CORROSION ISSUES RELATED TO DISPOSAL OF HIGH-LEVEL NUCLEAR WASTE IN THE YUCCA MOUNTAIN REPOSITORY

PEER REVIEWERS' PERSPECTIVE

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, VA 22201

ABSTRACT

The policy of the United States is to dispose of 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, Nevada, and intends to submit a license application to the U. S. Nuclear Regulatory Commission (NRC) for that repository in June 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 Nuclear Waste Policy Amendments Act of 1987, passed by Congress and signed by the President in late December of that year, established the U.S. Nuclear Waste Technical Review Board (Board) as an independent agency within the Executive Branch. The duties of the Board are to evaluate the technical and scientific validity of activities undertaken by the Secretary of Energy for managing and disposing of high-level nuclear waste. The Board consists of 11 members 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 geologists, hydrogeologists, risk analysts, transportation specialists, microbiologists, and other relevant disciplines. The Board membership always has included one or two corrosion experts. The Board is supported by a small permanent staff at the Board office in Arlington, Virginia. The role of the Board is not to drive the scientific or technical aspects of the Yucca Mountain Project, or to advise formally on what scientific or engineering data need to be generated to make disposal of high-level nuclear waste acceptable. However, the make-up of the Board and the format the Board uses when meeting with representatives of DOE and other entities, including NRC, the technical community, the State of Nevada, and the public, allow individual members, or small groups of members, to offer helpful technical advice to DOE. The Board provides data and information that will be helpful to the Secretary of Energy and Congress in their making fully informed decisions on the program for managing and disposing of high-level nuclear waste.

WASTE FORMS AND REPOSITORY CHARACTERISTICS

Most high-level nuclear waste consists of spent fuel from domestic nuclear electric power plants, but it also includes spent fuel from research and defense applications and high-level nuclear waste from reprocessing for both defense and commercial reasons. The waste is radioactive and emits both radioactivity and heat as it decays. DOE is responsible for developing a repository for the permanent underground disposal of high-level nuclear waste at a site in Nevada at Yucca Mountain, adjacent to the Nevada Test Site and about 75 miles northwest of Las Vegas. DOE is preparing an application for a license to construct the repository for submittal to the NRC. As of early January 2008, DOE plans to submit the application before the end of June 2008. A major part of the application will be the projection of the degree to which the components of the repository would work together to isolate radionuclides from the human environment for up to a million years.
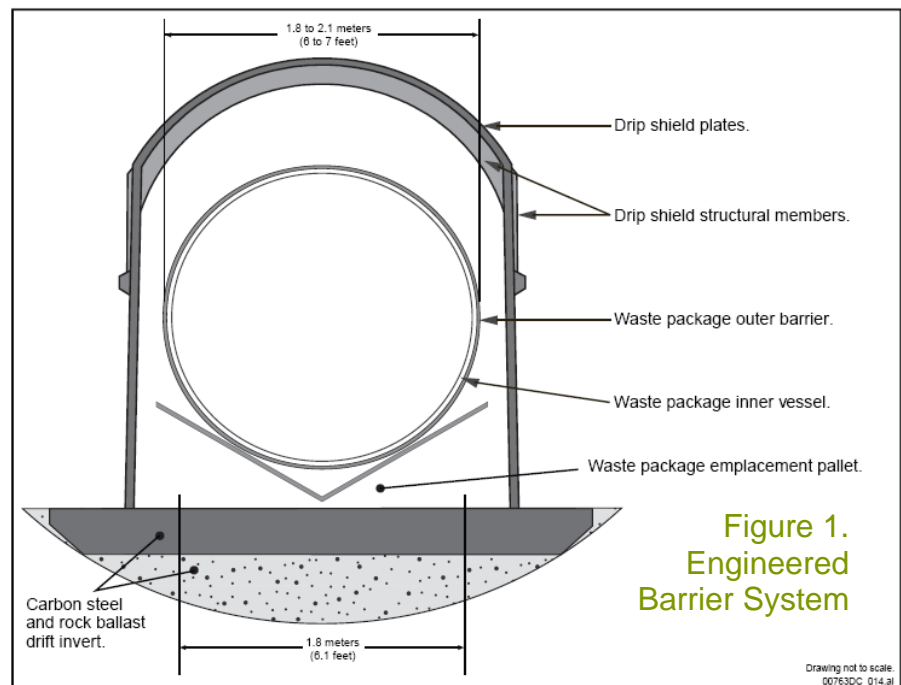
The repository would be located approximately 300 m underground as a series of tunnels with diameters of approximately 5.5 m. Its capacity is limited by statute to 70,000 metric tons of uranium. The repository would remain open and ventilated while being loaded and for several decades after being fully loaded; it then would be closed and permanently sealed. Of important note is that current plans for the repository do not include near-term or future retrieval after the vault has been sealed. The natural system, i.e., the geology of Yucca Mountain, and the engineered system would function together as a system to prevent or limit releases of radioactivity to the environment in amounts that could be harmful to human health.

