APPENDIX J

WASTE PACKAGE: EFFECTS OF SILICA ON CORROSION (RESPONSE TO CLST 1.06 AIN-1)

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 J

WASTE PACKAGE: EFFECTS OF SILICA ON CORROSION (RESPONSE TO CLST 1.06 AIN-1)

This appendix provides a response to Key Technical Issue (KTI) agreement Container Life and Source Term (CLST) 1.06 additional information needed (AIN)-1. This KTI agreement relates to the effect of silica on corrosion.

J.1 KEY TECHNICAL ISSUE AGREEMENT

J.1.1 CLST 1.06 AIN-1

Agreement CLST 1.06 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 and 13, 2000. Subissues 1 (effects of corrosion processes on the lifetime of the containers), 2 (effects of phase instability and initial defects on the mechanical failure and lifetime of the containers), 3 (the rate at which radionuclides in spent nuclear fuel are released from the engineered barrier subsystem through the oxidation and dissolution of spent nuclear fuel), 4 (the rate at which radionuclides in high-level radioactive waste glass are released from the engineered barrier subsystem), and 6 (effects of alternate engineered barrier subsystem design features on container lifetime and radionuclide release from the engineered barrier subsystem) were discussed at the meeting (Schlueter 2000).

Wording of the agreement is as follows:

CLST 1.06

> Provide the documentation on testing showing corrosion rates in the absence of silica deposition. DOE will document the results of testing in the absence of silica deposits in the revision of Alloy 22 AMR (ANL-EBS-MD-000003) prior to LA.

A response to CLST 1.06 was initially provided to the NRC in a licensing letter report (Ziegler 2002a). It was followed up by a supplement to the licensing letter report (Ziegler 2002b). The NRC review of the submittals resulted in an AIN request (Schlueter 2003). Accordingly, this appendix provides a response to the AIN as requested by the NRC.

Wording of the AIN is as follows:

CLST 1.06 AIN-1

> Additional information is needed addressing the effect of silica to support the assertion about the beneficial effect or insignificance of silica deposition on the corrosion rates measured in the long-term corrosion testing facility. Presentation of the complete results from the 5 year test data in addition to the results of short term electrochemical tests over a range of solution compositions and pHs taken under appropriate testing conditions are required. DOE should also provide

sufficient rationale for the relationship between the silica deposition in LTCTF and in the repository.

J.1.2 Related Key Technical Issue Agreements

CLST 1.06 AIN-1 is related to KTI agreements CLST 1.04 (Appendix R), CLST 1.05, CLST 1.06, CLST 1.07, CLST 2.07, TSPAI 3.12 and TSPAI 3.13.

J.2 RELEVANCE TO REPOSITORY PERFORMANCE

CLST 1.06 AIN-1 addresses a condition in which silica scales formed on waste packages may not be present as a protective layer against corrosion during the life of the repository. In this case, the corrosion rates may be underestimated for longer periods of time if the protective nature of silica was included in the models. Therefore, the effects of silica on long-term waste package corrosion performance need to be understood.

J.3 RESPONSE

This appendix presents additional technical information and clarification for KTI agreement CLST 1.06. CLST 1.06 relates to the corrosion behavior influenced by silica deposition. The test solutions used in the long-term corrosion testing contain dissolved silicates. These solutions are representative of some of the waters expected in the repository. Comparison of the test solutions with the expected waters was addressed in the response to KTI agreement items CLST 1.01, TSPAI 3.12 and TSPAI 3.13.

This appendix includes the results from several recent experiments to demonstrate that silica deposition has a minimal effect on the corrosion behavior of Alloy 22. The main points of this additional technical information can be summarized as follows:

- The results of immersion testing for approximately 280 days show that, the presence of silica in solution had little impact on the corrosion potential of Alloy 22. The short-term corrosion potential data were randomly spread, but no strong influence from silica was observed. See Figures J-1 and J-2.

- Short-term corrosion rates measured by the linear polarization resistance technique indicated that the corrosion rate of Alloy 22 was not influenced by silica; it was much more strongly influenced by other environmental factors, such as pH, aeration–deaeration, and temperature. See Figures J-3 and J-4.

