APPENDIX R

CONTINUED TESTING IN LONG TERM CORROSION TEST FACILITY (RESPONSE TO CLST 1.04)

Note Regarding the Status of Supporting Technical Information

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design bases at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

APPENDIX R

CONTINUED TESTING IN LONG TERM CORROSION TEST FACILITY (RESPONSE TO CLST 1.04)

This appendix provides a response to Key Technical Issue (KTI) Container Life and Source Term (CLST) 1.04. This KTI agreement relates to providing documentation on the path forward for the testing of Alloy 22 (UNS N06022) and titanium in the Long Term Corrosion Test Facility (LTCTF) at Lawrence Livermore National Laboratory.

R.1 KEY TECHNICAL ISSUE AGREEMENT

R.1.1 CLST 1.04

Agreement CLST 1.04 was reached during the U.S. Nuclear Regulatory Commission (NRC)/U.S. Department of Energy (DOE) Technical Exchange and Management Meeting on CLST held September 12 through 13, 2000, in Las Vegas, Nevada. Subissues 1, 2, 3, 4, and 6 were discussed at the meeting (Schlueter 2000).

Wording of the agreement is as follows:

CLST 1.04[1]

> Provide the documentation for Alloy 22 and titanium for the path forward items listed on slide 14. DOE will provide the documentation in a revision to AMR "ANL-EBS-MD-000003 and ANL-EBS-MD-000004" by LA.

There has been no submittal to the NRC related to this KTI agreement.

R.1.2 Related Key Technical Issue Agreements

KTI agreements related to CLST 1.04 include CLST 1.05, CLST 1.06, CLST 1.07, and CLST 1.15. These agreements support the understanding that long-term testing is necessary to determine the corrosion rate of Alloy 22 and other engineering alloys in environments that would span a series of predicted possible near-field environments at the repository site.

R.2 RELEVANCE TO REPOSITORY PERFORMANCE

The prediction of the lifetime of the containers in Yucca Mountain is based on the corrosion rate data gathered through immersion tests. Specimens of Alloy 22 and other engineering alloys have been in testing at the LTCTF since 1997. Specimens have been removed at intervals of 6 months, 1 year, 2 years, and 5 years. General corrosion rate data from these samples have been used to generate corrosion models for use in total system performance assessment (TSPA) of the

[1] Slide 14 reads, "Continue testing in the Long-Term Corrosion Test Facility (LTCTF); add new bounding water test environments to LTCTF (SSW and BSW); install thinner coupons in LTCTF with larger surface area to volume ratios e.g., 10 cm × 10 cm (presently use 5 cm × 2.5 cm) and thereby decrease measurement error; install high-sensitivity probes of Alloy 22 in some of the LTCTF vessels permits on-line measurements and monitoring of changes in corrosion rates; materials testing continues during performance confirmation."

repository. At this time, only one set of specimens remains to be removed in 2007, after 10 years of immersion. It is necessary to replenish the vessels with new specimens and electrolyte solutions that describe a broader range of expected environments and for longer exposure times to confirm corrosion rate models used in TSPA.

R.3 RESPONSE

The lifetime performance of the waste package has been documented in two analysis model reports. The data and degradation models for Alloy 22 are documented in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003a), and the data and models for Titanium Grade 7 (UNS R52400) and Titanium Grade 16 (UNS R52402) are documented in *General Corrosion and Localized Corrosion of the Drip Shield* (BSC 2003b). These two documents describe the passive behavior of the nickel and titanium alloys for the lifetime of the waste package based on general corrosion rates or penetration rates obtained through immersion testing of coupons in the LTCTF. The available data cover a time span of 5 years. These results are presented in this technical basis document and in the response to CLST 1.07 AIN-1 (Appendix A). The first point of CLST 1.04 is to continue testing in the LTCTF to obtain penetration rates for longer exposure times. As agreed, testing is continuing at the LTCTF. Immersion testing is being carried out in concentrated multicomponent solutions derived from well J-13 water. In addition, short-term testing using electrochemical methods in highly aggressive and bounding environments, such as calcium chloride, basic saturated water, and simulated saturated water, and other solutions has been conducted. Results of these tests will be presented in response to KTI agreements CLST 1.10 and CLST 1.11 (Appendix O).

