

Corrosion Issues Related to Disposal of High-Level Nuclear Waste in the Yucca Mountain Repository

David J. Duquette, Ronald M. Latanision, Carlos A. W. Di Bella, and Bruce E. Kirstein
United States Nuclear Waste Technical Review Board
2300 Clarendon Blvd., Suite 1300
Arlington, Virginia 22201, U.S.A.

ABSTRACT

The current policy of the United States is to dispose of spent nuclear fuel and high-level nuclear waste underground in geologic repositories. The U.S. Department of Energy (DOE) has been developing plans for a repository to be located at Yucca Mountain, in Nevada. In June 2008, DOE submitted an application to the U.S. Nuclear Regulatory Commission (NRC) for a construction license for that repository. NRC accepted the application for docketing in September 2008.

This paper discusses DOE's bases for and approach to modeling the localized and general corrosion aspects of the Alloy 22 outer shell of the container that DOE plans to use for encapsulating the waste in the repository. The modeling is necessary to predict the corrosion behavior for the container's extraordinarily long "service period" — more than a million years.

INTRODUCTION

The U. S. Nuclear Waste Technical Review Board (Board) was created by the Nuclear Waste Policy Amendments Act of 1987 as an independent federal agency within the Executive Branch. The duties of the Board are to evaluate the technical and scientific validity of activities undertaken by DOE within scope of the Nuclear Waste Policy Act (NWPA) of 1982, as amended, and advise the Secretary of Energy and Congress of the Board's findings, conclusions, and recommendations. The Board is composed of 11 members, who are nominated by the National Academy of Sciences and appointed by the President to 4-year terms. Board members, all of whom serve part-time, are chosen from a broad range of scientific and engineering disciplines, including geology, hydrogeology, geochemistry, risk analysis, transportation, chemical and nuclear engineering, and other relevant disciplines. The Board membership always has included 1 or 2 corrosion experts. The Board is supported by a small permanent staff. Two of the authors (DJD and RML) are Board members; the two other authors are part of the Board's staff.

The docketing of DOE's license application in September 2008 started an intensive review by NRC employees and contractors of supporting materials submitted with the license application. That review is part of NRC's process for determining from a radiological point of view whether the repository DOE proposes for Yucca Mountain can be constructed and operated safely and will protect the public and the environment before and after the repository is closed. The Board's ongoing peer review of the technical and scientific validity of DOE activities differs significantly from NRC's review. For example, many DOE activities within the scope of the NWPA, e.g., transportation, are not part of the license application. In addition, although safety is paramount, other attributes of an activity, such as cost, schedule, capacity, process integration,

non-radiological safety, and resource availability can be and are among the important considerations of the Board's evaluation. Finally, as part of its review of technical and scientific validity, the Board evaluates the depth of technical understanding of key processes. In contrast, the level of technical understanding of a process required by safety regulations is confined to what is necessary to show either that the process is not important for safety or that assumptions about the physical behavior of the process are conservative and indicate that the effect of the process on safety is bracketed.

All waste to be disposed of in the proposed repository will be contained in double-shell, welded-metal cylinders — the “waste package.” The outside diameters of the outer shells range from approximately 1.7m to approximately 2.0m and the lengths from approximately 3.5m to approximately 5.7m, depending on the form of the waste. The current design includes an outer shell of 25.4mm-thick Alloy 22. The current design for the inner shell is 50.8mm thick 316 stainless steel. The mass of a fully loaded waste package ranges from ~40,000 to ~74,000 kg. The Alloy-22 outer shell is the topic of this paper because its corrosion resistance accounts for most of the performance of the waste package in preventing or limiting releases. For most of the scenarios analyzed by DOE, very few waste packages will have failed after a million years. Thus, the waste package is an important barrier for isolating waste from the human environment. In its license application, DOE takes the inner shell into account for structural support of the outer shell so long as the outer shell is intact but assumes that the inner shell has essentially no corrosion resistance. While such an assumption, which is very conservative from a safety point of view, may be acceptable in a license application, it masks the true behavior of the waste package. Liquid water, which is necessary for corrosion of the stainless steel to occur, cannot contact the inner shell until the Alloy-22 outer shell is penetrated. In almost all cases, such penetration should not occur until temperatures in the waste package are low, i.e., <40°C. At such temperatures, the inner shell is likely to be a formidable corrosion barrier.

