susceptibility decreases with increasing values of repassivation slope (CRWMS M&O 2000 [DIRS 151564], Section 6.4.4). In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), the model parameter for repassivation slope is represented by a uniform distribution with an upper bound of 0.84 and a lower bound of 0.75, and the variation of the parameter value is due to uncertainty (CRWMS M&O 2000 [DIRS 151564], Section 6.4.4).

Threshold Stress Model for Crack Initiation—Although the slip dissolution model assumes that crack growth can initiate at any surface defect that can generate a stress intensity factor, regardless of defect size and tensile stress, examination of the relevant SCC literature indicates that there is a threshold stress below which SCC will not initiate on a “smooth” surface (i.e., free of surface breaking flaws). The uncertainty in the threshold stress for initiation of stress corrosion cracking is conservatively estimated to be approximately 20 to 30 percent of the material yield strength (CRWMS M&O 2000 [DIRS 148375], Section 6.5.2). The threshold stress and its uncertainty range are conservative and based on the determination of such thresholds for more susceptible alloy systems (e.g., stainless steels) exposed to very aggressive environments, such as boiling magnesium chloride. Uniform distribution between the bounds indicated above is assumed for the threshold stress uncertainty.

Closure-Weld Residual Stress Uncertainty—The stress profile (stress vs. depth) and corresponding stress intensity factor profile in the closure lid welds, before and after stress mitigation, are determined from analyses of measured residual stresses in welds as well as finite element modeling (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.2). The residual stress analysis shows that the dominant stress in the closure lid welds after stress mitigation is the hoop stress, which drives radial cracks through the closure lid weld region. The radial stress state, which drives circumferential cracks, does not remain tensile throughout the thickness of the closure lid weld region; therefore, there will be no through-wall cracking caused by circumferential cracks (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2 and Attachment I). This analysis indicates that only radial flaws are potential sites for through-wall SCC if it occurs.

The uncertainties in the residual stress profile (and corresponding stress intensity factor profile) were estimated from literature data (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.5). A separate uncertainty range was developed for each of three cases: optimum, realistic, and worst case. A stress uncertainty range of ± 5 percent was used to represent the optimum case that is achievable through stringent control of such processes as welding, stress mitigation, material variability, and other fabrication steps. The stress uncertainty range of ± 10 percent is used to represent the realistic case that is achievable through appropriate levels of process controls. The stress uncertainty range of ± 30 percent is used to represent the worst case that might result from inadequate control of the processes (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.5). The TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) considers an uncertainty range of the worst case (± 30 percent of yield stress) as the base case and evaluates the ranges of ± 10 percent and ± 5 percent in sensitivity analyses (CRWMS M&O 2000 [DIRS 151566], Section 4.1.8). Triangular distributions around the mean are assumed for the residual stress uncertainty.

Manufacturing Flaws in Closure Weld—An input to the SCC modeling approach is information regarding defects, incipient cracks, and manufacturing defects. Preexisting manufacturing flaws in the closure lid welds are the most likely sites for SCC failure. The frequency and size distributions for manufacturing flaws in the closure welds are based on published data for stainless steel pipe welds in nuclear power plants. The published data used to develop the manufacturing defect model utilize relevant welding techniques and post-weld inspection methods.

In the TSPA-SR analysis (CRWMS M&O 2000 [DIRS 153246]), preexisting surface-breaking defects and defects embedded in the outer 25 percent of the weld thickness are considered as potential sites for SCC crack growth (CRWMS M&O 2000 [DIRS 151549], Section 5.2). There is uncertainty associated with this assumption because, as general corrosion propagates, some of the existing surface-breaking defect flaws may disappear and some of the embedded defects may become surface-breaking defects. Use of this assumption is conservative because the WAPDEG model does not allow existing surface-breaking defects to be removed due to general corrosion processes during the simulation, leading to a greater number of defects capable of propagation. In addition, weld flaws are assumed to be randomly distributed spatially, as represented by a Poisson process (CRWMS M&O 2000 [DIRS 151549], Section 5.2). This assumption is reasonable for the manufacturing process being considered.

As described above, the residual stress analysis shows that the dominant stress in the closure lid welds after stress mitigation is hoop stress, which drives radial cracks through the closure lid weld region. This analysis indicates that only radial flaws are potential sites for through-wall SCC if it occurs. The TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumes that all manufacturing flaws are oriented in such a way that they could grow in the radial direction in the presence of hoop stresses. This is a highly conservative assumption. More realistically, most weld flaws, such as lack of fusion and slag inclusions, would be expected to be oriented within a few degrees of the weld centerline (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1). Available published data and limited flaw measurements from the viability assessment design mockups also show that most weld flaws (about 99 percent) tend to be oriented in a circumferential direction (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1). Analyses show it is extremely unlikely that cracks initiating from circumferential flaws grow in the radial direction (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1).

7.2.6 Hydrogen-Induced Cracking

Evaluation of hydrogen-induced cracking (HIC) is based upon a threshold hydrogen concentration. The drip shield design avoids any galvanic couple that would lead to the possibility of HIC. In the TSPA-SR analysis (CRWMS M&O 2000 [DIRS 153246]), a simple and conservative model was developed to evaluate the effects of HIC on the drip shield. The basic premise of the model is that failure will occur after the hydrogen content exceeds a certain limit, or critical value. This model is very conservative because it assumes that, once the environmental and material conditions can support that particular corrosion process, failure will be effectively instantaneous. The threshold hydrogen concentration value of 400 $\mu\text{g/g}$ was used initially for the HIC analysis of drip shield. Based on the threshold hydrogen concentration data for Titanium Grade 16, which is between 1,000 and 2,000 $\mu\text{g/g}$ (CRWMS M&O 2000 [DIRS 151559], Section 6.1.3), the threshold value for Titanium Grade 7 was updated to be at least 1,000 $\mu\text{g/g}$. This assumption is used because the threshold hydrogen concentration data are not available for Titanium Grade 7, and Titanium Grade 7 and 16 are similar alloys because of their similar chemical compositions (CRWMS M&O 2000 [DIRS 151559], Section 6.1.3).

A quantitative evaluation indicates that a wide margin of safety exists for the drip shield against the effects of HIC. Hydrogen concentration in the drip shield due to a galvanic couple with steel ground supports likely will not exceed the threshold value. The estimated hydrogen concentrations are less than the critical hydrogen concentration of 1,000 $\mu\text{g/g}$ (CRWMS M&O 2000 [DIRS 151559], Section 6.3.3). Analyses of a worst case scenario, which assumes local concentration of hydrogen from the galvanic coupling and impact of the contact area by a rockfall, conclude that hydrogen embrittlement is unlikely even though the hydrogen concentration may exceed the critical value. This is because the stress intensity factor induced by a rockfall is below the fracture toughness that may be degraded by hydrogen absorption (CRWMS M&O 2000 [DIRS 151559], Section 6.3.4). The analyses show that Titanium Grade 7 is an excellent choice of material for the drip shield with regard to degradation caused by HIC and that the drip shield is able to sustain the effects of HIC under expected conditions at the repository.

7.3 UNCERTAINTY ANALYSES

This section documents additional analyses conducted since the completion of the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) to quantify previously unquantified uncertainties in the waste package degradation model. The degradation processes for which uncertainties are quantified and/or reevaluated are:

- Chemical environment on the waste package and drip shield surfaces
- Aging and phase stability of Alloy 22 outer barrier
- Stress corrosion cracking of Alloy 22 outer barrier
- Passive film stability of Alloy 22 outer barrier
- General corrosion of Alloy 22 outer barrier

- Early waste package failure by improper heat treatment
- Other issues, including the threshold temperature for Alloy 22 localized corrosion and the effects of radiolysis on the Alloy 22 corrosion rate.

Natural analogues and industrial analogues, where available, are documented as multiple lines of evidence to support the degradation models and the uncertainty quantification. Where applicable, additional analyses are presented to address and quantify uncertainties in the waste package degradation processes that could be affected by alternative thermal operating modes.

7.3.1 Environments on Waste Package and Drip Shield Surfaces

7.3.1.1 Introduction

In order to understand waste package and drip shield performance in the potential repository, it is necessary to characterize the range of environments to which they might be exposed. These environments, combined with the material's properties, determine the potential degradation modes and the extent of the degradation.

The aqueous salt films that could form on these components will result either from hygroscopic salts that have been deposited on the surfaces or from evaporative concentration of dilute waters contacting these components. In order to determine the effect of aqueous films on the degradation of engineered barrier system (EBS) components, the brines that could form are characterized in terms of parameters that influence the corrosion processes. These parameters include pH, the hygroscopic characteristics of the salts, gas solubility (e.g., oxygen and carbon dioxide) in these waters, and the compositions of these waters.

Analysis of natural brines indicates that, in terms of pH, there are two types of brines: high pH sodium-carbonate-base brines, and near-neutral pH brines, which contain calcium and/or magnesium (Drever 1997 [DIRS 147480], Chapter 15). The high-pH brines do not contain significant calcium and magnesium because of the low solubility of magnesium-containing calcium carbonate and magnesium silicates under high pH conditions. These high pH brines may also contain a limited amount of soluble fluoride.

The near-neutral pH brines can contain soluble calcium and magnesium. Salt precipitates from these types of brines may contain chlorides of calcium and/or magnesium. These chloride salts are very hygroscopic (i.e., they form aqueous solutions at low relative humidities), and their saturated solutions have boiling points in excess of 160°C. Dissolution of pure chloride salts can result in very concentrated chloride solutions for low relative humidity conditions. This topic is discussed in Section 7.3.1.3.1.

The chemical composition of the waters also includes constituents that may only be present in small quantities due to solubility limitations. It is known, however, that some minor constituents, such as lead, arsenic, and mercury, may enhance the corrosion susceptibility of nickel alloys under specific conditions. A discussion of lead in the ambient system waters is presented in Section 7.3.1.3.3. Studies of arsenic and mercury in the ambient system waters are ongoing.

The contributions to aqueous solution formation by particulate matter and aerosols entrained in the ventilation air and by dust deposited with the drift are being actively investigated. Studies are underway to identify the soluble salt species contained in these sources, their contribution to the amount of salt deposited, and their projected contribution to the total amount of salt deposited. To supplement these studies, data obtained by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN 2001 [DIRS 154843]) for ionic species deposition are considered. These data are discussed in Section 7.3.1.3.4.

7.3.1.2 Goal of the Analyses

The following sections discuss information that supplements the analyses contained in previous documentation on this subject (CRWMS M&O 2000 [DIRS 151568]). The goal is to specify the environmental conditions that affect waste package and drip shield degradation as a function of temperature and relative humidity, considering lower- and higher-temperature operating modes of the potential repository. These environmental conditions include water composition, pH, presence of minor constituents, deliquescence points of deposited salts, and compositions of the aqueous solution at the deliquescence points.

Other goals of the analyses include reducing uncertainties pertaining to minor constituents that may be contained in waters that contact the waste packages and drip shields and uncertainties pertaining to soluble salts that may be deposited on these EBS components due to ventilation and drift dust.

7.3.1.3 New Analyses Since Total System Performance Assessment-Site Recommendation

7.3.1.3.1 Range of Water Chemistries on the Waste Package and Drip Shield

As an indication of the types of seepage waters that may contact waste packages and drip shields in the emplacement drifts, the range of water chemistries of saline lakes was considered. An examination of these lake waters indicates a wide range of compositions exists in nature (Drever 1997 [DIRS 147480]; see also Table 7.3.1-1 for examples). Table 7.3.1-1 notes lakes where chloride is the dominant anion, with significant amounts of calcium cation (e.g., Bristol Dry Lake, California). There are other lakes where the anion content includes significant amounts of sulfate and carbonate in addition to chloride (e.g., Alkali Valley, Oregon). The calcium and magnesium content in these high-carbonate lakes is very small.

Numerous factors influence the compositions of these saline lakes (Drever 1997 [DIRS 147480]). These include the compositions of the initial dilute water, which undergoes evaporative concentration; the partial pressure of carbon dioxide; and the mineralogy through which the waters that contribute to the lakes transverse. These processes must also be considered to specify the range of compositions of waters that may contact the drip shields and waste packages.

Numerous dilute waters have been sampled at Yucca Mountain. The compositions of these waters are listed in Table 7.3.1-2. Water from well J-13 has been well-characterized and its composition bounds established from numerous samplings (Harrar et al. 1990 [DIRS 100814]).

Compositions of the other waters are based on fewer measurements. The uncertainty in the measurements of pore water compositions (PERM-2 and PERM-3) is discussed in Section 6.

Applying the principal of the chemical divide (See Section 6) to evaporative concentration, the dilute waters of the well J-13 and the UZ-14 perched water form high pH sodium-carbonate-base brines. In contrast, the pore waters (PERM-2 and PERM-3 in Table 7.3.1-2) form near neutral pH brines that contain soluble magnesium and/or calcium. Of particular interest for corrosion concerns is the type of chloride salt that would form from evaporation to dryness. Halite (NaCl) has been identified as an evaporite mineral from a simulated well J-13 water and tachyhydrite ($Mg_2CaCl_6 \cdot 12H_2O$) has been identified from a simulated pore water (Rosenberg et al. 2000 [DIRS 152766]). The same reasoning for formation of $MgCl_2$ and/or $CaCl_2$ aqueous solutions can be applied to the brines that result from hygroscopic salts deposited on the waste packages and drip shields from particulate matter and aerosols entrained in the ventilation air and from drift dust.

The presence of chloride-containing salts allows for the possibility of formation of chloride-dominated waters, such as those seen in nature. The chemical separation of relatively pure chloride salts can occur in the host rock surrounding the drifts or on the waste packages or drip shields; therefore, the waters in contact with these EBS components could be chloride-dominated for at least some time period. With time, as the relative humidities increases and more salts become soluble, the composition of the waters in contact with drip shields and waste packages will contain other ionic species. It is well documented in the corrosion literature that anions such as nitrate, carbonate, fluoride, and sulfate can mitigate against the aggressiveness of chloride-enhanced corrosion (e.g., Thomas 1994 [DIRS 120498]). The project data confirm that the presence of these ions in solution reduces the aggressiveness of chloride ions to Alloy 22 corrosion (CRWMS M&O 2000 [DIRS 144229], Section 6.4.2). A recent project data indicates that nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solution at 120°C (Pasupathi 2001 [DIRS 155252]).

Previous analyses of the environment on the waste package outer barrier and drip shield focused on carbonate-base dilute waters contacting these EBS components (CRWMS M&O 2000 [DIRS 151568]), Section 6.4.2; see also Table 7.3.1-2 for composition of the dilute water). Experimental data and modeling indicate that these types of waters evolve into high-pH brines that do not contain significant amounts of soluble calcium or magnesium. Low to neutral pH variants of these waters were used in corrosion testing. The low pH variant is a sodium chloride-nitrate-sulfate solution at pH 2.7; the near-neutral pH solution was a high boiling point sodium-chloride-nitrate solution (CRWMS M&O 2000 [DIRS 151568], Section 6.4.2).

Present analyses also include non-carbonate base dilute waters contacting these EBS components. See Table 7.3.1-2 for composition of the dilute water. These waters will evolve into near-neutral pH brines that contain soluble calcium and magnesium, as has been confirmed experimentally (Rosenberg et al. 2001 [DIRS 152766]). The presence of these cations in the aqueous solutions could result in the formation of limited amounts of water that are stable at low relative humidities. However, the soluble amount of calcium and magnesium in these waters decreases during evaporative concentration due to the formation of insoluble precipitates, such as carbonates and silicates.

The quantity of highly concentrated water that may be in contact with the waste package and drip shield is limited by the amount of dilute water that must undergo evaporative concentration. As an example, a 1-L solution of 7.4 M $MgCl_2$, which will boil at 155°C (Casale 1967 [DIRS 155014]), requires the magnesium ion content from 5,400 L of PERM-2 water. In actuality, the availability of magnesium ions will be decreased significantly by the formation of insoluble precipitates; therefore, a larger quantity of dilute water would be necessary to supply the required amount of ions.

Modeling and experimental studies are ongoing to investigate the factors controlling the environments on the waste package and drip shield. In particular, the relationship between solution chemistry and partial pressure of CO_2 (P_{CO_2}) is of interest, since P_{CO_2} has a strong influence on the precipitation of insoluble magnesium and calcium species. An initial low-order approximation on the probability of the formation of magnesium and calcium chloride brines was attempted based on the combination of the different modeling runs done on the seven different water compositions (see Section 6.3.3.7.1). The initial approximation indicates that there would be a 14 percent chance of the starting water composition going toward a calcium/magnesium chloride brine due to evaporative concentration processes. However, the approximation is considered still qualitative and subjective, and cautions should be exercised in using the information in a quantitative analysis (see Section 6.3.3.7.1).

Modeling and experimental efforts are also focusing on minor constituents, such as lead, mercury, and arsenic, that may be present in the waters that contact the waste package and drip shield. These efforts focus on characterizing the availability of these species at Yucca Mountain, the solubility limits and the factors controlling solubility in natural waters, and the speciation of these components in solution. Corrosion studies of candidate materials in solutions based on these types of waters are ongoing. Some aspects of lead solubility in natural waters are discussed in Section 7.3.1.3.4.

7.3.1.3.2 Brine Formation Dependence on Relative Humidity

The formation of brines on EBS components and their characteristics are functions of incoming water chemistry, temperature, and relative humidity. It is assumed that the occurrence of brines on the components is controlled by the most hygroscopic salt contained in the deposited salts (CRWMS M&O 2000 [DIRS 151568], Sections 6.1 and 6.4.1; CRWMS M&O 2001 [DIRS 153265]). The composition of the brines may, however, include other ionic species that dissolve in the brines formed by the hygroscopic salts. Regardless of the deposited salts, the consequences for waste package degradation depend on the time, temperature, and relative humidity projections of any particular repository design.

For the deposited salts that evolve into high pH brines, aqueous solution formation is assumed to be controlled by the hygroscopic properties of sodium nitrate ($NaNO_3$) (Table 7.3.1-3). The deliquescence point of sodium nitrate varies from 50 percent relative humidity at the boiling point (120.6°C) (Kracek 1928 [DIRS 122125], pp. 351 to 373) of the saturated solution to 73 percent relative humidity at 30°C (Table 7.3.1-3). Hence, higher relative humidities are required for brine formation at lower temperatures. Other salts that may determine aqueous solution formation as a function of relative humidity include sodium chloride ($NaCl$). For

sodium chloride, the deliquescence point is nominally 75 percent relative humidity over a temperature range of 30° to 80°C (Table 7.3.1-3).

For the deposited salts that evolve into near-neutral pH brines, aqueous solution formation is assumed to be controlled by the hygroscopic properties of either calcium chloride (CaCl₂) or magnesium chloride (MgCl₂). Both of these salts are very hygroscopic (Table 7.3.1-3). The deliquescence point for magnesium chloride increases from 22 percent relative humidity at 100°C to 32 percent relative humidity at 30°C. No deliquescence point data for calcium chloride have been reported; however, the boiling point at sea level is 164.3°C (Kracek 1928 [DIRS 122125], pp. 351 to 373). The relative humidity at the boiling point (sea level) is about 15 percent.

7.3.1.3.3 Soluble Salts in the Ventilation Air

Particulate matter entrained in the ventilation air will introduce inorganic and organic material into the drifts that may affect the corrosion processes occurring on the waste package and drip shield. Hygroscopic salts, which are entrained in the ventilation air, may enhance the degradation of the EBS components by forming high ionic strength aqueous solutions at low relative humidities (CRWMS M&O 2000 [DIRS 151568], Section 6.1), facilitating electrochemical corrosion processes. The entrained organic matter could supply nutrients for microbiological activity. The Yucca Mountain Site Characterization Project (YMP) has an ongoing program to characterize the particulate matter in air in the vicinity of Yucca Mountain. Information from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN 2001 [DIRS 154843]) on the annual deposition of ionic species supplements this data collection.

The National Atmospheric Deposition Program/National Trends Network has been monitoring the deposition of several ionic species throughout the United States. The ionic species include chloride, sulfate (SO₄), nitrate (NO₃), sodium, calcium, magnesium, and potassium. Included in this program is a monitoring station at Red Rock Canyon (Site NV00) in Clark County, Nevada, where monitoring has been ongoing since 1985. The deposition rates (kilogram/hectare) of these ions are listed in Table 7.3.1-4.

The deposition rates for nitrate and sulfate are well in excess of the corrosively aggressive chloride. The nitrate and sulfate contents of waters have a mitigating effect on the aggressiveness of the chloride (see Section 7.3.5.4). In addition, sulfate ion may remove calcium from solution during evaporative concentration to brines as relatively insoluble calcium sulfate minerals (e.g., gypsum and hemi-hydrate). The calcium and magnesium content reported is due to carbonate.

7.3.1.3.4 Minor Constituents in Yucca Mountain Waters

Minor constituents, which may be present in waters that contact the EBS components, may enhance the degradation of these components. Minor constituents such as lead, arsenic, and mercury are of concern. The following discussion addresses the issues of lead content in natural waters and those phenomena that may limit the aqueous lead content. Future work will address the industrial experience of lead-, mercury-, and arsenic-enhanced corrosion and the content of

these elements in natural waters. These studies and laboratory testing for trace constituent solubility in concentrated brines are expected to improve uncertainties associated with minor constituents in water contacting the waste packages and drip shields.

Ambient Lead Groundwater Geochemistry at Yucca Mountain—Lead concentrations measured in groundwater in the vicinity of Yucca Mountain occur at trace levels (Perfect et al. 1995 [DIRS 101053]). The median lead concentrations of groundwater samples (those which had reported Pb concentration) collected within a 100,000-km² area in the southern Great Basin, which includes Yucca Mountain and the Nevada Test Site, is 9 ppb (Perfect et al. 1995 [DIRS 101053]; Lee 2001 [DIRS 155241]). The median value for Pb concentration was obtained from the data by using only those entries for which there is a reported Pb concentration. Of the 3,733 entries, 399 have values for Pb. A median of 9 ppb is obtained when only Pb concentration entries greater than or equal to zero are considered. This corresponds to 256 entries (Lee 2001 [DIRS 155241]). Two samples collected from the Obsidian Butte Brine Pond Site have lead concentrations near 3 ppm. The possible sources of lead at Yucca Mountain include trace concentrations present in the volcanic rock and foreign sources, perhaps wind-blown sediments or aerosols.

Waters with a range of chemical compositions are expected to come in contact with EBS components at Yucca Mountain. As discussed in Section 7.3.1.3.1, two types of water have received the most attention based on their chemical composition. The first type is water similar in composition to water from well J-13, a water-supply well near Yucca Mountain (Harrar et al. 1990 [DIRS 100814]). J-13 well water was used as the basis for estimating the chemistry of drift seepage water in a recent performance assessment (CRWMS M&O 1998 [DIRS 108004]). Perfect et al. (1995 [DIRS 101053]) reported J-13 well water analyses. In one sample, 3 ppb lead was detected; in the other sample, no lead was detected.

Another assessment of the chemistry of seepage water at Yucca Mountain suggests using a pore water-type composition from rocks in the Paintbrush (PTn) hydrostratigraphic unit in the unsaturated zone (UZ) above the repository (Sonnenthal and Bodvarsson 1999 [DIRS 117127]). The Paintbrush unit is a nonfractured tuff unit directly above the repository horizon unit, the Topopah Springs tuff (TSw). Although lead analyses of the Paintbrush pore water could not be found, it is likely that dissolved lead concentrations are similar to the trace concentrations reported in the surrounding groundwater.

The trace lead levels measured near Yucca Mountain are similar to lead concentrations measured in other natural groundwater. For example, dissolved lead is less than 1 ppb in the Gorleben aquifer in Germany (Lieser and Ament 1993 [DIRS 154845]). Even in groundwaters that contact lead-contaminated sediments, the levels are not high. For example, pore water measured in lead-contaminated estuarine sediments are less than 5 ppb (Carroll et al. 1999 [DIRS 154744]).

Dissolved lead concentrations in groundwater are controlled by lead adsorption on mineral surfaces and organic matter, as well as by precipitation of lead minerals (e.g., carbonates, sulfides, and phosphates) (Drever 1997 [DIRS 147480], pp. 189 to 192).

Current geochemical models may not adequately predict the processes that control lead concentration (e.g., EQ3/6 V7.2b). Ion exchange and sorption, which may reduce lead concentration, are not included in the models. Also, aqueous complexes that may be important in controlling lead concentration (Rickard and Nriagu 1978 [DIRS 154847]; Ferri et al. 1987 [DIRS 154849]; Bilinski and Schindler 1982 [DIRS 144730]) are not considered in these models.

The lead uptake onto minerals at Yucca Mountain has not been experimentally determined but, based on literature studies of other waters containing minerals found at Yucca Mountain (e.g., smectite, illite, zeolites, amorphous silica, cristobalite), it is expected that sorption of lead to those mineral surfaces is important in limiting lead concentration in groundwater at Yucca Mountain. For example, pure mineral separates suspended in groundwater show that lead is concentrated on quartz, kaolinite, calcite, and smectite (bentonite) surfaces. The greatest sorption coefficient (i.e., the ratio of lead on mineral phase to lead in solution) was measured for smectite (Freedman et al. 1994 [DIRS 155016]). The enhanced lead uptake is due to lead exchange for calcium in smectite interlayers (Siantar and Fripiat 1995 [DIRS 154850]; Nagy and Konya 1998 [DIRS 154851]). Roy et al. (1993 [DIRS 154852]) also report lead sorption to kaolinite and illite in complex ash-water suspensions at pH 12. In the absence of these minerals, lead remained dissolved in the solution.

Evaporative Evolution of Yucca Mountain Groundwaters and Lead Chemistry—Rosenberg et al. (2000 [DIRS 152766]) recently examined the evaporative evolution of both simulated J-13 well water and simulated PTn pore water from the UZ in a series of subboiling laboratory experiments, with and without crushed tuff present. The study did not include lead analysis, but is relevant nonetheless in terms of expected pH and mineral precipitation.

J-13 Well Water—The J-13 well water experiments indicate loss of calcium, magnesium, and HCO_3 from solution as carbonates, with magnesium likely going into a slightly disordered CaCO_3 phase. Evaporation produced an alkaline $\text{Na-HCO}_3\text{-CO}_3$ brine. The pH stabilized at about 10 after an approximately 50-fold concentration. After 1000-fold concentration, amorphous silica, aragonite, and calcite had precipitated from solution. Some clays also formed after complete evaporation.

Unsaturated Zone Pore Waters—After approximately 1000-fold concentration, the solution lost calcium and SO_4 , suggesting removal of these species as gypsum. Aqueous concentrations of magnesium, fluoride, HCO_3 , and SiO_2 also decreased with evaporation, suggesting some carbonate precipitation as well. The pH stabilized at about 6. Evaporation of this water produced a $\text{Na-K-Ca-Mg-Cl-NO}_3$ brine. The minerals recovered after complete evaporation contain a magnesium-smectite.

These experiments show that minerals that precipitate during evaporation of Yucca Mountain waters produce phases known to sorb lead (Wang and Stumm 1987 [DIRS 154853]). Additional experiments are in progress to determine the partitioning of lead between the precipitated minerals, candidate surfaces, and brine solutions during evaporative concentration.

7.3.1.4 Temperature Effect on Aqueous Solution Occurrence

The controlling factors for occurrence of aqueous solutions are relative humidity, temperature, and the particular salt. As discussed previously, the deliquescence point for most salts is temperature-dependent. In general, deliquescence points increase with decreasing temperature. However, ionic strengths of the salt solutions formed at the deliquescence points are very high, independent of temperature (CRWMS M&O 2000 [DIRS 151568], Section 6.4.1).

The effect of the hygroscopic nature of NaNO_3 on controlling the occurrence of aqueous solutions on the waste package and drip shield was discussed previously (CRWMS M&O 2000 [DIRS 151568], Section 6.4.1). The hygroscopic nature of MgCl_2 and CaCl_2 allows the formation of aqueous solutions at temperatures in excess of 155°C at very low relative humidities. The accelerating effect of temperature on corrosion will make these solutions more aggressive. A lower-temperature operating mode may offer an advantage in that if these salts are present, this higher-temperature corrosion mode will not occur.

As discussed in Section 7.3.1.3.1, the quantity of these salts and their saturated solutions that could form on the waste package and drip shield surfaces is expected to be limited. In addition, over the entire temperature range, the solutions will be very concentrated at the deliquescence point. With increasing relative humidity, aqueous solutions become more dilute and other, less hygroscopic salts deliquesce. The formation of mixed-ion solutions then becomes more probable. Hence, the time period when these conditions are operative is necessary for understanding their corrosive effect. Anions such as nitrate, carbonate, fluoride, and sulfate are known to mitigate against the aggressiveness of chloride-enhanced corrosion (Thomas 1994 [DIRS 120498]). The project data confirm that the presence of these ions in solution reduces the aggressiveness of chloride ions to Alloy 22 corrosion (CRWMS M&O 2000 [DIRS 144229], Section 6.4). A recent project data indicates that nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solutions at 120°C (Pasupathi 2001 [DIRS 155252]). An additional discussion on effects of environment on Alloy 22 corrosion is contained in Section 7.3.5.4.