The concept of defense in depth, or a multiple barrier system, is not unique to the US program. For example, In several international programs, high-level nuclear wastes will be isolated in repositories where the surrounding granitic environment is not only an effective barrier to migration of radionuclides, but is also generally reducing, and corrosion of the containers becomes a virtual nonissue. For example, in the Finnish, Swedish and possibly Canadian programs, arguably the most scientifically and technically advanced, spent nuclear fuel will be encased in copper containers in an environment where the redox potential is active to the reversible potential for dissolution of the copper. Thus, corrosion of the copper is impossible without violating the fundamental laws of thermodynamics, and the copper containers will be chemically stable for a theoretically infinite period of time, provided, of course, that the repository remains anoxic in character. In other European programs, e.g.

Belgium, Switzerland and possibly France, it is assumed that the clay is such an excellent barrier that only a short time (~10^3 years) of container integrity will be required.

In the U.S. program, the environment is oxidizing, and the principal barrier in the engineered system is the waste package, a double-shell cylinder consisting of a 50.8 mm 316 stainless-steel inner shell and a 25.4 mm Alloy 22[1] outer shell. See Figure 1. Depending on the type of waste, waste package diameters range from ~1.8 to ~2.1 m, and lengths from ~3.5 to ~5.7 m. The mass of fully loaded waste packages 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.

Figure 1. Engineered Barrier System

Besides the double-shell waste package, other barriers making up the engineered system include a stainless-steel canister just inside the stainless-steel inner shell, a titanium drip shield over the waste package intended to divert seepage water away from the containers, the zircaloy cladding that encapsulates almost all of the spent commercial fuel, and the waste itself. Although these items are important to the overall performance of the engineered barrier system, they will be discussed only peripherally in this presentation and therefore are not all shown in Figure 1.
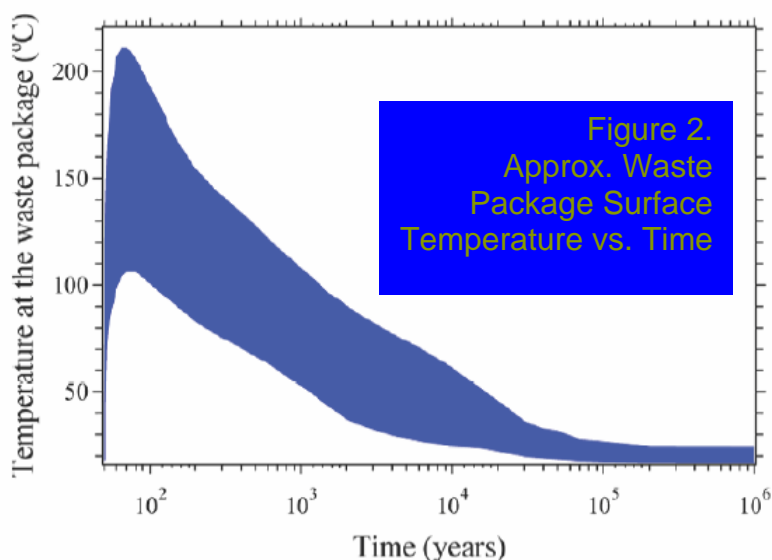
SERVICE CONDITIONS

Service period. From the point of view of engineered alloys, the most unusual service condition for the Alloy 22 outer shell of the waste package is the period of service. A panel of the National Research Council recommended in 1995[1] that compliance with a standard that sets a limit on the risk to individuals of adverse health effects from releases from the repository be measured at the time of peak risk.[2] Recent studies published by DOE indicate that the peak risk (as measured by peak dose) from the repository will occur more than a million years after repository closure.[2] The principal reason for the peak dose occurring so far into the future appears to be the longevity of the outer barrier of the waste package. This presents a uniquely long "service period" for a man-made material.