Projected service conditions in the repository

Temperature: Ventilation (natural and forced) will remove essentially all of the decay heat of emplaced waste for the 50-100⁺-year period while the repository is open. When the repository is closed and sealed, decay heat will dissipate into the rock surrounding the tunnels rather than into the ventilation air, and the waste package and rock temperatures will achieve peak values approximately 60-80 years after closure. Then temperatures will begin to decrease. In the current design, DOE's calculations indicate that waste package surface temperatures will fall within the blue band shown in Figure 1. The roughly thousand-year period when temperatures are above 96°C is known as the “thermal pulse.” The specific temperature of an individual waste package will depend on the thermal power of the waste in the package and the package's location in the repository. Figure 1 also incorporates uncertainties in thermal parameters, such as thermal conductivity of the rock, and is based on the assumption that the geology of the repository is stable for a million years. The calculations can be extrapolated beyond a million years as long as the geology remains stable.

Pressure: Since the repository rock is permeable and the repository will be located well above the water table, the pressure of the gas phase in the tunnels will be essentially atmospheric during waste emplacement and after repository closure. The repository will be located

approximately 300m below the surface at an elevation of approximately 1100m above sea level. Nominal atmospheric pressure at an elevation of 1100m is 89 kilopascal. The boiling point of pure water at this pressure is $\sim 96^{\circ}\text{C}$.

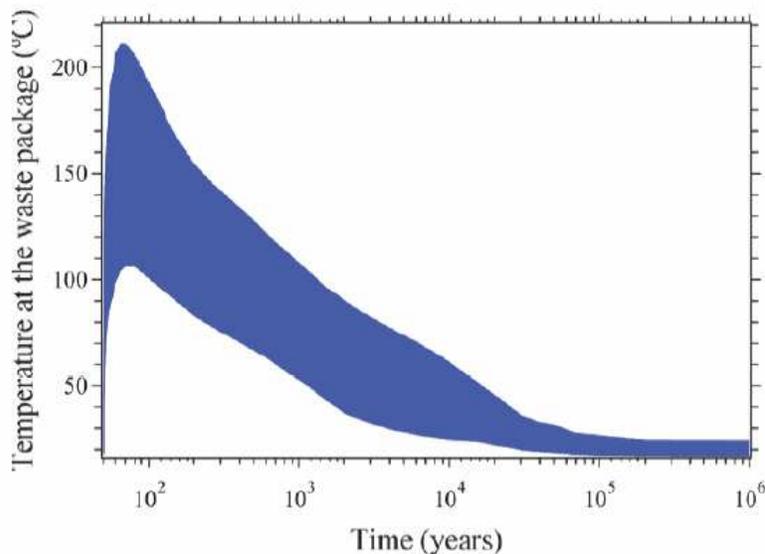


Figure 1. Approximate waste package surface temperature versus time since repository closure.

Chemistry: Atmospheric (dry) corrosion of Alloy 22 is not a significant concern; however, aqueous corrosion of Alloy 22 will occur, albeit slowly, whenever and wherever liquid water resides on the surface of the waste package. The chemistry of the water will be influenced by soluble solids present on waste package surfaces, e.g., salts and soluble organic compounds in dust deposited on the waste package during the long ventilation period, and by dissolved solids in water that drips onto waste packages. Based on samples of dusts in the air outside the portal of the underground Exploratory Studies Facility at Yucca Mountain, the dusts that deposit on waste packages during the ventilation period are likely to contain the following: calcium, sodium, magnesium, potassium, silicon, ammonium, chloride, sulfate, bicarbonate, nitrate, fluoride, formate, acetate, and propionate, among others.[1] Since the concentration of oxygen in the gas phase will be approximately 20 volume % at all times except during a portion of the thermal pulse, the environment will be mildly oxidizing. Anions present in the water tend to make it neutral-to-basic, but local situations could exist where, due to concentration, hydrolysis, radiolysis, or other processes, low-pH environments exist temporarily.

Humidity: As the tunnel rock heats up after closure, water remaining in the fractures and pores of the rock will vaporize, which will drive air away from the tunnels, resulting in a nearly pure steam atmosphere. After the rock reaches its peak temperature and cools to 96°C , water vapor will condense, drawing air back into the repository tunnels. The relative humidity in the tunnels will return to its natural state of greater than 90%.