- Presence of silica in NaCl solutions did not affect the general corrosion rate behavior. The general corrosion rate decreased as exposure time increased. See Figures J-5 and J-6.

Note that the corrosion rates presented in this document are only intended for determining the possible effects of silicates in test solutions. The results of the effects of silicates are applicable to both short term and long-term general corrosion rates.

The information in this report is responsive to agreement CLST 1.06 made between DOE and NRC and responsive to AIN request CLST 1.06 AIN-1. This report contains the information that DOE considers necessary for NRC review for closure of this agreement.

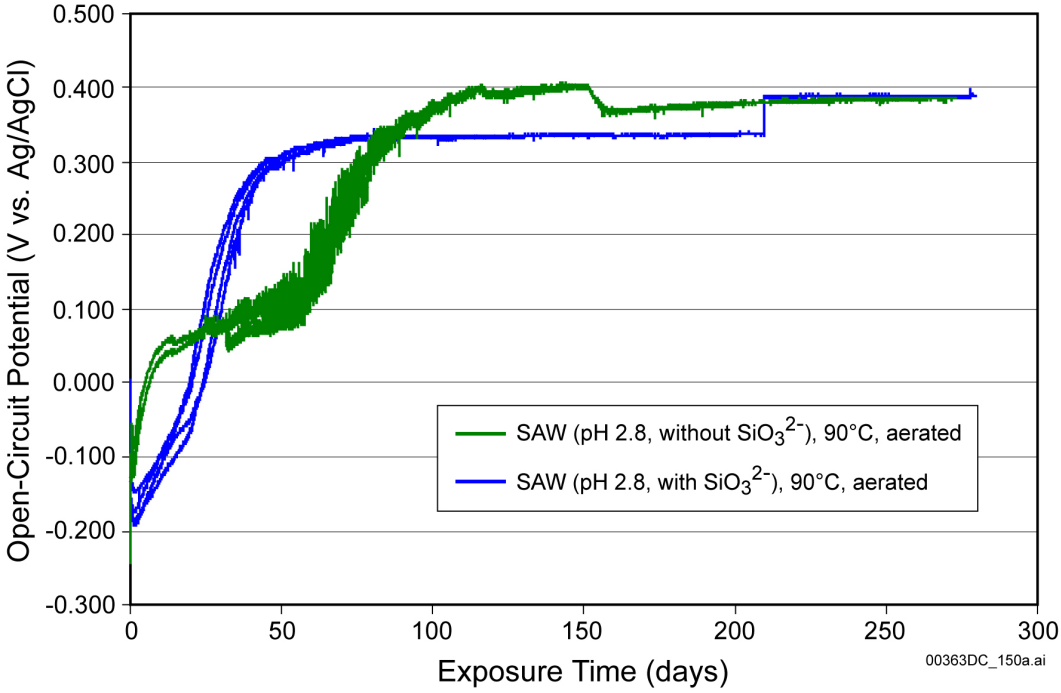
J.4 BASIS FOR THE RESPONSE

The experimental data presented in this report were obtained through electrochemical measurements in solutions with and without silicate. No measurement of silica deposition on the test specimens was made. However, the silicate content used in this study is 10 times higher than the silicate contents in the waters of the Long Term Corrosion Test Facility at Lawrence Livermore National Laboratory. This increase in silicate content, in addition to the testing at elevated water temperatures up to 95°C, enhances the probability of silica deposition on the surface of metal samples tested. This approach allows evaluating the silicate effects in short-term experiments.

J.4.1 Silica Effects on the Corrosion Potential

Figure J-1 shows the corrosion potential of Alloy 22 exposed in simulated acidified water, which is approximately 1,000 times more concentrated than well J-13 water and has a pH of approximately 3, with and without silicate. The presence of silicate in the water had no significant impact on the long-term corrosion potential. Although a difference was observed in short-term exposure up to the first 3 weeks, the corrosion potential in a SiO_3^{2-}-free simulated acidified water was higher (more noble) than that in SiO_3^{2-}-containing simulated acidified water. After 3 weeks, SiO_3^{2-}-containing simulated acidified water resulted in higher corrosion potential. The potential measurement on a platinum sample, which was placed along with the Alloy 22 sample in the same test cells, revealed that the redox potential was slightly higher in a SiO_3^{2-}-free environment at around 0.48 V (versus Ag/AgCl), compared to a redox potential of around 0.40 V (versus Ag/AgCl) in SiO_3^{2-}-containing simulated acidified water.