7.3.1.5 Summary and Conclusions

Aqueous films will develop on the waste package and drip shield surfaces either by deliquescence of hygroscopic salts or evaporative concentration of the dilute waters contacting these EBS components. The chemical characteristics of these aqueous films will determine the extent of the electrochemical corrosion processes that occur on these components.

The range of water chemistries that contact the waste package and drip shield is constrained by the natural system. Dilute natural waters can evolve into high-pH, sodium-carbonate brine or into near-neutral-pH brine. The high-pH brine is primarily composed of sodium salts, while the near-neutral-pH brine may contain calcium and/or magnesium ions. Precipitated salts from the near-neutral-pH brine may contain chlorides salts of magnesium and/or calcium. These are very hygroscopic salts (i.e., they form aqueous solutions at very low relative humidities). However, because the soluble amounts of calcium and magnesium ions in the solution would decrease significantly during evaporation by the formation of insoluble precipitates, large quantities of seepage water would be necessary to provide significant quantities of these ions in concentrated

solutions. Other salts may also dissolve to a limited extent in these aqueous solutions. In addition, with rising relative humidities other precipitated salts will deliquesce, and hence mixed-ion solutions are more likely. Anions such as nitrate, carbonate, fluoride, and sulfate are known to mitigate against the aggressiveness of chloride-enhanced corrosion (Thomas 1994 [DIRS 120498]). The project data confirm that the presence of these ions in solution reduces the aggressiveness of chloride ions to Alloy 22 corrosion (CRWMS M&O 2000 [DIRS 144229], Section 6.4). A recent project data indicates that nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solutions at 120°C (Pasupathi 2001 [DIRS 155252]).

The ventilation system could bring soluble salts into the drifts. The extent of this contribution to the chemical composition of aqueous films in contact with the waste packages and drip shields may be estimated from rain deposition data. Sulfate and nitrate concentrations are higher than the chloride concentration, and calcium and magnesium are in the form of carbonate salts. The sulfate ions would remove calcium from concentrated solutions as calcium sulfate. The contribution of the soluble salts entrained in the ventilation air would then be expected to diminish the amounts of magnesium and calcium chloride solutions that might form.

The concentration of lead in natural dilute waters is low, and lead is not expected to concentrate to a significant extent because of precipitation as an insoluble species. Acidic conditions, where the solubility is high, are not expected to occur.

7.3.2 Aging and Phase Stability

7.3.2.1 Overview

7.3.2.1.1 Goal of Model

In the mill annealed condition, Alloy 22 is primarily a single-phase, face-centered cubic (FCC) solid solution with excellent corrosion resistance in a wide range of environmental conditions. Over time, other phases can precipitate out and degrade both the mechanical properties and the corrosion resistance of the alloy. The goal of this model is to determine whether the single-phase solid solution is stable under repository conditions, and if not, how fast other phases might precipitate. Precipitation kinetics in the annealed base metal, as well as in the annealed and laser-peened welds, must be modeled. In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), a corrosion enhancement factor ranging from 1.0 to 2.5 was applied to the closure welds to bound the effects of any phase instabilities. The new scientific data in this section are presented to increase confidence in the conservatism of this approach. The new data, however, do not yet indicate that the enhancement factor should be removed.

7.3.2.1.2 Background

The time it takes for these precipitation reactions to occur increases as the temperature decreases. At the expected repository temperatures, the kinetics of these precipitation reactions are too slow to measure experimentally. For this reason, the rates at which they occur are measured at temperatures that are high with respect to expected repository temperatures and then extrapolated to lower temperatures. Extrapolation from the relatively short laboratory time frame (tens of years) to the long repository time frame (tens of thousands of years) must be done over durations

spanning orders of magnitude. Because of the extended time period over which the extrapolation is done, small changes in the short-term data can have a large effect on the predicted results (CRWMS M&O 2000 [DIRS 147639], pp. 133, 134, 139, Figure 98). Theoretical calculations should be used to establish confidence in such extended extrapolations.

Several of the phases that form in Alloy 22 are Frank-Kasper, tetrahedrally close-packed (TCP) phases (Shoemaker and Shoemaker 1988 [DIRS 154989], pp. 19 to 45, Section 4): μ , P, and σ . These phases tend to be rich in molybdenum and/or chromium (Raghavan et al. 1984 [DIRS 154707], p. 789, Tables III and IV). Since these elements are largely responsible for the corrosion resistance of Alloy 22, precipitation of TCP phases can lead to degradation of the corrosion properties. The TCP phases are also very brittle and tend to precipitate (at least initially) on grain boundaries, leading to a reduction in the toughness and, to a lesser extent, the ductility of Alloy 22 (Summers et al. 1999 [DIRS 146915], pp. 922 to 923, Figures 2 and 3). As discussed below, the available data suggest that precipitation of these phases would be kinetically inhibited at expected repository temperatures. These data, however, were qualitative and had a large uncertainty associated with them; they were taken over a five-year time period and extrapolated to 10,000 years. A bounding argument was made in *Aging and Phase Stability of Waste Package Outer Barrier* (CRWMS 2000 [DIRS 147639], Section 6.2) to account for uncertainty in the short-term data. With the bounding structure, it was determined that the corrosion rate of Alloy 22 was enhanced by a factor of 2.5 (CRWMS M&O 2000 [DIRS 144229], Section 6.7.3). Theoretical calculations have since been done (see Section 7.3.2.2) to support the short-term experimental data. These calculations require more quantitative experimental support to reduce uncertainties. The amount of precipitation is currently being quantified as a function of time and temperature in order to do this.

At temperatures below approximately 600°C, long-range ordering (LRO) occurs in Alloy 22. This ordering has been linked to an increase in the susceptibility of similar nickel-chromium-molybdenum alloys to hydrogen embrittlement and stress corrosion cracking. It was tentatively concluded from very limited short-term data that LRO would not occur as long as the temperature was kept below about 260°C (CRWMS M&O 2000 [DIRS 147639], Section 6.5). New data, discussed below, indicate that this temperature limit is conservative. Again, theoretical calculations have been done to determine the rate at which ordering occurs, but conclusions from these calculations will remain uncertain until some experimental validation is done.

Welding produces a cast microstructure with chemical segregation regardless of the alloy used. In Alloy 22, segregation of primarily molybdenum causes TCP phases to precipitate during welding (Cieslak et al. 1986 [DIRS 104966], p. 2041). The chemical segregation of an as-welded structure, as well as these TCP phases, can result in degradation of the mechanical and corrosion properties of Alloy 22 welds when compared to the base metal. Although no enhanced corrosion rate was seen for welded Alloy 22 samples in long-term immersion tests involving chemical environments relevant to the potential repository at Yucca Mountain (CRWMS M&O 2000 [DIRS 144229], Section 6.5.2), no sensitive measurements have yet been made on Alloy 22 welds with a thickness that would be typical of the current waste package design in relevant environments. Data available from Alloy 22 immersion testing using the standard American Society for Testing and Materials (ASTM) G28A method (ASTM 3.02, *Standard Test Methods of Detecting Susceptibility to Intergranular Corrosion in Wrought, Nickel-Rich,*

Chromium-Bearing Alloys [DIRS 154712]) with a boiling solution of 50 percent H₂SO₄ and 42 g/l of Fe₂(SO₄)₃ indicate that the weld could have a corrosion rate that is approximately 2 to 2.5 times that of the annealed Alloy 22 base metal (Summers et al. 2000 [DIRS 154854], Figure 5; Heubner et al. 1989 [DIRS 107792], p. 256, Table 4). A similar enhancement of the corrosion rate of Alloy 22 welds was seen in boiling 2.5 percent HCl (Summers et al. 2000 [DIRS 154854], Figure 12). In 4M chloride solution at 95°C (pH = 8), the general corrosion rate of Alloy 22 welds was found to be comparable to the base metal (Dunn et al. 1999 [DIRS 154481], pp. 3 to 5). An enhancement factor of 2.5 for the general corrosion rate of unannealed Alloy 22 welds over that of annealed base metal is reasonable, and may even be conservative.

Growth of TCP phases in Alloy 22 welds due to thermal aging causes a further reduction of the corrosion resistance and mechanical properties of the weld. The kinetics of the reactions that occur in the weld may be different than those discussed above for the base metal because the precipitates are already nucleated in the weld and there is chemical segregation. New preliminary data (see Section 7.3.2.2) do not indicate that further nucleation and growth of TCP phases in Alloy 22 welds will occur at temperatures below approximately 200°C. Given the short-term nature of these data, conclusions will remain uncertain until theoretical calculations that take into consideration the numerous phases involved, their compositions, and segregation in the weld are performed and experimentally validated.

The planned solution and induction annealing of Alloy 22 welds will likely improve their corrosion resistance and mechanical properties. Growth of TCP phases in the welds will also occur at a rate somewhere between that seen for TCP phase nucleation and growth in annealed Alloy 22 base metal and that seen for unannealed weld metal. Heating outside the intended hot zone during induction annealing could nucleate TCP phases in the surrounding base metal, which may locally affect corrosion resistance and precipitation kinetics. The effect of such TCP phase nucleation is currently being investigated. Cold work due to laser peening may enhance both the corrosion rate of the weld and the TCP phase precipitation and LRO kinetics; these effects are also currently under investigation.

7.3.2.2 New Scientific Data Supporting the Model

This section discusses new scientific data and analyses conducted for thermal aging and phase stability of Alloy 22 since the completion of the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). As discussed previously, in the TSPA analysis, a corrosion enhancement factor with a range of 1.0 to 2.5 was applied to the closure welds to bound the effects of any phase instabilities. The new scientific data and analyses in this section support and enhance confidence in the conservatism of this approach. The new data, however, do not yet indicate that the enhancement factor should be removed.

7.3.2.2.1 Critical Temperature for Long-Range Ordering

The current model (CRWMS M&O 2000 [DIRS 147639], Section 6.5) for LRO in Alloy 22 was determined from the shortest times at which LRO was observed in Alloy 22 (annealed base metal). The model indicates that LRO is not likely to occur in 10,000 years as long as the temperature is kept below approximately 260°C for significant time periods (CRWMS

M&O 2000 [DIRS 147639], Section 6.5). This critical temperature is reached by solving Equation 5 in *Aging and Phase Stability of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 147639], Section 6.5) for a time of 8.8×10^7 hours (10,000 years), noting that T is temperature in Kelvin. New data (Figure 7.3.2-1) indicate that a critical temperature of 300°C is more realistic for the same time period.

A sample aged for 1,000 hours at 482°C was examined with transmission electron microscopy. No evidence of LRO was observed. This point falls very close to the line in Figure 7.3.2-1, suggesting that the new data are more realistic than the data used in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). As an estimate for the uncertainty in the critical temperature, the data were extrapolated using the points at 538°C for 100 hours and 482°C for 1,000 hours in one case, and the points at 482°C for 1,000 hours and 427°C for 20,000 hours in another. The critical temperatures obtained for these cases were 289°C and 309°C, respectively. A realistic critical temperature for the occurrence of LRO in 10,000 years is thus $300 \pm 11^\circ\text{C}$. This value may be conservative because the kinetics are calculated for an isothermal anneal (i.e., at a constant temperature). The waste package temperature in the repository peaks below 200°C and decreases over time (CRWMS M&O 2000 [DIRS 148384], Section 6.3.1). The extrapolation of short-term data over long time periods is being verified theoretically.

7.3.2.2.2 Theoretical Modeling of Precipitation of Tetrahedrally Close-Packed Phases and Long-Range Ordering in Alloy 22

Theoretical modeling was performed to determine phase diagrams and other thermodynamic properties of the phases that form in Alloy 22. It was also used to calculate the rate at which the relevant phase transformations occur (Turchi 2001 [DIRS 154934]).

The stability of the binary nickel-chromium, nickel-molybdenum, and molybdenum-chromium alloys and of the ternary nickel-chromium-molybdenum alloys was investigated. The study also focused on the role of additional solutes, such as silicon, carbon, cobalt, niobium, tantalum, and tungsten, on stability, ordering, and precipitation in Alloy 22. Figure 7.3.2-2 shows, as an example, the phase fraction versus temperature for Alloy 22 using a composition of 21.2Cr-13.5Mo-4Fe-3W-2Co-0.5Mn-0.3V-0.08Si-0.01C-bal. Ni (wt. percent). These results indicate that the TCP phases (P and probably μ) are stable at repository temperatures and will form if they are not kinetically inhibited. It is also apparent in Figure 7.3.2-2 that preparing samples for measurements of the corrosion and mechanical properties must be done considering the temperature range at which the relevant phases form. The phases that would be stable under potential repository conditions form at temperatures below approximately 800°C. Sigma phase forms at higher temperatures, but is not stable at the lower temperatures expected in the potential repository.

Kinetic and thermodynamic modeling were combined and applied to the study of diffusion-controlled transformations (Turchi 2001 [DIRS 154943]). These kinetic studies were focused on the time-dependent formation of complex TCP phases and LRO in terms of phase evolution from the FCC matrix for times up to 10,000 years. To date, a first series of calculations has been performed to predict the time-temperature-transformation (TTT) diagram for the case of the 10 percent transformation of an FCC-based nickel-chromium matrix in the ordered Ni_2Cr phase where experimental results were available (Karmazin 1982

[DIRS 154881]). A second series of simulations was done for the case of a ternary nickel-chromium-molybdenum alloy with a nominal composition of 55.7Ni-21.1Cr-13.5Mo (wt. percent). The transformation of P-phase from the FCC-based matrix ranging from 1 to 20 percent was considered as a function of time and temperature. These results are superimposed over the TTT diagrams reported in *Aging and Phase Stability of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 147639], Figure 96) in Figure 7.3.2-3. The results in Figure 7.3.2-3 are comparable to those in *Aging and Phase Stability of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 147639], Figure 96). A quantitative analysis of phase formation in samples annealed at various temperatures and for several aging times is being done to reduce uncertainties in this study's conclusions. In these simulations, grain boundary formation is not considered. Precipitation on grain boundaries, which is observed, occurs at a faster rate than bulk precipitation, which was treated here.

7.3.2.2.3 Weld Stability

Gas-tungsten-arc welds, which were made from 0.5-inch thick Alloy 22 base metal in a single V groove configuration using nine passes, were examined using optical microscopy at magnifications of 200 and 400 times. These welds were produced and aged at 593°, 649°, 704°, and 760°C for times up to 1,000 hours at Haynes International, Inc. in Kokomo, Indiana (Summers et al. 2000 [DIRS 154854]). Volume fraction measurements were also made. The measurements to date are preliminary. The amount and size of precipitates in the welds vary with position in the weld. For example, relatively few and smaller precipitates tend to be present near weld pass boundaries, while many larger precipitates tend to be present at the top of the last weld pass (CRWMS M&O 2000 [DIRS 147639], Figure 68). The measurements presented here represent averages over several positions in the weld. Future studies will correlate precipitate amount with location in the weld. These welds are also much thinner than those called out in the current waste package design. Welding conditions, such as heat input, that might affect the starting weld structure and the subsequent precipitation kinetics will be different for thicker welds. A study of precipitation kinetics in thicker welds is currently planned. Also, several phases are expected in Alloy 22 welds; σ , μ , and P have been observed (Cieslak et al. 1986 [DIRS 104966], p. 2041). The growth kinetics for each of these phases may be different. In the base metal, it is likely that the amount of σ -phase precipitating is small at temperatures below about 750°C and that μ - and P-phases are similar. In the weld, however, the amount of σ -phase may be quite high due to chemical segregation. More refined studies that take these factors into account are being done to reduce uncertainties associated with conclusions drawn about weld stability.

In the as-welded condition, the volume fraction of precipitates measured was 0.029 at 200-fold magnification and 0.025 at 400-fold magnification. The times required for this volume fraction to increase to 0.05 and 0.10 are listed as a function of temperature in Table 7.3.2-1. These times are plotted against reciprocal temperatures in Figure 7.3.2-4.

The data in Figure 7.3.2-4 are for isothermal conditions. The temperature of the repository is expected to peak below 200°C and decrease over thousands of years. Weld stability does not appear to be a problem for Alloy 22. Because the extrapolation is done over very long times from relatively short-term data, very small changes in the measured data can cause a shift in the extrapolated cutoff temperature to give a 10,000-year life of a hundred degrees or more.

Theoretical calculations similar to those being made for TCP phase precipitation will be done to account for any uncertainties associated with segregation in the welds, the different phases present, and the other experimental difficulties mentioned above.

7.3.2.3 Effect of Temperature on Precipitation Kinetics

The time to cause precipitation reactions in Alloy 22 is exponentially dependent on temperature. For example, a curve fit to the data in Figure 7.3.2-1 yields:

$$time = 3.0 \cdot 10^{-13} \exp\left(\frac{27098}{T}\right) \quad (\text{Eq. 7.3.2-1})$$

where T is temperature in Kelvin and $time$ is in hours. This exponential temperature dependence is very strong. Solving Equation 7.3.2-1 for $T = 673$ K (400°C) yields a time of 90,000 hours (10 years). At 573 K (300°C), the time is 10^8 hours (10,000 years), an increase of four orders of magnitude. Further reductions in temperature have similar orders of magnitude increases in time.

The temperature dependence in Equation 7.3.2-1 assumes the temperature remains constant. The temperature of the waste package is not expected to be constant. It has been calculated to peak below about 200°C and decrease over time (CRWMS M&O 2000 [DIRS 153246], Section 3.3.3). Thus, estimates based on isothermal conditions are conservative. Because of the strong temperature dependence of the rate of these precipitation reactions, the margin in the conclusion that phase instabilities will not occur greatly increases as temperature decreases.

7.3.2.4 Alternative Lines of Evidence to Support Model

7.3.2.4.1 Critical Temperature for Precipitation of Tetrahedrally Close-Packed Phases

The data available for the phase stability of Alloy 22 base metal used in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) did not indicate that precipitation of TCP phases is likely even at 300°C for 10,000 years (CRWMS M&O 2000 [DIRS 147639], Section 6.2). These data, however, had a large degree of uncertainty, so a bounding argument was made to account for this uncertainty. The mechanical and corrosion properties of aged Alloy 22 have been measured (Rebak et al. 2000 [DIRS 146910]). The times to give a degradation of the Charpy impact toughness from 264 to 150 ft-lb and the times to cause an increase in the corrosion rate, measured with the ASTM G28A procedure (ASTM 3.02 [DIRS 154712]), from 0.8 to 2.03 mm/year were extrapolated to 10,000 years. These data are reproduced with estimated error bars in Figure 7.3.2-5. The uncertainty associated with these data is much less than that associated with the data in *Aging and Phase Stability of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 147639], Section 6.2). Extrapolation of these data indicates that the phase instabilities that cause this property degradation will not occur in 10,000 years, even at temperatures much higher than 300°C .

According to Figure 7.3.2-5, the time at which the ASTM G28A (ASTM 3.02 [DIRS 154712]) corrosion rate reaches 80 mpy is approximately 7 hours at 704°C . The time at which the Charpy impact toughness decreases to 150 ft-lb is 60 hours at 704°C . The fully aged structure used as a

bounding case for the TSPA-SR model was created by aging Alloy 22 base metal for 173 hours at 700°C (CRWMS M&O 2000 [DIRS 153246]). These data indicate that the microstructural changes responsible for the degradation of the mechanical and corrosion properties at relatively high temperatures are not likely to occur under expected repository conditions.

7.3.2.4.2 Natural Analogues

Awaruite is a naturally occurring, ordered iron-nickel metallic mineral with an approximate stoichiometry of Ni_3Fe . It was first discovered in Awarua, New Zealand, but has been found at various locations around the world (Krishnarao 1964 [DIRS 154746], p. 443). Josephinite, a rock found in Josephine County, Oregon, contains grains of awaruite that are larger than other sources of awaruite. Josephinite also has, in some instances, a unique mixture of minerals that has been tied to changes in the local environment and higher temperatures associated with hornblende diorite dikes from igneous intrusions (Dick 1974 [DIRS 154749], p. 297; Göpel et al. 1990 [DIRS 154750], p. 26). The age of these dike intrusions has been measured, using potassium-argon dating, at approximately 150 to 155 million years (Dick 1974 [DIRS 154749], p. 292). Other nearby rocks also associated with the formation of josephinite have been dated, using lead isotopes, at 159 ± 8 million years (Göpel et al. 1990 [DIRS 154750], p. 24). Thus, the age of josephinite is on the order of 150 million years.

Some samples of josephinite contain taenite (the high-temperature, disordered, FCC Ni-Fe metallic phase) as well as awaruite. The composition and amount of each of these phases in the two-phase mixture have been fit to the Fe-Ni phase diagram, showing that these phases formed in the temperature range of 460° down to about 400°C (Botto and Morrison 1976 [DIRS 154716]). The fact that the composition and amount of these phases fits the phase diagram at the higher temperatures indicates that no changes have occurred at lower temperatures. Taenite is not stable below about 350°C; α -Fe and awaruite are the stable phases at ambient temperatures. The fact that taenite, not α -Fe, is present in josephinite also indicates that no changes have occurred in the 150 million years since these samples formed.

Out of necessity, phase stability is studied at temperatures greater than those expected in the repository so the rate at which phase changes occur can be measured. These rates are measured as a function of temperature, and the functional relationship is extrapolated to the lower repository temperatures. The stability of the metallic structures in josephinite over millions of years suggests no low-temperature mechanism with rates significantly greater than those predicted exists, thus providing confidence in the implicit assumption that the high-temperature mechanisms used to extrapolate kinetics are the same as the low-temperature mechanisms that will be active under repository conditions.

7.3.3 Stress Corrosion Cracking

Stress corrosion cracking is a potential degradation mode that can result in penetration of the waste package outer barrier material (Alloy 22). Stress corrosion cracking of materials may occur when an appropriate combination of material susceptibility, tensile stress, and environment is present. The current analysis assumes conservatively that, in the presence of tensile stress, Alloy 22 is susceptible to stress corrosion cracking in any environment that can have a stable water film form on the waste package surface, irrespective of the chemistry of the water film

(CRWMS M&O 2000 [DIRS 151566], Section 5.7). This is based on industrial experience with stress corrosion crack failures of recirculating coolant pipes in a boiling water reactor. The recirculating coolant is high-purity, neutral-pH water (ASM International 1987 [DIRS 103753], p. 930).

The closure of the waste package outer barrier is designed to include two lids with two separate post-weld stress mitigation processes: laser peening of the inner lid welds and induction annealing stress relief of the outer lid welds. This two-lid design and stress mitigation strategy form part of the basis for the stress corrosion crack model. In the TSPA-SR stress corrosion cracking is assumed to occur only in the regions around the closure welds of the waste package outer barrier because the residual stress in the closure welds cannot be relieved completely by stress mitigation techniques (CRWMS M&O 2000 [DIRS 151566], Section 5.6). It is assumed that all welds used in the fabrication of the waste package outer barrier (other than the closure welds) and the Titanium Grade 7 drip shield are fully annealed, and thus are not subject to stress corrosion cracking (CRWMS M&O 2000 [DIRS 151564], Section 5.0). The approach is also employed in the current analysis. Stress corrosion cracking of the drip shield is possible under the applied stresses resulting from rockfall; however, it is assumed to be of low consequence to drip shield performance, so it is not modeled in the analysis described in *Stress Corrosion Cracking of the Drip Shield, the Waste Package Outer Barrier, and the Stainless Steel Structural Material* (CRWMS M&O 2000 [DIRS 151564], Section 6.5.5).

7.3.3.1 Goal of the Analysis

The TSPA-SR analysis uses the slip dissolution model for stress corrosion crack analysis of the waste package (CRWMS M&O 2000 [DIRS 151566], Section 3.2.4). The slip dissolution model calculates the stress corrosion crack propagation rate, V , as a function of the local exposure environment (represented by parameter n for the repassivation rate [or repassivation slope] at the crack tip) and the stress intensity factor, K_I (CRWMS M&O 2000 [DIRS 151564], Section 6.4.4):

$$V = \bar{A}(K_I)^{\bar{n}} \quad (\text{Eq. 7.3.3-1})$$

where V is the crack growth rate in mm/s and K_I is the stress intensity factor in MPa (m)^{1/2}. Parameters \bar{A} and \bar{n} in the above equation are expressed in terms of the repassivation rate, n , as follows:

$$\bar{A} = 7.8 \times 10^{-2} n^{3.6} (4.1 \times 10^{-14})^n \quad (\text{Eq. 7.3.3-2})$$

$$\bar{n} = 4n \quad (\text{Eq. 7.3.3-3})$$

The slip dissolution model has been used in the boiling water reactor industry as a crack propagation prediction tool (ASM International 1987 [DIRS 103753], p. 930) and is accepted by the NRC (Carpenter and Lund 1999 [DIRS 154988]). The time-to-failure from stress corrosion cracking (i.e., the time to through-wall penetration by a stress corrosion crack) is determined by integrating the calculated propagation rate. Thus, the residual stress and corresponding stress intensity factor are important parameters in the stress corrosion cracking analysis for the slip

dissolution model (CRWMS M&O 2000 [DIRS 151549], Section 6.4). Another important parameter is the threshold stress for stress corrosion crack initiation. The current model assumes that stress corrosion cracking initiates only if the threshold stress is exceeded at the tip of an “intrinsic” flaw or a weld flaw (CRWMS M&O 2000 [DIRS 151564], Section 6.5.2). In addition, because stress corrosion cracks initiated from weld flaws are likely the ones that fail waste packages (CRWMS M&O 2000 [DIRS 151566], Section 6.5.2), the size, frequency, and orientation of weld flaws are also important to the stress corrosion cracking analysis of waste packages. The goal of the analyses discussed in this section is to reexamine the uncertainties and conservatism in the important stress corrosion cracking model parameters in the TSPA-SR analysis (CRWMS M&O 2000 [DIRS 153246]) and to quantify and update their uncertainties by incorporating the data and analyses that have become available since the completion of the TSPA-SR.

7.3.3.2 Identification of Unquantified Uncertainties in Total System Performance Assessment-Site Recommendation

As discussed above, this section reviews approaches to treating uncertainties associated with the stress corrosion cracking model parameters in the TSPA-SR model. This section also identifies stress corrosion cracking model parameters for which uncertainties were not quantified or for which an excessive conservatism was employed in the analysis. In particular, the important stress corrosion model parameters reviewed in this section are:

- Parameter n in the slip dissolution model
- Residual stresses in the outer and inner closure lid welds of the Alloy 22 waste package outer barrier
- Threshold stress for stress corrosion crack initiation in the Alloy 22 outer barrier
- Orientation of weld flaws in the waste package outer barrier closure welds
- Plugging of stress corrosion cracks in the drip shield and waste package outer barrier by calcite precipitation.

Parameter n in the Slip Dissolution Model—In the slip dissolution model, the rate of repassivation at the crack tip is captured by the parameter n , referred to as the repassivation slope. A characteristic of the slip dissolution (or film rupture model) is that stress corrosion crack susceptibility decreases with increasing values of n (CRWMS M&O 2000 [DIRS 151564], Section 6.4.4). In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), because limited data were available under repository conditions, the parameter was evaluated based on data for stainless steel in boiling water reactors (CRWMS M&O 2000 [DIRS 148375], Section 3.2.2). Because stainless steels are more prone to stress corrosion cracking than Alloy 22, the parameter estimates are considered conservative. In the *WAPDEG Analysis of Waste Package and Drip Shield Degradation* (CRWMS M&O 2000 [DIRS 151566], Section 4.1.9), n is represented by a uniform distribution with an upper bound of 0.84 and a lower bound of 0.75, and the variation of the parameter value is assumed to be due to uncertainty.

From recently obtained longer-term data for Alloy 22 under repository-relevant conditions, the model parameter n and its uncertainty have been reevaluated. The parameter is now represented by a uniform distribution with an upper bound of 0.920 and a lower bound of 0.843 (CRWMS M&O 2000 [DIRS 151564], Section 6.4.4). As for the TSPA-SR case (CRWMS M&O 2000 [DIRS 153246]), variation in the parameter value is assumed to be due to uncertainty. With the updated uncertainty distribution for n , the through-wall penetration time of a 20-mm thick Alloy 22 layer by stress corrosion cracking increases significantly relative to that obtained using the previous uncertainty distribution (CRWMS M&O 2000 [DIRS 151549], Section 6.4.5). The updated uncertainty distribution for n represents the current state of knowledge, and no further characterization and quantification of uncertainty in n is attempted in the current analysis.

Closure-Weld Residual Stress Uncertainty—The closure welds of the outer and inner lid of the waste package outer barrier will be treated by induction heating and laser peening, respectively, to mitigate stresses and generate compressive stress at the surface and down to a significant depth. The stress mitigation treatments will be limited to the closure weld area. In particular, the induction heating will be performed in such a way that other areas are not heated to undesirable temperatures. The resulting residual stress profiles in both of the closure lids were calculated, as a function of depth (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.2). As discussed in the *Abstraction of Models of Stress Corrosion Cracking of Drip Shield and Waste Package Outer Barrier and Hydrogen Induced Corrosion of Drip Shield* (CRWMS M&O 2000 [DIRS 151549], Section 6.3), hoop stress is the dominant stress to potentially drive radial cracks through the wall thickness. Therefore, the profile with the highest hoop stress was used as a mean stress profile for the outer and inner closure lid welds.