Liquid Water: Corrosion is not a concern during the period before repository closure because the dry desert air used for ventilating the repository will preclude formation of liquid water on the waste package surfaces. After the thermal pulse, the saturation of the pores in the rock will return to $\sim 90\%$, and the relative humidity will be greater than 90%. Under such high-

relative humidity conditions, water films at least a few molecules thick are likely to be present on waste package surfaces, and general corrosion will occur. The film will exist at lower relative humidities, or the film will be thicker at the same relative humidity, if there are soluble salts on waste package surfaces, because the salts will dissolve in the film and depress the equilibrium vapor pressure of the resultant solution. Waste packages surfaces will be coated with a 50-100⁺-year accumulation of dust, which will contain some soluble salts. Due to deliquescence, liquid water in the form of concentrated brines also can exist on waste package surfaces at temperatures well above the boiling point of pure water if certain salts are present. For example, mixtures of sodium and potassium chlorides and nitrates can deliquesce at temperatures above 200°C at atmospheric pressure if the vapor phase over the salts is essentially pure steam. Whether other mixed salt combinations that might exist on waste package surfaces could form brines at high temperatures via deliquescence is still under debate. The possible formation of brines, the composition of the brines, and the presence or absence of solid dust particles or solids resulting from the precipitation of insoluble species, are relevant to the corrosion performance of the Alloy-22 outer barrier of the containers.

EXPERIMENTS AND MODELS

Reference 2 describes the Alloy-22 general and localized corrosion models used in DOE's license application and the analyses and experimental data underlying the models.[2] This paper deals with some of the issues the Board sees in some of the models, with particular emphasis on recent experimental work that became available too late to be incorporated into Reference 1. The recent work includes work sponsored by the State of Nevada at the Institute for Metal Research (IMR) of the Chinese Academy of Sciences [3-5], work sponsored by NRC at the Center for Nuclear Waste Regulatory Analyses (CNWRA)[6], and work sponsored by the DOE at Sandia National Laboratories (SNL).[7,8] We also touch briefly on the issue of "oxide wedging."

General Corrosion

Base general corrosion rate: Personnel at Lawrence Livermore National Laboratory (LLNL) produced much of the general corrosion data that DOE relied on to develop a model of the long-term general corrosion behavior of Alloy 22 in repository-relevant environments. LLNL personnel designed, built, and then operated for approximately 10 years baths approximately half-full of solutions¹ in which samples of Alloy 22 and other materials that were reference materials or alternate candidates for use in a repository at Yucca Mountain were exposed. Some samples were completely immersed; some were at the water line; and some were in the vapor space above the solutions. The corrosion rates for the immersed samples were higher than other samples. Therefore data from only the immersed samples were used to develop the model. Approximately half of the baths were maintained at 60°C; the other half were maintained at 90°C. Corrosion rates were determined by weight loss.

¹ Four different solution compositions were used. All were based on the composition of the water in the aquifer below the proposed repository location, a sodium carbonate water. Each composition was adjusted to reflect concentration processes and possible acidification or alkalization. The compositions of the solutions in the baths are listed in Reference 1.

Two geometric sample configurations were used in the baths. One set (samples with crevice formers attached) showed greater average weight loss than the other set (boldly exposed samples). DOE conservatively decided to use only the set showing the greater average weight loss as the basis for its model of the Alloy-22 general corrosion rate. There were no discernible differences between average weight losses at 60°C and at 90°C. The samples used for the model had been immersed in the baths for approximately 5 years. The mean general corrosion rate determined from the data was approximately 8nm/yr. Assuming a general corrosion rate of 8nm/yr and no other forms of Alloy-22 degradation, the outer layer of the waste package would last an astounding 3 million years.

Weight loss data from samples immersed for 9½ years in the baths were not available when the model was frozen. Evaluation of the 9½-year samples just began earlier this year. The 5-year data, data from samples with less time in the baths, and shorter-term electrochemical data indicate that the Alloy-22 general corrosion rate decreases with time, as would be expected. It is anticipated that the 9½-year data will show that trend continuing, although eventually the corrosion rate would reach an equilibrium value corresponding to the limiting passive current density. In its modeling of general corrosion, DOE conservatively used a fixed general corrosion rate based on the corrosion rate averaged over the entire 5 year period rather than a corrosion rate that decreases with time or even the instantaneous corrosion rate at the end of the 5-year period. This is very conservative; in our opinion DOE's model for general corrosion significantly overpredicts recession rates at below-boiling temperatures.