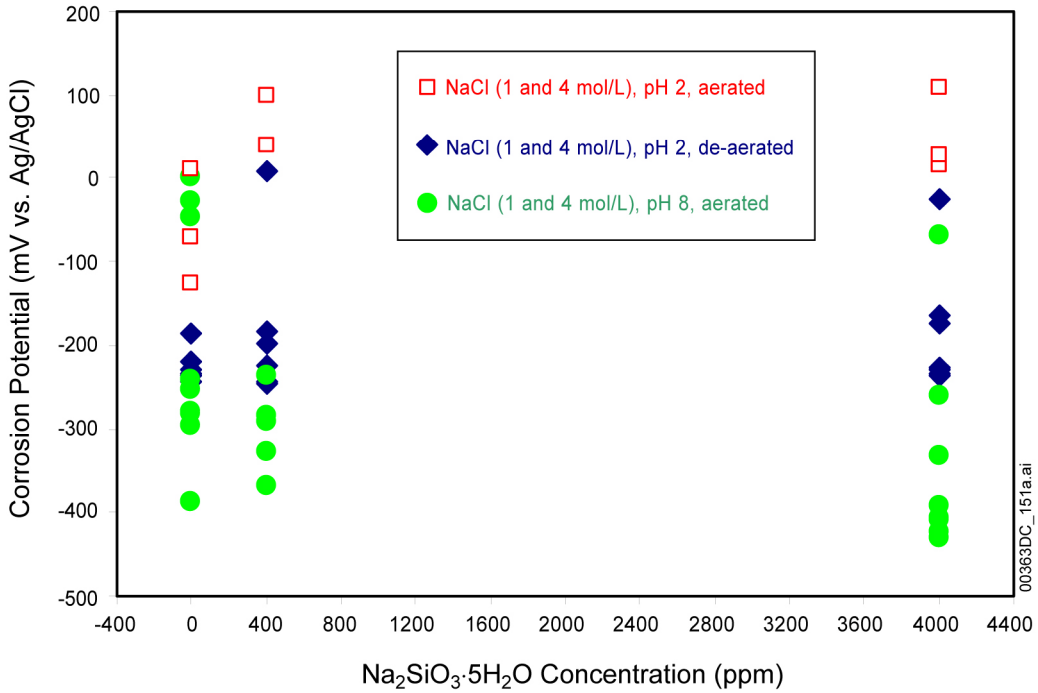
Figure J-2 shows corrosion potential measurements after 24 hours exposure at 95° C as a function of silicate additions. $Na_2SiO_3{\cdot}5H_2O$ was added into the 1 or 4 mol/L NaCl solutions for studying the silica effects. A 400 ppm $Na_2SiO_3{\cdot}5H_2O$ is equivalent to about 40 ppm silicon in the water, which is comparable to the silicate content in groundwater at the repository site. The test parameters included chloride concentrations, pH, and aeration. In general, the short-term corrosion potential of Alloy 22 in NaCl-based solutions revealed no discernable effect on silicate. Figure J-2 also shows that the corrosion potential was affected primarily by the solution pH and aeration. Under aerated conditions, a slight increase in corrosion potential with the addition of silicate was observed. Overall, the corrosion potential of Alloy 22 is not significantly affected by the presence of silicate. Other than the random spread of data observed in corrosion potential measurements, no strong dependency on silicate concentration was observed. For example, at pH 8, the corrosion potential showed wider spread, with or without the silicate. It is likely that this spread will be reduced with a longer-term exposure, as equilibrium is approached, similar to the behavior shown in Figure J-1.



Source: DTN: LL040206212251.069.