Because no measured data are available for the waste package design, the uncertainties in the residual stress were addressed in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) by considering three scenarios (optimum, realistic and worst case) for welding and post-weld mitigation operations and assigning separate uncertainty ranges for each scenario (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.5). The uncertainty bounds for individual scenarios were based on literature data. The optimum case is the best case scenario that is achievable through stringent control of such processes as welding, stress mitigation, material variability, and other fabrication steps, and is represented by the stress uncertainty range of ± 5 percent of the yield strength. The realistic case is assumed achievable through appropriate levels of process controls, and is represented with the stress uncertainty range of ± 10 percent of the yield strength. The worst case is a case that might result from inadequate control of the processes, represented with the stress uncertainty range of ± 30 percent of the yield strength (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.5). The TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) considers the uncertainty range of the worst case (± 30 percent of the yield strength) as the base case, and evaluates the ranges of ± 10 percent and ± 5 percent of the yield strength in sensitivity analyses (CRWMS M&O 2000 [DIRS 151566], Section 6.2.2.5). The triangular distributions around the mean and the bounds (i.e., ± 5 , ± 10 , and ± 30 percent of the yield strength) are assumed for the residual stress uncertainty. The TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) base case uncertainty bounds are highly conservative, based on information available in the literature and considering the strict process control and inspections that will be implemented during the waste package manufacturing process.

Additional analyses have been conducted since the completion of the TSPA-SR (CRWMS M&O 2000 [DIRS 153246] to further quantify the residual stress uncertainty and remove the conservatism in the base case. In the absence of measured data for the waste package design, those analyses focused on relevant literature data for similar stress mitigation techniques applied to similar materials (Offer 1983 [DIRS 154454]; Chrenko 1980 [DIRS 154451]; Shack and Ellingson 1980 [DIRS 154456]; Pasupathi 2000 [DIRS 149968]). The outer closure lid weld region of the waste package outer barrier will be induction annealed (CRWMS M&O 2000 [DIRS 144128], Section 6.4). Consideration of the literature data resulted in a revision of the symmetric upper and lower bounds on the stress and stress intensity factor profile uncertainty distribution from ± 30 percent to ± 21.4 percent. The inner closure lid weld region of the waste package outer barrier will be laser peened (CRWMS M&O 2000 [DIRS 144128], Section 6.4). Consideration of the literature data resulted in the development of a cumulative distribution function for the symmetric upper and lower bounds on the stress and stress intensity factor profile uncertainty distribution. Details of the analyses and uncertainty quantification approach are described in Sections 7.3.3.3.1 and 7.3.3.3.2 for the outer lid and inner lid welds, respectively.

Threshold Stress for Crack Initiation—Although the slip dissolution model assumes crack growth can initiate at any surface flaw that can generate a stress intensity factor, regardless of flaw size and tensile stress, examination of relevant literature (Erbing Falkland 2000 [DIRS 149956], p. 661, Figure 8; Haynes International 1998 [DIRS 154463]) indicates that there is a threshold stress below which stress corrosion cracking will not initiate on a “smooth” surface (i.e., free of surface breaking flaws). In the absence of relevant Alloy 22 test results, literature results on Stainless Steel Type 304 were used to assess the expected stress corrosion crack susceptibility of Alloy 22 in terms of initiation threshold stress. These results were obtained in very aggressive boiling magnesium chloride or in 0.1 M sodium chloride solutions dripped onto stressed specimens heated to 200°C. Under these very aggressive conditions, lower-bound initiation threshold stresses of 20 to 30 percent of the yield strength were observed, so this range was conservatively selected for waste package design applications. Accordingly, in the TSPA analysis, the uncertainty in the threshold stress for initiation of stress corrosion crack is conservatively estimated to be approximately 20 to 30 percent of the Alloy 22 yield strength (CRWMS M&O 2000 [DIRS 151564], Section 6.5.2). A uniform distribution between the bounds is assumed for the threshold stress uncertainty.

However, in these very aggressive environments, initiation stress threshold values for higher nickel-content stainless steels and nickel-base alloys may exceed 80 percent of the yield strength. In the case of Alloy 22 U-bends (10 to 15 percent strain) in boiling magnesium chloride, the initiation threshold may exceed approximately 200 percent of the yield strength (Erbing Falkland 2000 [DIRS 149956], p. 661, Figure 8; Haynes International 1998 [DIRS 154463]). The literature data and YMP measured data generated since completion of the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) were used to reevaluate the initiation threshold stress and quantify its associated uncertainty. In Section 7.3.3.3.3, it is concluded that the initiation threshold stress should be sampled from a uniform distribution between 80 and 90 percent of the yield strength. Details of the analysis and approach are described in Section 7.3.3.3.3.

Orientation of Manufacturing Flaws in Closure Weld—The waste package analysis considers both incipient cracks and manufacturing flaws. Preexisting manufacturing flaws in the closure

lid welds are the most likely sites for waste package failure by stress corrosion cracking. Therefore, characteristics of flaws in the waste package closure welds are important input to the waste package stress corrosion cracking analysis. In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), the frequency and size distributions for manufacturing flaws in the closure welds were developed based on published data for stainless steel pipe welds in nuclear power plants (CRWMS M&O 2000 [DIRS 152097], Section 6.2.1.1). The published data used to develop the manufacturing defect model are those utilizing welding techniques and post-weld inspection methods that are relevant to waste package manufacturing (CRWMS M&O 2000 [DIRS 152097], Section 6.2.1.1).

As discussed previously, the hoop stress is the dominant stress in the closure lid welds, which drives radial cracks through the closure lid weld region. This analysis indicates that only radial flaws are potential sites for through-wall stress corrosion cracking, if it occurs. The TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumes conservatively that all manufacturing flaws are oriented in such a way that they could grow in the radial direction in the presence of hoop stresses (CRWMS M&O 2000 [DIRS 151566], Section 5.5). This is a highly conservative assumption. Considering additional literature information and limited measured data from the mockups developed for the viability assessment analysis, analyses were conducted to quantify the uncertainty associated with the orientation of weld flaws in the waste package closure welds. It was determined in Section 7.3.3.3.4 that, based on weld flaw orientation, the fraction of weld flaws capable of propagation in the radial direction should be sampled from a lognormal distribution with a mean of one percent, an upper bound of 50 percent, and lower bound of 0.02 percent. Details of the analysis and approach, along with the quantified uncertainty, are described in Section 7.3.3.3.4.

Plugging of Stress Corrosion Cracks by Calcite Precipitation—Analyses have shown that stress corrosion cracking of the drip shield is possible under the applied stresses resulting from rockfall (CRWMS M&O 2000 [DIRS 149574]). However, the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumed that stress corrosion cracking failure of the drip shield is of low consequence to the intended performance of the drip shield; therefore, it was not modeled in the analysis (CRWMS M&O 2000 [DIRS 153802], Section 3.2.1). The basis of the assumption made in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) was as follows. Cracks in passive alloys, such as Titanium Grade 7 or Alloy 22, tend to be very tight (i.e., small crack opening displacement) by nature (CRWMS M&O 2000 [DIRS 151564], Section 6.5.5). The opposing sides of through-wall cracks will continue to corrode at very low passive corrosion rates until the gap region of the tight crack opening is “plugged” by the corrosion product particles and mineral precipitates, such as carbonate, present in the water. Any water transport through this oxide/salt-filled crack area will occur mainly by diffusion-type transport processes (CRWMS M&O 2000 [DIRS 151564], Section 6.5.5). Thus, the effective water flow rate through cracks in the drip shield would be expected to be extremely low and should not contribute significantly to the overall radionuclide release rate from an underlying failed waste package. Therefore, because the primary role of the drip shield is to keep water from contacting the waste package, stress corrosion cracking of the drip shield is of low consequence to waste package performance.

Quantitative bounding analyses have been undertaken to determine whether calcite and other minerals can precipitate at a sufficiently high rate to plug cracks resulting from stress corrosion. In addition to corrosion products, mineral deposits and possibly particulates could increase the

volume of materials and plug the crack faster. The analyses will also determine the time frame at which calcite and other minerals can precipitate in the stress corrosion cracks. The calculation depends mainly on two parameters: the evaporation at the surface of the waste package or drip shield, in particular in the vicinity of cracks, and the precipitation rate of minerals (Nicot 2001 [DIRS 154452]). The analyses focus on the extended cooldown period (from 2,000 to 100,000 years) that occurs after the boiling period (50 to 1,000 years), when stress corrosion cracks still have an impact on the performance of the waste packages. The analyses consider calcite and amorphous silica as minerals that potentially precipitate within the stress corrosion cracks. The analyses consider two end-member scenarios for potential water flow characteristics in the cracks: film flow and water bridging across the crack opening (Nicot 2001 [DIRS 154452], Section 5.3.3). The water bridging scenario employs highly conservative assumptions, such as no corrosion of the crack wall, no mixing of the bridging water with the outside environment, no water transport along the crack wall, and no consideration of mineral precipitate in the presence of fine particulates of corrosion products along the crack wall.

The analysis results show that for the film flow scenario, cracks are plugged by mineral precipitates within a decade (Nicot 2001 [DIRS 154452], Tables 6-3 and 6-5). For the conservative scenario (i.e., water bridging scenario), plugging of stress corrosion cracks takes 600 to 1,000 years if the crack opening occurs prior to 20,000 years (Nicot 2001 [DIRS 154452], Tables 6-4 and 6-6). Considering the conservatism employed in the water-bridging scenario, the time to plugging the cracks would be sooner than the bounding estimates. Because the time periods required for the crack plugging by mineral precipitates are much shorter than the time steps used in the TSPA analysis (CRWMS M&O 2000 [DIRS 153246]), the assumption for the crack plugging is well justified. No further characterization and quantification of uncertainty in the time to plugging the stress corrosion cracks is attempted in the current analysis.

7.3.3.3 Quantification of Model Parameter Uncertainties

This section discusses additional analyses conducted to quantify uncertainties of the important stress corrosion cracking model parameters identified in Section 7.3.3.2. The analyses include new measured data from ongoing YMP testing programs and any new analyses developed. The analyses also incorporate additional literature data and information relevant to the current waste package design and repository exposure environments. As discussed in Section 7.3.3.2, the stress corrosion cracking model parameters to be considered further for uncertainty quantification are:

- Residual stresses in the outer and inner closure lid weld regions of the Alloy 22 waste package outer barrier
- Threshold stress for stress corrosion crack initiation in the Alloy 22 outer barrier
- Orientation of weld flaws in the waste package outer barrier closure welds.

No further uncertainty quantification beyond the discussion presented in Section 7.3.3.2 is undertaken for the parameter n in the slip dissolution model and plugging of stress corrosion cracks in the drip shield and waste package outer barrier by calcite precipitation.

7.3.3.3.1 Uncertainties in Residual Stress in Outer Lid Closure Welds

As discussed in Section 7.3.3, the closure welds of the outer lid of the waste package outer barrier will be treated by induction heating to mitigate stresses and generate compressive stress at the surface and down to a significant depth. The induction heating treatment will be limited to the closure weld area, and will be performed in such a way that other areas are not heated to undesirable temperatures. The resulting residual stress profiles as a function of depth in the outer closure lid welds were calculated (CRWMS M&O 2000 [DIRS 151564], Section 6.2). As discussed in the *Abstraction of Models of Stress Corrosion Cracking of Drip Shield and Waste Package Outer Barrier and Hydrogen Induced Corrosion of Drip Shield* (CRWMS M&O 2000 [DIRS 151549], Sections 5.3 and 6.3.1.1), the profile with the highest hoop stress from the calculated residual stress profiles was used as a mean stress profile for the outer closure lid weld region. This section provides the technical basis and an approach to quantifying the uncertainty in the calculated mean residual stress. It is assumed in this analysis that the stress measurement uncertainty is the primary contributor to the total uncertainty in the residual stress. Because no stress profile data are available for the waste package design, the uncertainty quantification is based on literature data generated for similar stress mitigation techniques, such as the induction heat treatment process referred to as Induction Heating Stress Improvement (IHSI) (Offer 1983 [DIRS 154454]).

The measurement of residual stresses in components may involve the use of one or more techniques to obtain the total stress state. The techniques used may require the destruction of the component to determine the residual stresses, or they may be performed in a totally nondestructive manner. Because the data generated for IHSI utilized the mechanical (strain gage stress relief) and x-ray residual stress techniques for measurement, these two techniques are therefore the focus of this analysis, and the errors and accuracy associated with those techniques are quantified. Those are two of the most popular residual stress measurement techniques. The x-ray residual stress technique is a nondestructive technique; the strain gage stress relief technique is a destructive technique (Offer 1983 [DIRS 154454]).

X-Ray Diffraction Residual Stress Measurements—The x-ray diffraction technique is the most routinely used nondestructive technique for determining surface residual stresses. It determines the stress by measuring the interplanar spacings in the material. If subsurface residual stresses must be measured, then material can be removed (making this method a destructive technique) and the measurement repeated.

The x-ray technique for measuring residual stress is based on the fact that the lattice spacings (d-spacings) of the atomic planes in a crystalline material are altered by stress. The lattice spacings can be measured by determining the angular position of the diffracted x-ray beam (Bragg's Law). This technique is strictly valid for measurements of stress in a material that is homogeneous, isotropic, and elastic. Wrought austenitic stainless steels and wrought nickel alloys generally meet these requirements.

One of the assumptions made in performing x-ray residual stress measurements is that the penetration depth of the x-ray beam is small, so in the volume being examined, the stress perpendicular to the surface is zero because of the lack of constraint at the surface. For steels and nickel alloys using chromium K-alpha radiation, as used in the evaluations reported for the

IHSI-treated welds (Offer 1983 [DIRS 154454]), this assumption is valid because most of the diffracted energy comes from a depth of less than 0.013 mm.

The approach used in making x-ray residual stress measurements on IHSI-treated welds used in the current analysis utilized a combination of strain gage and x-ray results to obtain the total surface residual stress. The error in the strain gage measurement results is within 1.0 ksi (Chrenko 1980 [DIRS 154451]). X-ray residual stress measurements were then performed on the full-thickness pieces of pipe. The total original inside surface residual stress present at a certain location was obtained by algebraically combining the x-ray residual stress with the stress relaxed at that location when the piece was cut out of the original pipe.

Chrenko (1980 [DIRS 154451]) reports that the accuracy of the x-ray residual stress measurements for the types of samples used in the IHSI study was ± 34.5 to 48.3 MPa.

Strain Gage Stress Relief Residual Stress Measurements—The strain gages can also be used to obtain near-surface and through-thickness residual stress results by application initially to the outer diameter and inner diameter surfaces of the pipe. When the full thickness bar is parted out, both the outer diameter and inner diameter gages are read. The parting out stress is used for both x-ray and future strain gage residual stress information.

Detailed measurements of the residual stress distributions indicate that, except for the rapidly varying surface stresses, the distribution of residual stress through the thickness of the 101.6 mm weldments investigated is reasonably linear in most cases (Shack and Ellingson 1980 [DIRS 154456]). For a linear distribution, the bulk residual stress as measured by strain gages on the inner and outer surfaces of full wall-thickness specimens gives a good measure of the stress available to drive the crack (Shack and Ellingson 1980 [DIRS 154456]). For thicker pipes (19 mm thick and greater), the approach used—measuring the strain relieved on the inner diameter and outer diameter surfaces, slicing along the neutral plane, then strain gaging the newly created surfaces and repeating the process on thinner and thinner strips—allows investigators to continue the approximation process to the level of accuracy required for the specific application.

Based on the measured data reported in Offer (1983 [DIRS 154454]), the through-thickness strain gage data produced for the IHSI-treated welds was obtained at 3.18 to 6.35 mm increments of depth. For these final thicknesses, linear interpolation was performed to estimate the residual stress state.

Quantification of Uncertainty Due to Measurement Error—The sources of measurement error for the x-ray diffraction residual stress technique are: (1) local surface residual stresses due to cold work, (2) errors in parting out stresses associated with strain gages, and (3) inhomogeneous grain structure. Total error is estimated to be ± 34.5 to 48.3 MPa.

The sources of measurement error for the strain gage residual stress technique are: (1) parting out stresses due to removal of bar by machining, (2) additional machining on neutral surfaces to produce thin strips, and (3) interpolation of results in finite thickness strips.

In reviewing the strain gage residual stresses at various azimuthal locations in a given pipe (Offer 1983 [DIRS 154454]), it was noted that the results usually varied less than ± 69 MPa. If it is assumed that this variation is the result of real variations in residual stress due to the welding process added with measurement error, then the measurement error must be less than ± 69 MPa (10 ksi). The accuracy of the actual strain gage residual stress values is ± 6.9 MPa (1 ksi) (Chrenko 1980 [DIRS 154451]).

Based on the analyses of the x-ray and strain gage measurement errors (Chrenko 1980 [DIRS 154451]) and the azimuthal variation of strain gage residual stresses (Offer 1983 [DIRS 154454]), it is concluded that the measurement error associated with strain gage measurement of surface and through-thickness residual stresses after the induction heating stress mitigation can be bounded by ± 69 MPa. Assuming a yield strength of 322 MPa of Alloy 22 at 125°C, the residual stress uncertainty in the outer lid closure welds is bounded by ± 21 percent of yield strength of Alloy 22. The same uncertainty bounds are also applied to the corresponding stress intensity factor profile. For comparison, the TSPA-SR base case (CRWMS M&O 2000 [DIRS 153246]) uses ± 30 percent of yield strength for the bounds of residual stress uncertainty (CRWMS M&O 2000 [DIRS 151566], Section 4.1.8).

7.3.3.3.2 Uncertainties in Residual Stress in Inner Lid Closure Welds

As discussed in Section 7.3.3, laser peening has been proposed to mitigate stresses and generate compressive stresses at the surface and down to a significant depth in the closure weld region of the inner lid of the Alloy 22 waste package outer barrier. The resulting residual stress profiles, after laser-peening treatment, were calculated as a function of depth in the inner closure lid weld region (CRWMS M&O 2000 [DIRS 151564], Section 6.2). From the calculated residual stress profiles, the profile with the highest hoop stress was used as a mean stress profile for the entire inner closure lid weld region (CRWMS M&O 2000 [DIRS 151549], Section 6.3.1.1). This section provides the technical basis and approach to quantifying the uncertainty in the calculated mean residual stress. It is assumed in this analysis that the total uncertainty in the residual stress is due to the stress measurement uncertainty. Because there are no data available for residual stress of laser-peened closure lid welds of the waste package design, literature data available for similar stress mitigation techniques were used to quantify the uncertainty in the residual stress in the inner closure lid weld region.

The uncertainties in the residual stress and stress intensity factor profiles for the laser-peened closure welds of the Alloy 22 waste package inner lid are estimated from stress states measured on shot-peened Incoloy 908 samples (Pasupathi 2000 [DIRS 149968]). The use of data obtained for Incoloy 908 is appropriate for this application because Incoloy 908 is a nickel-based superalloy similar to Alloy 22 (Pasupathi 2000 [DIRS 149968]). Furthermore, the analyses in this section are meant to develop a material-independent scaling term, the fractional uncertainty, which can be multiplied by the yield strength of the material under study to obtain the stress and stress intensity factor uncertainty distributions. A total of 17 stress measurements, along with their estimated measurement error, were used to estimate the observed fractional uncertainty for the data. The residual surface stresses are centered on a value consistent with the reference value of the materials' yield strength. The uncertainty in the values is consistent with a normal distribution, as shown in the following discussions.

The 17 stress measurements used in the current analysis are from a report from the Plasma Fusion Center of the Massachusetts Institute of Technology (Pasupathi 2000 [DIRS 149968], Table VI). X-ray diffraction residual stress techniques were employed to measure the stress at the surface of a shot-peened Incoloy 908 sample. A measurement error was estimated for each measurement, which results from the random error in the determination of the diffraction peak angular position and the empirically determined value of the x-ray elastic constant. Those parameters are required for calculating stress from strain measurements. This measurement error is used to weight the values for estimating the mean and standard deviation of the stress values. The observed trend in the errors is that lower (more negative) stress values have more error associated with them. The consequence of this is that the weighted mean estimate is higher in value than the unweighted estimate.

Analysis of the data shows that they can be treated as a normal distribution. This is demonstrated graphically by the fractile and probability plots of the data values compared with the normal distribution values, as shown in Figures 7.3.3-1 and 7.3.3-2. The plots show that the data values follow the normal distribution values reasonably closely.

The descriptive statistics of the sample are listed in Table 7.3.3-1. The weighted mean is calculated to be -899.2 MPa. This is consistent in magnitude with the reference yield strength for this material, 896 MPa. The weighted standard deviation of the data is calculated to be 45 MPa. With these values, the fractional uncertainty, defined as the ratio of the standard deviation to the absolute value of the mean, is about five percent.

Confidence values may be estimated for the fractional uncertainty (FU) by assuming that the mean is fixed and known (i.e., contributes little to the uncertainty variation) and that the ratio of the sample variance to the variance follows a chi-square distribution with $(n-1)$ degrees of freedom, $\chi^2(n-1)$, under the normal assumption (Bulmer 1979 [DIRS 111961], Chapter 8, pp. 129-132). The fractional uncertainty is sampled as follows:

$$FU \sim \sqrt{\frac{(n-1) \cdot s^2}{\chi^2(n-1)}} \cdot \frac{1}{\bar{x}} \quad (\text{Eq. 7.3.3-4})$$

Parameters in the equation are defined in Table 7.3.3-1. Using these assumptions, the median value for the fractional uncertainty is 0.051. A portion of the resulting cumulative distribution function is reproduced in Table 7.3.3-2.

In the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), the residual stress uncertainty model for the waste package closure welds used, as its upper bound, the yield strength scaling factor (F) (CRWMS M&O 2000 [DIRS 151549], Section 6.3.1). In the current residual stress uncertainty model, the upper bound is three times the fractional uncertainty (FU) value derived from Equation 7.3.3-4. For the mean case, the bounds of the residual stress uncertainty are ± 15.3 percent of the yield strength, and those of the 95th percentile case are ± 21.3 percent of the yield strength. For comparison, the TSPA-SR base case uses ± 30 percent of the yield strength for the bounds of residual stress uncertainty.

For each realization of the WAPDEG analysis, the fractional uncertainty (FU) was sampled and multiplied by 3, and a value for z (representing the uncertainty variation away from the mean) was sampled from a triangular distribution with a lower bound of -1, an upper bound of 1, and a mode of 0 (CRWMS M&O 2000 [DIRS 151549], Attachments II and III). These values were then multiplied together, yielding a new z value, which was passed to the stress corrosion cracking model (CRWMS M&O 2000 [DIRS 151549], Attachments II and III). Note that the yield strength scaling factor (F) in the TSPA-SR stress corrosion cracking model (CRWMS M&O 2000 [DIRS 151549], Attachments II and III) is no longer necessary because it has been incorporated into the product and is therefore set to 1, thus having no effect on the model. The stress corrosion cracking model then evaluated the uncertainty scaling factor and calculated the stress and stress intensity factor profiles to be used for the current realization.

7.3.3.3.3 Threshold Stress for Initiation of Stress Corrosion Cracking in Alloy 22

Initially, in the absence of relevant Alloy 22 stress corrosion cracking test results, literature results on Stainless Steel Type 304 were used to assess the expected susceptibility of Alloy 22 in terms of initiation stress threshold. These results were obtained in either very aggressive boiling magnesium chloride or in 0.1 M sodium chloride solutions dripped onto stressed specimens heated to 200°C. Under these very aggressive conditions, lower-bound initiation stress threshold of 10 to 30 percent of yield strength was observed. This range was conservatively selected for waste package design applications. In these same very aggressive environments, initiation stress threshold values for higher nickel-content stainless steels and nickel base alloys may exceed 80 percent of the yield strength. In the case of Alloy 22 U-bends (10 to 15 percent strain) in boiling magnesium chloride, the initiation stress threshold may exceed approximately 200 percent of the yield strength (Erbing Falkland 2000 [DIRS 149956], p. 661, Figure 8; Haynes International 1998 [DIRS 154463]).

More recently, a series of constant load and slow strain rate stress corrosion initiation tests was performed in more relevant test environments to assess the expected stress corrosion susceptibility of Alloy 22 in terms of stress threshold for crack growth initiation. In addition, highly stressed U-bend specimens of Alloy 22 were examined after up to two years of exposure in a range of environments in the Long-Term Corrosion Test Facility. These crack initiation tests were performed on Alloy 22 specimens with machined surfaces typical of those expected on the waste package, and no evidence of stress corrosion crack initiation has been found to date. These tests included:

- Constant load tests at 105° to 125°C on approximately 100 specimens (Figures 7.3.3-3 and 7.3.3-4) with a range of stresses up to approximately 250 percent of yield strength in concentrated J-13 well water solutions (equivalent to being evaporatively concentrated to approximately 5500-fold, pH = 12.4). Details of the testing solution composition are given in *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 151568], Section 6.12). These tests included a range of metallurgical conditions, including annealed, welded, thermally aged and cold-worked material. No stress corrosion crack initiation was observed on any Alloy 22 specimen in any of these tests out to approximately 2,500 hours of exposure.

- Alloy 22 U-bend tests (estimated stress at approximately 200 percent of yield strength) at 90°C, including annealed and as-welded materials exposed up to two years in the Long-Term Corrosion Test Facility over a range of expected and bounding waste package surface environmental conditions (simulated concentrated water [approximately 1000-fold J-13 well water, pH = 8], simulated acidic water [approximately 1000 to 3000-fold J-13 well water, pH = 2.7], and simulated dilute water [approximately 10-fold J-13 well water, pH = 9.9]). Details of the testing solution composition are given in *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 151568], Section 6.12). The materials did not exhibit any cracking during the exposure period.
- Slow strain rate tests at 76° to 105°C covering a range of relevant and bounding environments (including trace element lead additions) and applied potentials (Table 7.3.3-3). Examination of these results indicates a high degree of stress corrosion crack resistance at open circuit potentials in relevant environments, even in the presence of dissolved lead at pH values as low as 3. If beneficial buffer ions are not present (e.g., in a chloride-rich 4 M NaCl solution), the potential for either stress corrosion crack or crevice corrosion exists at applied potentials greater than approximately 350 mV versus Ag/AgCl. However, it should be noted that the expected waste package surface environments will be buffered and less prone to stress corrosion cracking.

In addition to the various SCC initiation tests cited above, fracture mechanics type crack growth tests have been performed at 110°C in near-saturated (approximately 50,000 fold) J-13 well water at a pH of 13.43 (Andresen et al. 2000 [DIRS 154462], pp. 2 and 6). In these tests, a sharp flaw generated by fatigue pre-cracking the specimens is subjected to slow load cycling in the desired test environment at stress intensities of 30 or 45 MPa·m^{1/2} until an active stress corrosion (or corrosion fatigue) crack is initiated. The crack is then forced to continue growing by very slow load cycling. With time, the cycling frequency is reduced in steps, and eventually, the sample is held under constant load and the crack growth rate measured. For Alloy 22, this growth rate is extremely low and tends to arrest with time at constant load. The measured growth rate on 20 percent cold-worked Alloy 22 samples was approximately 4×10^{-10} mm/s, a rate that is near the lower limits of such measurements. For materials with such low growth rates, and under the constant loading conditions representative of the waste package closure welds (i.e., no load cycling occurs), there is a high probability that even if an actively growing stress corrosion crack were to initiate, it would subsequently arrest after a small amount of growth (Andresen et al. 2000 [DIRS 154462], p. 5).

Based on these recent tests, the stress threshold can be conservatively increased to a range of 80 to 90 percent of yield strength. A uniform distribution is assumed between the bounds, and the entire distribution represents uncertainty in the stress threshold. Although a still higher value could be justified based on the recently available Alloy 22-specific test results, it is prudent to limit the upper bound value to 90 percent of yield strength at this time to provide a safety margin, considering the relatively limited test exposure times compared to the waste package emplacement period under consideration.

7.3.3.3.4 Uncertainties in Orientation of Manufacturing Flaws in Closure Lid Welds

As discussed in Section 7.3.3.2, the residual stress analyses showed that the hoop stress is the dominant stress in the closure lid welds; thus, only radial flaws are potential sites for through-wall stress corrosion cracking, if it occurs, in the presence of hoop stress. The stress corrosion cracking analysis in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumed conservatively that all manufacturing flaws are oriented in such a way that they could grow in the radial direction in the presence of hoop stresses (CRWMS M&O 2000 [DIRS 151566], Section 5.6).

Only two weld methods are being considered for the fabrication process, gas metal arc and tungsten inert gas methods. These welding processes are designed to eliminate slag inclusions, a common flaw in other welding techniques. The most common flaws for gas metal arc and tungsten inert gas are lack of fusion flaws due to missed side wall or lack of penetration in the side wall. These flaws are generally large and readily detected by ultrasonic and radiographic inspections. Because both ultrasonic and radiographic methods will be used for post-weld inspections, there should be no large undiscovered flaws. Furthermore, flaws from the lack of fusion are, by definition, oriented in the direction of the weld bead, and thus are not subject to the applied hoop stress profile (CRWMS M&O 2000 [DIRS 152753]).