Unfortunately, the 60°C and 90°C temperatures and the environments in the baths were too similar to discern variations in corrosion rate with temperature or environment. DOE's model assumes the base general corrosion rate for Alloy 22 applies for 60°C and any environment to be encountered in Yucca Mountain. To adjust the general corrosion rate for temperature DOE used short term, electrochemical (polarization resistance) experiments at different temperatures to determine the variation of general corrosion rate with temperature.

DOE performed polarization resistance measurements at 60, 80, and 100°C in solutions made by dissolving various amounts of sodium chloride and potassium nitrate to obtain solutions ranging between 1 and 6 molal chloride and 0.05 and 3.0 molal nitrate. A total of 360 polarization resistance measurements were made, and corrosion rates were calculated from the measurements.

The corrosion rates then were fit to a classical Arrhenius relationship,

$$\ln(R_T) = \ln(A) - E_a/RT$$

where R_T is the generalized corrosion rate, nm/yr,
 A is the preexponential factor, nm/yr,
 E_a is the apparent activation energy, J/mol,
 R is the gas constant, 8.314 J/mol K, and
 T is temperature, K.

The resultant fit yielded an apparent activation energy of 40.78 kJ/mol with a standard deviation of 11.75 kJ/mol.

Recent CNWRA data. CNWRA measured corrosion rates of Alloy 22 in highly concentrated solutions of NaCl-NaNO₃-KNO₃ at atmospheric pressure and temperatures ranging from 130 to 220°C.[6] The test durations ranged from 80 to 140 days. The results appear consistent with the temperature-dependent Alloy-22 general corrosion rate model developed by DOE. However, corrosion rates appear to vary with composition of the solutions, i.e., the samples immersed in low pH (pH = ~3) solution had higher corrosion rates than samples immersed in higher pH solutions (pH~7) at the same temperature.²

Earlier, similar tests run at CNWRA in the same starting solution over the same temperature range gave different results.[9] Corrosion rates were significantly higher and showed no correlation with temperature. The major differences between the recent tests and the earlier tests were; (1) The earlier tests had shorter durations (30 to 80 days versus 80 to 140 days); and (2) Water captured in the vent bubbler (see Figure 2a) was recycled in the recent tests; in the earlier tests, deionized water was used to make up losses.