NOTE: SAW = simulated acidified water. The noise in the curves has been excluded for a better viewing of corrosion potential trending.

Figure J-1. Corrosion Potential of Alloy 22 in Simulated Acidified Water, with and without Silicate, at 90°C, Aerated



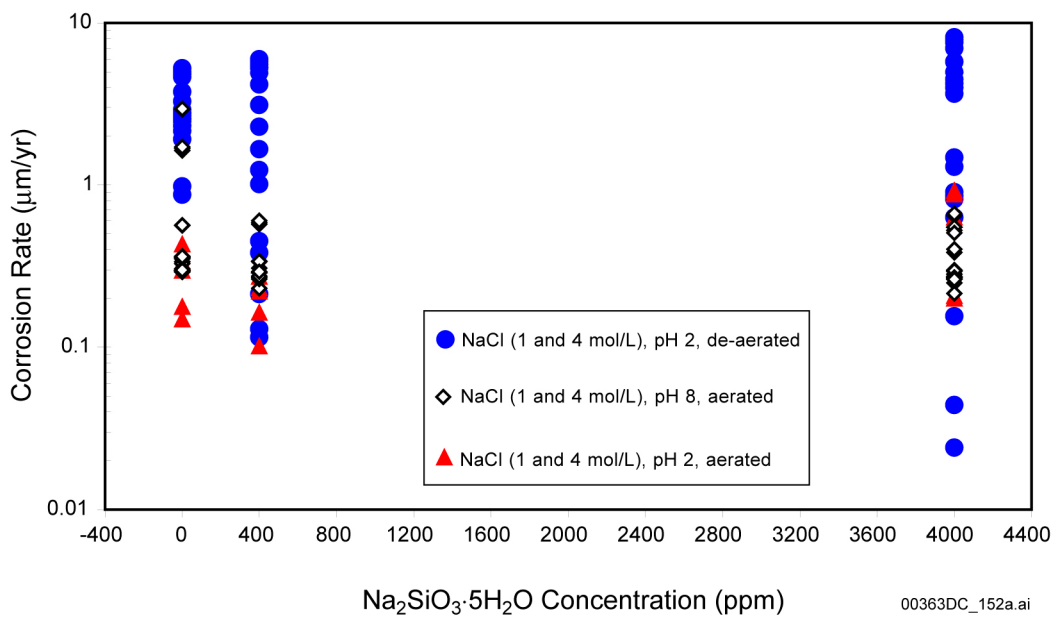
Source: DTN: LL040206312251.070.

Figure J-2. Corrosion Potential of Alloy 22 after 24 Hours in NaCl-Based Solution at 95°C

J.4.2 Silica Effects on the Corrosion Rate Measured by Polarization Techniques

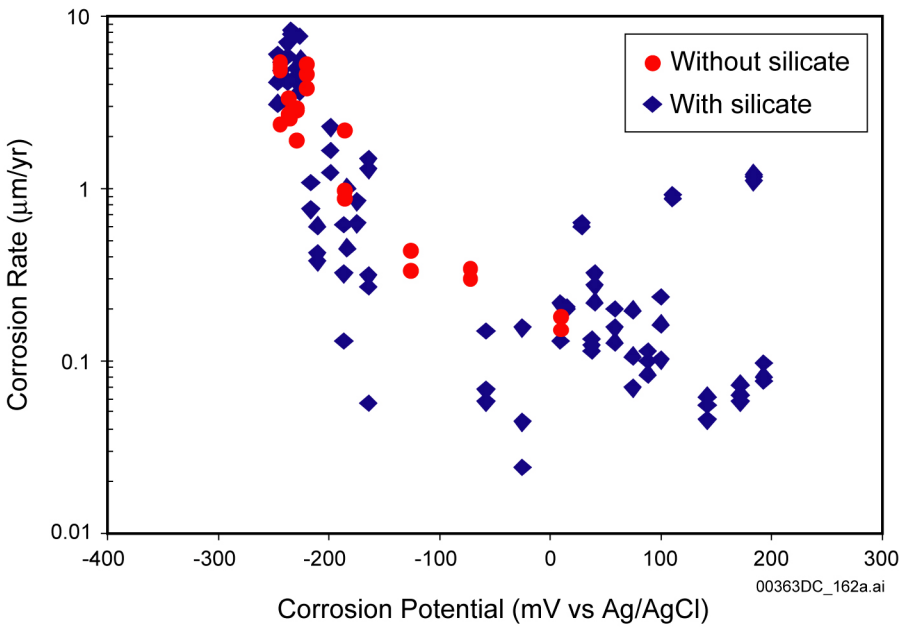
Figure J-3 shows the corrosion rate of Alloy 22 measured using the linear polarization resistance technique after 24 hours of exposure to NaCl solutions. The test parameters were the same as those for the results shown in Figure J-2. Overall, the measured corrosion rate did not reveal noticeable increase caused by the presence of silicate in the solutions. As in the case with the corrosion potential measurements, solution pH and aeration affected the measured corrosion rates more than the presence of silicate. For example, Figure J-3 shows that the corrosion rate was lowest in aerated solutions with a pH equal to 2. A slight increase was observed when pH was increased to 8. The short-term corrosion rate increased most significantly when the solution was deaerated with nitrogen gas. The corrosion rate, however, had little relation with the amount of silicate in solution. The effects of pH, solution chemistry, and applied potentials are discussed in greater detail in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003).