The observations noted above are supported by the limited data available from the lid welds on a 4-inch thick carbon-steel cylinder mockup using multiple passes for the viability assessment waste package design. Overall, sixteen indications were detected by ultrasonic testing on the bottom lid weld. Thirteen of these were classified as potential lack of fusion flaws because of their location at the weld fusion zone and their orientation parallel to the weld groove orientation. The other three indications were due to laminations in the base metal. Similarly, on the top lid welds of the same cylinder, three indications were detected; all were classified as lack of fusion very near the base of the weld root. The orientation of all of these indications was planar with respect to welding direction (CRWMS M&O 1998 [DIRS 107722]).

Shcherbinskii and Myakishev (1970 [DIRS 149953]) describe a statistical treatment of weld flaw orientations based on analysis of a significant data set of flaw orientation measurement and conclude that planar-type weld flaws, detected ultrasonically, tend to be predominately oriented parallel to the direction of the weld center line. More than 98 percent of the flaws detected fall within ± 16 degrees of the weld center line in the case of steam pipe welds (e.g., the tails of the distributions decrease to less than 2 percent probability as the azimuth angle approaches 90 degrees (Shcherbinskii and Myakishev 1970 [DIRS 149953], Figure 1)). A similar conclusion, drawn from the data for plate welds (Shcherbinskii and Myakishev 1970 [DIRS 149953], Figure 2), indicates that statistical distribution of the flaws with respect to the orientation angle can be approximated with a centered normal distribution with a maximum standard deviation of 5 degrees. This yields a probability of 99 percent that a flaw is oriented within about ± 13 degrees of the weld centerline. This suggests that less than one percent of these flaws have a potential to undergo stress corrosion cracking (i.e., radial crack propagation) under the action of the applied hoop stresses. Visual inspection of both the figures suggests a maximum probability of less than 2 percent at an azimuth between 12 and 16 degrees.

In summary, most weld flaws, such as lack of fusion and slag inclusions, would be expected to be oriented within a few degrees of the weld centerline (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1). Available published data and YMP limited flaw measurements from the viability assessment design mockups also show that most weld flaws (about 99 percent) tend to be oriented in the circumferential direction (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1). Recent analyses showed it is extremely unlikely that cracks initiating from circumferential flaws grow in the radial direction (CRWMS M&O 2000 [DIRS 151564], Section 6.5.1). Based on the information presented above, the uncertainty in the fraction of weld flaws in the waste package closure welds, which are capable of growing in the radial direction in the presence of hoop stress, is represented as a lognormal distribution with a mean of one percent, upper bound of 50 percent, and lower bound of 0.02 percent. The entire range of the distribution is assumed to be due to uncertainty. Considering the data in Shcherbinskii and Myakishev (1970 [DIRS 149953]), the mean of one percent is reasonably conservative.

7.3.3.4 Uncertainties Associated with Lower-Temperature Operating Mode

This section discusses model and parameter uncertainties associated with a lower-temperature operating mode.

Temperature Threshold for Stress Corrosion Cracking of Alloy 22—The range of temperatures evaluated for the stress corrosion cracking susceptibility of Alloy 22 in repository-relevant environments, such as concentrated J-13 well-type waters, is limited to date. For the relevant environments studied, stress corrosion crack propagation has been observed on fatigue pre-cracked fracture mechanics-type specimens over the temperature range of 95° to 110°C in basic saturated water, simulated acidic water, and simulated concentrated water (Andresen et al. 2000 [DIRS 154462]). Previous double cantilever beam specimens tested at Lawrence Livermore National Laboratory in less relevant unbuffered solutions (5 wt.% NaCl, pH = 2.7) indicated crack growth at 90°C (Roy et al. 1998 [DIRS 119544]). No testing was conducted for other temperatures. In contrast to the observed stress corrosion crack initiation and growth observed on pre-cracked (defected) specimens, no stress corrosion crack initiation has been reported on a “smooth” surface. Initiation tests to date include U-bend specimens exposed up to two years in the LTCTF in simulated concentrated, acidic, and dilute water environments at 60° and 90°C and in 15 to 20 percent basic saturated water at 105° to 125°C for up to 2,500 hours of exposure (Andresen et al. 2000 [DIRS 154462]) at levels exceeding yield stress. In slow strain rate tests, stress corrosion cracking was not initiated in Alloy 22 tested at 90°C in 5 wt.% NaCl, pH = 2.7 solutions (Roy et al. 1999 [DIRS 154455]). However, the available literature indicates that stress corrosion crack initiation can occur at higher temperatures on stressed Alloy 22 C-bend samples at 200°C in acidified Salton Sea-type brines (Kolts 1986 [DIRS 154453], Table 2). Alloy 22 was also tested in 25 wt.% NaCl, pH = 2 solutions with 135 ppm PbCl₂ at 200°C, but no cracking was observed after one week of exposure (Kolts 1986 [DIRS 154453], Table 2). Under more aggressive conditions, stress corrosion crack initiation and growth was observed on an Alloy 22 U-bend specimen tested in pH = 0.53, 1000-fold J-13 water solutions containing about 1,300 ppm lead at 250°C (Barkatt and Gorman 2000 [DIRS 154496]). In contrast, slow strain rate tests performed recently at Lawrence Livermore National Laboratory at a more realistic temperature of 76°C, either in pure aerated water containing 1 wt.% PbCl₂ or simulated acidic water with 100 ppm Pb (NO₃)₂ added, showed no evidence of stress corrosion crack initiation.

Although test results for Alloy 22 below 90°C in potentially relevant environments are limited (the only reported results are the U-bends tested in the LTCTF at 60°C and slow strain rate test results at 76°C), insight can be gained on the likely temperature dependency and potential threshold temperature for initiation and growth of cracks by examining literature information for other austenitic corrosion-resistant alloys where lower temperature results are available. One extensive series of test results on temperature dependency was obtained on pre-cracked Stainless Steel Type 304 and 304L fracture mechanics specimens in aerated 22 wt.% NaCl solutions, as well as more limited data in 42 wt.% MgCl₂ solutions (Speidel 1981 [DIRS 154457], Figure 10). In this series of tests, stress corrosion crack initiation and growth was observed on non-sensitized specimens over the test range from 50° to 130°C and on sensitized specimens down to room temperature. Increasing the nickel content above about 32 wt.% and the molybdenum content above about 5 wt.% significantly increased stress corrosion cracking resistance by increasing the threshold stress intensity factor, although the effect of lower temperatures was not reported for these highly corrosion-resistant alloys. Other results from the literature showed no stress corrosion crack initiation on U-bends of Alloys 800, 825, and 600 exposed for five years to a marine environment at Kure Beach at ambient temperature (Sedriks 1996 [DIRS 105113], p. 286). However, other results on non-sensitized stainless steels indicate that stress corrosion cracking can occur at room temperature in marine environments (Sedriks 1996 [DIRS 105113], p. 287). In one reported case, cracking was observed after less than 11 months of ambient exposure under dust containing up to 3.5 wt.% of water-soluble chloride in a Swiss tunnel (Sedriks 1996 [DIRS 105113], p. 288).

In summary, based on available results, there is currently no basis for establishing a threshold temperature below which stress corrosion cracking will not occur in Alloy 22 in chloride-containing environments, although the high nickel and molybdenum content (about 56 wt.% nickel and 13 wt.% molybdenum) in the alloy would tend to indicate that stress corrosion cracking is very unlikely below about 50°C.

7.3.4 Long-Term Passive Film Stability of Alloy 22

Long-term stability of the passive film on the surface of the Alloy 22 waste package outer barrier is one of the key issues that determine the long-term performance of the waste packages in the potential repository. A comprehensive testing and analysis program has been initiated to understand and develop a predictive model for the long-term stability of the passive film under expected repository exposure conditions. This section provides a brief description of the conceptual understanding of the passivity and passive film formation and growth on highly corrosion-resistant alloys relevant to Alloy 22.

7.3.4.1 Introduction

The corrosion models in the waste package degradation analysis for the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) are based on relatively short-term testing data. As discussed in Section 7.3.4.2, corrosion performance of highly corrosion-resistant alloys like Alloy 22 depends on the integrity of the thin, compact, adherent passive film formed on the alloy surface in contact with the corrosive environment. Extrapolation of the measured short-term corrosion rates over a repository time frame assumes that the integrity of this passive film remains stable over very long times. In addition, the individual corrosion models incorporated in the WAPDEG model

are empirical in nature. Because of the long service life of waste packages (10,000 years), empirical methods and models inherit significant uncertainties in long-term projection of corrosion degradation.

This section discusses the approach to developing a mechanistic predictive model for long-term performance of the Alloy 22 waste package outer barrier under expected repository exposure conditions. The mechanistic model, referred to as the generalized corrosion model (GCM), is based on two models: the mixed potential model (MPM) (Macdonald 1992 [DIRS 154719]) for predicting the electrochemical corrosion potential (ECP) and the corrosion current density, and the point defect model (PDM) (Macdonald 1999 [DIRS 154721]), which describes the growth and breakdown of the passive film that exists on the alloy surface. The model is in an early stage of development and requires experimental data for Alloy 22 under repository exposure conditions to estimate the value of its parameters.

Also discussed in this section are the features and application of the GCM using example calculations performed with the current (early developmental stage) version of the model. The present example calculations are limited to general corrosion processes and employ simplifying assumptions and data on other material. This is necessary because of the limited data available for Alloy 22 under repository conditions. The example calculation results for general corrosion processes discussed in this section should be viewed as preliminary and qualitative in nature.

7.3.4.2 Conceptual Description of Passivity and Passive Film Stability

Passivity can be defined as a phenomenon concerned with the formation of a thin, compact, and adherent oxide or oxyhydroxide film that protects a metal and alloy from corrosive degradation. It has now been accepted that the passive film is not a single layer, but rather has a stratified structure (Macdonald 1992 [DIRS 154720]; Marcus and Maurice 2000 [DIRS 154738], pp. 145 to 150). According to this bilayer model, the passive film consists of an inner layer of oxide and an outer layer of hydroxide or oxyhydroxide. The inner oxide layer plays the role of a barrier layer against corrosion, and the outer layer plays the role of an exchange layer.

Passive Film Formed on Metals—In general, the chemical composition and thickness of passive films depend on the nature of the metal, the pH of the electrolyte in which the metal is passivated, and the electrochemical potential (Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]). For example, for nickel that can passivate in solutions over a wide range of pH, the passive film is generally composed of nickel(II) cations with an inner layer of NiO and an outer layer of Ni(OH)₂. More noble (positive) passivation potential can enhance the development of a continuous oxide layer in the inner part of the film (Marcus and Maurice 2000 [DIRS 154738], pp. 142 to 153).

The passive films formed on metal surfaces are generally not electronic conductors, but rather semiconductors or insulators. The electronic structures of passive films can be determined by photoelectrochemical measurements. However, the structural analyses are rather difficult, inherent to the nanometer thickness of passive films and the roughness of the surfaces because of dissolution. The passive film formed on nickel (in 0.05 M H₂SO₄) has shown crystallites, the size of which are reduced with increasing potential. The shape of crystallites also changes with potential (Marcus and Maurice 2000 [DIRS 154738], pp. 145 to 153). Another factor that should

be considered is active dissolution, which occurs as long as the surface is not completely passivated. The dissolution rate increases exponentially with increasing potential (Tafel's law); dissolution may create new sites for oxide nucleation and can, thus, favor a higher density of oxide nuclei (Marcus and Maurice 2000 [DIRS 154738], pp. 145 to 153). The passive film formed on nickel has revealed crystallinity, with the surface exhibiting terraces and steps. On the other hand, the passive oxide film formed on chromium can have a nanocrystalline structure. These oxide nanocrystals are cemented together by the chromium hydroxide outer layer, making the passive film extremely protective against corrosion-induced damage.

Passive Film Growth Mechanisms—As summarized in the literature (Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]), the barrier oxide layer (inner layer) forms by the generation of oxygen vacancies (and hence new film) at the metal/film interface, balanced in the steady state by dissolution of the barrier layer at the barrier layer/outer layer interface. The outer layer forms via the hydrolysis and precipitation of cations transmitted through the barrier layer or by hydrolytic restructuring of the barrier layer/outer layer interface. The distinctly different origins of the barrier and outer layers are amply demonstrated by the fact that both layers may incorporate alloying elements from the alloy substrate, but only the outer layer incorporates species from the solution. Furthermore, with respect to the laboratory frame of reference, the barrier layer grows into the substrate metal, whereas the outer layer grows outwards into the solution (Macdonald 1992 [DIRS 154719]; Macdonald 1999 [DIRS 154721]). Thus, while the growth of the barrier layer is exclusively due to the generation of oxygen vacancies at the metal/barrier layer interface, the growth of the outer layer is commonly (but not exclusively) due to the transmission of cations through the barrier layer, either through cation vacancies or as cation interstitials, and their eventual emission at the barrier layer/outer layer interface. The origin of the outer layer is not exclusively due to cation transmission, because it may also form via hydrolytic restructuring of the barrier layer at the barrier layer/outer layer interface (Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]).

Current is carried by all charged species in the barrier layer, including cation vacancies (V_M'), cation interstitials (M_i^{z+}), and oxygen vacancies (V_O''), which are generated and annihilated at the interfaces (Figure 7.3.4-1, Reactions 1 to 6), and by dissolution of the barrier layer (Figure 7.3.4-1, Reaction 7), depending on whether a change in oxidation state occurs (Macdonald 1992 [DIRS 154719]; Macdonald 1999 [DIRS 154721]). The principal mode of transport of the defects is migration under the influence of a strong electric field, the magnitude of which is postulated to be established by the potential differences across the film and interfaces and by buffering due to Esaki (band-to-band) tunneling within the barrier layer. Because a barrier layer exists on all passive metals, all barrier layers are oxygen vacancy conductors to an extent that, in the steady-state, is determined by the dissolution rate of the film. However, other defects may dominate the structural and electronic defect structures of the barrier layer. For example, the defect structure of the barrier layer on nickel is dominated by cation vacancies, while that on zinc is dominated by cation interstitials, even though oxygen vacancies exist in both cases.

Chromium Enrichment in Passivated Nickel-Base Alloys—Chromium concentration plays a significant role in the passivation of austenitic nickel-base alloys, such as Alloy 600 and Alloy 690. The passive films in these alloys can be described by the bilayer model

(Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]). The concentration of Cr^{+3} in the inner oxide layer is higher than the nominal chromium content of the alloy (Lorang et al. 1990 [DIRS 154718]; Marcus and Maurice 2000 [DIRS 154738], p. 153). The mechanism of surface enrichment of chromium in the barrier layer has been developed within the framework of the PDM (Zhang and Macdonald 1998 [DIRS 154743]; Zhang and Macdonald 1998 [DIRS 154742]) and is based on the selective oxidation of the elements at the alloy/barrier layer interface, differences in transport properties of the species in the barrier layer, and selective oxidation of the elements at the barrier layer/outer layer interface. In the specific case of the passive film on iron-chromium alloys, enrichment of the barrier layer in chromium appears to entail the dissolution of iron and the oxidative segregation of chromium (Marcus and Maurice 2000 [DIRS 154738], p. 153). Iron atoms are detached from the surface and go into solution as ions, whereas chromium atoms are rapidly oxidized and the passive film forms by the nucleation and growth of a Cr_2O_3 -like phase (Marcus and Maurice 2000 [DIRS 154738], p. 153). However, the barrier layers on iron-chromium and nickel-chromium alloys are not pure chromium oxide (Cr_2O_3), and they still contain significant amounts of other metal species, such as nickel, ferrous, and ferric ions (Lorang et al. 1990 [DIRS 154718]). Finally, it is important to note that the accurate description of alloy segregation phenomena requires solving the “moving boundary” (i.e., Stefan’s) problem, because the interfaces at which the segregation reactions occur and the phases bounded by these interfaces move differently with respect to the laboratory frame of reference. This is the approach adopted in the PDM (Zhang and Macdonald 1998 [DIRS 154743]; Zhang and Macdonald 1998 [DIRS 154742]).

Role of Molybdenum—The exact mechanism of the effect of molybdenum on the corrosion resistance of nickel-chromium-molybdenum alloys is not fully understood. However, there is a consensus that molybdenum reduces the rate of anodic dissolution in the active state (Marcus and Maurice 2000 [DIRS 154738], pp. 155 to 158), but it is not clear whether this observation is relevant to the corrosion of a passive alloy. In this model, molybdenum is postulated to be located preferentially at local defects on the surface, which normally act as dissolution sites. The slowing down of the dissolution rate could be due to the increased metal-metal bond strength where molybdenum is present (Marcus and Maurice 2000 [DIRS 154738], pp. 155 to 158). Further, the presence of molybdenum counteracts the deleterious effect of species such as sulfur in that it bonds to sulfur and then dissolves, thus eliminating the detrimental effect of sulfur (Marcus and Maurice 2000 [DIRS 154738], p. 158). With regard to dissolution in the passive state, no consistent relationship has emerged between the passive current density and the molybdenum content of the alloy (e.g., Bojinov et al. 2001 [DIRS 154715]).

An analytical prediction of the role played by molybdenum (or any alloying element) in inhibiting passivity breakdown on alloys is provided by the point defect model (Urquidi and Macdonald 1985 [DIRS 154741]), which is found to account quantitatively (within the accuracy of the experimental data) for the impact of molybdenum on the pitting resistance of 18 chromium-8 nickel stainless steels (e.g., AISI Type 304 versus Type 316). In this model, highly oxidized alloy elements that are present substitutionally in the barrier layer lattice form immobile, positively charged centers. For example, recognizing that the barrier layer on chromium containing stainless steels and nickel-base alloys is essentially Cr_2O_3 , substitution of Mo^{6+} into a chromium cation vacancy would produce the immobile species $\text{Mo}_{\text{Cr}}^{3+}$. This species may interact electrostatically with the mobile, negatively charged cation vacancies ($\text{V}_{\text{Cr}}^{3-}$) that are

responsible for passivity breakdown via condensation at the metal/film interface under supra breakdown conditions (Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]). Thus, the solute-vacancy interaction reduces the free cation vacancy concentration and diffusivity, which results in a positive shift in the breakdown voltage and a lengthening of the induction time (i.e., the alloy becomes more resistant to passivity breakdown). The electrostatic interaction is described rigorously in terms of ion-pairing theory that is commonly employed to describe ionic interaction in solutions. This solute-vacancy interaction model (Urquidi and Macdonald 1985 [DIRS 154741]) successfully accounts for the positive shift in the breakdown voltage upon adding molybdenum to the alloy without the need for arbitrary, adjustable parameters. Most importantly, the solute-vacancy interaction model accounts for why molybdenum must be present in the barrier layer at concentrations greater than about 2 percent for significant protection to be achieved.

Finally, complexing between Mo_{Cr}^{3*} and a defect will only occur if the defect is negatively charged (i.e., if the defect is a cation vacancy). However, the Cr_2O_3 passive film on chromium containing alloys is normally n-type in electronic character; hence, the dominant defect is either a cation interstitial or an oxygen vacancy, both of which are formally positively charged. Consequently, there should be little solute (Mo_{Cr}^{3*}) – vacancy (V_O^{**} or M_i^{Z+}) interaction and pairing, and molybdenum should have little consistent impact on the passive current density, as observed.

7.3.4.3 Approach to Mechanistic Modeling of Long-Term Passive Film Stability

This section describes an approach to developing a mechanistic predictive model for the long-term performance of waste packages (i.e., Alloy 22 outer barrier) under expected repository exposure conditions. Development of the mechanistic model, referred to as the GCM, is underway.

The individual corrosion models incorporated in the WAPDEG model are empirical. Because of the long service life of waste packages (10,000 years), such empirical methods and models inherit significant uncertainties in long-term projection of corrosion degradation. In particular, empirical models, which may be best expressed in statistical form (e.g., in the form of extreme value statistics) for such long-term projections, require a large database of “identical systems” with relationships that are governed by some underlying distribution function (e.g., a Poisson distribution function). However, in the case of geological isolation of the waste over extremely long time periods, no such systems or associated databases exist, so there are significant uncertainties in the application of empirical statistical methods to the prediction of damage.

An alternative strategy is a mechanistic approach, which is based on the philosophy that future events can be predicted on the basis of the natural laws that are invariant in space and time. These mechanistic/deterministic models require that the path over which the system will evolve in the future be specified in sufficient detail to provide a prediction of the desired accuracy. Furthermore, the process (or processes) by which degradation occurs must be described in terms of a physically realistic mechanism, the quality of which ultimately governs the accuracy and veracity of the prediction. Nevertheless, deterministic prediction of corrosion damage is now well established and has been applied in the prediction of general and localized corrosion

damage in a variety of systems, including condensing heat exchangers (Macdonald et al. 1994 [DIRS 154735]) and water-cooled nuclear reactors (Macdonald 1999 [DIRS 154721]).

All deterministic models comprise constitutive equations (which describe relationships between components and parameters in the mechanisms) and constraints (that constrain the solutions to those that satisfy the relevant natural laws). Because corrosion is an electrochemical process, the relevant natural laws are the conservation of charge, the conservation of (equivalent) mass, and Faraday's law, which specifies the equivalence of mass and charge (96,487 coulombs/equivalent). Because the natural laws are the summation of previous scientific experience, much of which is not directly related to the mechanism of interest, deterministic models are broadly based and extraordinarily resilient. Most importantly, they require little calibration, and then only to derive values for poorly known model parameters if these parameters cannot be determined by independent experiment.

The algorithm used in the GCM is based on two models: the MPM (Macdonald 1992 [DIRS 154719]) for predicting the electrochemical corrosion potential and the corrosion current density (I_{corr}), and the PDM (Macdonald 1999 [DIRS 154721]), which describes the growth and breakdown of a passive film on the alloy surface. Because the MPM and the PDM are deterministic, the resulting GCM is also deterministic.

The MPM is based on the physical condition that charge conservation must be obeyed in the system (Macdonald 1992 [DIRS 154719]); that is, because electrochemical reactions (corrosion reactions) transfer charge across a metal/solution interface at rates measured by the partial currents, the reactions are constrained by the charge conservation constraint. These partial currents depend on the potential drop across the metal/solution interface.

The PDM has been developed to provide a mechanism-based description of the growth and breakdown of the passive oxide films that form on metal surfaces when in contact with oxidizing environments (Macdonald 1992 [DIRS 154720]; Macdonald 1999 [DIRS 154721]). The PDM is based upon a number of postulates and assumptions:

- The passive film is a bilayer structure made up of a highly defective barrier (inner) layer that forms from the metal substrate and an outer layer that forms by the hydrolysis and subsequent precipitation of an oxide, oxyhydroxide, or hydroxide. The outer layer has a low inherent defect concentration and generally contains species that are co-precipitated from the solution (Section 7.3.4.1).
- The defects contained within the barrier (inner) layer include cation vacancies ($V_M^{x'}$), cation interstitials (M_i^{x+}), and oxygen vacancies (V_O^{**}). These point defects are generated and annihilated at the metal/barrier layer and barrier layer/solution interfaces in a series of elementary reactions (Figure 7.3.4-1).
- The barrier (inner) layer is responsible for the phenomenon of passivity. However, the outer layer may contribute significantly to the total interfacial impedance, and hence may control the rate of charge transfer.

- A single metal oxidation state exists within the barrier layer. This assumption is too restrictive to accommodate all systems, including iron, where the barrier layer comprises magnetite containing both iron(II) and iron(III) species. A more general model that recognizes the presence of multiple oxidation states in the barrier layer is under development.

In general, it is expected that one defect will dominate the defect structure of the barrier layer. The physics governing the identity of the dominant defect is discussed by Macdonald (1999 [DIRS 154721]). The identity of the principal defect is determined by the relative energies of formation of the defects in the barrier layer. For a barrier layer with a high cation oxidation state (e.g., WO_3 on W), the energies of formation of cation vacancies and cation interstitials are much greater than the energy of formation of an oxygen vacancy, so that the passive film on tungsten, for example, is an oxygen vacancy conductor. For systems with low cation oxidation states (e.g., nickel and zinc), the energies of formation of cation vacancies and cation interstitials are lower than the energy of formation of the oxygen vacancy. Accordingly, the barrier layers on these metals are expected to be cation vacancy or cation interstitial conductors. Experiments show that the barrier layer on nickel is a cation conductor, while that on zinc is consistent with the dominant defect being a zinc interstitial (Macdonald 1999 [DIRS 154721]). The passive film on Alloy 22 is presumably defective Cr_2O_3 , which occupies a position that is between the two extremes outlined above. Accordingly, it is not possible to predict, a priori, the dominant defect in the barrier layer. However, electrochemical studies suggest that the passive current is independent of voltage, which is consistent with the dominant defect being a cation interstitial or an oxygen vacancy. While this issue must be resolved by experiment, the dominant defect is assumed to be the cation interstitial in the current model development. In addition, the steady-state thickness of the barrier layer, including the dependence of the contacting solution on pH, is expressed in terms of the same parameters in the PDM.

7.3.4.4 Application of the General Corrosion Model

In this section, applications of the mechanistic GCM (currently under development) are discussed. Example calculations with the current version of the model are included in the discussion, though they are limited to general corrosion processes. Because the model is in an early stage of development and experimental data for Alloy 22 under repository exposure conditions is needed to estimate the model parameter values, simplifying assumptions and data for less corrosion-resistant materials (such as stainless steel) are employed in the example calculations.

7.3.4.4.1 Summary of the Current Version of the General Corrosion Model

The current version of the GCM (under development) modifies the older MPM (Macdonald 1992 [DIRS 154719]) by using the PDM (Macdonald 1999 [DIRS 154721]) to calculate the partial anodic current density, and by using a modified Butler-Volmer equation for the redox reactions to recognize that the corrosion processes occur on the surface under a thin electrolyte film. The current GCM used to simulate general corrosion processes differs in a number of important respects from the earlier MPM, used to model the electrochemical properties of nuclear reactors (e.g., corrosion processes in boiling water reactor primary coolant circuits) (Macdonald 1992 [DIRS 154719]). This section summarizes the most important of these differences.

The GCM incorporates the PDM (Macdonald 1999 [DIRS 154721]) to describe the anodic processes occurring at the metal surface. In the present version of the model, it is assumed that the barrier layer is a cation interstitial conductor, but other conduction mechanisms are readily assumed by changing parameter values. Recent work by Bojinov et al. (2001 [DIRS 154715]) using a modification of the PDM suggests that the barrier layer on iron-chromium-molybdenum alloys is an oxygen vacancy conductor, but it is not known whether this conclusion also applies to Alloy 22, which is a nickel-base alloy. Finally, in applying the PDM to the MPM, it is assumed that the temperature dependencies of the standard rate constants in the model can be described by Arrhenius factors of the type $\exp[-E_a(1/T - 1/T_o)/R]$, where E_a is the activation energy, T is temperature in Kelvin, and $T_o = 298.15$ K.

The current GCM considers corrosion beneath a thin liquid film that forms on the surface through evaporative concentration. In the current calculations, the thin electrolyte film is assumed to contain a single electrolyte, which for the present purposes is assumed to be sodium chloride plus the requisite H^+ and counter anion as determined from the pH. The solubility of oxygen and the mean molal activity coefficient are calculated from the sodium chloride concentration, the former by using Sechenov's coefficients for carbon dioxide (which are assumed to hold also for oxygen) for temperatures up to 200°C, as given by Naumov et al. (1974 [DIRS 154739]), and the latter from the extensive data of Liu and Lindsay (1972 [DIRS 154717]) on the thermodynamics of the NaCl-H₂O system.

No redox species other than hydrogen and oxygen are considered in the model. This assumption reflects the general opinion that the radiation dose rates at the surface are not sufficiently large to produce significant amounts of radiolysis products, such as H₂O₂. However, the radiolysis products are considered in the thin layer MPM that was developed a number of years ago to explore the impact of radiolysis on the electrochemical and corrosion properties of a high-level nuclear waste canister (Urquidi and Macdonald 1985 [DIRS 154741]). That study, which focused on copper alloys, suggested that there could be observable radiolysis effects, but that finding depends strongly on the dose rate that is assumed to exist at the canister surface.

The MPM was originally developed for describing electrochemical and corrosion processes in the heat transport circuits of boiling water reactors (Macdonald 1992 [DIRS 154719]); hence, it assumed that pH was not a variable. However, the pH is a system variable in the present application, so the expressions for the exchange current densities of the hydrogen-electrode reaction and the oxygen-electrode reaction have been modified by inclusion of the factor $(C_{H^+} / 10^{-pK_w/2})^{\text{expon}}$, where $pK_w = -\log(K_w)$, K_w is the activity product of water at the prevailing temperature and C_{H^+} is the concentration of hydrogen ion, which is calculated from the known pH. The exponent is set equal to 0.5 for Alloy 22. A similar factor is introduced for the dependence of the exchange current density on the activity of water (a_w), in this case in the form of a_w^p , where $p = 1.4$ for the hydrogen-electrode reaction (Anderko et al. 2001 [DIRS 154714]) and $p = 1.0$ for the oxygen-electrode reaction. The latter value was assumed in lieu of experimental data for Alloy 22. Finally, it is assumed that the temperature dependencies of the exchange current densities for the hydrogen-electrode reaction and the oxygen-electrode reaction can be described by an Arrhenius factor of the form $\exp(-14244/RT)$, where T is temperature in Kelvin, as per the original MPM (Macdonald 1992 [DIRS 154719]).