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[1] UNS N06022: Co 2.5% max, Cr 20-22.5%, Fe 2-6%, Mn 0.5% max, Mo 12.5-14.5%, W 2.5-3.5%, Ni balance.
[2] Within the period of geologic stability of Yucca Mountain, which the panel opined is on the order of a million years.

Temperature. Radioactive materials in the waste emit radiation and thermal energy as they decay. The rates of radiation and thermal energy emissions from the waste in a waste package decline with time as shorter-lived radionuclides decay away to insignificant quantities. For example, the thermal power of a particular waste package containing 21 assemblies of spent fuel from a specific pressurized water reactor might be approximately 12 KW when it is emplaced in the repository. Most of this heat would result from the decay of Cs-137 and Sr-90, radioisotopes with half-lives of approximately 30 years. The thermal power of that same package would be only about 700 W 1,000 years later, when the Cs-137 and Sr-90 would be essentially gone and Am-241, a radioisotope with a half-life of approximately 430 years, would be providing the majority of the decay heat. After 10,000 years, the thermal power would be 120 W for the same package, and Pu-239, with a half-life of ~24,000 years, would be providing most of the decay heat. Natural and forced ventilation are expected to remove essentially all of the decay heat of emplaced waste while the repository is open. As soon as the repository is closed and sealed, heat is dissipated into the rock surrounding the tunnels instead of into the ventilation air, and the waste package and rock heat up quickly to peak values. Temperatures then slowly decrease from their peak values as the rate of decay heat from the waste packages decreases. The temperature of the surface of the waste package is important for corrosion. Figure 2 shows the approximate temperature of the waste package surface as a function of time, assuming that the repository is closed 50 years after the first waste package is emplaced. The curve is a band because waste package surface temperatures vary depending on location in the repository, the thermal power of the waste in the package, and other variables. Figure 2 is based on DOE's current plans for loading and closing the repository. The curve can be changed by placing packages closer or farther apart in the tunnels, by placing more or less waste in each package, by changing the duration of ventilation, and other design or operational changes. Note that the peak temperature reaches approximately 210°C during the "thermal pulse" — too low for atmospheric (gas phase) corrosion of Alloy 22 to be significant.

Pressure. The tunnels would be open to the atmosphere during emplacement. Because the repository rock is permeable and the repository would be located well above the water table, the pressure of the gas phase in the tunnels would remain essentially atmospheric after repository closure.

Chemistry. Because of the great span of the service period, aqueous corrosion of the Alloy 22 outer shell of the waste package is a concern. Aqueous corrosion will occur to some degree whenever 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, such as salts, silica, and soluble organic compounds in dust deposited on the waste package during

Figure 2. Approx. Waste Package Surface Temperature vs. Time

the long ventilation period, and by dissolved solids in water that drips onto waste packages when the temperatures are low enough for liquid water to exist. Based on samples of dusts in the air near the portal of the underground Exploratory Studies Facility at Yucca Mountain, the expectation is that the dusts that deposit on waste packages during the ventilation period are likely to contain the following moieties: calcium, sodium, magnesium, potassium, ammonium, chloride, sulfate, bicarbonate, nitrate, fluoride, formate, acetate, and propionate.[3] Because oxygen will be present in the gas phase at all times except during part of the thermal pulse, the environment is mildly oxidizing. Anions in the water tend to make the average pH neutral-to-basic, but local situations could exist where, because of concentration, hydrolysis, radiolysis, or other processes, low-pH environments could exist temporarily.