Figure J-4 shows a compilation of measured corrosion rates at a solution pH of 2, as a function of corrosion potential over a range of water chemistries and temperatures. All corrosion rates obtained from NaC1-only (or silicate-free) solutions were run at 95°C for baseline purposes, and corrosion rates from silicate-containing solutions were run at both 60°C and 95°C. Therefore, wider corrosion potential spread was included in Figure J-4. Nevertheless, no silicate effect on corrosion was observed.



Source: DTN: LL040206312251.070.

Figure J-3. Corrosion Rate Measured by Linear Polarization Technique after a 24-Hour Exposure in NaCl-Based Solution at 95°C



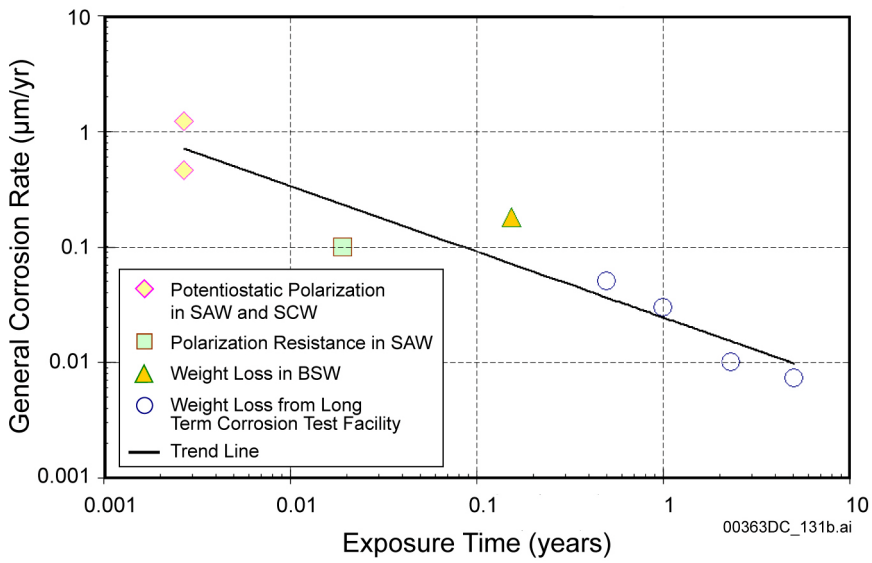
Source: DTN: LL040206312251.070.

NOTE: The compiled data include corrosion rate measured in pH 2 NaCl-based solutions with all compositions, temperatures, and with aeration and deaeration.