The potential scale employed in this work is the standard hydrogen electrode (SHE) scale, but that scale is not particularly useful for comparison with experimental data, which commonly are reported on the saturated calomel electrode (SCE) scale or the saturated silver/silver chloride electrode scale. However, conversion factors from one scale to another are temperature-dependent. In the current version of the model, the potential is reported on the SCE and SHE scales.

7.3.4.4.2 Example Simulation for Application of the Current Generalized Corrosion Model for General Corrosion Process

The model developed for the present analysis has not been optimized because of the unavailability of parameter input data for Alloy 22 under thin electrolyte films in simulated repository environments. Accordingly, the parameter values employed in the calculations described below generally refer to stainless steels, as used in previous applications of the MPM (Macdonald 1992 [DIRS 154719]), or are best estimates. One of the principal reasons for developing the model in its present form is to focus attention on the parameters that need to be measured experimentally. Future work will prioritize these parameters, using the present model to perform extensive sensitivity analyses. Finally, this model is under development and still requires additional work before it can be considered reasonably complete. Nevertheless, the model is capable of yielding realistic parameter values, and optimization is expected to produce predictions that are in accord with experimental observations. This view is based on previous experience with this model in predicting corrosion potentials in the primary coolant circuits of water-cooled nuclear reactors.

By way of illustration, the current model was used to calculate the electrochemical corrosion potential and the corrosion current density as a function of oxygen partial pressure and temperature (Macdonald 2001 [DIRS 154736], pp. 18 to 22). The results are given in Figures 7.3.4-2 and 7.3.4-3. The thin electrolyte film on the metal surface is assumed to be saturated in sodium chloride. The electrochemical corrosion potential displays a typical sigmoid variation with the log of oxygen partial pressure, and the potential becomes more negative with increasing temperature (Figure 7.3.4-2). Furthermore, the actual values are typical of stainless steels in aerated brines.

Figure 7.3.4-3 shows the predicted corrosion current density as a function of the partial pressure of oxygen (Macdonald 2001 [DIRS 154736], pp. 18 to 22). No dependence of the corrosion current density (i_{corr}) on the oxygen partial pressure (p_{O_2}) is noted. This is a consequence of assuming that the passive film is a cation interstitial conductor and that no change in oxidation state exists between the cation in the barrier layer and the metal species in the solution. Hence, the steady-state anodic partial current density is independent of potential. This relationship would hold if the oxygen vacancy was assumed to be the principal defect in the barrier oxide layer, provided that no change in oxidation state occurred upon film dissolution or ejection of a cation from the barrier layer at the barrier layer/solution interface. On the other hand, if the principal defect is the cation vacancy, or if the oxidation state of chromium changes upon barrier layer dissolution (Reaction 7, Figure 7.3.4-1) or upon cation ejection (Reactions 4 and 5, Figure 7.3.4-1), regardless of the identity of the principal defect, the corrosion current density will be potential-dependent. The current model incorporates all of these possible processes through the PDM.

Figure 7.3.4-4 shows the calculated electrochemical corrosion potential versus the thickness of the thin electrolyte film that is assumed to exist on the alloy surface (Macdonald 2001 [DIRS 154736], pp. 18 to 22). The data display two regions of interest: that at very low thickness values (corresponding to thin-film behavior) and that at large thickness values (corresponding to thick-film or bulk-electrolyte behavior). In both cases, the film is assumed to be quiescent, which is considered to be a good approximation for the thin-film scenario but not for the thick-film scenario. The assumption is inappropriate in the latter case because bulk systems are characterized by mass transport process other than diffusion (e.g., natural convection), so the model underestimates the limiting currents for the transport of oxygen and hydrogen ions to the metal surface. This has the effect of shifting the calculated electrochemical corrosion potential in the negative direction (Figure 7.3.4-4). The model needs to be improved to account for these processes.

Figures 7.3.4-5 and 7.3.4-6 show the calculated electrochemical corrosion potential and corrosion current density, respectively, as a function of pH for the assumed conditions of 100°C, 0.21-atm oxygen partial pressure, 0.01-cm electrolyte film thickness on the alloy surface, and saturated sodium chloride solution (Macdonald 2001 [DIRS 154736], pp. 18 to 22). The electrochemical corrosion potential is predicted to shift in the negative direction, and the corrosion current density is predicted to decrease exponentially with increasing pH. The origins of these shifts are complex and involve equilibrium and kinetic factors. Nevertheless, these relationships are observed commonly in experimental data.

7.3.4.5 Other Lines of Evidence to Support the Long-Term Passive Film Stability Model

Josephinite, a rock containing nickel-iron metallic minerals (Section 7.3.2.4), is about 150 million years old. It formed from the reduction of nickel- and iron-bearing minerals in the environment created by serpentinization of igneous rocks. Because the environment and temperature change with time during the formation of josephinite, its structure and mineral content changes from sample to sample, and even within individual samples (Botto and Morrison 1976 [DIRS 154716], p. 272).

The metallic mineral tends to be concentrated in the interior of josephinite samples (Figure 7.3.4-7). Because the environment in which josephinite forms becomes less and less reducing with time, there tends to be a relatively thick nonmetallic outer layer on these samples that protects the metal within. In some regions, however, the metallic nickel-iron apparently is at or near the surface. According to Botto and Morrison (1976 [DIRS 154716], p. 243), nickel-iron metal is sometimes seen at the surface of josephinite samples where the serpentine layer has been worn off during movement in streams. Whether metal is present on the surface of josephinite samples is currently being verified.

Current waste package corrosion modeling is based on relatively short-term testing. The corrosion rate in these tests is determined by a relatively thin passive film that controls the rate of oxide penetration into the bulk. Extrapolation of the measured corrosion rates over a repository time frame assumes that the integrity of this passive film remains stable over long times. Although the composition of the nickel-iron metallic mineral in josephinite differs from that of Alloy 22, if metal were found to be present on the surface of josephinite samples, that

would imply that a passive film can remain stable over long time periods, even in wet environments.

7.3.5 General Corrosion of Alloy 22

7.3.5.1 Goal of the Analysis

General corrosion is the relatively uniform thinning of materials without significant localized corrosion. The mode of general corrosion differs depending on the local environment. The repository environment will result in three different general corrosion modes: dry oxidation, humid-air corrosion, and aqueous-phase corrosion. The threshold relative humidity for both humid-air and aqueous-phase corrosion is based on the deliquescence point of sodium nitrate salt (CRWMS M&O 2000 [DIRS 151568], Section 7.0; CRWMS M&O 2000 [DIRS 144229], Section 4.1.2). Humid-air corrosion is defined as a corrosion condition in the absence of dripping water; aqueous-phase corrosion requires the presence of dripping water. Dry oxidation (dry-air corrosion) occurs at any relative humidity below the threshold for humid-air corrosion. Because the rates are extremely small under the expected repository thermal conditions, dry oxidation is expected to have no significant impact on waste package (CRWMS M&O 2000 [DIRS 144229], Section 6.1) or drip shield performance (CRWMS M&O 2000 [DIRS 144971], Section 7.0), so it is not considered in the current analysis.

The measured general corrosion rates of Alloy 22 from the immersion tests in the LTCTF have consistently indicated no discernible effect of temperature on the general corrosion rate, at least over the temperature range tested (60° to 90°C). The tests have also indicated no discernible effect of solution chemistry on measured general corrosion rates. Solutions considered in the testing include simulated dilute water, simulated concentrated water, simulated acidic water, and the saturated vapor environments above these waters (CRWMS M&O 2000 [DIRS 144229], Sections 6.5.2 and 6.9.1). Although no immersion tests have been conducted in simulated saturated water to date, cyclic polarization experiments have been conducted (CRWMS M&O 2000 [DIRS 144229], Section 6.4.2 and 6.4.3). Analyses have shown that the weight-loss method used in the LTCTF is not sensitive enough to quantify the effect of repository-relevant exposure conditions on the Alloy 22 general corrosion rate (CRWMS M&O 2000 [DIRS 144229], Section 6.5.3).

As discussed in Section 7.3.4, the passive dissolution (general corrosion) of highly corrosion-resistant alloys such as Alloy 22 is governed by the transport properties of reacting species (e.g., metal ions, oxygen ion, vacancies and interstitials) in the very thin (typically a few nanometers), compact, adherent passive film that forms on the alloy surface in contact with the corrosive environment and the dissolution rate of the passive film. These processes are influenced by the characteristics of the passive film, electrochemical potential across the film, and the chemistry of solution contacting the film. Chromium and nickel oxides, which are the major constituents of the passive film of nickel-chromium-molybdenum alloys like Alloy 22 (Lorang et al. 1990 [DIRS 154718]), are stable and exhibit extremely low dissolution rates over a wide range of solution chemistry (see Section 7.3.4.2). The transport properties of the reacting species and reaction rates in the passive film are considered thermally activated processes (see Section 7.3.4.4.1), so the general corrosion rate of the Alloy 22 waste package outer barrier is expected to have a certain level of temperature dependency. However, as discussed above, the

TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumed temperature-independent constant rates for general corrosion of the Alloy 22 outer barrier. This lack of temperature dependency of the general corrosion rate has been identified as one of the unquantified uncertainties in the waste package degradation model (Table 7-1). Because waste package temperatures are variable from location to location in the repository and change with time (i.e., decrease with time after their peak shortly after waste emplacement), the general corrosion degradation rate of waste packages is expected to be variable over time and across the repository. In addition, different general corrosion degradation behaviors of waste packages may result from alternative thermal operating modes.

The goal of the current analysis is to construct a model for the temperature dependence of general corrosion of the Alloy 22 waste package outer barrier by analyzing the limited data developed since the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). Three alternative models are developed and discussed in Section 7.3.5.3. The temperature-dependent general corrosion models are incorporated into the waste package degradation analysis to study the effect of the previously unquantified uncertainty on waste package degradation. Also presented in this section is a qualitative analysis of the effects of the chemical environment on corrosion of the Alloy 22 waste package outer barrier.

7.3.5.2 Identification of Unquantified Uncertainties in Total System Performance Assessment-Site Recommendation

The distribution of general corrosion rates for Alloy 22 used in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) is based on weight-loss data from the LTCTF over a two-year period (CRWMS M&O 2000 [DIRS 144229], Section 6.9.1). The test program includes sample coupons exposed to a variety of test media (e.g., water chemistry and temperature) to cover a range of exposure conditions relevant to the potential repository. The corrosion data for Alloy 22 gathered to date from the LTCTF indicate that the general corrosion rate for humid-air and aqueous-phase corrosion is about the same (i.e., water chemistry has no significant effect). The data also show little sensitivity to potential repository temperature for the water chemistry and temperature ranges considered in the test program. The general corrosion rates were corrected for the effects of potential formation of silica scale deposits on the sample surfaces. Silica deposition was estimated to potentially increase the corrosion rate determined from weight-loss measurements by as much as 0.063 $\mu\text{m}/\text{yr}$ (CRWMS M&O 2000 [DIRS 144229], Section 6.5.5; CRWMS M&O 2000 [DIRS 153802], Section 3.1.5.4.2).

The TSPA-SR (CRWMS M&O 2000 [DIRS 153246], Section 3.4.1.2) conservatively assumed that the rate of humid-air corrosion is represented by the same corrosion rate distribution used for aqueous-phase corrosion. It was further assumed that the corrosion rate is constant and does not decrease with time at times greater than two years. Because the general corrosion rate is expected to decrease with exposure time (see Section 7.3.5.4.2), the current general corrosion models are reasonably conservative representations of the corrosion behavior of the highly corrosion-resistant materials used for the waste package outer barrier (and drip shield) under expected repository conditions.

The general corrosion rate distributions for Alloy 22 and Titanium Grade 7 include substantial uncertainties (CRWMS M&O 2000 [DIRS 144229], Sections 6.5.2 and 6.9.1; CRWMS

M&O 2000 [DIRS 144971], Section 6.5.2; CRWMS M&O 2000 [DIRS 152542], Section 6). Most of these uncertainties result from insufficient resolution of the weight-loss measurements of the sample coupons due to the extremely low corrosion rate of the materials in the test media. The uncertainty in the measured general corrosion rates is not fully quantifiable, and the fraction of the total variance in the corrosion rate distribution that is attributed to spatial variability (and, conversely, to uncertainty) is not known. The approach in the waste package and drip shield degradation analysis in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) assumes that this fraction is uncertain and could range from pure uncertainty to pure variability (CRWMS M&O 2000 [DIRS 151566], Section 6.4.7).

As discussed previously, because the passive dissolution (general corrosion) rate of Alloy 22 depends on the transport properties of the reacting species (e.g., metal ions, oxygen ion, vacancies, and interstitials) and reaction rates in the thin, compact adherent passive film, which are considered thermally activated processes (see Section 7.4.4.4.1), a certain level of temperature dependency of the general corrosion rate of the Alloy 22 waste package outer barrier is expected. Therefore, among those uncertainties in the Alloy 22 general corrosion rate, the lack of temperature dependence of the general corrosion rate is the most likely source of unquantified uncertainty for the expected exposure conditions in the potential repository. Therefore, the current analysis attempts to quantify the temperature dependence of the general corrosion rate using the limited project and literature data available for Alloy 22 under repository-relevant exposure conditions. Additionally, the current analysis assumes that the entire variation of the current Alloy 22 general corrosion model (i.e., the general corrosion rate distribution resulting from the two-year weight-loss measurements from the LTCTF) is due to uncertainty. This is based on the error analysis results of the weight-loss measurement data of Alloy 22 samples (CRWMS M&O 2000 [DIRS 144229], Section 6.5.3).

7.3.5.3 Quantification of Temperature Dependence of Alloy 22 General Corrosion Rate

In this section, three alternative temperature-dependent general corrosion rate models for the Alloy 22 outer barrier are derived, assuming the temperature dependency follows an Arrhenius relationship (Scully et al. 2001 [DIRS 154513], p. 31). For all models, it is assumed that the current general corrosion rate distribution derived from the two-year weight-loss measurements (CRWMS M&O 2000 [DIRS 152542]) is representative for an exposure temperature of 60°C. The rate at any other temperature is determined by the Arrhenius equation, given a slope term (or activation energy term) is known. The Arrhenius equation for the general-corrosion rate is:

$$R = \exp\left[c_0 - \frac{c_1}{T}\right] \quad (\text{Eq. 7.3.5-1})$$

where

- R = general-corrosion rate
- T = temperature (Kelvin)
- c_0 = intercept term
- c_1 = slope term

Assuming the current general corrosion rate distribution from the LTCTF is at 60°C and given the slope term is known, the intercept term is determined by the equation:

$$c_0 = \ln(R_o) + \frac{c_1}{T_o} \quad (\text{Eq. 7.3.5-2})$$

where R_o is the rate sampled from the general corrosion rate distribution assumed to be at T_o and T_o is 333.15 K (60°C).

The temperature dependency in the first two models is determined from a set of passive current density data collected from potentiostatic polarization experiments (Scully et al. 2001 [DIRS 154513], Section 1.4; Lee 2001 [DIRS 154891]). The first model was developed using the entire data set. The second model was developed using the same data set, except for one apparent outlier point.

7.3.5.3.1 Temperature-Dependent Alloy 22 General Corrosion Model I

To determine the Arrhenius-equation slope (c_1) for the temperature dependency of the Alloy 22 general corrosion rate for repository-relevant conditions, passive current density data collected from potentiostatic polarization experiments were used (Scully et al. 2001 [DIRS 154513], Section 1.4; Lee 2001 [DIRS 154891]). Tests were performed on air-aged Alloy 22 crevice specimens at pH levels of 2.75 and 7.75 and temperatures of 80°, 85° and 95°C. All specimens were in a non-deaerated aqueous environment containing LiCl, Na₂SO₄, and NaNO₃, with [Cl⁻] versus [SO₄²⁻] + [NO₃⁻] ratios of 10 to 1 and 100 to 1. The passive dissolution rates (i.e., general corrosion rates) were calculated from the measured passive current density using Faraday's law, as discussed in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 144229], Section 6.5.1). A total of twelve passive current densities were determined, as seen in Table 7.3.5-1, for the various combinations of the exposure condition parameters (temperature, pH, and [Cl⁻] versus [SO₄²⁻] + [NO₃⁻] ratio). Each current density is reported with an estimated median value and average value (with a reported standard error). The average values are used in the slope determination.

The Arrhenius equation slope for this data set was calculated by determining the correlation between the natural log rates and the reciprocal of the temperatures in Kelvin. The last two columns in Table 7.3.5-2 are the deviation from the average for each variable, multiplying the temperature deviations by the rate deviations (cross product) and itself (squared). Taking the ratio of the two column sums, as seen in Table 7.3.5-2, results in a value of 7,997 K for the value of c_1 , the slope term. The model fit of the data is shown in Figure 7.3.5-1.

Dividing the slope term by the gas constant results in the more familiar activation energy term as 66 kJ/mole. Figure 7.3.5-2 shows the cumulative distribution functions (CDFs) for the Alloy 22 general corrosion rate that result from the model. The 60°C CDF represents the general corrosion rate used in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). The 100th percentile rate is approximately 0.14 μm/yr, and the 50th percentile rate is approximately 0.045 μm/yr. At 125°C, which is close to the boiling point of a saturated NaNO₃ solution (i.e., the maximum temperature for having a stable aqueous solution for corrosion in the presence of NaNO₃ salt), the 100th percentile rate is approximately 7 μm/yr (approximately a 60-fold

increase from the 60°C rate), and the 50th percentile rate is approximately 2.2 µm/yr (approximately a 50-fold increase from the 60°C rate). At ambient temperatures (25°C), the 100th percentile rate decreases to 0.008 µm/yr (8 nm/yr) and the 50th percentile rate to approximately 0.0025 µm/yr (2.5 nm/yr). In this updated model, the general corrosion rates decrease approximately three orders of magnitude for a temperature range from the maximum temperature for corrosion (125°C) to ambient temperature (25°C). The waste package temperatures are expected to be variable from location to location in the repository and to decrease with time after their peak shortly after waste emplacement. Because of spatial and temporal variability in the waste package temperature, this updated temperature-dependent model causes significant variability in the general corrosion degradation rate of waste packages.

7.3.5.3.2 Temperature-Dependent Alloy 22 General Corrosion Model II

Examining the residual values in model I, one data point (identified in bold in Table 7.3.5-1) was over twice as large in magnitude as all the other residuals. This large residual corresponds to the specimen from the test condition of 95°C, 2.75 pH, and 100:1 electrolyte ratio. Based on model I, a *t*-statistic of 2.264 was calculated. This value is the number of standard deviations by which the suspected value differs from the value predicted by the model. The *p*-value, or probability that a legitimate value will differ from the model by this number of standard deviations (for a value this extreme, both small and large), is 0.047. Comparing the relative error in the data set between the median values and the average values, the suspect value has a relative error of 11.39 compared to the next largest relative error value of 0.43. Examining the standard deviations associated with each average value, the suspected value's standard deviations ranges from 22 to 146 times larger than the others do. This indicates the error associated with this value is at least an order of magnitude larger than the other averages. The above discussion indicates that the data point in question is clearly an outlier. All of the evidence discussed above indicates either that a more robust estimation should be performed that is not as sensitive to outliers (e.g., median regression or weighted regression), or that the outlier should be removed from the data set and the analysis be redone to see how much the suspect value actually affects the results.

Removing the outlier and determining the Arrhenius equation slope from the remaining eleven current density averages results in a value of 4372.96 K for the value of *cI*, the slope term. Dividing the slope by the gas constant results in the more familiar activation energy term as 36 kJ/mole. The model fit of the data without the outlier is shown in Figure 7.3.5-3. Comparing Figure 7.3.5-3 with Figure 7.3.5-1 shows that removing the outlier from the model not only decreases the slope, but also reduces the predictor bounds.

Figure 7.3.5-4 shows the CDFs for the Alloy 22 general corrosion rate model, excluding the outlier point. The 60°C CDF represents the general corrosion rate used in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). At 125°C, the 100th percentile rate is approximately 1.2 µm/yr (approximately a 25-fold increase from the 60°C rate) and the 50th percentile rate is approximately 0.4 µm/yr (approximately 9-fold increase from the 60°C rate). At ambient temperatures (25°C), the 100th percentile rate decreases to 0.03 µm/yr (30 nm/yr) and the 50th percentile rate to approximately 0.01 µm/yr (10 nm/yr). In this updated model, the general corrosion rates decrease approximately two orders of magnitude for a temperature range from the maximum temperature for corrosion (125°C) to ambient temperature (25°C). The corrosion rates and rate variation with temperature observed using this model are more realistic than those

obtained with the previous model (including the outlier point). Furthermore, as discussed above, exclusion of the outlier decreases the activation energy term by approximately 30 kJ/mole.

7.3.5.3.3 Temperature-Dependent Alloy 22 General Corrosion Model III

A recent experiment was conducted over a broader temperature range for which a passive current density was collected from a potentiostatic polarization experiment (Lloyd et al. 2001 [DIRS 155186]; Lee 2001 [DIRS 154871]). The potentiostatic experiment was performed at a potential of 350 mV (vs. Ag/AgCl) in a 1.0 M NaCl (pH = 1) solution. The temperature was raised in increments, starting at 25° and ending at 85°C. The passive current density was measured at five temperature levels: 25°, 45°, 65°, 75°, and 85°C. A steady-state current density measurement was determined at each temperature level. The passive dissolution rates (i.e., general corrosion rates) were calculated from the measured passive current density using Faraday's law, as discussed in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 144229], Section 6.5.1). The passive current density data and the calculated passive dissolution rate (general corrosion rate) are given in Table 7.3.5-3.

Determining the Arrhenius slope from these five measurements results in a value of 3,852 K for the slope term, cl . Dividing the slope term by the gas constant results in the more familiar activation energy term as 32 kJ/mole. This slope was determined from these five passive dissolution rate values by applying the same analysis performed for the previous two models. Figure 7.3.5-5 shows the CDFs for the general corrosion rates at 25°, 60°, and 125°C calculated with Alloy 22 General Corrosion Model III. Comparing Figure 7.3.5-5 with Figure 7.3.5-4 shows that the third model (32 kJ/mole activation energy term) results in a temperature behavior similar to the second model (36 kJ/mole activation energy term). Since WAPDEG (Version 4.0) results from these two models would be similar, only the results with the second general corrosion model (36 kJ/mole activation energy term) are presented in Section 7.4.

7.3.5.4 Effects of Environment on the Corrosion of Alloy 22

As discussed previously, the corrosion data from the LTCTF show little dependence on the chemistry of the test solutions. These long-term tests (exposure times greater than two years) were supplemented with short-term cyclic polarization tests, which also showed no discernible dependence on chemistry (CRWMS M&O 2000 [DIRS 144229], Sections 6.4.2, 6.4.3, 6.5.1 and 6.5.2). This was expected for a corrosion-resistant material such as Alloy 22 and types of test environments containing ions such as nitrates and sulfates, which tend to buffer the effects of chlorides (Thomas 1994 [DIRS 120498]; CRWMS M&O 2000 [DIRS 144229], Section 6.4; Pasupathi 2001 [DIRS 155252]). However, it is necessary to understand the types of environments in which material corrosion would show dependence on chemistry and if there is a potential for the evolution of such environments at Yucca Mountain. Available data are limited, and a comprehensive testing and analysis program is underway to determine the bounds of environments beyond which accelerated corrosion is possible. However, the available information can be used to develop qualitative conclusions.

In the present design, which includes a drip shield, the expected environment on the waste package as long as the drip shield functions is largely determined by the temperature and relative

humidity history and the characteristics of dust particles present on the surface (see Section 7.3.1.3.3). The environment is also affected by the ionic species deposited from the soluble salts transported by the ventilation air. Preliminary data from the analysis of dust particles in the Exploratory Studies Facility show that the samples contain significant amounts of soluble chlorides, nitrates, and sulfates. Data from the atmospheric deposition monitoring program (see Section 7.3.1.3.3) also show that significant amounts of nitrates, chlorides, and sulfates are deposited from the atmosphere and available to interact with the materials in the emplacement drifts, including the waste package and drip shield. Based on this, the possibility of formation of a potentially more aggressive chloride-only solution on the waste package from deliquescence of the soluble salts in the dust particles or from the atmospheric deposition was considered. However, a review of the data shows that formation of "pure" chloride solutions on the surface of the waste package is highly unlikely because of the significantly greater amounts of nitrates and sulfates present (see Section 7.3.1.3.1). The buffering effect of these ions against the corrosive aggressiveness of chloride ions is well known (Thomas 1994 [DIRS 120498]; CRWMS M&O 2000 [DIRS 144229], Section 6.4; Pasupathi 2001 [DIRS 155252]).

When and if the drip shields fail to perform their intended function (i.e., divert dripping water from the surface of the waste package), the waste package may be susceptible to aggressive chemistries that could lead to accelerated general and localized corrosion. Previous analyses to determine the expected environment on the waste package surface used carbonate-based waters (J-13 well water-type), which resulted in high pH brines upon evaporative concentration (see Section 7.3.1). Alloy 22 corrosion rates due to the aqueous film formed from the deliquescence of the salt deposits from the solutions are very low because of the beneficial effects of the buffering nitrate and sulfate ions. Development of a chloride-only environment containing sodium chloride, while not likely, is not expected to have a significant effect on corrosion rates (Dunn et al. 2001 [DIRS 154511]).

More recent analyses (see Sections 7.3.1 and 6.3.3.7.1) have included the evolution of non-carbonate based dilute waters (such as pore water in the host rock) on the waste package and drip shield surfaces. These waters, in contrast to the J-13 well water-type, may evolve into brines containing chlorides of calcium and magnesium, since these cations are not completely removed by precipitation as carbonates and silicates. The presence of magnesium/calcium chlorides is significant because these could result in the formation of highly corrosive solutions at low relative humidities (20 to 30 percent) and have been shown to cause localized corrosion at elevated temperatures. An initial low-order approximation on the probability of the formation of magnesium and calcium chloride brines was attempted based on the combination of the different modeling runs done on the seven different water compositions (see Section 6.3.3.7.1). The initial approximation indicates that there would be a 14 percent chance of the starting water composition going toward a calcium/magnesium chloride brine due to evaporative concentration processes. However, the approximation is considered qualitative and subjective, and cautions should be exercised in using the information in a quantitative analysis (see Section 6.3.3.7.1).

However the possibility of development of saturated solutions of "pure" magnesium and calcium chloride salts is very unlikely for two reasons. First, the formation of an aqueous film containing these salts will also result in the dissolution of other soluble anions, such as nitrates and sulfates, thereby producing a more benign buffered solution (see Section 7.3.1.3.1). This will continue as the relative humidity increases in the repository. Anions such as nitrate, carbonate, fluoride, and

sulfate are known to mitigate against the aggressiveness of chloride-enhanced corrosion (Thomas 1994 [DIRS 120498]). The project data confirm that the presence of these ions in solution reduces the aggressiveness of chloride ions to Alloy 22 corrosion (CRWMS M&O 2000 [DIRS 144229], Section 6.4). Recent project data indicate that nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solutions at 120°C (Pasupathi 2001 [DIRS 155252]). Second, the soluble amounts of calcium and magnesium in these waters are very limited, since many of the available cations are removed during evaporative concentration due to the formation of insoluble mineral precipitates (see Section 7.3.1.3.1).

Another potential environmental constituent that could affect the long-term corrosion behavior of Alloy 22 is the presence of lead salts. Presence of lead in test solutions (up to several thousand ppm) has been shown to cause localized corrosion and stress corrosion cracking in Alloy 22 (Barkatt and Gorman 2000 [DIRS 154496]). Development of such an environmental scenario is also highly unlikely because the amount of measured lead concentration in Yucca Mountain waters is very low (several ppb). In addition, preliminary tests conducted in lead containing buffered (mixed ionic) solutions have shown no deleterious effects (see Section 7.3.3.3.3).

Thus, a qualitative review of available information suggests that development of environments in which corrosion of Alloy 22 shows a measurable dependence on the chemistry of the environment is highly unlikely. It also suggests that the potential for the development of environments leading to localized corrosion of Alloy 22 is unlikely. As discussed below, a sensitivity analysis is conducted to study potential effects of magnesium and calcium chloride salts on general corrosion of the Alloy 22 outer barrier.

Sensitivity Analysis for Effects of Magnesium and Calcium Salts on Waste Package Degradation—As discussed above and in Section 7.3.1.3, development of magnesium and calcium chloride salts on the waste package and drip shield surfaces is possible under expected repository conditions. However, the formation of an aqueous film containing these salts will also result in the dissolution of other soluble anions, such as nitrates and sulfates, thereby producing a more benign buffered solution (see Section 7.3.1.3.1). This will continue as the relative humidity increases in the repository. A recent project data indicates that nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solutions at 120°C (Pasupathi 2001 [DIRS 155252]). Therefore, the potential for the development of environments leading to localized corrosion of Alloy 22 is unlikely. However, because of low deliquescence points of these salts (see Table 7.3.1-2b), general corrosion of waste package and drip shield could initiate much earlier while the temperatures at the surfaces are still sufficiently high.