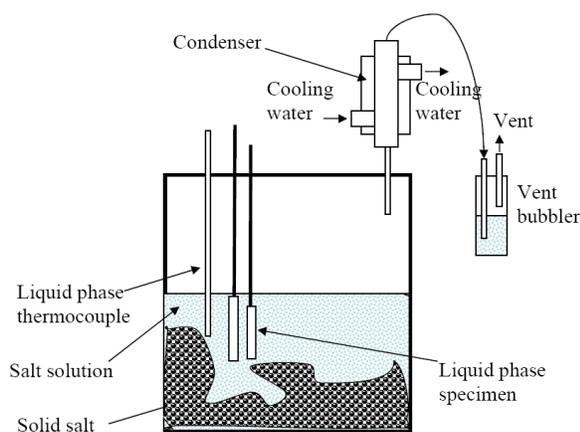


Figure 2a. CNWRA Apparatus Simplified Schematic

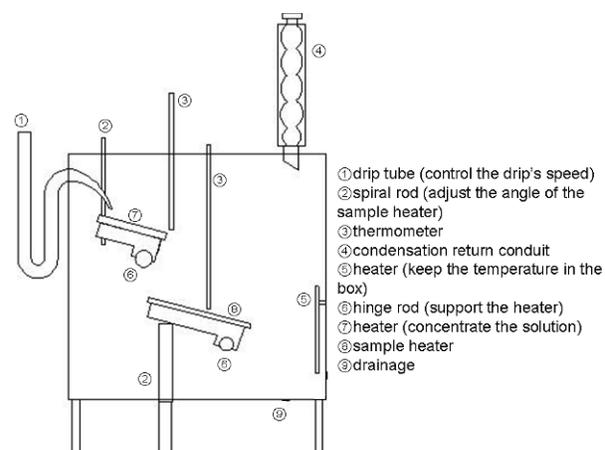


Figure 2b. IMR Apparatus Simplified Schematic

Recent IMR Data. Personnel at IMR, using equipment with many apparent similarities to the equipment used in the CNWRA studies discussed above, studied corrosion of Alloy 22 at atmospheric pressure at ~160°C.[3,4] Instead of a concentrated solution of NaCl-NaNO₃-KNO₃ used by CNWRA, the IMR work used “simulated unsaturated zone pore water” of various concentrations. Both CNWRA and IMR reported the amounts of salts used to make up their test solutions, but did not report the composition of the solutions. The IMR also used a test solution made up of magnesium chloride hexahydrate to which a small amount of magnesium nitrate hexahydrate had been added ([Cl]/[NO₃]~50). Instead of immersing the sample, IMR researchers dripped solutions onto an inclined plate maintained at 100°C, from which the heated solution dripped onto an Alloy-22 sample heated to 160°C. The duration of the IMR tests ranged from 10 to 30 days. Figure 2b shows a schematic of the IMR apparatus. The pHs of the

² The pHs reported above are for samples of solution that were diluted by a factor of 10 to prevent crystallization. Therefore the pHs of the solutions themselves are likely to be lower than reported above.

solutions were measured before the solutions were introduced into the apparatus and as the solutions were draining from the samples. The pHs of the virgin solutions were essentially neutral (from ~6 to ~7.3); the pHs of the solutions draining from the samples were acidic (pHs from ~1 to ~3.3). No quantitative corrosion results were reported. However, photographs and photomicrographs of the test samples show severe corrosion, which the IMR investigators believe is crevice corrosion.

Discussion. The Board has little concern about general corrosion of Alloy 22 at temperatures below boiling because DOE's model appears very conservative. Weighing of the samples (at SNL) that resided in the LLNL baths for 9½ years has been underway for several months. No results have been reported yet. If corrosion rates determined by weighing the 9½-year samples do not show a continuing trend of a decrease in mean general corrosion rate (averaged over time) with residence time in the bath, we may be concerned with the validity of the data. We recognize that the general corrosion rate will eventually reach an equilibrium value. However, this point had not been reached after 5 years in the baths.

The new CNWRA and IMR data give reason for concern about general corrosion of Alloy 22 at temperatures above boiling. The CNWRA results indicate that the general corrosion rate of Alloy 22 may vary with composition of the environment, i.e., at lower pHs the general corrosion rate of Alloy 22 may be higher. This is not an unexpected finding, but it appears to contradict DOE's model, which predicts no variation in the general corrosion rate of Alloy 22, regardless of composition of the solution in contact with the metal (within the range of compositions that DOE expects to be present at Yucca Mountain). The IMR experiments indicate the possibility of severe corrosion for a scenario of no drip shield, large temperature differences between the tunnel walls and the waste package surface, and with acid gasses condensing within the brine on waste package surfaces. We do not know what the possibility of that scenario is. The likelihood of the scenario should be explored by DOE. Performing the experiments on titanium Grade 7, the material proposed for the drip shield, also would be worthwhile. (The DOE model for titanium predicts a higher general corrosion rate for titanium Grade 7 than for Alloy 22.) Both the new CNWRA data and the new IMR data raise the possibility of problematic general corrosion rates at above boiling temperatures.

The Arrhenius form of the DOE model for the general corrosion rate of Alloy 22 is appropriate, particularly since the temperature range of interest is so narrow, 25-200°C. The value for the apparent activation energy is reasonable. It is likely that the corrosion rates obtained from the polarization resistance measurements are greater than they will be at steady state, but since the purpose of the experiments was to determine the variation of corrosion rate with temperature and not to determine the rate itself, this does not seem to be a significant limitation. Limiting the solutions tested to chloride- and nitrate-containing solutions, not varying the pH of the solutions, and limiting the temperature range of the polarization resistance tests to 60-100°C do not seem appropriate. However, even assuming the most severe conditions that might be encountered in the repository, it appears — barring the evidence from the IMR tests — unlikely that the containers will fail due to general corrosion of the Alloy 22 for millennia.

Localized Corrosion

DOE treats Alloy-22 localized corrosion differently depending on the environment in which the localized corrosion may occur. If the environment is due to liquid water dripping onto the waste package (seepage), then localized corrosion is modeled as described below. If the environment is due to the deliquescence of salts deposited on the waste package (e.g., during the ventilation phase) localized corrosion is screened out as inconsequential.