Figure J-4. Corrosion Rates as a Function of Corrosion Potential in pH 2 Solutions

J.4.3 Long-Term Corrosion Rate Results from the Long Term Corrosion Test Facility

Figure J-5 includes the weight loss data from the immersion tests running in the Long Term Corrosion Test Facility at the Lawrence Livermore National Laboratory. More than 100 samples have been measured over a 5-year period. Figure J-5 represents the mean values of data generated from the more than 100 samples of Alloy 22 measured at 90°C. The testing conditions in the Long Term Corrosion Test Facility 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 test coupons were immersed in the liquid aqueous solution and also exposed to the vapor phase (above the solution) where condensation occurred. Simulated acidified water and simulated concentrated water are both approximately 1,000 times more concentrated than well J-13 water and have pH values of approximately 3 and 10 respectively. Simulated diluted water is approximately 10 times more concentrated than well J-13 water and has a pH of approximately 10.



Source: BSC 2003, Figure 6-25.

NOTE: SAW = simulated acidified water; SCW = simulated concentrated water; BSW = basic saturated water; LTCTF = Long Term Corrosion Test Facility.

Figure J-5. General Corrosion Rate of Alloy 22 in Multi-ionic Solutions at 90°C

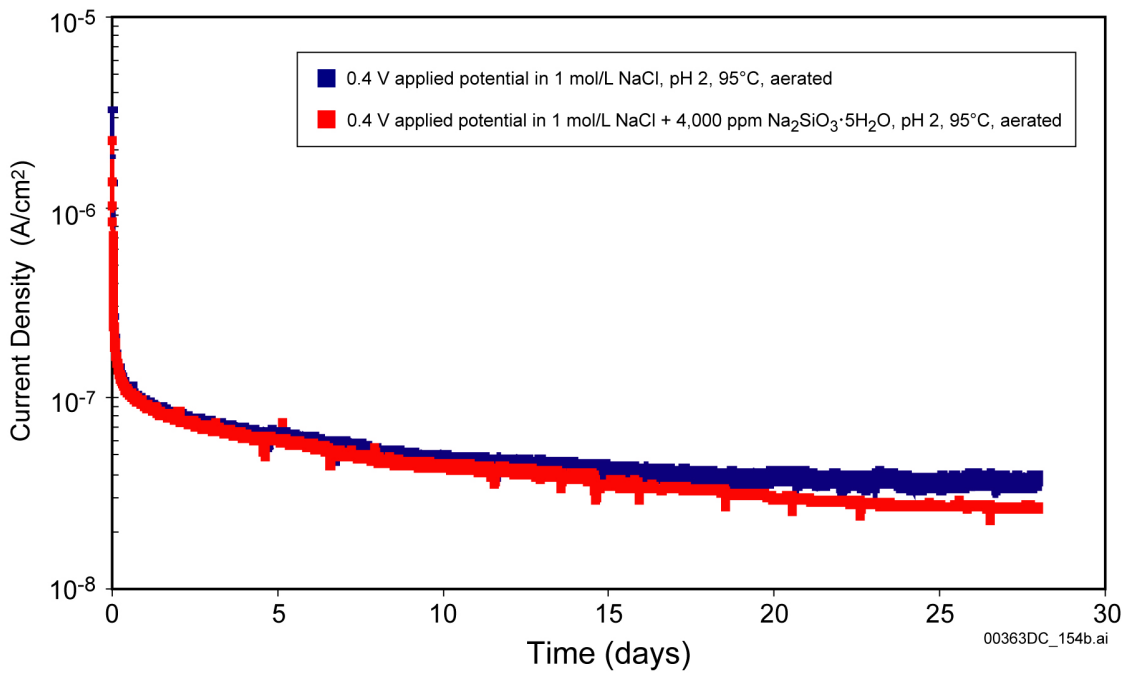
Figure J-5 also includes corrosion rates for Alloy 22 measured in electrochemical tests (the linear polarization resistance, and potentiostatic polarization measurements). Corrosion rates measured via electrochemical methods are also reported in *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (BSC 2003) and in the literature (Evans and Rebak 2002; Lian et al. 2003; Rebak et al. 2002). For example, potentiostatic polarization measurements performed on Alloy 22 in 95°C, 0.028 mol/L NaCl solution without silicate present and polarized to a potential of 100 mV (SCE) yield a current density of 1.1×10^{-8} A/cm^2, equivalent to a corrosion rate of about 0.1 µm/yr after about 200 hours (Pensado et al. 2002, p. 4-2). This rate falls slightly below the corrosion rate of about 0.2 µm/yr estimated in Figure J-5 for the exposure time, suggesting a lack of any effect of silicate on the general corrosion rate.