In order to investigate potential effects of the possible presence of magnesium and calcium chloride salts on the waste package and drip shield surfaces, a sensitivity analysis was conducted using a relative humidity threshold for the initiation of general corrosion based on the deliquescence points of magnesium chloride salt ($MgCl_2$) (see Table 7.3.1-2b). Use of this threshold will allow general corrosion to initiate at an earlier time. This allows for the potential of general corrosion at lower relative humidities and higher temperatures (around 14 percent RH at 164°C). The general corrosion rate used is temperature-dependent General Corrosion

Model II (Section 7.3.5.3.2) and considered to be 100 percent uncertainty. Figure 7.3.5-8 shows a graph of the general corrosion rate cumulative distribution functions at 25, 60, 120, and 165°C for General Corrosion Model II. The median general corrosion rate at 165°C is about 1.05 $\mu\text{m}/\text{yr}$ and the upper bound rate is about 3.16 $\mu\text{m}/\text{yr}$.

The simulation parameters used are similar, with the exception of the relative humidity threshold, to those presented in Section 7.4.3.3. The temperature and relative humidity histories of the waste package and drip shield surfaces are sampled from the thermal hydrology time histories for the entire repository (see Section 7.4.3.2). Figure 7.3.5-9 shows the upper-bound, mean, and 95th, 75th and 25th percentile confidence intervals of the failure profile for the waste packages with time, which result from the use of a relative humidity threshold for the initiation of general corrosion based on the deliquescence points of magnesium chloride salts. Lower-bound and 5th percentile confidence interval are not shown in the figure. The upper-bound profile indicates that the earliest possible failure time for a waste package is approximately 20,000 years, 5,000 years later than in the Baseline Waste Package Degradation Model hereafter referred to as the nominal case (Section 7.4.1). The failure profiles in the figure are similar to the failure profiles of the case using the relative humidity threshold based on the deliquescence points of NaNO_3 salt (see Table 7.3.1-2b), as shown in Figure 7.4-22 (Section 7.4.3.3). As discussed below, all breaches before 55,500 years are due to crack penetrations. The median estimate of the first breach time of the upper-bound profile is approximately 118,000 years (30,500 years for the nominal case and approximately 2,000 years earlier than the simulation shown in Figure 7.4-22). For the mean profile, approximately 80 percent of the waste packages fail by the end of the simulation time (1 million years). This is the same fraction as in the simulation shown in Figure 7.4-22. The time to fail 10 percent of the waste packages for the upper-bound and mean profiles is approximately 66,000 and 194,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case). These times are 6,000 and 8,000 years earlier, respectively, than those for the simulation presented in Figure 7.4-22.

Figure 7.3.5-10 shows the first patch penetration profiles of the waste packages with time, which result from the use of a relative humidity threshold for the initiation of general corrosion based on the deliquescence points of magnesium chloride salts (see Table 7.3.1-2b). The first patch breach times of the upper-bound and 95th percentile profiles are approximately 55,500 and 92,000 years, respectively. Comparison of the patch breach profiles with the failure (first breach) profiles (Figure 7.3.5-9) indicates that the initial breach (or failure) of the waste packages is mostly by SCC penetration in the closure lid welds of the Alloy 22 waste package outer barrier. For the 75th percentile profile, the first patch penetration time is approximately 228,000 years. For the mean profile, approximately 71 percent of the waste packages have patch failures by the end of the simulation time (1 million years).

In summary, the effect of the use of a relative humidity threshold for the initiation of general corrosion based on the deliquescence points of magnesium chloride salt is insignificant. The failure times are a few thousand years earlier, and approximately one percent more patch failures result. As seen in Table 7.3.1-2b, the use of the deliquescence points of magnesium chloride salt, which is more hygroscopic than NaNO_3 salt, causes an earlier corrosion initiation and increased general corrosion rates at higher temperatures of the Alloy 22 outer barrier (see Figure 7.3.5-8). This insensitivity of waste package degradation to the more aggressive

corrosion initiation threshold is due mostly to the fact that the time period, during which the waste package temperature is above the boiling temperature of NaNO₃ salt (120.6°C, see Table 7.3.1-2b) and the waste packages are subject to higher general corrosion rates, is much shorter than the waste package lifetime.

7.3.5.5 Other Lines of Evidence to Support Alloy 22 General Corrosion Model

This section discusses alternative lines of evidence in support of the Alloy 22 general corrosion model used in the TSPA. Literature data and industrial analogues are presented as alternative lines of evidence for the time dependence of the general corrosion rate (i.e., the general corrosion rate decreases with exposure time).

Time-Dependent General Corrosion Behavior of Alloy 22—The general corrosion rates used for Alloy 22 in the waste package degradation analysis are based on the two-year weight-loss results from the LTCTF (CRWMS M&O 2000 [DIRS 144229], Section 6.9.1). These results were conservatively selected for extrapolation over repository time scales based on the observation that the measured corrosion rate is continuing to decrease with time (Figure 7.3.5-6).

The trend of decreasing general corrosion rate with time is consistent with the expected corrosion behavior of passive alloys such as Alloy 22 under repository-type aqueous conditions. Similar passive behavior has also been observed for nickel-, chromium-, and molybdenum-type corrosion-resistant alloys. For example, Alloy C is found to retain a very thin passive film, indicated by the retained mirror-like finish after 44 years of exposure at Kure Beach to a marine environment (i.e., salt air with alternate wetting and drying as well as the presence of surface deposits) (Baker 1988 [DIRS 154510], p. 134). More recent examination of specimens from this alloy after more than 50 years of exposure indicates that the samples continue to maintain a mirror-like finish and passive film behavior (McCright 1998 [DIRS 100289], Figure ES-1). Under these same conditions, the less corrosion-resistant Alloy 600 exhibited a corrosion rate of 0.008 µm/yr after 36 years of exposure. These long-term results provide corroborative support for the expected excellent long-term passive corrosion behavior of Alloy 22 under chloride-containing aqueous environments that are relevant to repository exposure conditions.

In addition, the time-dependent corrosion behavior can be inferred by the long-term monitored corrosion results (represented by loss in tensile strength measurements) on passive-type aluminum alloys exposed to a marine environment (ASM International 1987 [DIRS 103753], p. 911, Figure 42). The initial rate is relatively high at short times (less than one year), but the rates drop off rapidly with increasing exposure time. This is the expected behavior for alloys where the passive film grows by a parabolic diffusion-controlled process or by a logarithmic process.

7.3.6 Early Waste Package Failure: Improper Heat Treatment

An extensive literature review was conducted for the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) to collect information to develop scenarios and conditions that could lead to early failure of waste packages. From this literature review and analysis, a number of potential mechanisms were identified that could lead to early waste package failures under repository conditions (CRWMS M&O 2000 [DIRS 147359]). Those mechanisms were further evaluated to

develop the probability of their occurrence and the consequence of the mechanism to waste package failures under repository conditions (CRWMS M&O 2000 [DIRS 147359], Section 6.1 and 6.2). All the mechanisms except weld flaws in the waste package closure welds were screened out based on a low probability of occurrence (CRWMS M&O 2001 [DIRS 153937], Section 6.2.12). The analysis results for weld flaw frequency and size were used as inputs to the waste package SCC analysis (CRWMS M&O 2000 [DIRS 151549], Section 6.2.2; see also Section 7.2.5).

A recent reevaluation of the potential early failure mechanisms in *Analysis of Mechanisms for Early Waste Package Failure* (CRWMS M&O 2000 [DIRS 152097]) has concluded that improper heat treatment of waste packages needs to be considered in the waste package and TSPA analysis. This is necessary because the consequence of improper heat treatment could lead to a gross failure of affected waste packages, although the probability of this occurrence is very low. Accordingly, improper heat treatment of waste package is considered in the current waste package degradation analysis. As discussed below, the affected waste packages are assumed to fail with a non-mechanistic failure mode.

Estimation of the Number of Affected Waste Packages—The probability of improper heat treatment of a waste package is estimated in *Analysis of Mechanisms for Early Waste Package Failure* (CRWMS M&O 2000 [DIRS 152097], Section 6.2.3). The main probability component is the branch on the event tree (CRWMS M&O 2000 [DIRS 152097], Section 6.2.3.1, Figure 9, Branch 10) in which the furnace suffers a nondetectable failure and a subsequent independent test fails to detect the improper treatment (CRWMS M&O 2000 [DIRS 152097], Section 6.2.3). This event tree is assumed to apply both for the heat treatment of the waste package before the waste loading and for the induction annealing of the closure weld regions. The current analysis further assumes that the waste package undergoes a second independent inspection before waste loading with a failure probability of one in a hundred, which corresponds to an human error probability of failure to follow a written operating procedure (CRWMS M&O 2000 [DIRS 152097], Section 6.2.3.1). The given probability of an improper heat treatment is p , where $p = 2.21 \times 10^{-5}$ (CRWMS M&O 2000 [DIRS 152097], Figure 9). Combining the two failure modes, the total failure probability is $1.01 \times p = 2.23 \times 10^{-5}$.

A Poisson distribution is used to model the number of waste packages that suffer an improper heat treatment in the repository. The Poisson distribution assumes that the affected waste packages are independent. This assumption is reasonable considering that improper heat treatment is caused by non-detected equipment malfunctioning and non-reported operator errors. The appropriate parameter for the distribution is the expected number of improperly heat-treated waste packages. Assuming there are 11,770 waste packages (CRWMS M&O 2000 [DIRS 148384], Section 6.3.4, Table 6-31) and the probability of improper heat treatment is 2.23×10^{-5} , then the expected number of improperly heat-treated waste packages is the product of these two numbers (0.263). Given this value as the mean of the Poisson distribution, probabilities for the number of packages that are improperly heat-treated are calculated from the Poisson distribution function. The resulting probabilities for the number of waste packages improperly heat-treated per repository are given in Table 7.3.6-1. The results show that there is a 76.9 percent chance that no single waste package is improperly heat-treated. The probability of having at least one waste package improperly heat-treated is 20.2 percent, and the probability of having two waste packages affected is 2.6 percent. The probability of having three waste

packages with improper heat treatment is about 0.2 percent. Assuming a total of 100 realizations for the waste package degradation analysis using the WAPDEG model, those probabilities provide that 77 out of 100 realizations would have no waste packages affected by improper heat treatment. Out of 100 realizations, 20 realizations would have at least one waste package affected and 3 realizations would have two waste packages affected. Because improper heat treatment is a low probability event, it is modeled directly in the TSPA analysis presented in Volume 2 (McNeish 2001 [DIRS 155023]).

Consideration of Improper Heat Treatment in Waste Package Performance Analysis–

Disposal containers will be subjected to heat treatment processes to relieve stresses as part of the manufacturing process. A disposal container becomes a waste package after being loaded with waste and sealed (CRWMS M&O 2000 [DIRS 152104], Section 1.0). These processes include solution annealing of containers before being loaded and local induction annealing for stress mitigation of the outer lid welds of the waste package outer barrier.

Improper heat treatment would be caused by heating and subsequent cooling operations outside the specified operation ranges. The most likely causes would be operator error or equipment malfunctioning when out-of-range operations are not reported or detected. Operations that could damage waste package integrity include heating the container to undesirable temperatures for an extended period of time or improper cooling following the heating process. Any of these operations could result in extensive precipitation of undesirable secondary phases, both on grain boundaries and in the grain interiors (grain bulk) of the Alloy 22 waste package outer barrier. This could lead to severe aging and phase instability problems, which would result in significant degradation of the container's mechanical properties (CRWMS M&O 2000 [DIRS 147639], Section 6.3 and Section 7.3.2.1.2 of this volume) and an increased susceptibility to localized corrosion of the outer barrier (CRWMS M&O 2000 [DIRS 147639], Section 1.1; Dunn et al. 2001 [DIRS 154511], Figure 1; see also Section 7.3.2). Therefore, waste packages that are improperly heat-treated may be subject to SCC and enhanced general and localized corrosion.

As indicated, the improper heat treatment event is modeled directly in the current TSPA analysis. In evaluating the potential of early failures by improper heat treatment and its consequence, a non-mechanistic failure of the outer and inner closure lids of the waste package outer barrier is assumed as well as the failure of the closure lid of the stainless steel structural inner shell. Details of the TSPA implementation are discussed in Volume 2 (McNeish 2001 [DIRS 155023]). The following assumptions are employed:

- Those waste packages affected are assumed to fail immediately when they undergo corrosion.
- The area on the waste package affected by improper heat treatment is assumed to be equal to the closure weld patches because improper heat treatment is most likely to occur during the induction annealing of the outer closure lid welds of the waste package outer barrier (CRWMS M&O 2000 [DIRS 151564], Section 6.2.2.4).

- The materials of the entire affected area are assumed to be lost upon failure of the waste packages because the affected area will be subjected to SCC and highly enhanced localized and general corrosion.
- The weld region of the inner closure lid of the outer barrier and the closure lid of the stainless steel structural inner shell fail at the same time when the outer closure-lid weld region fails.

The above assumptions are conservative because only the weld region of the outer-lid of the outer barrier would be affected by potential improper heat treatment during the stress mitigation heat treatment (e.g., induction annealing), and the inner-lid of the outer barrier is not likely affected. The conservative assumptions were made to avoid detailed analyses for estimating “more realistic” open area of the affected waste package. In a more realistic scenario, the breached weld patches of the affected waste package would remain with the waste package until the weakened areas affected by a major mechanical impact or corroded away by general corrosion.

7.3.7 Other Issues

This section documents additional analyses and information that are not associated with those discussed in the previous subsections.

7.3.7.1 Margin for Localized Corrosion Susceptibility for the Range of Thermal Operating Modes

Two parameters commonly used for assessing thresholds below which localized corrosion will not occur in a given alloy/environment system are critical crevice temperature (CCT) and critical potential (e.g., repassivation potential). The current approach in the waste package performance analysis uses critical potential as the threshold parameter (CRWMS M&O 2000 [DIRS 147648], Sections 6.3.1 and 6.4.1; CRWMS M&O 2000 [DIRS 151566], Sections 4.1.5 and 4.1.6). The use of CCT is also discussed in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* analysis model report (CRWMS M&O 2000 [DIRS 144229], Section 6.4.3). In considering the advantages of lower-temperature operating modes, the use of a CCT parameter is more informative than a critical potential. There are industrial standards for evaluating CCT (e.g., ASTM G-48 and Materials Technology Institute (MTI) standard MTI-2). The CCT values for Alloy 22 evaluated in these tests could be as low as approximately 58°C (Table 7.3.7-1). Although useful in ranking a range of alloys, these standard tests utilize aggressive environments (in particular, a ferric chloride solution) that are not directly relevant to expected waste package surface environments because the potential for ferric chloride generation is very remote. Although not directly relevant, testing with ferric chloride solution may be used for a conservative lower bound for the expected CCT for magnesium and calcium chloride solutions. Although unlikely to develop, a limited quantity of such solutions could evolve from non-carbonate waters that might be present on the waste package surface from either dripping or deliquescence of the salts contained in deposits on the waste package surface (see Section 7.3.1).

Recent test results by the NRC (Dunn et al. 1999 [DIRS 154481], p. 3-10, Figure 3-10) and Lawrence Livermore National Laboratory for relatively pure concentrated sodium chloride

solutions (pH range of 2.5-8.0; see Table 7.3.7-1) are somewhat more germane than the results with ferric chloride solution, but they are still not directly relevant to potential waste package surface environments. These results with concentrated sodium chloride solutions yield CCT values as low as 85°C, which can be used as a conservative lower-bound CCT. Of more direct relevance are the CCT values that can be derived from specimens exposed to a range of relevant environments (simulated acidic water, simulated dilute water, and simulated concentrated water) at 90°C in the LTCTF. Other relevant data can be derived from the cyclic polarization tests that were conducted for a broader range of relevant environments (CRWMS M&O 2000 [DIRS 144229], Sections 6.4 and 6.5). These test environments all contain realistic concentrations of one or more beneficial buffer ions (nitrate, sulfate, carbonate, and silica ions), which are expected to be present along with chloride ions in the solutions contacting the waste package surface. The CCT values obtained in these tests, as summarized in Table 7.3.7-1, yield a CCT value of at least 90°C (the maximum temperature employed in the LTCTF). These values are greater than 120°C for all relevant test environments, as determined from extrapolation of the measured cyclic polarization corrosion potentials and critical potentials versus test temperature to the point of intersection, as discussed in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000 [DIRS 144229], Section 6.4.3).

Another basis for assessment of CCT can be derived from the Halar creviced (at each end of gage length) slow strain rate tests performed at Lawrence Livermore National Laboratory. The tests were conducted for conditions that included a range of temperatures from 76° to 105°C, applied potentials from open circuit potential to 400 mV vs. Ag/AgCl, and a range of relevant environments. This test yields a very conservative CCT because the passive film is continuously fractured and reformed throughout the test. Examination of the results previously discussed in Section 7.3.3.3.3 (Table 7.3.3-3) indicates that the normal range of fracture ductility without corrosion effects is about 50 to 60 percent for both the uncreviced and creviced cases. In near-neutral 4M NaCl solutions, a CCT of 98°C occurs between 350 and 400 mV vs. Ag/AgCl (Tests ARC22-123 and ARC22-117), whereas in basic saturated water (pH 13, Test ARC22-120), it lies above 105°C even at 400 mV vs. Ag/AgCl. However, if both nitrate and sulfate ions are removed, leaving primarily NaCl (approximately 3M) in solution, crevice corrosion occurs between 200 and 300 mV vs. Ag/AgCl (Test ARC22-122 vs. ARC22-126) at 98°C, indicating that the pH 13 NaCl solution is more aggressive for Alloy 22 than the near-neutral solution. At highly oxidizing conditions (400 mV vs. Ag/AgCl), simulated concentrated water (Test ARC22-112) appears to be a more aggressive environment than basic saturated water (Test ARC22-119), with a CCT value of 76°C or less. However, at a lower but still highly oxidizing condition (317 mV vs. Ag/AgCl), no crevice corrosion is observed at 76°C in the environment. Under the expected case of open circuit potential, no crevice corrosion is observed at 76°C in any of the environments tested, including those with lead additions (Tests ARC22-13 and ARC22-16 to 18), even under very aggressive, continuous straining conditions.

As discussed above, the CCT value for Alloy 22 in the range of relevant environments and expected corrosion potentials (approximately -200 mV vs. Ag/AgCl) (CRWMS M&O 2000 [DIRS 144229], Section 6.4.2) is greater than 90°C, and very likely greater than 120°C. Additional margin would be obtained from lower-temperature operating modes because of the difference in temperature dependencies between the corrosion and repassivation potentials. The corrosion potential rises only slightly with decreasing temperature (due to increasing oxygen solubility), as described by the Nernst equation, and the repassivation potential increases rapidly

with decreasing temperature, as observed over a broad range of sodium chloride concentrations (Cragolino et al. 1999 [DIRS 152354], p. 2-33, Figure 2-11). This increasing difference in potentials with decreasing temperature would also provide margin for any upward drift of corrosion potential with time, as well as for any decrease in repassivation potential over long time periods. These potential changes with time may occur due to potentially decreasing protectiveness of the passive film on Alloy 22, which could be caused by some unexpected passive film degradation mechanism. It also provides margin for unexpected (but possible) environments that may lack beneficial buffering ions or contain higher than expected trace element concentrations, including dissolved lead.

7.3.7.2 Effects of Radiolysis on Alloy 22 Corrosion Rates

Section 7.3.1 discusses the highly unlikely potential for the development of an aqueous environment very early after waste package emplacement due to the presence of magnesium and calcium chloride salts in the deposited salts from the non-carbonate based pore water. Because of this, it is possible that the radiation levels at the outer surface of the waste packages may be high enough to result in the formation of more aggressive conditions due to radiolysis. To address this condition, a brief review of the available information was conducted.

Engineering calculations of the expected radiation levels at the surface of the waste package have been performed. For a bounding-case waste package containing 21-PWR fuel assemblies (75 GWd/MTU burnup and 5-year decay), the maximum surface radiation level in the fueled region was calculated to be 1,039 rem/hour (BSC 2001 [DIRS 153752]). This value is an upper bound at the time of emplacement. For an assumed ventilation period of 50 years, during which time no aqueous environment is expected, this value decays down to levels in the range of 85 to 90 rem/hour (BSC 2001 [DIRS 153752]). The calculated levels are further reduced to approximately 25 rem/hour at 100 years after emplacement.

The effects of radiation on waste package materials corrosion will differ depending on the environment (i.e., dry, humid, or wet). At relative humidities where a thin film of liquid can form from the deliquescence of the deposited salts, and if dissolved nitrogen from air is present in the water film, radiation could lead to formation of acidic conditions, and thus enhanced corrosion rates. However, there is little information available in the literature on the effects of radiation on Alloy 22. Limited data are available on the effects of radiation fields on the corrosion of nickel alloy C-4 in highly aggressive $MgCl_2$ brines. There was no observable influence from the radiation field below 1,000 rem/hour (Smailos et al. 1990 [DIRS 154820]; Shoemith and King 1999 [DIRS 112178]). Above these levels, localized corrosion was observed. Based on these limited data, it is concluded that even in the presence of $MgCl_2$ brines, the radiation levels are not high enough to result in an enhancement of corrosion rates of the Alloy 22 outer barrier.

7.3.7.3 Additional Natural and Archaeological Analogues

Although corrosion data for Alloy 22 are available only for a two-year time period, there are abundant data from analogues that suggest that corrosion rates should be very low in an open space within an unsaturated environment. A vault excavated into limestone at the base of the great pyramid of Giza contained a disassembled cedar boat that was well-preserved in spite of its

4,500-year-old age. The tombs in the valley of the kings of Egypt were carved into limestone within an unsaturated zone. The tomb of Meketre contained 24 wooden boxes, each with painted figurines, which were all well preserved after nearly 4,000 years (Stuckless 2000 [DIRS 151957]). Several items that are more delicate than metals and alloys were recovered from the tomb of Tutankhamen, including reed baskets of fruit, bread, and dried cornflowers. Even an iron knife, which was free of rust when pulled from its scabbard, was preserved within the unsaturated zone for approximately 3,500 years (Stuckless 2000 [DIRS 151957]).

Some of the oldest examples of metal preserved within the unsaturated zone come from a cave in Israel. Bronze items have been nearly perfectly preserved for almost 6,000 years. Other items preserved in the cave and pictured in a recent issue of National Geographic (Ozment 1999 [DIRS 155058]) include ivory, wood, and fabric. Although the climate in this example is drier than that of southern Nevada, it shows how well the unsaturated zone can protect even nondurable materials.

The durability of the iron (99.7 percent) pillar of Asoka, India, is attributed to its location in a relatively dry environment and to its having minimal impurities. Johnson and Francis (1980 [DIRS 125291], p. 6.5) indicate that the pillar was constructed by forge-welding together many solid disks. They suggest that conditions during welding may have been favorable for formation of corrosion-resistant oxides.

Stuckless (2000 [DIRS 151957]) reviews examples of metal and other materials preserved in Europe, where the environments are wetter than those of Israel or southern Nevada. Examples from Roman mines excavated into the unsaturated zone include a copper plaque from Riotinto, Spain, that is nearly 2,000 years old. Other items from around the same period include iron and bronze tools, a bronze pump, leather ore buckets, hemp, and a wooden Archimedian screw.

7.3.7.3.1 Cask of Nails

An ancient hoard of buried nails has been used in a study of the corrosion of iron. These nails were found on the site of the most northerly fortress of the Roman Empire at Inchtuthil, Scotland. An estimated total of over a million nails were buried in a 5-m deep pit and covered with 3 m of compacted earth in a successful attempt to hide the nails from Pictish tribes when the fortress was abandoned in 87 A.D. (Miller et al. 1994 [DIRS 126089]). The fortress was excavated in the 1950s, when the surviving nails (850,000 or so) were unearthed. Although the nails were composed of iron, they were heterogeneous in composition, with regions of high and low carbon contents. The surfaces of all the nails exhibited some corrosion, but the degree of corrosion was greatly controlled by location within the hoard. The nails toward the inside of the hoard showed minimal corrosion, limited to formation of a thin corroded layer; those on the outside of the hoard, especially near the top, were corroded to the extent that they formed a solid crust. This example serves to illustrate the protective role of a corrosion-formed crust in reducing or preventing further corrosion.

7.3.7.3.2 Meteorites

Naturally occurring metal and metallic oxides also demonstrate low corrosion rates in the environment of the southwestern United States. Iron from the meteorite that created Meteor

Crater in Arizona has existed at the surface of the earth for thousands of years. At Yucca Mountain, ilmenite (FeTiO_2) and magnetite (Fe_3O_4) have existed within the unsaturated zone for the entire history of the mountain without visible alteration.

It has been suggested that iron meteorites may be good analogues of steel alloy waste packages. Iron meteorites are essentially nickel-iron alloys (nickel content usually ranges between 5 and 11 wt. percent, with a maximum of 60 wt. percent) with minor amounts of cobalt (0.3 to 1.0 wt. percent) and traces of chromium (5 to 2500 ppm), chlorine (1 to 10 ppm), and titanium and vanadium (0.5 to 5.0 ppm) (Johnson and Francis 1980 [DIRS 125291], p. 4.2). Although iron meteorites lack the high chromium concentration of Alloy 22, their validity as an analogue would be increased by the ability to monitor such present environmental parameters as pH, Eh, soil moisture, etc., and to estimate past environmental parameters in the setting where they fell to earth. This means that only meteorites that can be traced to their depositional sites would yield useful information for such a study.

The presence or absence of a fusion crust (i.e., a magnetite (Fe_3O_4)-wüstite (Fe_{1-x}O) rind formed by rapid oxidation during atmospheric descent) may be a factor in the range of weathering that occurs at sites where meteorites fragment both on descent and upon impact. At Canyon Diablo, Arizona, meteoritic material that developed a fusion crust during descent was, with the exception of silica-coated metal particles, more resistant to weathering than masses formed on impact, which developed a thin fusion crust (Johnson and Francis 1980 [DIRS 125291], p. 4.20).

The nickel content of a meteorite appears to affect its resistance to corrosion. Phases with 20 to 30 wt.% nickel (ataxites) have frequently shown superior resistance to terrestrial corrosion than phases with less nickel. By measuring potentials between selected phases, Buddhue (Johnson and Francis 1980 [DIRS 125291], p. 6.4) determined that corrosion over a period of centuries consumed kamacite (Fe-7.5 percent Ni) while preserving phases such as taenite (Fe-25 percent Ni), schreibersite ($\text{Fe, Ni}_3\text{P}$) (Johnson and Francis 1980 [DIRS 125291], p. 6.4) as the meteorite mineral most resistant to corrosion), and draubreelite (FeCr_2S_4). The better-preserved phases are higher in chromium and nickel.

Johnson and Francis (1980 [DIRS 125291]) investigated general corrosion of more than 40 iron artifacts and a few meteorites, and obtained a rate of uniform corrosion of 0.1 to 10 $\mu\text{m}/\text{yr}$ over a range of environmental conditions. Chapman et al. (1984 [DIRS 127768]) used a corrosion rate of 1 $\mu\text{m}/\text{yr}$ (in the middle of this range) to obtain a lifetime of 5×10^4 years for the mechanical stability of the Nagra (Switzerland) waste package container.

Johnson and Francis (1980 [DIRS 125291], p. 6.7) noted that dry and tomb-like environments were the most benign to all ancient materials because lack of moisture condensation suppressed corrosion. They further suggested that if temperatures are below the range where rapid oxidation occurs (varying by metal), elevated temperatures (above the dew point) are an advantage to preservation of metals.

7.4 EFFECT OF UPDATED UNCERTAINTIES ON WASTE PACKAGE PERFORMANCE

This section evaluates the effects of using updated data (i.e., updated and quantified uncertainties) in the corrosion models of waste package performance described in Section 7.3. The WAPDEG model is used in the analysis. The analysis is conducted by comparing the results of the baseline (or nominal case) WAPDEG analysis with the results of a new WAPDEG analysis conducted using updated corrosion models.

7.4.1 Baseline Waste Package Degradation Model

All simulations were conducted using Version 4.0 of the WAPDEG software and Version 6.04.007 of the GoldSim software. The baseline integrated WAPDEG model, the model used to produce the analyses presented in this section, differs slightly from the model used in the initial TSPA-SR (CRWMS M&O 2000 [DIRS 148384]). The baseline model is referred to as the updated WAPDEG model in the *WAPDEG Analysis of Waste Package and Drip Shield Degradation* (CRWMS M&O 2000 [DIRS 151566]), and the initial TSPA-SR WAPDEG model (CRWMS M&O 2000 [DIRS 153246]) is referred to as the current WAPDEG model. The baseline WAPDEG model incorporated some of the updated and quantified uncertainties in the corrosion models (see Section 7.3) completed after the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]) was issued. Differences between the baseline WAPDEG model and the current WAPDEG model include:

- The radii of the Alloy 22 waste package outer barrier closure lid used in the baseline WAPDEG model are slightly larger than those used in the current WAPDEG model.
- The treatment of the weld flaw abstraction model has been updated. The input parameters and functional forms used in the baseline WAPDEG weld flaw model are based on analyses presented in the process level and abstraction analysis model reports (CRWMS M&O 2000 [DIRS 152097]; CRWMS M&O 2000 [DIRS 151549]).
- The lower bound on the distribution for the location parameter for the probability of nondetection of weld flaws is larger in the baseline WAPDEG model than the bound used in the current WAPDEG model.
- The baseline WAPDEG model uses one more input than the current WAPDEG model in its treatment of the weld flaw abstraction model (i.e., the fraction of surface-breaking flaws).
- The baseline WAPDEG model uses a revised threshold stress uncertainty for SCC initiation that is uniformly distributed between 10 percent and 40 percent of the yield strength. The current WAPDEG model uses a threshold stress uncertainty that is uniformly distributed between 20 percent and 30 percent of the yield strength.
- The baseline WAPDEG model has an updated uncertainty range for parameter n , the crack growth exponent (sometimes referred to as the repassivation slope) of the slip dissolution model. In the baseline WAPDEG model, n is given by a uniform

distribution between 0.843 and 0.920. In the current WAPDEG model, n is given a uniform distribution between 0.75 and 0.84.