Localized Corrosion due to Seepage. DOE's model for localized corrosion due to seepage is based in part on the assumption that seepage onto the waste package cannot occur when the surface of the waste package is above 120°C. For waste package surface temperatures at and below 120°C, DOE assumes that localized corrosion will initiate on the portion of the waste package surface contacted by seepage if the composition, temperature, and pH of the seepage water are such that the corrosion potential, E_{corr} , of Alloy 22 immersed in a surrogate for the seepage water is equal to or greater than the critical potential, E_{crit} . The critical potential is also a function of the composition, temperature, and pH of the seepage water contacting the waste package. The Board concurs that this general approach is a reasonable *conceptual* model for initiation of localized corrosion. Initiation is particularly important because DOE assumes that seepage-based localized corrosion, once initiated, will penetrate rapidly and will not stifle.

The data for the determination of E_{corr} and E_{crit} were obtained in separate experiments. To determine E_{corr} , DOE measured open circuit potentials versus time for various Alloy-22 samples in model aqueous solutions over a temperature range of 25-90°C for periods of up to 3 years and then used multiple linear regression on the data to fit a model for E_{corr} as a function of nitrate and chloride concentrations, temperature, and pH, i.e., $E_{\text{corr}} = f_1([\text{NO}_3], [\text{Cl}], T, \text{pH})$.

To determine E_{crit} , DOE used the ASTM G61-86 cyclic potentiodynamic polarization (CPP) technique to determine the repassivation potentials for a number of creviced Alloy-22 samples in a variety of aqueous solutions. E_{crit} was taken as the potential value where the reverse CPP scan intersected the forward CPP scan. The resultant data were fit to express critical potential as a function of nitrate concentration, chloride concentration, and temperature, i.e., $E_{\text{crit}} = f_2([\text{NO}_3], [\text{Cl}], T)$.

Discussion. DOE assumes that localized corrosion of Alloy 22 will initiate if E_{corr} , as represented by function f_1 , is greater than E_{crit} , as represented by function f_2 . The data on which function f_1 is based are long-term data — up to 3 years in many cases but at least 8 months in all cases. On the other hand, the data on which function f_2 is based are short-term data — a matter of approximately a day for each CPP curve. The question then must be asked if mixing long-term data and short-term data to form the basis for predicting localized corrosion initiation is appropriate. If so, is it likely to overpredict the occurrence of localized corrosion or underpredict it? In addition, despite the long term nature of the corrosion potential experiments, it is not clear that all the experiments had reached a stable value by the end of the tests, and some of the test results were “noisy” at the end of the tests, also making their stability questionable.

A problem with interpreting some of the data used to develop the localized corrosion model is that DOE's long-term corrosion tests in the baths at LLNL, many of which were on

creviced samples, apparently do not corroborate the model DOE has developed by fitting E_{corr} and E_{crit} equations to the electrochemical corrosion potential and CPP data. For example, according to the localized corrosion model, a few of the tests used to develop the generalized corrosion model discussed above should have shown localized corrosion. However, none of them did. Similarly, other long-term corrosion tests that the model indicates should have developed localized corrosion did not. With a single exception, the only tests where the model predicted localized corrosion and localized corrosion did occur were in highly concentrated solutions of calcium chloride with minor amounts (or none) of calcium nitrate. Such solutions are not very likely to exist in the repository. In summary, the model used to predict localized corrosion under seepage conditions appears to be overly conservative in that it predicts that localized corrosion will occur in many instances where experimental data indicate that it will not occur — at least not in the time frame of the experiments.

Propagation. If seepage-based localized corrosion initiates, DOE's model assumes that it will propagate at a constant rate, chosen from a logarithmic linear distribution ranging from 12.7 $\mu\text{m}/\text{yr}$ to 1270 $\mu\text{m}/\text{yr}$. Apparently, these values were selected from Alloy-22 uniform corrosion rates in highly aggressive solutions extracted from the product literature of one of the manufacturers of Alloy 22. In our opinion, such data only should be used to compare the relative corrosion resistance of different alloys, and localized corrosion rates, in general, are much higher than uniform corrosion rates. However, using the highest published corrosion rates results in penetration of the waste packages, once localized corrosion has been initiated, in a matter of less than 2,000 years, which, for a million-year (or more) period of concern, is essentially instantaneously.

It is not clear from currently available documentation how DOE models what happens after the waste package is penetrated by localized corrosion, i.e., what the area, morphology, and geometry of the penetration(s) are. One approach could be to assume that the entire area contacted by seepage disappears when penetration occurs. This would be an extremely conservative view and inconsistent with the very nature of localized corrosion. An even more extreme assumption would be to assume that the entire waste package disappears at the time of penetration. In either case, the corrosion resistance of the container alloys essentially becomes irrelevant, and the containment of radionuclides becomes the responsibility of the natural barriers.