The data in the analysis model report show that the uncertainty in the measured corrosion rate after 5-year exposure is significantly improved over those measured after 1-year and 2-year exposures. The weight loss data from the 1-year and 2-year exposures were affected by silica deposits on the surfaces due to an ineffective cleaning process, leading to large uncertainties in the corrosion rates and the question of possible beneficial effects of silica in the measured values. A correction for the presence of silica was applied to the measured weight loss values. In the case of the 5-year data, more sensitive measurements and better cleaning procedures were utilized and no correction for residual deposition from the solution was needed. Results shown in Figure J-5, including the short-term electrochemical data, show that the general corrosion rate of Alloy 22 follows the trend for passive metal (that is, the decrease in corrosion rate with increase in exposure time, likely due to decrease in passive dissolution rate on a more chemically stable passive film), corroborating the conclusion that the effects of silicates are insignificant.

J.4.4 Potentiostatic Polarization Tests in Studying Silicate Effects

To study the silicate effect on the general corrosion rate decaying as a function of time, potentiostatic polarization tests were performed on Alloy 22 in a 1 mol/L NaCl solution and in a 1 mol/L NaCl + 4,000 ppm $Na_2SiO_3 \cdot 5H_2O$ solution. In acidic (pH 2) solutions, a 0.4 V (versus Ag/AgCl) constant potential was applied to the disc specimen for 1 month. The potential value of 0.4 V was selected based on the steady open circuit potential indicated in Figure J-1 and therefore, represents expected corrosion behavior after a long-term exposure. The test results shown in Figure J-6 reveal minimal differences in the measured current densities at 3.45×10^{-8} A/cm^2 in the SiO_3^{2-}-free solution compared to 2.67×10^{-8} A/cm^2 in the SiO_3^{2-}-containing solution. Similar results were seen in near-neutral (pH 8) solutions with an applied potential at 0.2 V (versus Ag/AgCl). Figure J-7 shows 1.31×10^{-7} A/cm^2 in the SiO_3^{2-}-free solution compared to 1.42×10^{-7} A/cm^2 in the SiO_3^{2-}-containing solution.

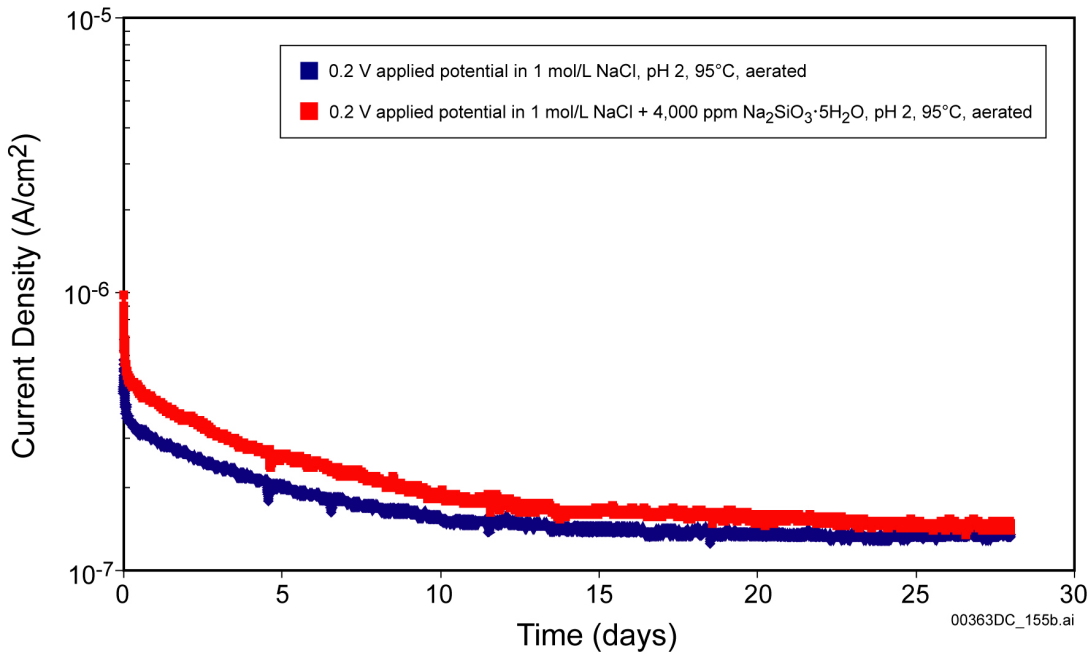
The potentiostatic polarization test results for exposures of about 30 days clearly indicate that any potential effects of silica deposition will have an insignificant impact on general corrosion rates.