Results of a WAPDEG analysis (i.e., waste package and drip shield failure time and number of crack, pit, and patch penetrations) are reported as a group of degradation profile curves that represent the potential range of the output parameters. The results are presented for the upper and lower bounds, mean, and 95th, 75th, 25th, and 5th percentiles as a function of time for the following output parameters:

- Waste package first breach (or failure)
- Drip shield first breach (or failure)
- Waste package first crack penetration
- Waste package first patch penetration
- Waste package crack penetration numbers per failed waste package
- Waste package patch penetration numbers per failed waste package
- Drip shield patch penetration numbers per failed drip shield.

Localized corrosion does not initiate for either the waste package (Alloy 22 outer barrier) or the drip shield because the exposure conditions on the drip shield and waste package surface are not severe enough to initiate localized corrosion. In the current conceptual model, the drip shields will be fully annealed before being placed in the emplacement drift, and rockfall-induced SCC is the only potential mechanism for a through-wall crack penetration of the drip shield. However, the SCC cracks will be short and tight and plugged with corrosion products and precipitates such as calcite (see Section 7.3.3.2). Therefore the rockfall-induced SCC cracks will not compromise the intended design function of the drip shield (i.e., diversion of dripping water). SCC of the drip shield is not considered further in the current analysis. Thus, for the drip shield, the first patch breach time profile is the same as the failure time profile.

The upper-bound, lower-bound, mean, and 95th, 75th, 25th, and 5th percentile curves do not correspond to individual realizations. They are summary statistics related to consideration of 100 realizations. In the bullets below, the origin of the upper-bound, lower-bound, mean, and 95th, 75th, 25th, and 5th percentile curves for first breach of the waste package are discussed. Similar wording could be applied to discussion of the origins of the drip shield first breach curves, waste package first crack penetration curves, etc.

- At each point in time, the upper-bound curve shows the realization with the greatest fraction of failed waste packages calculated in any one of the 100 realizations. This may not be the same realization at each point in time. The upper bound curve becomes non-zero at the time of failure of the first waste package in all 100 realizations. Note that the upper-bound curve represents a case with an extremely low probability, and the same is true for the lower-bound curve discussed below.
- At each point in time, the 95th percentile curve shows the realization with the 95th greatest fraction of waste packages failed (i.e., 95 realizations out of 100 have a smaller fraction of failed waste packages). This may not be the same realization at each point in time. The 95th percentile curve becomes non-zero at the time when at least 5 realizations have at least 1 waste package failure.

- At each point in time, the 75th percentile curve shows the realization calculated in any one of the 100 realizations with the 75th greatest fraction of failed waste packages, (i.e., 75 realizations out of 100 have a smaller fraction of waste packages failed). This may not be the same realization at each point in time. The 75th percentile curve becomes non-zero at the time when at least 25 realizations have at least 1 waste package failure.
- At each point in time, the 25th percentile curve shows the realization calculated in any one of the 100 realizations with the 25th greatest fraction of failed waste packages (i.e., 25 realizations out of 100 have a smaller fraction of waste packages failed). This may not be the same realization at each point in time. The 25th percentile curve becomes non-zero at the time when at least 75 realizations have at least 1 waste package failure.
- At each point in time, the 5th percentile curve shows the realization calculated in any one of the 100 realizations with the 5th greatest fraction of failed waste packages (i.e., 5 realizations out of 100 have a smaller fraction of waste packages failed). This may not be the same realization at each point in time. The 5th percentile curve becomes non-zero at the time when at least 95 realizations have at least 1 waste package failure.
- At each point in time, the mean curve shows the mean of all the fractions of failed waste packages in the 100 realizations. The mean curve becomes non-zero at the time of failure of the first waste package in all 100 realizations.

The effect of the updated and quantified uncertainties in the corrosion models (see Section 7.3) on waste package performance is evaluated by comparing results of the WAPDEG analysis using the updated corrosion models with the results of the baseline WAPDEG analysis. The nominal case results are discussed first in this section. Details concerning the development of the nominal case WAPDEG analyses can be found in the *WAPDEG Analysis of Waste Package and Drip Shield Degradation* (CRWMS M&O 2000 [DIRS 151566]).

WAPDEG results for the following cases are presented and described in the following sections:

- Baseline WAPDEG model
- Updated weld residual stress profile uncertainty bounds for the Alloy 22 waste package outer and inner closure lid weld regions
- Updated stress threshold uncertainty for stress corrosion cracking (SCC) crack growth initiation
- Updated general corrosion models assuming 100% uncertainty in the general corrosion rates
- Updated general corrosion models incorporating the temperature-dependent general corrosion rate
- Integrated Models using the temperature-dependent general corrosion models discussed in Section 7.3.5.

The upper and lower bounds, mean, and 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach (failure) profile for the waste packages with time for the baseline WAPDEG model were calculated (Figure 7.4-1). The upper-bound profile, which is the upper extreme of the probable range of the first breach time, indicates that the earliest possible first breach time for a waste package is approximately 15,000 years. Note that the estimated earliest possible first breach time has an extremely low probability. It can be shown by comparison with the upper-bound profile in Figure 7.4-4 (showing the first crack breach profiles of waste packages with time) that the first breach is by SCC crack penetration. The median estimate (50 percent of waste packages failed) of the first breach time of the upper bound profile is approximately 35,000 years. The median estimate of the first breach time of the mean profile is approximately 108,000 years. The time to fail 10 percent of the waste packages for the two profiles is approximately 23,000 and 56,000 years, respectively.

Figure 7.4-2 shows the first breach profiles of drip shields with time for the baseline WAPDEG model. As discussed earlier, the drip shields are not subject to localized corrosion, and SCC of the drip shield is not considered in the current analysis. Therefore, the first breach profiles shown in the figure are by general corrosion only. The upper and under sides of the drip shield are exposed to conditions in the emplacement drift and subject to corrosion. In addition, both sides experience the same exposure conditions regardless of whether the drip shields are dripped on or not. Thus, in the analysis, the general corrosion rate for the drip shields is sampled twice independently, once for the patches on the upper side and once for the patches on the under side. This results in reduced variability in the degradation profiles and a fast failure rate (i.e., many drip shields failing over a short time). This is shown in the upper-bound profile, in which the drip shield first breach starts at approximately 20,000 years and 50 percent of the drip shields fail within a couple of thousand years after the initial failure. Similar trends are also seen with the 95th, 75th, and median profiles. In terms of the number of patch penetration openings per failed drip shield with for the baseline WAPDEG model (Figure 7.4-3), the upper-bound profile shows that as the drip shields fail, a large number of patches are perforated over a relatively short time period (i.e., a few thousand years). There are kinks in the upper-bound curve in Figure 7.4-3 at early times (e.g., at 30,000 years) because the number of failed drip shields increases rapidly at these times (Figure 7.4-2). This causes the average number of patch penetrations per failed drip shield to decrease significantly at these times.

Figures 7.4-4 and 7.4-5 show, respectively, the first crack penetration and first patch penetration profiles of the waste packages with time for the baseline WAPDEG model. The first crack breach times of the upper-bound and 95th percentile profiles are approximately 15,000 and 20,000 years, respectively (Figure 7.4-4), and the first patch breach times of the upper-bound and 95th percentile profiles are approximately 33,000 and 43,000 years, respectively (Figure 7.4-5). Comparison of the first crack and patch breach profiles with the first breach profiles in Figure 7.4-1 indicates that the initial breach (or failure) of the waste packages is likely by SCC penetration in the Alloy 22 waste package outer barrier closure lid welds. For the 75th percentile profiles in the figures, the first crack and patch penetration times are approximately 32,500 and 58,000 years, respectively.

Figure 7.4-6 shows the profile for the average number of crack penetrations per failed waste package for the baseline WAPDEG model. As discussed for Figure 7.4-4, the upper-bound and 95th percentile profiles show the first crack penetration at approximately 15,000 and 20,000 years, respectively. The mean profile never develops more than 25 crack penetrations per waste package. SCC cracks in passive alloys such as Alloy 22 tend to be tight (i.e., have a small crack opening displacement) (CRWMS M&O 2000 [DIRS 151564], Section 6.5.5). The opposing sides of through-wall SCC cracks will continue to corrode at low passive corrosion rates until the gap region of the tight crack opening is “plugged” by the corrosion product particulates and precipitates such as calcite. Any water transport through this oxide/salt-filled crack area will be mainly by diffusion-type processes (CRWMS M&O 2000 [DIRS 153940], Section 6.4.3). Refer to Section 7.3.3.2 for a summary discussion on the recent analysis of plugging of SCC cracks by calcite precipitates. Thus, the effective water flow rate into the waste packages and the radionuclide release rate from the waste packages through the SCC cracks would be expected to be extremely low.

Figure 7.4-7 presents the profile for the average number of patch openings per failed waste package for the baseline WAPDEG model. For the upper-bound profile, which represents an extremely low probability case, the first patch breach occurs at approximately 33,000 years (also see Figure 7.4-5), and approximately 12 patches of the failed waste packages (approximately 1.2 percent of the waste package surface area) are breached by 100,000 years. For the mean profile, there will be approximately 2 patch openings in each of the failed waste packages by 100,000 years.

7.4.2 Effect of Updated and/or Quantified Uncertainties in the Stress Corrosion Cracking Model Parameters

7.4.2.1 Weld Flaw Orientation

Uncertainty in the fraction of weld flaws that are capable of growing in a radial direction in the presence of hoop stress is quantified in Section 7.3.3. As discussed in that section, hoop stress is the dominant stress that can grow through-wall radial cracks resulting in waste package failure. The WAPDEG model assumes that, if SCC occurs, only those flaws could grow in a radial direction in the presence of hoop stress. A sensitivity study was conducted using the WAPDEG model (CRWMS M&O 2000 [DIRS 151566]) in which the fraction of the weld flaws considered capable of propagation in the radial direction was sampled from a bounded lognormal distribution with a median value of 0.01 (1 percent) and ± 3 standard deviations bounds (0.0002 and 0.50). This is obtained by multiplying the fraction of flaws (CRWMS M&O 2000 [DIRS 151566], Section 6.4.11) considered to be capable of propagation by the sampled value.

Figure 7.4-8 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time incorporating the updated uncertainty for weld flaw orientation. The upper-bound profile, which is the upper extreme of the probable range of the first breach time, indicates that the earliest possible first breach time for a waste package is approximately 20,000 years (15,000 years for the nominal case). The median estimate (50 percent of waste packages failed) of the first breach time of the upper-bound profile is approximately 55,000 years (30,500 years for the nominal case). The median estimate of the first breach time of the mean profile is approximately 120,000 years

(108,000 years in the nominal case). The time to fail 10 percent of the waste packages for the two profiles (the upper-bound and mean profiles) is approximately 34,500 and 70,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case).

7.4.2.2 Residual Stress Uncertainty Bounds

A second sensitivity study was conducted, based on the revised models, to determine the uncertainty in the stress and stress intensity factor profiles. In this analysis, the uncertainty bounds of residual stress of the Alloy 22 waste package outer closure lid welds (induction annealed) were set to ± 21.4 percent of the yield strength (Section 7.3.3.3.1), and the residual stress uncertainty bounds of the Alloy 22 waste package inner closure lid welds (laser peened) were sampled from a cumulative distribution function (Table 7.3.3-2). In the WAPDEG model nominal case simulations, the residual stress uncertainty bounds for both of the Alloy 22 waste package outer barrier closure lids were set to ± 30 percent (CRWMS M&O 2000 [DIRS 151566], Section 6.5.1). The residual stress uncertainty bounds used in this sensitivity study would increase the minimum depth at which SCC crack growth could initiate (Figures 7.4-11 and 7.4-12), delaying the waste package first breach times relative to the nominal case simulations. Details of the residual stress uncertainty model implementation are presented in *WAPDEG Analysis of Waste Package and Drip Shield Degradation* (CRWMS M&O 2000 [DIRS 151566], Section 6.4.12).

Figure 7.4-9 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time incorporating the updated stress uncertainty bounds for the outer and inner lids of the waste package outer barrier. The upper-bound profile, which is the upper extreme of the probable range of the first breach time, indicates that the earliest possible first breach time for a waste package is approximately 20,000 years (15,000 years for the nominal case). The median estimate (50 percent of waste packages failed) of the first breach time of the upper-bound profile is approximately 48,000 years (30,500 years for the nominal case). The median estimate of the first breach time of the mean profile is approximately 106,000 years (108,000 years for the nominal case). The time to fail 10 percent of the waste packages for the two profiles is approximately 33,000 and 57,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case).

7.4.2.3 Updated Threshold Stress Uncertainty for Stress Corrosion Crack Initiation

A third sensitivity study was conducted, based on the revised models, to determine the uncertainty in the stress threshold necessary for SCC crack initiation. In this analysis, the stress threshold was considered to vary uniformly between 80 and 90 percent of the Alloy 22 yield strength. Figure 7.4-10 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time incorporating the updated stress threshold uncertainty for SCC crack initiation. The upper-bound profile, which is the upper extreme of the probable range of the first breach time, indicates that the earliest possible first breach time for a waste package is approximately 30,000 years (15,000 years for the nominal case). The median estimate (50 percent of waste packages failed) of the first breach time of the upper-bound profile is approximately 82,500 years (30,500 years for the nominal case). The median estimate of the first breach time of the mean profile is

approximately 140,000 years (108,000 years in the nominal case). The time to fail 10 percent of the waste packages for the two profiles is approximately 62,000 and 90,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case). In this case, crack and patch beach times are comparable (i.e., neither failure mode can be considered to dominate the overall failure behavior of the waste packages).

Figures 7.4-11 and 7.4-12 (CRWMS M&O 2000 [DIRS 151549], Figures 11 and 13) show the median stress profiles in the Alloy 22 outer and inner closure lid weld regions, along with stress profiles with the uncertainty bounds of ± 5 , ± 10 , and ± 30 percent of the yield strength. Also shown in the figures is the lower bound of the stress threshold distribution (80 percent of the yield strength). For the Alloy 22 waste package outer lid, the crack tip has to reach a depth of approximately 11 mm before crack growth can initiate (Figure 7.4-11). A greater level (near 30 percent) of uncertainty is necessary for any SCC cracks to begin propagation in the Alloy 22 inner lid. This would lead to few cracks penetrating the inner lid. However, because the WAPDEG model conservatively assumes that manufacturing flaws (which are treated in WAPDEG as preexisting cracks) maintain their depth relative to the general corrosion penetration front at all times (CRWMS M&O 2000 [DIRS 151566], Section 5.7), there can be a significant number of crack penetrations. The WAPDEG results for the upper-bound average number of cracks per failed waste package incorporating the updated stress threshold uncertainty for SCC crack initiation (Figure 7.4-13) indicate that cracks do not start penetrating the Alloy 22 inner lid until approximately 35,000 years (less than 5,000 years after the first patch penetration, but significantly delayed relative to the nominal case value of 15,000 years). The average number of cracks per failed waste package never exceeds approximately 15 cracks, whereas in the nominal case approximately 33 cracks per failed waste package are estimated.

7.4.3 Effect of Updated and Quantified Uncertainties in Alloy 22 General Corrosion

This section discusses the WAPDEG sensitivity analysis results using the updated uncertainty in the Alloy 22 general corrosion rate distribution (Section 7.4.3.1). Also presented in this section are the effects of the previously unquantified uncertainty in the temperature effect on the Alloy 22 general corrosion rate on the waste package degradation. As discussed in Section 7.3.5.3, three alternative temperature-dependent general corrosion rate models were developed for the Alloy 22 outer barrier assuming the temperature dependency follows an Arrhenius relationship. These models are: 1) temperature-dependent Alloy 22 general corrosion model I (Section 7.3.5.1); 2) temperature-dependent Alloy 22 general corrosion model II (Section 7.3.5.2); and 3) temperature-dependent Alloy 22 general corrosion model III (Section 7.3.5.3). Because the model II and III behave similarly, only the WAPDEG analysis results using the model I and II are documented in this section.

7.4.3.1 General Corrosion Rate Uncertainty

A sensitivity study was conducted in which all variance in the general corrosion rates for Titanium Grade 7 and Alloy 22 was considered to be solely due to uncertainty (i.e., 100 percent uncertainty). Details of the general corrosion rate uncertainty model implementation can be found in the *WAPDEG Analysis of Waste Package and Drip Shield Degradation* (CRWMS M&O 2000 [DIRS 151566], Section 6.4.7). Figure 7.4-14 shows the first breach profiles of drip shields with time assuming 100% uncertainty in the general corrosion rates for the Alloy 22

waste package outer barrier and the Titanium Grade 7 drip shield. Because the drip shields are subject to general corrosion only (i.e., not subject to localized corrosion and SCC not considered), the first breach profiles shown in the figure are from general corrosion only. In the upper-bound profile, the drip shield first breach starts at approximately 20,500 years, and all the drip shields fail within a few years after the initial failure. The slight variability in drip shield failure time is due solely to variability in general corrosion initiation time caused by variability in the temperature and relative humidity profiles used in the analysis. For the 95th percentile, all drip shields fail at 37,000 years. The 75th percentile curve shows the drip shield failures at 77,000 years.

Unlike the drip shield degradation model, the waste package degradation model has sources of variability other than the general corrosion rates. In each WAPDEG realization, the number of manufacturing flaws per waste package and their sizes are sampled from a cumulative distribution function (representing variability) derived from parameters (CRWMS M&O 2000 [DIRS 151566], Section 6.4.11). The general corrosion initiation time is variable; it depends on the time at which the critical relative humidity threshold for corrosion initiation is satisfied, which in turn depends on the thermal-hydrologic history files used for the given waste package (CRWMS M&O 2000 [DIRS 151566], Section 6.4.8). The effects of MIC, and aging and phase stability are modeled with enhancement factors, which are used as multipliers to the general corrosion rate, and are considered to be 100 percent variable (CRWMS M&O 2000 [DIRS 151566], Section 6.3.2 and 6.3.3). The MIC enhancement factor applies to the entire Alloy 22 waste package surface (CRWMS M&O 2000 [DIRS 151566], Section 4.1.10), while the aging and phase stability enhancement factor applies only to the Alloy 22 closure lid weld regions (CRWMS M&O 2000 [DIRS 151566], Section 4.1.11).

Figure 7.4-15 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time assuming 100 percent uncertainty in the general corrosion rates for the Alloy 22 waste package outer barrier and the Titanium Grade 7 drip shield. The upper-bound profile indicates that the earliest possible first breach time for a waste package is approximately 15,000 years, similar to the nominal case. The median estimate of the first breach time of the upper-bound profile is approximately 40,000 years (30,500 years for the nominal case). The median estimate of the first breach time of the mean profile is approximately 120,000 years (108,000 years for the nominal case). The time to fail 99 percent of the waste packages for the mean profile is approximately 700,000 years (approximately 300,000 years in the nominal case). The use of the 100 percent uncertainty assumption results in a broader (spread over a longer time) mean failure curve than the nominal case. This is because in the nominal case, even if a low median general corrosion rate is sampled for a waste package, variability around that median could allow for higher corrosion rates for the patches of the waste package. With the use of 100 percent uncertainty, no such variability exists.

7.4.3.2 Temperature-Dependent Alloy 22 General Corrosion Model I

This section documents the WAPDEG results using the Alloy 22 temperature-dependent general corrosion model I. The temperature dependence of this model is based on the passive current density data collected from potentiostatic polarization experiments by Scully et al. (2001 [DIRS 154513], Section 1.4; also see Section 7.3.5.3.1).

Figure 7.4-16 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time incorporating the temperature-dependent general corrosion model for the Alloy 22 outer barrier. The upper-bound profile, which is the upper extreme of the probable range of the first breach time, indicates that the earliest possible first breach time for a waste package is approximately 15,000 years, similar to the nominal case. The median estimate (50 percent of waste packages failed) of the first breach time of the upper-bound profile is approximately 204,000 years (30,500 years for the nominal case). For the mean profile, approximately 23 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of the waste packages for the two profiles is approximately 62,500 and 625,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case).

Figure 7.4-17 shows the first patch penetration profiles of the waste packages with time incorporating the temperature-dependent general corrosion model for the Alloy 22 outer barrier. The first patch breach times of the upper and 95th percentile profiles are approximately 272,000 and 592,000 years, respectively. Comparison of the first patch breach profiles with the first breach profiles (Figure 7.4-16) indicates that the initial breach (or failure) of the waste packages is all by SCC penetration in the closure lid welds of the Alloy 22 outer barrier. For the 75th percentile profile, the first patch penetration time is approximately 944,000 years. For the mean profile, approximately 6 percent of the waste packages have patch failures by the end of the simulation time (1 million years).

Thermal-Hydrologic History Sampling—If the general corrosion model is not temperature dependent, then the thermal-hydrologic history files used have little effect on the results of a WAPDEG simulation. The primary role of the thermal-hydrologic history file would be to determine the corrosion initiation time, since the critical relative humidity for corrosion initiation is a function of exposure temperature (CRWMS M&O 2000 [DIRS 151566], Section 6.4.8). Small variations in the corrosion initiation time would have little effect on the simulation results, particularly since the waste package lifetime exceeds significantly typical corrosion initiation times. For this reason, 14 thermal-hydrologic history files were used to represent the variability in thermal-hydrologic exposure conditions (CRWMS M&O 2000 [DIRS 151566], Section 6.4.1).

Development of a temperature-dependent general corrosion model for the Alloy 22 outer barrier necessitates considering all possible thermal-hydrologic history files in WAPDEG simulation. In the WAPDEG model developed for the TSPA-SR, three infiltration scenarios (low, medium, and high) were considered (CRWMS M&O 2000 [DIRS 148384], Section 6.3.1). The low infiltration scenario is considered to occur for 17 percent of the simulations, the medium infiltration scenario is considered to occur for 48 percent of the simulations, and the high infiltration scenario is considered to occur for 35 percent of the simulations. These values are in agreement with those found in the TSPA-SR model document (CRWMS M&O 2000

[DIRS 148384], Section 6.3.1). The repository is divided into about 600 spatial locations (CRWMS M&O 2000 [DIRS 148384], Section 6.3.1). At each location, thermal-hydrologic histories (e.g., waste package temperature and relative humidity, drip shield temperature, relative humidity, and other factors versus time) are developed for two waste package types (CSNF and codisposed waste forms), resulting in a total of approximately 1,200 different histories for each infiltration scenario. Each history is assigned a weight based on the fraction of repository area that the spatial location represents. The histories are binned (i.e., grouped) based on the percolation flux range into which they can be grouped (e.g., Bin 1 = 0 to 3 mm/yr, and Bin 2 = 3 to 10 mm/yr) (CRWMS M&O 2000 [DIRS 148384], Section 6.3.1). There are up to 5 bins for each infiltration scenario, although some bins do not have any time histories in them. In the potential repository design, 11,770 waste packages are modeled (3,910 codisposed and 7,860 CSNF) (CRWMS M&O 2000 [DIRS 148384], Section 6.3.4).

A thermal hydrology preprocessor (MkTable Version 1.00) was developed to prepare the temperature and relative humidity history input to the WAPDEG analysis. MkTable is executed before each realization of the WAPDEG code. It reads the total number of CSNF and codisposed waste packages (generally supplied by the TSPA-SR model (CRWMS M&O 2000 [DIRS 148384])) as discussed above and, based on the infiltration scenario under consideration (also supplied by the TSPA-SR model), randomly samples a set of 15 thermal-hydrologic histories to be used by the WAPDEG code in simulating waste package degradation for the given realization. The histories are chosen consistent with the fraction of codisposed and CSNF waste packages in the potential repository and with the weights assigned to each individual thermal-hydrologic history file.

Figure 7.4-18 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time incorporating the temperature-dependent general corrosion model for the Alloy 22 outer barrier with thermal-hydrologic history sampling. The upper-bound profile indicates that the earliest first breach time for a waste package is approximately 6,000 years, earlier than in the nominal case. As discussed below, all breaches before 24,000 years are due to crack penetrations. The median estimate of the first breach time of the upper-bound profile is approximately 190,000 years (30,500 years for the nominal case). For the mean profile, approximately 25 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of the waste packages for the two profiles is approximately 24,000 and 550,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case).

Figure 7.4-19 shows the first patch penetration profiles of the waste packages with time incorporating the temperature-dependent general corrosion model for the Alloy 22 outer barrier with thermal-hydrologic history sampling. The first patch breach times of the upper and 95th percentile profiles are approximately 24,000 and 92,000 years, respectively. Comparison of the patch breach profiles with the first breach profiles (Figure 7.4-18) indicates that the initial breach (or failure) of the waste packages is mostly by SCC penetration in the closure lid welds of the Alloy 22 waste package outer barrier. For the 75th percentile profile, the first patch penetration time is approximately 670,000 years. For the mean profile, approximately 7 percent of the waste packages have patch failures by the end of the simulation time (1 million years).

Integrated Model I Simulation-The integrated model I waste package degradation simulation using the temperature-dependent Alloy 22 general corrosion model I with thermal-hydrologic history sampling consists of a combination of the parameters studied in the individual one-off analyses documented in the preceding sections. These include:

- The temperature-dependent Alloy 22 general corrosion model I with thermal-hydrologic history sampling
- The fraction of weld flaws capable of propagation given by a ± 3 standard deviation truncated lognormal distribution (mean = 0.01, +3 standard deviations = 0.5, -3 standard deviations = 0.0002) (Section 7.4.2)
- The stress threshold for the initiation of SCC given by a uniform distribution between 80 and 90 percent of the Alloy 22 yield strength (Section 7.4.2)
- The uncertainty bounds of residual stress for the Alloy 22 waste package outer closure lid welds (induction annealed) set to ± 21.4 percent of the yield strength (Section 7.3.3.3.1)
- The residual stress uncertainty bounds of the Alloy 22 waste package inner closure lid welds (laser peened) sampled from a cumulative distribution function (Section 7.3.3.3.1, Table 7.3.3-2).

The results of using these simulation parameters are shown in Figures 7.4-20 and 7.4-21.

Figure 7.4-20 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time for the integrated model I. The upper-bound profile indicates that the earliest first breach time for a waste package is approximately 30,000 years, later than the 15,000 years for the previous nominal case. As discussed below, almost all breaches are due to patch penetrations. The median estimate of the first breach time of the upper-bound profile is approximately 876,000 years (30,500 years for the previous nominal case). For the mean profile, approximately 2.5 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of the waste packages for the upper-bound profile is approximately 392,000 years (23,000 years for the previous nominal case).

Figure 7.4-21 shows the first crack penetration profiles of the waste packages with time for the integrated model I. Due to the low fraction of manufacturing flaws capable of propagating and the high stress threshold for initiation of crack growth, little cracking is observed. The first crack breach time of the upper-bound and 95th percentile profiles is approximately 68,000 and 552,000 years, respectively. Comparison of the first crack breach profiles with the first breach profiles (Figure 7.4-20) indicates that the initial breach (or failure) of the waste packages is generally by patch penetration. For the mean profile, approximately 0.2 percent of the waste packages have crack failures by the end of the simulation time (1 million years).

7.4.3.3 Temperature-Dependent Alloy 22 General Corrosion Model II

This section documents the WAPDEG analysis results using the Alloy 22 temperature-dependent general corrosion model II, which was developed using the same data for the model I except one outlier (see Section 7.3.5.3.2). The WAPDEG analysis was conducted with the thermal-hydrologic histories sampled randomly.

Figure 7.4-22 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time. The upper-bound profile indicates that the earliest first breach time for a waste package is approximately 20,000 years, 5,000 years later than in the nominal case. As discussed below, all breaches before 55,500 years are due to crack penetrations. The median estimate of the first breach time of the upper-bound profile is approximately 120,000 years (30,500 years for the nominal case). For the mean profile, approximately 80 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of the waste packages for the two profiles is approximately 72,000 and 202,000 years, respectively (23,000 and 56,000 years, respectively, for the nominal case).

Figure 7.4-23 shows the first patch penetration profiles of the waste packages with time. The first patch breach times of the upper and 95th percentile profiles are approximately 55,500 and 94,000 years, respectively. Comparison of the patch breach profiles with the first breach profiles (Figure 7.4-22) indicates that the initial breach (or failure) of the waste packages is generally by SCC penetration in the closure lid welds of the Alloy 22 waste package outer barrier. For the 75th percentile profile, the first patch penetration time is approximately 228,000 years. For the mean profile, approximately 70 percent of the waste packages have patch failures by the end of the simulation time (1 million years).