Localized corrosion due to deliquescence. That brines can form on waste package surfaces at temperatures up to $\sim 200^\circ\text{C}$ due to deliquescence is well established. Therefore, the possibility of localized corrosion (and other forms of aqueous corrosion) during the thermal pulse period is a concern. Localized (crevice) corrosion has been observed in autoclave (pressurized) experiments performed on Alloy 22 in aqueous solutions of 2.5m and 6.4m Cl^- with $[\text{NO}_3^-]/[\text{Cl}^-]$ ratios of 0.5 or 7.4 at temperatures of 160°C and 220°C .^[10] Localized corrosion was observed in all cases, but was not anticipated in the solutions with nitrate to chloride ratios of 7.4.³ The test solutions were made by dissolving sodium chloride, sodium

³ The minimum nitrate to chloride ratio necessary to inhibit localized corrosion has not been determined over the full range of temperatures that waste package surfaces may experience. Moreover, the minimum ratio appears to increase with temperature and may be a function of other variables, also.

nitrate, and potassium nitrate in water. Brines containing sodium, potassium, chloride, and nitrate cannot form at atmospheric pressure in the higher end of the temperature range of interest unless the nitrate to chloride ratio of the brine is well above 1. However, if the nitrate concentrations are lower than anticipated, or if the nitrate is removed by chemical, physical, or biological processes (e.g., by reacting with organic materials in the dust deposited during ventilation), whether the stable brine would decrease in amount, form a metastable brine or solidify (thus being rendered innocuous) has not been determined. In addition, whether other brines could form at high temperatures from other mixtures of salts that may exist at Yucca Mountain has not been explored systematically. In other words, in our view the possibility of other high-temperature corrosive environments has not been conclusively ruled out.

The Board sponsored a public workshop on localized corrosion in September 2006 to discuss deliquescence-based corrosion of Alloy 22 in repository-relevant environments.[11] At that workshop, DOE presented a strong case suggesting that the nitrate to chloride ratios in the repository would be sufficiently high that localized corrosion could not occur. DOE representatives also suggested that, if those assumptions were incorrect, the propagation of localized corrosion would effectively be stifled, because (a) migration rates for nitrate into occluded regions are higher than chloride migration rates, and repassivation would occur within the occluded regions; and/or (b) the amount of water and/or aggressive species are so low that the occluded regions would effectively be “starved” as the damage propagated and localized corrosion would essentially halt. The Board made two recommendations to DOE as a result of the workshop: (1) determine the level of nitrate needed to inhibit localized corrosion over the *entire* temperature range (i.e., up to ~200°C), and (2) determine the relative migration rates for the migration of nitrate and chloride ions into crevices. At this time it appears that the first of these recommendations is in DOE’s corrosion test plan for fiscal year 2009.[8]

At or below a waste package surface temperature of 120°C, i.e., for waste package surface temperatures for which DOE believes seepage-based localized corrosion is possible, thin films of brines may form due to deliquescence of salt mixtures in the dust deposited on the packages. There is essentially no difference between films caused by seepage and films caused by deliquescence, although the films caused by deliquescence could be thinner. Therefore the $E_{\text{corr}} \geq E_{\text{crit}}$ model DOE uses to determine whether localized corrosion due to seepage would initiate should apply equally well to the determination of whether deliquescence-based localized corrosion would initiate. Yet DOE seemingly has chosen to ignore the possibility of deliquescence-based localized corrosion at low temperatures, with no apparent explanation. This is a shortcoming that DOE needs to explain or rectify.

Oxide Wedging

The 2 cylinders that make up the waste package do not have an interference fit. Design specifications call for the outer diameter of the inner, 316 stainless steel cylinder to be 4 to 10 mm less than the inner diameter of the outer, Alloy-22 cylinder. Thus, there would be a small gap between the 2 cylinders. If the outer cylinder is penetrated, water could enter the gap space between the cylinders, causing corrosion of both the inner wall of the outer cylinder and the outer wall of the inner cylinder. Corrosion products of both metals have lower densities than the parent metals, and therefore the gap will eventually fill with corrosion products. Further

corrosion could result in local stresses that might exacerbate waste package degradation, either by simple deformation or by introducing the possibility of stress corrosion cracking.