Source: DTN: LL040206312251.070.

NOTE: Both tests used 0.4 V (versus Ag/AgCl) applied potential for nearly a month.

Figure J-6. Results of Potentiostatic Polarization Tests in 1 mol/L NaCl and 1 mol/L NaCl + 4,000 ppm $Na_2SiO_3 \cdot 5H_2O$, pH 2, Aerated



Source: DTN: LL040206312251.070.

NOTE: Both tests used 0.2 V (versus Ag/AgCl) applied potential for nearly a month.

Figure J-7. Results of Potentiostatic Polarization Tests in 1 mol/L NaCl and 1 mol/L NaCl + 4,000 ppm $Na_2SiO_3 \cdot 5H_2O$, pH 8, Aerated

J.4.5 Summary of Silica Effects on Corrosion under Repository Conditions

As described in the above sections, the effect of silica on corrosion processes is not discernable for a range of waters tested. The silica content of the test waters used in the Long Term Corrosion Test Facility for developing the 5-year corrosion data conforms to the ranges of water chemistry anticipated at the repository.

J.5 REFERENCES

J.5.1 Documents Cited

BSC (Bechtel SAIC Company) 2003. *General Corrosion and Localized Corrosion of Waste Package Outer Barrier*. ANL-EBS-MD-000003 REV 01. Las Vegas, Nevada: Bechtel SAIC Company. ACC: DOC.20030916.0010.

Evans, K.J. and Rebak, R.B. 2002. "Passivity of Alloy 22 in Concentrated Electrolytes Effect of Temperature and Solution Composition." *Corrosion Science, A Retrospective and Current Status in Honor of Robert P. Frankenthal, Proceedings of the International Symposium.* Frankel, G.S.; Isaacs, H.S.; Scully, J.R.; and Sinclair, J.D., eds. Proceedings Volume 2002-13. 344-354. Pennington, New Jersey: Electrochemical Society. TIC: 254801.

Lian, T.; Estill, J.C.; Hurst, G.A.; and Rebak, R.B. 2003. "Passive and Transpassive Dissolution of Alloy 22 in Simulated Repository Environments." *Corrosion/2003, 58th Annual Conference & Exposition, March 16-20, 2003, San Diego, California. Paper No. 03694,* Houston, Texas: NACE International. TIC: 254906.

Pensado, O.; Dunn, D.S.; Cragnolino, G.A.; and Jain, V. 2002. *Passive Dissolution of Container Materials—Modeling and Experiments.* CNWRA 2003-01. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. TIC: 254056.

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Ziegler, J.D. 2002b. "Transmittal of Supplement to Report Addressing Key Technical Issue (KTI) Agreements Container Life and Source Term (CLST) 1.05, 1.06, 1.07, and 2.07." Letter from J.D. Ziegler (DOE/ORD) to J.R. Schlueter (NRC), November 1, 2002, 1104024968, OLA&S:TCG-0060, with enclosure. ACC: MOL.20030213.0007.

J.5.2 Data, Listed by Data Tracking Number

LL040206212251.069. Long Term Corrosion Potential Measurements. Submittal date: 03/29/04.

LL040206312251.070. Silicate Effects on Corrosion of Alloy 22. Submittal date: 03/29/04.