Humidity. Before repository closure, the average relative humidity in the tunnels will be very low because of the low relative humidity of the arid desert air used for ventilation. As the tunnel rock heats up after closure, however, water remaining in the pores of the rock will vaporize, driving the air away from the tunnels and resulting in an atmosphere that is essentially entirely water vapor. After the rock passes its peak temperature and begins to cool, water vapor will begin to condense and air will be drawn back into the repository volume. After the rock surrounding the tunnels cools to below the boiling point of water (96°C at the elevation of the proposed repository, approximately 1000 m above sea level), condensing water vapor and water slowly percolating downward through the mountain from surface precipitation will resaturate most of the pores of the rock surrounding the tunnels, resulting in a relative humidity of near 100 percent, particularly when the temperature of the waste package surface also drops below the boiling point of water.

Liquid water. As the relative humidity approaches 100 percent, at least a thin film of water (perhaps only a few molecules thick) will exist on waste package surfaces. The film will exist at lower relative humidities if there are soluble salts on waste package surfaces, because the salts will depress the equilibrium vapor pressure of the water. Thus, the assumption must be that liquid water will exist on the surface of a waste package whenever the surface temperature is below 96°C.

Liquid water also can exist on waste package surfaces at temperatures above boiling, indeed well above boiling, via deliquescence if certain salts are present. For example, certain salt mixtures, such as 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. However 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 highly relevant to the performance of the Alloy 22 outer shells of the containers.

CORROSION ISSUES

Alloy 22 is an extremely corrosion-resistant material, and the apparent service conditions, except for the required extraordinarily long service life, are relatively benign. This long service life makes both localized corrosion and generalized corrosion significant concerns. Stress corrosion cracking (SCC) also is a concern, but there is no evidence that

significant SCC of Alloy 22 will occur in even the harshest proposed environments that are expected to be encountered in the repository. DOE and NRC are pursuing some limited studies of SCC of Alloy 22.

General Corrosion

Base general corrosion rate. DOE has developed a comprehensive set of long-term (5 years) experimental data for the general corrosion rate of Alloy 22 at temperatures of 60°C and 90°C in solutions that are believed to be relevant to Yucca Mountain.[4] Soon, the dataset will be augmented by 9½-year data. The 5-year data and data with less time exposure indicate that general corrosion rates decrease with time, as would be expected. The expectation also is that the 9½-year data will show the trend continuing. In its modeling of general corrosion, DOE conservatively uses a fixed 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. The model that DOE uses is equivalent to assuming that the passive layer is shed every 5 years for a new passive layer to begin building. DOE's model for general corrosion overpredicts recession rates significantly, in our opinion.

Unfortunately, however, the 60°C and 90°C temperatures and the environments used to determine the base general corrosion rate are too close, or too similar, to discern variation in corrosion rate with temperature or environment. DOE assumes that the base general corrosion rate applies for 60°C and any environment to be encountered in Yucca Mountain. Then DOE uses short-term, electrochemical (polarization-resistance) experiments at different temperatures to determine the variation of general corrosion rate with temperature. As might be expected, the short-term experiments showed higher general corrosion rates than the long-term experiments.

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.[4]

The corrosion rates then were fit to an Arrhenius-type relationship,

$$R_T = A \exp(E_a/RT)$$

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.

Comments. The Arrhenius form is appropriate, particularly because the temperature range of interest is so narrow, 25ºC - 210ºC. The value for the apparent activation energy is reasonable. The corrosion rates obtained from the polarization-resistance measurements are unlikely to be stable, but because the purpose of the experiments was to determine the variation of corrosion rate with temperature and not 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 60-100ºC do not seem appropriate. However, even assuming the most severe conditions that might be encountered in the repository, it appears unlikely that the containers would fail because of general corrosion of the Alloy 22 for millennia. A semiquantitative illustration of the metal loss due to corrosion has been provided by Payer.[5] (See Figure 3.) Payer pointed out that the thickness of the Alloy 22 outer shell of the waste package corresponds approximately to the height of a stack of 12 U.S. quarters and that for below-boiling corrosion rates of 1µm/yr to 0.01µm/yr, 1,600 to 160,000 years would be required to penetrate the thickness of just one quarter.