As mentioned above, testing has been continued, and, in addition to short-term electrochemical tests, longer-term high-temperature tests have been conducted. These tests conducted on thin foil samples in autoclaves cover a temperature range of 120°C to 220°C. Environments used for the tests include near-saturated, high molar concentrations of sodium and potassium brines (chloride and nitrate) that are expected from dust deliquescence. As shown in Table R-1, the results are in agreement with the data from the LTCTF tanks after a 5-year exposure period, where the maximum corrosion rate observed was 23 nm/yr. The negative corrosion rates seen in the table signify an increase in weight due to oxide formation or scale that could not be removed during cleaning. The standard deviation shown represents the sample-to-sample variation between samples tested (three samples were tested for each condition). The measurement uncertainty is 6 nm/yr, which is generally less than the sample-to-sample variation. All of the corrosion rates measured at the elevated temperatures in the concentrated brines would result in less than 2 mm of general corrosion in 10,000 years, which is an extremely low corrosion rate. At the time the CLST 1.04 agreement was reached, high sensitivity probes were planned to be installed in the next generation of test tanks. However, after further evaluation of this approach, it was concluded that the timely development of high sensitivity probes was not viable for corrosion-resistant alloys, such as Alloy 22 and Titanium Grade 7. Instead, the sensitivities of the corrosion rate measurements and uncertainties in the measurements have been addressed and documented in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003a) and in *General Corrosion and Localized Corrosion of the Drip Shield* (BSC 2003b). These issues are also addressed in Section R.4.1 and in the responses to KTI agreements CLST 1.07 AIN-1 (Appendix A) and CLST 1.06 AIN-1 (Appendix J).

Table R-1. Alloy 22 Corrosion Rates by Weight Loss in Autoclave Testing

Solution		Corrosion Rate (nm/yr) at 120°C	Corrosion Rate (nm/yr) at 140°C	Corrosion Rate (nm/yr) at 160°C	Corrosion Rate (nm/yr) at 220°C
NO_3/Cl Ratio	Total Molality				
0.05	6.7	—	-17 ±21[b]	—	—
0.31	8.4	31 ±3[a]	-23 ±3[a]	5 ±30[a]	50 ±26[b]
0.5	9.6	—	14 ±17[b]	—	—
6.7	21.2	-2 ±32[a]	56 ±15[a]	108 ±31[a]	—

Source: DTN: LL040502512251.099.

NOTE: [a] Exposure time: 157 days.
[b] Exposure time: 130 days.
There is no significant general corrosion of Alloy 22 in saturated salt brines at temperatures between 120°C and 220°C. Maximum corrosion rate observed on samples after 5 years in the LTCTF environments is 23 nm/yr.

To carry on the testing for longer times and during the performance confirmation stage, the installation of a new series of vessels containing specimens and coupons of Alloy 22, Titanium Grade 7, and other alloys in a series of electrolyte solutions that span the possible environments in contact with the waste package during its lifetime is planned (see Section R.4). A set of the new specimens will be fabricated from foil material, which offers a high surface area–to–volume ratio and, therefore, may increase the sensitivity in penetration rate measurement.

The information in this report is responsive to agreement CLST 1.04 made between the DOE and NRC. The report contains the information that the DOE considers necessary for NRC review for closure of this agreement.