DOE screens out oxide wedging as inconsequential.[12] That is, DOE omits the phenomenon from the total system performance assessment (TSPA-LA) in its license application on the basis that oxide wedging would have an insignificant effect on dose. The rationale advanced by DOE for screening oxide wedging out is that oxide wedging would result in enhanced degradation of the inner vessel, preventing it from acting as an effective substrate from which the corrosion products could exert stresses on the outer vessel. Even if the corrosion products were to exert stresses on the outer vessel, DOE argues that the effects are sufficiently accounted for by conservative modeling — specifically by assuming a maximized stress corrosion crack area and by taking no credit for the decreased rate of transport of radionuclides through the corrosion products.

DOE commissioned an independent review of TSPA-LA. The results of the review were published earlier this year.[13] The reviewers agreed that screening out oxide wedging was appropriate. However, they found DOE's rationale deficient. The reviewers suggested that stresses caused by oxide wedging would be ameliorated by stretching of the Alloy 22, which is highly ductile. The reviewers also pointed out that any cracks (e.g., cracks caused by stress corrosion cracking) in the Alloy-22 vessel would fill with water and corrosion products, resulting in very slow transport of oxygen to the stainless steel inner vessel, thereby limiting the rate of corrosion of the inner vessel. The corrosion products in the gap between the inner and outer cylinder also would retard oxygen transport. The reviewers criticized DOE for not considering this scenario. We agree with the reviewers.

CONCLUSIONS

The waste package is an extremely important barrier. In most scenarios, few waste packages will have failed after a million years, and most of those that have failed have relatively few penetrations. The technical bases for the corrosion performance of the Alloy-22 outer shell of the waste package at below-boiling temperatures appear robust, although the model for localized corrosion at below-boiling temperatures appears overly conservative. There are fewer data at high temperatures, however, and it is not apparent that all of the above-boiling corrosion data are consistent. DOE has plans to address high-temperature corrosion issues. We encourage DOE to execute the plans soon. Treating deliquescence-based localized corrosion and seepage-based localized corrosion of Alloy 22 differently, as DOE does in the corrosion models in its license application, seems inappropriate since the mechanisms are likely to be the same.

The million-plus year service life for Alloy 22 is a unique and unprecedented materials engineering challenge. Even though the general corrosion data are of high quality and their extrapolation for 10^6+ years is based on conservative application of physical and chemical principles, one is uneasy predicting or bounding behavior for this long a period. The corrosion community has not had to deal with anything approaching such a long service life. Perhaps the single largest unknown in predicting the corrosion behavior of Alloy 22 in the repository environment is the specific chemistry of the environment in the repository horizon, in occluded regions such as metal to metal crevices, in deliquesced brines under dust, etc. A further

complication is the evolution of the chemical environment with time, which could result in depletion of nitrates due to reaction with organic materials in deliquescent brines.

While the general corrosion of the containers may be reasonably predicted, or at least bounded, it appears that deliquescence of certain salts that can cause liquid water to be present at temperatures well above the boiling point of pure water introduces many uncertainties about localized corrosion (and, to a lesser extent, general corrosion) at elevated temperatures. It should not be concluded, however, that localized corrosion of the Alloy 22, even if it should result in a breach of the containers, will necessarily compromise the integrity of the repository. Even assuming complete penetration of the Alloy 22 by localized corrosion, before the first spent fuel material would contact the repository environment the inner stainless steel shell of the waste package would also have to corrode and aggressive species would have to be transported across the gas within that shell to the fuel rod assemblies followed by penetration of the zircaloy cladding on the assemblies. Even then, before radionuclides can reach the biosphere, degradation of the spent fuel must occur, followed by transport of the degraded spent fuel material across the gap between the assembly and the wall of the container, transport through a presumably limited localized corrosion penetration zone of the container, and transport across the repository environment into the walls of the repository with subsequent geological confinement (perhaps the ultimate isolation step).

Accordingly, because “defense in depth,” a concept that has been adopted by virtually every national nuclear waste isolation program, must be followed, corrosion of the containers will not necessarily compromise the entire concept. Nevertheless, an understanding of the corrosion processes that may lead to damage to the containers is imperative. If it can be shown that the containers will contain the waste during the entire period of statutory emplacement, scientific and technical credibility may lead to public credence.

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