Figure 3. Corrosion Illustration

Localized Corrosion

For predicting the postclosure performance of the Alloy 22 outer barrier of the waste package with regard to localized corrosion, DOE divides localized corrosion into two parts: localized corrosion caused by seepage of water onto the waste package surface, and localized corrosion due to deliquescence of hydroscopic salts in dust deposited on the waste package by ventilation in the 50-100 year (or longer) period before closure of the repository.

Localized Corrosion Due to Seepage

DOE assumes that seepage onto the waste package cannot occur when the surface of the waste package is above 120°C and therefore that localized corrosion of the waste package due to seepage cannot occur when the surface of the waste package is above 120°C. At and below 120°C, DOE assumes that localized corrosion will initiate on the part of the waste package surface contacted by seepage if the composition, temperature, and pH of the seepage water are such that the corrosion potential of Alloy 22, E_{corr}, immersed in 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. In general, the Board has concurred that this 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.

To determine E_{corr}, DOE has measured open-circuit potentials versus time for various Alloy 22 samples in model aqueous solutions over a temperature range of 25-90ºC for periods

of up to 3 years. DOE then uses multiple linear regression on the data to fit a model for E_{corr} as a function of nitrate concentration, chloride concentration, temperature, and pH, i.e.:

$$E_{corr} = f([NO_3], [Cl], T, pH)$$

where E_{corr} is corrosion potential in mV vs. a saturated silver chloride electrode,
        [NO_3] is the nitrate ion concentration, molal
        [Cl] is the chloride ion concentration, molal,
        T is temperature, °C, and
        pH is the negative logarithm of the hydrogen ion concentration.

Figure 4 is an illustration of a small portion of the data used for fitting the E_{corr} function. It shows corrosion potential versus time for a number of Alloy 22 samples in various environments at 90ºC . More information about the dataset shown in Figure 4 and other data used to fit the function, f, can be found in Reference 4.
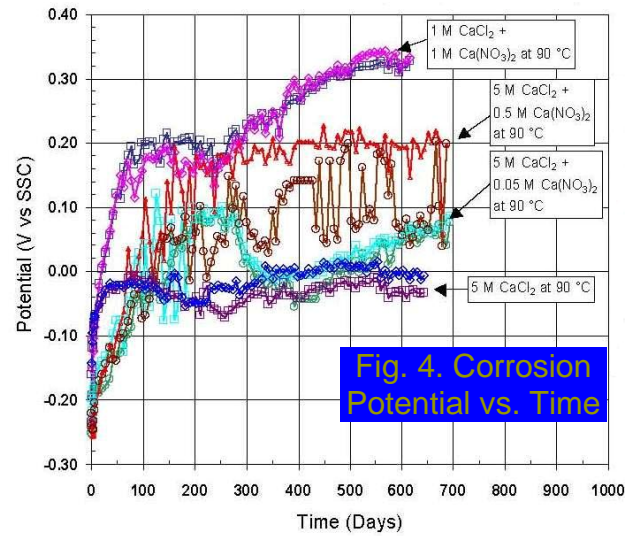
To determine E_{crit}, DOE uses the ASTM G61-86 cyclic potentiodynamic polarization (CPP) technique to determine the repassivation potentials[3] for a number of Alloy 22 samples in a variety of aqueous solutions. Figure 5 is a stylized representation of a typical CPP curve for a highly corrosion resistant alloy. The crossover point, E_R, is where the forward scan intersects the reverse scan. The resultant data were fit to express critical potential as a function of nitrate concentration, chloride concentration, and temperature, i.e.:

Fig. 4. Corrosion Potential vs. Time

$$E_{crit} = g([NO_3], [Cl], T)$$

where E_{crit} is critical potential in mV vs. a saturated silver chloride electrode, and [NO_3], [Cl], and T are as defined above.

More information about the data and the function, g, may be found in Reference 4.