R.4 BASIS FOR THE RESPONSE

R.4.1 Corrosion Rates Measurements

Confidence has been established in the value of the general corrosion rate that can be expected for Alloy 22 under repository conditions. During 2002, the corrosion rates of Alloy 22 and Titanium Grade 16 were measured for more than 100 coupons of each alloy exposed for over 5 years in the LTCTF. The testing conditions in the LTCTF included three different electrolyte solutions (simulated acidified water, simulated dilute water, and simulated concentrated water) and two temperatures (60°C and 90°C). For each electrolyte solution, the coupons were immersed in the liquid aqueous solution and also exposed to the vapor phase (above the solution) where condensation occurred. (Simulated acidified water is approximately 1,000 times more concentrated than well J-13 water and has a pH of approximately 3. Simulated dilute water is approximately 10 times more concentrated than well J-13 water and has a pH of approximately 10. Simulated concentrated water is approximately 1,000 times more concentrated than J-13 water and also has a pH of approximately 10.) Alloy 22 and Titanium Grade 16 were tested in both the mill-annealed wrought condition and in the as-welded condition. Moreover, under each condition mentioned above, Alloy 22 was tested in creviced and noncreviced conditions. Taking into account the variables mentioned above (two temperatures, three solutions, two phases, two metallurgical states, and two types of coupons), both alloys were tested in a wide range of relevant conditions. Nevertheless, the overall corrosion rate obtained after 5 years of immersion was extremely low (well below

100 nm/yr). Results show that, in general, the corrosion rate of Alloy 22 was lower than the corrosion rate of Titanium Grade 16. The specific values of the corrosion rates for Alloy 22 in each condition and the analysis of the results (influencing variables) are fully documented in this technical basis document, in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003a), and by Wong, Fix et al. (2003) and Wong, Lian et al. (2004). The corrosion rate values for titanium alloys are documented in *General Corrosion and Localized Corrosion of the Drip Shield* (BSC 2003b) and by Wong, Estill et al. (2003).

The corrosion rate of Alloy 22 follows a logical trend for passive metals; that is, the corrosion rate decreases as the exposure time increases. This has been shown both for weight loss tests and electrochemical methods (e.g., polarization resistance). Corrosion rates measured via electrochemical methods are reported in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003a) and by Evans and Rebak (2002), Lian et al. (2003), and Rebak and Estill (2003). The data in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003a) show that the uncertainty in the measured corrosion rate continues to decrease with exposure time. For example, for Alloy 22, the maximum corrosion rates measured at 6-month, 1-year, and 2-year exposures were 730, 100, and 70 nm/yr, respectively. The mean corrosion rates for the three exposure periods were 50, 30, and 10 nm/yr, respectively. In comparison, for the samples exposed for 5 years, the maximum measured corrosion rate was 23 nm/yr, and the mean corrosion rate was 7.24 nm/yr (in the creviced samples). For the noncreviced (weight-loss) specimens, the maximum rate was 12 nm/yr, and the mean corrosion rate was 2.75 nm/yr. This reduced uncertainty is due to more sensitive measurements, better cleaning procedures, and no correction for residual deposition of silica from the solution, employed in the analysis for the 5-year exposure specimens.

R.4.2 Immersion Tests

The discussion that follows applies to Alloy 22 and other nickel alloys (e.g., Alloy C-4 (UNS N06455), Alloy 825 (UNS N08825), and Alloy 625 (UNS N06625)), as well as to Titanium Grade 7 and other titanium alloys (e.g., Titanium Grade 16, Titanium Grade 12 (UNS R53400), and Titanium Grade 24 (UNS R56405)).

The testing in the LTCTF is designed to obtain corrosion (penetration) rates by the weight loss method. Testing and calculation of corrosion rates are carried out according to guidelines given in American Society for Testing and Materials standards (ASTM G 1-90; ASTM G 31-72). In the weight (mass) loss method, coupons of the alloy under study are immersed in the corrosive medium in question for a certain period of time. Assuming uniform penetration or thinning of the coupon, the corrosion rate or penetration rate is calculated by dividing the weight loss during immersion by the exposed area and the immersion time (Equation R-1; ASTM G 1-90, Section 8) as follows:

$$CR(mm/yr) = 8.76 \times 10^4 \frac{W_i - W_f(g)}{A(cm^2) \cdot t(h) \cdot \delta(g/cm^3)} \qquad \text{(Eq. R-1)}$$

where W_i is the initial (prior to immersion) weight (mass) of the coupon, W_f is the final weight of the coupon, A is the surface area of the coupon exposed to the corroding electrolyte, t is the immersion time, and δ is the density of the studied alloy. The constant in the formula accounts for the conversion between centimeters and millimeters and between hours and years.