Integrated Model II Simulation-The integrated model II waste package degradation simulation using the temperature-dependent Alloy 22 general corrosion model II (excluding the outlier) with thermal-hydrologic history sampling consists of a combination of the individual one-off studies documented in the preceding sections. These include:

- The temperature-dependent Alloy 22 general corrosion model II (excluding the outlier) with thermal-hydrologic history sampling
- The fraction of weld flaws capable of propagation given by a ± 3 standard deviation truncated lognormal distribution (mean = 0.01, +3 standard deviations = 0.5, -3 standard deviations = 0.0002) (Section 7.4.2)
- The stress threshold for the initiation of SCC given by a uniform distribution between 80 and 90 percent of the Alloy 22 yield strength (Section 7.4.2)
- The uncertainty bounds of residual stress for the Alloy 22 waste package outer closure lid welds (induction annealed) set to ± 21.4 percent of the yield strength (Section 7.3.3.3.1)

- The residual stress uncertainty bounds of the Alloy 22 waste package inner closure lid welds (laser peened) sampled from a cumulative distribution function (Section 7.3.3.3.1, Table 7.3.3-2).

The results of using these simulation parameters are shown in Figures 7.4-24 and 7.4-25.

Figure 7.4-24 shows the upper-bound, lower-bound, mean, 95th, 75th, 25th, and 5th percentile confidence intervals of the first breach profile for the waste packages with time. The upper-bound profile indicates that the earliest first breach time for a waste package is approximately 120,000 years, later than the 15,000 years for the previous nominal case. As discussed below, almost all breaches are due to patch penetrations. The median estimate of the first breach time of the upper-bound profile is approximately 318,000 years (30,500 years for the previous nominal case). For the mean profile, approximately 63 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of the waste packages for the upper-bound profile is approximately 210,000 years (23,000 years for the previous nominal case). The time to fail 10 percent of the waste packages for the median profile is approximately 422,000 years (23,000 years for the previous nominal case).

Figure 7.4-25 shows the first crack penetration profiles of the waste packages with time. Due to the low fraction of manufacturing defects capable of propagating and the high stress threshold for initiation of crack growth, little cracking is observed. The first crack breach time of the upper-bound and 95th percentile profiles is approximately 120,000 and 260,000 years, respectively. Comparison of the first crack breach profiles with the first breach profiles (Figure 7.4-24) indicates that the initial breach (or failure) of the waste packages is generally by patch penetration. For the mean profile, approximately 8 percent of the waste packages have crack failures by the end of the simulation time (1 million years).

The temperature-dependent Alloy 22 general corrosion model I (including the outlier) results in earlier first waste package failure times than the model II obtained by excluding the outlier however, fewer realizations have waste package failures and those that do have fewer failed waste packages. For the mean waste package failure curves for the two models, the temperature-dependent Alloy 22 general corrosion model II (excluding the outlier) results in 63 percent of the waste packages failed by the end of the simulation time (1 million years) while the temperature-dependent Alloy 22 general corrosion model I (including the outlier) results in only 2.5 percent of the waste packages (see Section 7.4.3.1) failed by the end of the simulation time.

7.4.4 Recommended Nominal Case for Volume 2

The recommended model for use in Supplemental Science and Performance Analysis Volume 2 (i.e., the model recommended to be used in the Total System Performance Assessment Model to analyze total system performance; McNeish 2001 [DIRS 155023]) is integrated model II using the temperature-dependent Alloy 22 general corrosion model II (excluding the outlier) with thermal-hydrologic history sampling. Analysis and discussion in Section 7.3.5.3 clearly indicate that there is an outlier in the Alloy 22 data set on which both models are based. The effect of including the outlier in the model development process increases the activation energy from 36 to 66 kJ/mol or approximately 83 percent. The use of the larger slope results in higher than

expected general corrosion rates (up to 7 $\mu\text{m}/\text{yr}$) at higher temperatures and lower than expected general corrosion rates at low temperatures (on the order of 3 nm/yr). This results from the effect of the outlier on the slope determined. The use of the lower slope produces more reasonable general corrosion rates (up to 1.2 $\mu\text{m}/\text{yr}$ at higher temperatures and about 30 nm/yr at lower temperatures). The work of Smailos et al. (1990 [DIRS 154820], Table 5) shows that the corrosion rate of Alloy C-4 (a less corrosion resistant alloy than Alloy 22) in highly concentrated Q-Brine solutions (Smailos et al. 1990 [DIRS 154820], Table 2) for the composition of Q-Brine is less than 1 $\mu\text{m}/\text{yr}$ at 150°C. For these reasons, the temperature-dependent Alloy 22 general corrosion model II (excluding the outlier) is more realistic and better suited to distinguishing between different thermal operating modes.

7.5 SUMMARY AND PARAMETERS PROVIDED TO TOTAL SYSTEM PERFORMANCE ASSESSMENT

The analyses conducted to quantify conservatism and uncertainties in the waste package degradation models and parameters were discussed in the previous sections. Also included in these discussions were data and information obtained subsequent to the development of analysis model reports for the various degradation mechanisms. Results of the integration of these models into the WAPDEG analyses were included in these discussions as well.

Previous analyses of the possible environments on the surfaces of the waste package and drip shield focused on carbonate-base dilute waters. These waters, when concentrated by evaporation, result in high pH brines. More recent analyses have included non-carbonate base dilute waters. These are similar to the pore waters in the host rock and, when evaporatively concentrated, evolve into near-neutral pH brines with dissolved calcium and magnesium ions. The presence of these cations in aqueous solution could result in the formation of limited amounts of calcium and magnesium chloride salt solutions that are stable at low relative humidities. However, because the available amounts of calcium and magnesium ions in the solution would decrease significantly during evaporation by the formation of insoluble precipitates, large quantities of seepage water would be necessary to provide concentrations sufficient to result in aggressive environments. However, the formation of an aqueous film containing these salts will also result in the dissolution of other soluble anions, such as nitrates and sulfates, thereby producing a more benign buffered solution. This will continue as the relative humidity increases in the repository. Nitrate ions can mitigate against the aggressiveness of chloride ions to Alloy 22 corrosion even in nearly saturated calcium chloride solutions at 120°C (Pasupathi 2001 [DIRS 155252]). Therefore, the potential for the development of environments leading to localized corrosion of Alloy 22 is unlikely. Because of low deliquescence points of these salts, general corrosion of waste package and drip shield could initiate much earlier while the temperatures at the surfaces are still sufficiently high.

A sensitivity analysis for potential effects of increased general corrosion rates of the waste package outer barrier due to the possible presence of magnesium and calcium chloride salts has shown that the effect is insignificant. This insensitivity of waste package degradation to the more aggressive corrosion initiation threshold is due mostly to the fact that the time period, during which the waste package temperature is above the boiling temperature of NaNO_3 salt (120.6°C, see Table 7.3.1-2b) and the waste packages are subject to higher general corrosion rates, is much shorter than the waste package lifetime.

New analyses to evaluate potential environments also included assessments of the presence of potentially deleterious minor constituents, such as lead. The measured concentrations of lead in the waters at Yucca Mountain are very low. In addition, a review of data in the literature shows that sorption of lead to the surface of minerals such as smectite and calcite will limit the amount of lead in solution. Evaporative concentration of Yucca Mountain waters has shown that lead is likely removed from the solution as lead-containing mineral precipitates, and, therefore, the amount of lead available in solution is expected to be insignificant.

Aging and phase stability of Alloy 22 was reevaluated using new data and analyses. These analyses confirm the prior conclusion that aging of the Alloy 22 waste package outer barrier will not pose a problem. Since this conclusion is based on limited data, alternative lines of evidence were evaluated, including mechanical property changes due to aging, natural analogues, and theoretical modeling. All of these corroborate the conclusion that for the estimated peak waste package temperatures of 200°C or lower, aging effects such as long-range ordering or grain boundary and bulk precipitation of secondary phases will not affect waste package performance.

In the case of stress corrosion cracking of the Alloy 22 barrier, new analyses were conducted to quantify the uncertain parameters and remove some of the conservatism in the previous analyses for the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]). Models of the residual stress uncertainty, the threshold stress for stress corrosion cracking initiation, and the orientation of manufacturing flaws were revised based on new data, literature reviews, and analyses. In addition, the analyses included an evaluation of the effects of temperature on stress corrosion cracking, which showed that there is currently no basis for establishing a temperature threshold for stress corrosion cracking. Some of the new data evaluated included SCC test data on Alloy 22 in solutions containing lead. The data show that under very aggressive (unrealistic) conditions (pH of 0.53, 250°C, and 1,300 ppm lead), Alloy 22 may fail because of stress corrosion cracking. However, tests under acidic conditions with the anions that are present in the Yucca Mountain groundwater (1 wt percent lead in mixed-ion solutions at a pH of 2.7 and 76°C) show no stress corrosion cracking failures. Overall, the technical bases for the stress corrosion cracking model were improved significantly with the new data and analyses.

In the corrosion models used to predict the long-term corrosion behavior of Alloy 22 in the TSPA-SR (CRWMS M&O 2000 [DIRS 153246]), data from relatively short-term tests (two years of exposure) were used. Extrapolation of two-year data to predict performance over thousands of years was based on the assumption that the passive film on the surface would remain stable over a long period. To reduce the uncertainties associated with this assumption, a comprehensive testing and analysis program has been initiated. A mechanistic conceptual model for predicting the behavior of the passive film has been developed, and this conceptual model, along with associated model parameters, is being implemented into the passive film stability model. Preliminary calculations have been performed using values for model parameters that are based on stainless steels in nuclear power plant piping. A testing program is underway to provide data relevant to Alloy 22 for the conditions expected in the potential repository. When completed, the passive film stability model will be incorporated into the integrated WAPDEG model to analyze the effects of long-term passive film stability on waste package performance. The DOE's current position is that the passive film on Alloy 22 would remain stable under the exposure conditions expected in the potential repository. Data from ongoing testing programs

and detailed mechanistic modeling will provide useful information to determine the long-term stability of the passive film under repository-relevant exposure conditions.

Previous analyses of Alloy 22 general corrosion were based on data from weight-loss measurements on samples exposed for approximately two years. Because of the low corrosion rates in the material, the data showed significant uncertainties that are due mostly to measurement uncertainty (see Section 7.3.5.2). As a result, the data showed no discernible effects of temperature, environment, or exposure times on corrosion rates. New analyses based on new electrochemical data have been conducted to evaluate the effects of temperature. While the correlation developed is based on limited data over a small temperature range, the model provides a basis for evaluating waste package performance over ranges of time and location in the potential repository.

Potential early failures of waste packages by improper heat treatment are included in the waste package and TSPA analysis. Although the probability of the occurrence is very low, the consequence of improper heat treatment could lead to a gross failure of affected waste packages. The analysis results show that the probability of having at least one waste package improperly heat-treated is 20.2 percent, and the probability of having two waste packages affected is 2.6 percent. The probability of having three waste packages with improper heat treatment is about 0.2 percent. Assuming a total of 100 realizations for the waste package degradation analysis using the WAPDEG model, those probabilities provide that 77 out of 100 realizations would have no waste packages affected by improper heat treatment. Out of 100 realizations, 20 realizations would have at least one waste package affected and 3 realizations would have two waste packages affected.

Based on the additional analyses documented in this report, the following corrosion models and/or parameters are recommended for the waste package degradation analysis:

- Temperature-dependent Alloy 22 general corrosion model II (excluding one outlier from the passive current density data) with the total variance of the general corrosion rates from the weight-loss measurements due to uncertainty and the thermal-hydrologic histories sampled (see Section 7.3.5.3.2)
- The fraction of weld flaws capable of propagation in the radial direction given by a ± 3 standard deviation truncated lognormal distribution with a mean of 0.01 and bounded between 0.5 (+3 standard deviations) and 0.0002 (-3 standard deviations) (see Section 7.3.3.3.4)
- The stress threshold for the initiation of stress corrosion cracking given by a uniform distribution between 80 and 90 percent of the Alloy 22 yield strength (see Section 7.3.3.3.3)

- The uncertainty bounds of residual stress of the Alloy 22 waste package outer closure lid welds (induction annealed) set to ± 21.4 percent of the yield strength (see Section 7.3.3.3.1)
- The uncertainty bounds of residual stress of the Alloy 22 waste package inner closure lid welds (laser peened) sampled from a cumulative distribution function (see Section 7.3.3.3.2 and Table 7.3.3-2).

Because early waste package failure caused by improper heat treatment is a low probability event, it is modeled directly in the TSPA presented in Volume 2 (McNeish 2001 [DIRS 155023]) and not included in the waste package degradation analysis result summary that is discussed below. The new analyses, data, and models were incorporated into the integrated WAPDEG V4.0 model. The upper-bound profile, which is the upper extreme (very low probability) of the probable range of the first breach time, indicates that, not considering early waste package failures, the earliest first breach time for a waste package is approximately 120,000 years (Figure 7.4-24), much later than the 15,000 years for the previous baseline model (Figure 7.4-1) and the 10,000 years of the TSPA-SR base case (CRWMS M&O 2000 [DIRS 151566], Figure 18). Almost all breaches are due to patch penetrations by general corrosion. The median estimate (50 percent of waste packages failed) of the first breach time of the upper-bound profile is approximately 318,000 years (Figure 7.4-24), compared to 35,000 years for the previous baseline model (Figure 7.4-1). For the mean profile, approximately 63 percent of the waste packages failed by the end of the simulation time (1 million years). The time to fail 10 percent of waste packages for the upper-bound profile is approximately 250,000 years, compared to 23,000 years for the previous baseline model. These failure times are significantly longer than the TSPA-SR results (CRWMS M&O 2000 [DIRS 153246]).

Overall, new data and analyses have been developed to quantify the uncertainties in the waste package degradation models, and these have improved the technical bases for the assessment of waste package performance. The analysis results with the new baseline waste package degradation model having incorporated the quantified uncertainties of the key degradation models demonstrate that the waste package performance analysis results in the TSPA-SR base case (Figure 7.4-1 of this volume) are conservative and provide sufficient margins in the predictions of waste package performance.

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Table 7.3.1-1. Compositions of Brines from Saline Lakes in Western North America

Species	Concentration (milligram/kilogram)				
	Alkali Valley, Oregon	Carson Sink, Nevada	Mono Lake, California	Searles Lake, California	Bristol Dry Lake, California
SiO ₂	542	19	14	–	–
Ca	–	261	4.5	16	43,296
Mg	–	139	34	–	1,061
Na	117,000	56,800	21,500	110,000	57,365
K	8,850	3,240	1,170	26,000	33,294
HCO ₃	2,510	322	5,410	–	–
CO ₃	9,1400	–	10,300	27100	–
SO ₄	46,300	786	7,380	46,000	223
Cl	45,700	88,900	13,500	121,000	172,933
Total	314,000	152,000	56,600	336,000	279,150
pH	10.1	7.8	9.6	Not reported	Not reported

Source: Eugster and Hardie 1978 [DIRS 100743].

Table 7.3.1-2. Compositions of Yucca Mountain Waters

Species	Concentration (mg/L)		
	Well J-13 water	PERM-2	PERM-3
	(carbonate base water)	(non-carbonate base water)	(non-carbonate base water)
K	5.04	7	9
Na	45.8	61	62
Ca	13.0	106	97
Mg	2.01	16.6	17.4
SiO ₂	61.0	66	75
HCO ₃	128.9	Not reported	Not reported
Cl	7.14	110	123
F	2.18	Not reported	Not reported
SO ₄	18.4	111	120
NO ₃	8.78	3	10

Source: CRWMS M&O 2000 [DIRS 151568], Tables 14 and 15.

Table 7.3.1-2b. Deliquescence Point Data of Pure Salts of MgCl₂, NaCl, and NaNO₃

Temperature (°C)	Deliquescence Point (percent)		
	MgCl ₂	NaCl	NaNO ₃
0	33.66	75.51	--
5	33.60	75.65	78.57
10	33.47	75.67	77.53
15	33.30	75.61	76.46
20	33.07	75.47	75.36
25	32.78	75.29	74.25
30	32.44	75.09	73.14
35	32.05	74.87	72.06
40	31.60	74.68	71.00
45	31.10	74.52	69.99
50	30.54	74.43	69.04
55	29.93	74.41	68.15
60	29.26	74.50	67.35
65	28.54	74.71	66.64
70	27.77	75.06	66.04
75	26.94	75.58	65.56
80	26.05	76.29	65.22
85	25.11	--	65.03
90	24.12	--	65.00
95	23.07	--	--
100	21.97	--	--
108.67	--	--	--
120.6	--	73.90	50.10
164.27	14.80 ^a	--	--

Source: Greenspan 1977 [DIRS 104945], Table 2.

NOTE: ^a Data for CaCl₂ salt.

Table 7.3.1-3. National Atmospheric Deposition Program/National Trends Network Deposition Data for Site NV00, Red Rock Canyon, Clark County, Nevada

Deposition Rate (kilogram/hectare)								
Year	Ca	Mg	K	Na	NH ₄	NO ₃	Cl	SO ₄
1985	1.00	0.142	0.054	0.215	0.29	1.97	0.34	1.26
1986	0.53	0.083	0.025	0.148	0.29	1.84	0.21	1.10
1987	0.74	0.101	0.036	0.194	0.45	2.70	0.30	1.37
1988	0.80	0.119	0.092	0.203	0.23	1.77	0.26	1.08
1989	0.31	0.043	0.013	0.076	0.23	0.70	0.06	0.38
1990	1.75	0.251	0.040	0.170	0.90	2.69	0.31	1.39
1991	1.84	0.254	0.047	0.271	0.47	3.07	0.39	1.76
1992	0.91	0.108	0.036	0.241	0.61	3.23	0.35	2.20
1993	1.02	0.143	0.063	0.262	0.57	3.39	0.36	1.73
1994	1.25	0.147	0.026	0.102	0.36	1.57	0.15	0.77
1995	0.88	0.122	0.045	0.213	0.56	3.26	0.28	1.67
1996	1.45	0.122	0.047	0.148	0.21	1.57	0.16	0.65
1997	0.87	0.070	0.038	0.101	0.42	1.80	0.16	1.05
1998	1.47	0.198	0.055	0.206	0.74	4.41	0.36	1.97
1999	0.75	0.088	0.014	0.088	0.55	2.39	0.18	1.06

Source: NADP/NTN 2001 [DIRS 154843].

Table 7.3.2-1. Preliminary Measurements of Time to Give Precipitate Volume Fractions of 0.05 and 0.10 in Aged Alloy 22 Welds

Temperature (°C)	Time to Give 5% Precipitates (Hours)	Time to Give 10% Precipitates (Hours)
760	5.7	15
704	32	87
649	105	469
593	210	1065

Source: Summers 2001 [DIRS 155018].

Table 7.3.3-1. Descriptive Statistics of Surface Residual Stress Data of Shot-Peened Samples

Estimator	Unweighted	Weighted
Mean (\bar{x}) (MPa)	-902.3	-899.2
Standard error (MPa)	10.8	10.9
Median (MPa)	-896	-
Mode (MPa)	-891	-
Standard deviation (s) (MPa)	44.3	44.8
Sample variance (s^2)	1965.2	2006.7
Fractional uncertainty	0.049	0.050
Kurtosis	0.5	-
Skewness	0.3	-
Range (MPa)	179	-
Minimum (MPa)	-987	-
Maximum (MPa)	-808	-
Count (n)	17	-

Source: Bullard 2001 [DIRS 155035].

Table 7.3.3-2. Cumulative Density Function Values of Fractional Uncertainty

Probability	Fractional Uncertainty
0.50	0.051
0.90	0.065
0.95	0.071
0.99	0.083
0.999	0.100

Source: Bullard 2001 [DIRS 155035].

Table 7.3.3-3. Slow Strain Rate Test Results for Alloy 22

Specimen ID	Test Environment	Applied Potential (mV vs. Ag/AgCl)	Crevice	Temperature (°C)	Summary Results
ARC22-12	Air	N/A	N/A	Room Temp.	Full ductility (58% strain to failure nominal)
ARC22-123	4M NaCl	350	None	98	Full ductility (55% strain to failure nominal)
ARC22-117	4M NaCl	400	Halar	98	SCC at gage (6% strain to failure)
ARC22-120	BSW pH 13	400	None	105	Full ductility (52% strain to failure nominal)
ARC22-119	BSW pH13	400	Halar	105	Full ductility (61% strain to failure nominal)
ARC22-115	BSW pH 13, no NO ₃	400	Halar	105	Full ductility (56% strain to failure nominal)
ARC22-129	BSW pH 13, no SO ₄	400	Halar	105	Full ductility (60% strain to failure nominal)
ARC22-128	BSW pH 13, no NO ₃ or SO ₄	400	Halar	98	Severe crevice corrosion at gage 4% strain to failure
ARC22-126	BSW pH 13, no NO ₃ or SO ₄	300	Halar	98	Crevice corrosion at gage 22% strain to failure
ARC22-122	BSW pH 13, no NO ₃ or SO ₄	200	Halar	98	Full ductility (60% strain to failure nominal)
ARC22-124	BSW pH 13, no NO ₃ or SO ₄	100	Halar	98	Full ductility (60% strain to failure nominal)
ARC22-127	BSW pH 13, no NO ₃ or SO ₄	Open Circuit	Halar	98	Full ductility (60% strain to failure nominal)
ARC22-125	SSW pH 6.25	400	Halar	100	Full ductility (53% strain to failure nominal)
ARC22-112	SCW	400	Halar	76	Some impact on ductility (41% strain to failure)
ARC22-113	SCW	317	Halar	76	Full ductility (53% strain to failure nominal)
ARC22-15	SAW	Open circuit	Halar	76	Full ductility (60% strain to failure nominal)
ARC22-13	1% PbCl ₂ , pH 4, aerated water	Open circuit	N/A	95 to 76	Full ductility (57% strain to failure nominal)
ARC22-16	Pb in SAW pH 3	Open circuit	Halar	76	Full ductility (60% strain to failure nominal)
ARC22-17	Pb in SAW pH 3	Open circuit	Halar	76	Full ductility (60% strain to failure nominal)
ARC22-18	Pb in SAW pH 3	Open circuit	Halar	76	Full ductility (60% strain to failure nominal)

Source: Pasupathi 2001 [DIRS 154935].

NOTE: BSW = basic saturated water; SSW = simulated saturated water; SCW = simulated concentrated water; SAW = simulated acidified water; N/A = not applicable. Specimens were tested at a strain rate of 1.66×10^{-6} per second, which is a reasonably conservative strain rate. Halar is a polymeric coating material used to create crevice on the specimens.

Table 7.3.5-1. Passive Current Density Data from Potentiostatic Polarization Experiments for Alloy 22

Material	pH	Electrolyte	Temperature	Passive Current Density (A/cm ²)		
				Median	Average	Std. Dev.
C22	2.75	10:1	95	1.6518E-07	1.4792E-07	5.6918E-08
			85	1.2847E-07	1.3076E-07	2.0348E-08
			80	6.1482E-08	8.6809E-08	7.0242E-08
	2.75	100:1	95	1.4224E-07	8.1326E-07	1.8234E-06
			85	1.0094E-07	1.2480E-07	5.8973E-08
			80	7.1118E-08	7.3412E-08	1.2407E-08
	7.75	10:1	95	1.7435E-07	1.6255E-07	3.4218E-08
			85	1.0507E-07	9.6353E-08	5.6074E-08
			80	1.3765E-07	1.3508E-07	5.1741E-08
	7.75	100:1	95	1.8353E-07	2.0494E-07	8.0975E-08
			85	1.4224E-07	1.4224E-07	1.7168E-08
			80	1.2847E-07	1.2939E-07	3.4114E-08

Source: Lee 2001 [DIRS 154891].

NOTE: The entry in bold is identified as an outlier. Testing was conducted with crevice specimens in non-deaerated solutions.

Table 7.3.5-2. Calculations for the Temperature Dependence Term for the Alloy 22 General Corrosion Rate Model

Temp (°C)	Passive Current Density (A/cm ²)	1/Temp (K ⁻¹)	Ln(Rate)		Cross-Product Deviations	Squared Deviations
95	1.4792E-07	0.002716284	-15.72656244		-5.03878E-07	4.06261E-09
85	1.3076E-07	0.002792126	-15.84986627		-1.39672E-06	1.46493E-10
80	8.6809E-08	0.002831658	-16.25955079		-2.71128E-05	2.66619E-09
95	8.1326E-07	0.002716284	-14.02220919		-0.000109137	4.06261E-09
85	1.2480E-07	0.002792126	-15.89655338		-1.96179E-06	1.46493E-10
80	7.3412E-08	0.002831658	-16.42718163		-3.57684E-05	2.66619E-09
95	1.6255E-07	0.002716284	-15.63225176		-6.51511E-06	4.06261E-09
85	9.6353E-08	0.002792126	-16.15524792		-5.09289E-06	1.46493E-10
80	1.3508E-07	0.002831658	-15.81741606		-4.28305E-06	2.66619E-09
95	2.0494E-07	0.002716284	-15.40054284		-2.12839E-05	4.06261E-09
85	1.4224E-07	0.002792126	-15.76578315		-3.79024E-07	1.46493E-10
80	1.2939E-07	0.002831658	-15.86044838		-6.50503E-06	2.66619E-09
	Averages	0.002780023	-15.73446782	Sum	-0.00021994	2.75012E-08
					Ratio	7,997

Source: Bullard 2001 [DIRS 155034].

Table 7.3.5-3. Passive Current Density Data from Potentiostatic Polarization Experiments and Calculated Passive Dissolution Rate for Alloy 22

Material	E_{cont} (mV vs. Ag/AgCl)	Electrolyte	pH	Temperature	Passive Current Density (A/cm^2)	Passive Dissolution Rate (mm/yr)
Alloy 22	350	1 M NaCl	1.0	25	1.29E-08	1.238 E-04
Alloy 22	350	1 M NaCl	1.0	45	2.24E-08	2.147 E-04
Alloy 22	350	1 M NaCl	1.0	65	5.45E-08	5.232 E-04
Alloy 22	350	1 M NaCl	1.0	75	7.23E-08	6.944 E-04
Alloy 22	350	1 M NaCl	1.0	85	1.10E-07	1.052E-04

Source: Lee 2001 [DIRS 154871].

NOTE: E_{cont} is the controlled applied potential to polarize the specimens. Testing was conducted with cylindrically shaped specimens.

Table 7.3.6-1. Poisson Probabilities for Improper Heat Treatment of Waste Packages

Number of Packages	Probability	Cumulative Probability
0	0.76896	0.76896
1	0.20202	0.97098
2	0.02654	0.99752
3	2.32392E-3	0.99984
4	1.52634E-4	0.99999
5	8.01996E-6	1.00000

Source: Bullard 2001 [DIRS 155036].

Table 7.3.7-1 Critical Crevice Temperatures for Alloy 22

Test Environment	Concentration	pH	Estimated	Estimated	Estimated Critical Crevice Temperature (°C)	Reference
			E_{rp}	E_{corr}		
			mV vs. SHE	mV vs. SHE		
NaCl Solution	0.5M Cl ⁻	2.5 or 8	620		95	Dunn et al. 1999 [DIRS 154481]
NaCl Solution	1.0M Cl ⁻	2.5 or 8	550		85	Dunn et al. 1999 [DIRS 154481]
NaCl Solution	4.0M Cl ⁻	2.5 or 8	300		85	Dunn et al. 1999 [DIRS 154481]
NaCl Solution	4.0M Cl ⁻	~7	<350	-40	<100	Dunn et al. 1999 [DIRS 154481]
LTCTF Acidified 1000-fold well J-13 water (SAW)	0.8M Cl ⁻	2.7	780	~40	>90 ^a	CRWMS M&O 2000 [DIRS 144229], Table 3
50,000-fold well J-13 water	~3 M Cl ⁻	13	~600	-40	>100	CRWMS M&O 2000 [DIRS 144229], Table 24
50,000-fold well J-13 water without sulfate and nitrite ions	~3 M Cl ⁻	13	<600	-40	<98	Table 7.3.3-3 of this volume
SCW, SAW, SDW exposed in LTCTF		2.7 to 8			>90	CRWMS M&O 2000 [DIRS 144229], Table 3
Cyclic Polarization results in full range of potential environments				~-40	>120	CRWMS M&O 2000 [DIRS 144229], Section 6.4.3
4% NaCl/0.1%Fe ₂ (SO ₄) ₃ /0.01M HCl	as shown	2		~600	102	Haynes International 1997 [DIRS 100896]
6% FeCl ₃ + 1% HCl	as shown	<1.2 ^b		>800	58	Agarwal and Herda 1997 [DIRS 107676], Table 5

Source: ^b ASM = ASM International 1987 [DIRS 133378], p. 304.

NOTES: E_{rp} = repassivation potential; E_{corr} = corrosion potential; LTCTF = Long-Term Corrosion Test Facility at Lawrence Livermore National Laboratory; SAW = simulated acidic water; SCW = simulated concentrated water; SDW = simulated dilute water.

^a Maximum aqueous crevice corrosion rate less than 0.07 µm/yr after two years.