Comments. DOE assumes that localized corrosion of Alloy 22 will initiate if E_{corr}, as represented by function f, is greater than E_{crit}, as represented by function g. The data on which function f is based are long-term data — up to 3
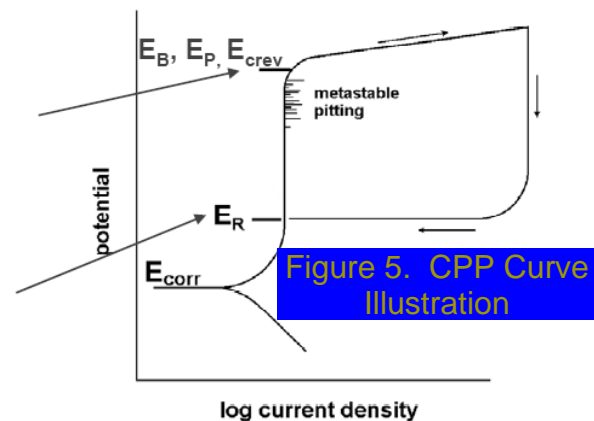

Figure 5. CPP Curve Illustration

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[3] Repassivation potential is taken as the point at which the reverse scan curve crosses the forward scan curve. E_{crit} is assumed to equal the repassivation potential.

years in many cases but at least 8 months in all cases. On the other hand, the data on which function g is based are short-term data — a matter of a few days. The question of whether mixing short-term data and long-term data to form the basis for predicting localized corrosion initiation is appropriate then must be asked. If so, is doing so 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 (Figure 4 is not atypical), also making the stability of the test results questionable.

A problem with interpreting some of the data is that DOE's tests of long-term corrosion, many with crevice formers and others boldly exposed, apparently do not corroborate the model that DOE has developed by fitting E_{corr} and E_{crit} equations to the electrochemical data. For example, according to the localized corrosion model, some of the tests used to develop the generalized corrosion model discussed above should have shown localized corrosion. However, none of them did. Similarly, many 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 occurred 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. Once localized corrosion initiates, the assumption is that it will propagate at a constant rate, ranging from 12.7 µm/yr to 1270 µm/yr.[4] 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 should be used only 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 above results in penetration of the waste packages, once localized corrosion has been initiated, in a matter of 20 years, which, for a million-year (or longer) 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. Even more extreme 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 dangerous radionuclides becomes the responsibility of the waste form and natural barriers.

Localized Corrosion Due to Deliquescence

Brines can form on waste package surfaces at temperatures of up to 210°C because of deliquescence, so the possibility of localized corrosion during the thermal pulse period

(essentially the ~100- to 1000-year period immediately after repository closure, during which the waste package surfaces are above boiling) 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 $[NO_3^-]/[Cl^-]$ ratios of 0.5 or 7.4 at temperatures of 160°C and 220°C.[6] Localized corrosion was observed in all cases but was not anticipated in the solutions with nitrate-to-chloride ratios of 7.4.[4] The test solutions were made by dissolving sodium chloride, sodium nitrate, and potassium nitrate. 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 physical or biological processes, 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, the possibility of other high-temperature corrosive environments has not been ruled out.

The Board sponsored a workshop on localized corrosion in September 2006 to discuss deliquescence-based corrosion of Alloy 22 in repository-relevant environments. At that meeting, DOE presented a strong case suggesting that the nitrate-to-chloride ratios in the repository were sufficiently high that localized corrosion could not occur. In addition, several workshop participants suggested that 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 is 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 210ºC), and (2) determine the relative migration rates for the migration of nitrate and chloride ions into crevices. At this time, neither of these recommendations appears to have been implemented, and thus the possibility of localized corrosion due to deliquescence at high temperatures remains uncertain.

At lower temperatures, i.e., waste package surface temperatures of 100ºC and below, many pure salts and salt mixtures will persist on waste package surfaces that can deliquesce in the near-100 percent relative humidity environment that will exist in the repository after the thermal pulse. Some of these salts can form corrosive brines, according to the E_{corr}, E_{crit} localized corrosion model discussed above.

OBSERVATIONS

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 a conservative application of physical and chemical principles, predicting or bounding behavior for this long a period leaves one with a vague

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

uneasiness. 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.

Although the general corrosion of the containers may be reasonably predicted, 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, generalized corrosion) at elevated temperatures.