R.4.3 Continued Testing in the Long Term Corrosion Test Facility

The current electrolyte solutions in the continued LTCTF testing are simulated acidified water, simulated concentrated water, and simulated dilute water. The temperatures are 60°C and 90°C. Specimens include weight loss coupons, creviced coupons, and U-bend specimens. Materials include nonwelded and welded. The following alloys are currently under testing: (1) nickel-based Alloy 22, Alloy C-4, Alloy 625, Alloy G-3 (UNS N06985), and Alloy 825; and (2) Titanium Grade 7, Titanium Grade 16, and Titanium Grade 12. The evolution of solution in the vessels is being monitored yearly. In addition to the long-term testing in the test vessels, short-term electrochemical studies have been conducted and documented in response to KTI agreements CLST 1.10 and CLST 1.11 (Appendix O).

In addition, plans are to continue testing during the performance confirmation period. It is planned to install new vessels starting in fiscal year 2005, with new ranges of predicted environments including bounding environments and new types of alloys to reflect current design specifications of the waste package.

Types of specimens planned include general (weight loss), localized corrosion (multiple crevice assemblies), stress corrosion cracking, galvanically coupled samples from waste package and drip shield materials and from structural materials. A range of metallurgical conditions will also be included. In addition, thin section coupons will be included to determine weight loss with more accuracy and to decrease measurement error. These foils will be approximately 40 μm thick; in a size of 5 by 5 cm, they provide a surface area–to–volume ratio approximately 50 times higher than the currently tested 3-mm-thick coupons.

Test environments will cover the range of predicted environments, including those expected from dust deliquescence, trace elements, and those simulating the effects of occluded geometries due to deposits and biofilm.

This is a long-term testing plan that will extend throughout the performance confirmation period. Although CLST 1.04 specifies the electrolytes simulated saturated water and basic saturated water, the new testing matrix will focus on testing in electrolyte solutions expected to evolve at ranges of relative humidity and temperature in the repository.

High Sensitivity Probes–As described earlier, the Project adopted an alternate approach to using high-sensitivity probes for determining the sensitivities in corrosion rate measurements. The alternate approach involves the monitoring of E_{corr} and the polarization resistance (an indicator of corrosion rate) of selected creviced and noncreviced specimens. The evolution of E_{corr} and polarization resistance in time will be an indication of the alloy remaining active or becoming passive with a protective oxide film on the surface as time progresses. The sensitivities in the corrosion rate measurements and the effects of silica deposition are further addressed in response to CLST 1.07 AIN-1 (Appendix A) and CLST 1.06 AIN-1 (Appendix J).

R.5 REFERENCES

R.5.1 Documents Cited

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Wong, L.L.; Lian, T.; Fix, D.V.; Sutton, M.; Rebak, R.B. 2004. "Surface Analysis of Alloy 22 Coupons Exposed for Five Years to Concentrated Ground Waters," *Corrosion/2004.* Paper No. 04701. Houston, Texas: NACE International. TIC: 255873.

R.5.2 Codes, Standards, and Regulations

ASTM G 1-90 (Reapproved 1999) 1999. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.* West Conshohocken, Pennsylvania: American Society for Testing and Materials. TIC: 238771.

ASTM G 31-72 (Reapproved 1999) 1972. *Standard Practice for Laboratory Immersion Corrosion Testing of Metals.* West Conshohocken, Pennsylvania: American Society for Testing and Materials. TIC: 249897.

R.5.3 Data, Listed by Data Tracking Number

LL040502512251.099. Weight Loss Measurements and Weight Loss Corrosion Rates from Alloy 22 Foil Specimens. Submittal date: 06/11/2004.

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