It should not be concluded, however, that localized corrosion of Alloy 22, even if it results in a breach of the containers, will necessarily compromise the integrity of the repository. Even assuming complete penetration of Alloy 22, corrosion of the inner stainless steel must occur, followed by transport of aggressive species across the gas within the container to the fuel rod assemblies and penetration of the zircaloy cladding on the assemblies, before the first spent-fuel material will be in contact with the repository environment. Corrosion of the spent fuel then must occur, followed by transport of the corroded 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) before radionuclides can reach the biosphere.

Accordingly, although the "defense-in-depth" concept adopted by virtually every national nuclear waste isolation program must be followed, corrosion of the containers will not 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 will lead to public credence.

CONCLUSIONS

Much of this discussion has been based on the opinions of members of the Board and its staff on the current state of the corrosion evaluation programs of DOE regarding the proposed disposal containers for high-level civilian and military radioactive waste to be emplaced at Yucca Mountain. It must be reiterated that these discussions are individual opinions and not Board opinions. It also should be reiterated that the Board does not set requirements for the technical programs of DOE related to nuclear waste disposal, but only reports to the Secretary and Congress on the relevance and quality of the technical aspects of the program for the safe disposal of high-level nuclear waste in Yucca Mountain. In this spirit, we offer the following opinions.

Because of the extremely long service life, we agree that caution is appropriate in predicting long-term corrosion. Conservatism is applied to predicting general corrosion — including the assumption that the general corrosion rate does not decline with time and using an average rate taken over a 5-year period rather than the rate at the end of the period. We

agree that applying these conservatisms is prudent, although their application significantly overstates the true corrosion rate.

Overconservatism, however, may lead to distortion in decision-making, and this possibility may be the case for the model for localized corrosion due to seepage, where conservatisms are piled on top of conservatisms to the point of predictions being unrealistic. Although there well could be insignificant localized corrosion due to seepage, DOE's models predict that potential releases of radionuclides from waste packages due to localized corrosion could be significant. This elevates, perhaps incorrectly, the importance of the titanium drip shield, because it functions to keep seepage off of waste packages.

Although DOE's models for localized and generalized corrosion of Alloy 22 have many conservatisms, there are three instances of nonconservatisms — or at least uncertainties — in the models, and all have to do with deliquescence. One is the possibility of localized corrosion at high temperatures (above the boiling point of pure water) due to formation of brines by deliquescence of salts in the dust deposited on waste package surfaces. Although DOE has a large body of data and analyses to support the position that localized corrosion due to deliquescence at high temperatures would be insignificant, that body is not quite enough, in our opinion. Experiments for determining the minimum ratios of nitrate to chloride that are protective need to be carried out over the *entire* high-temperature range (i.e., 120ºC - 210ºC), and transference numbers for nitrate and chloride need to be determined for this temperature range. The second nonconservatism is DOE's omission of localized corrosion due to deliquescence at below-boiling temperatures. Although localized corrosion due to deliquescence could well be insignificant at below-boiling temperatures, DOE has not done analyses to show that this would be the case. The third nonconservatism, or at least uncertainty, was addressed in a recent letter from the Board to DOE.[8] The nitrate-to-chloride ratio is important for preventing localized corrosion. Therefore, DOE should show that preventive nitrate-to-chloride ratios persist under repository conditions by investigating the full range of factors that could affect nitrate-to-chloride ratios, such as reactions with organic materials in the dust, acid gas devolatilization, radiolysis, etc.

Last, as discussed above under "<u>Service period</u>," a panel of the National Research Council recommended that health effects from the repository be measured at the time of peak risk. Because the risk comes from releases of radionuclides from the repository, and the repository cannot have releases until after waste packages fail, and because the time of peak risk probably would fall after approximately half of the waste packages fail, it is reasonable to ask when this time would occur. According to results presented in the draft SEIS (reference 2), DOE's models predict that only about 10 percent of the waste packages would have failed at a million years, and less than 0.5 percent of the area of those waste packages would be gone at that time. Clearly then, the peak risk would come later. As recommended by the panel, DOE should carry out the calculations to the time of peak dose.

ACKNOWLEDGEMENT

and 7, respectively. The views in this paper are those of the authors and not necessarily those of the U.S. Nuclear Waste Technical Review Board.

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