UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD
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November 25, 2003

Dr. Margaret S. Y. Chu
Director
Office of Civilian Radioactive Waste Management
U.S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585

Dear Dr. Chu:

We are pleased to transmit a technical report prepared by the Nuclear Waste Technical Review Board (Board) that includes additional analyses supporting the Board's conclusions related to corrosion in its October 21, 2003, letter to you. Although the enclosed report touches on a variety of corrosion issues, its main focus is the potential for deliquescence-induced localized (or crevice) corrosion of the Alloy 22 waste packages in the Department of Energy's proposed high-temperature repository design. The conditions used by the Board for its analyses were presented by the DOE at the Board's January and May 2003 meetings. The report also evaluates the vaporization barrier and capillary barrier concepts that were discussed at the May meeting. Appended to the report are some additional technical comments by Dr. Michael Corradini.

Based on its review of data gathered by the DOE and the Center for Nuclear Waste Regulatory Analyses, the Board believes that all the conditions necessary to initiate localized corrosion of the waste packages will likely be present during the thermal pulse because of the deliquescence of salts on waste package surfaces, and thus it is likely that deliquescence-induced localized corrosion will be initiated during the thermal pulse. Corrosion experiments indicate that localized corrosion is likely to be initiated if waste package surface temperatures are above 140°C and if concentrated brines, such as would be formed by the deliquescence of calcium and magnesium chloride, are present. Limited data examined to date indicate that dust, which would be present in the proposed tunnels and which would be deposited on waste packages, contains calcium chloride and magnesium chloride salts in amounts sufficient for the development of concentrated brines through deliquescence. (Crevices are widespread on the waste packages, arising from their design as well as from contacts between the metal and dust particles.)

Thus, the Board believes that under conditions associated with the DOE's current high-temperature repository design, widespread corrosion of the waste packages is likely to be initiated during the thermal pulse. Once started, such corrosion is likely to propagate rapidly even after conditions necessary for initiation are no longer present. The result would be perforation caused by localized corrosion of the waste packages, with possible release of radionuclides.

The Board is aware that the DOE believes that the conditions in the repository will not promote significant corrosion. The DOE points to data, gathered using thermogravimetric apparatus (TGA), to demonstrate that the conditions necessary to initiate localized corrosion will be present only briefly. The Board has evaluated these data and finds them inadequate to support the DOE's claim for the following reasons.

- Brines used in the TGA experiments may not be representative of those that would form on the waste packages because of deliquescence.
- The metallic coupons used in the experiments did not contain crevices.

- The TGA experiments have been run only over narrow ranges of temperature and relative humidity.
- The experimental apparatus is an "open" system that may not approximate short-term behavior of the microenvironment associated with crevices.
- The results from other experiments conducted by the DOE seem contradictory.

The DOE also holds that the conditions under which localized corrosion might occur are extreme and unlikely. The information provided to the Board to date, however, does not form a compelling basis for that contention. For example, the DOE maintains that the presence of nitrates and an insufficient amount of calcium chloride in the proposed repository tunnels will limit localized corrosion. The DOE's own data, however, indicate that nitrate may not be protective at temperatures higher than 140°C. Furthermore, as noted above, the Board has concluded that more than enough chloride would be present in the dust from the tunnels to lead to widespread localized corrosion.

Thus, the DOE's belief that the geochemical environment on the waste package surfaces *will not* lead to corrosion lacks a strong technical basis. Absent that basis, the Board cannot ignore the clear and unambiguous implications of the corrosion and deliquescence experiments.

As stated in our October 21 letter, the Board realizes that decision-makers must take into account considerations beyond technical and scientific ones when making program decisions. However, because of the significance of the waste packages to the proposed repository system, the Board believes that the potential for localized corrosion during the thermal pulse should be addressed. From a technical perspective, the problems related to localized corrosion that are described by the Board in the enclosed report could be avoided if the repository design and operation were modified. The data currently available indicate that perforation of the waste packages caused by localized corrosion is unlikely if their temperatures are kept below 95ºC.

The Board looks forward to continuing its review of the DOE's investigations at Yucca Mountain, including those dealing with the integrity of the waste packages.

Sincerely,

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Michael L. Corradini, Chairman

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U.S. Nuclear Waste Technical Review Board

November, 2003

Executive Summary

At meetings of the U. S. Nuclear Waste Technical Review Board (Board) held in May and September 2003, the U. S. Department of Energy (DOE) made five presentations about how its high-temperature repository design proposed for Yucca Mountain in Nevada might behave. The presentations included an extended discussion of how the natural system and the waste packages might function over many thousands of years. This paper presents the Board's views on the validity of the DOE's technical arguments, made at those meetings, about repository behavior. The paper concentrates on the first 1,000 years after the repository is closed. During that time, commonly referred to as the "thermal pulse," temperatures within the repository's drifts would be above the boiling point of water, reaching a high of 160°C to 180°C. In the following evaluation, the Board also considers other related issues and relies on technical analyses carried out by the DOE but not presented at the May or September meetings.

This paper is not designed to present an exhaustive analysis of the entire repository system as proposed by the DOE. Some elements of that system are not addressed at all, such as the role the interior waste package and the design of the waste form might play in inhibiting the mobilization of radionuclides and how the unsaturated zone below the repository horizon and the saturated zone might delay transport of radionuclides.

Drift Conditions During the Thermal Pulse

The DOE maintains that its temperature calculations for repository tunnel temperatures during the thermal pulse are sufficiently accurate or conservatively modeled. The Board believes that the calculations may be inaccurate because (1) the DOE's rock-mass thermal conductivity estimates for the lower lithophysal rock (where at least 80 percent of the drifts will be located) may be too high; (2) the insulating effect of rockfall and drift degradation on the waste package surface are not included in the DOE's models; and (3) the effects of in-drift and in-rock natural ventilation and air circulation after repository closure have not been accounted for. The DOE argues that relative humidity in repository tunnels also is adequately or conservatively modeled. The Board believes that the relative humidity calculations may be inaccurate because they depend on inaccurate temperature calculations and because they do not take into account the effects of natural ventilation and air circulation after the repository is closed.

Localized Corrosion of the Alloy 22 Layer of the Waste Package

Deliquescence-induced corrosion. Deliquescence is the absorption of atmospheric water vapor by a solid salt to the point where the salt dissolves into a saturated solution. All salts that are soluble in water exhibit the property of deliquescence to some degree. Deliquescence is important because it is a mechanism by which liquid water could exist on waste package surfaces during the thermal pulse.

All the conditions necessary for deliquescence will be present during the thermal pulse for nearly all waste packages. The DOE, however, believes that corrosion will not take place because the period of existence of conditions necessary for crevice corrosion would be too brief for measurable corrosion to occur and because there always will be sufficient amounts of nitrate to inhibit localized corrosion. In addition, the DOE believes that insufficient chloride, which is needed for corrosion, is present at Yucca Mountain to do significant damage to the waste packages.

The Board believes that the experimental evidence is not adequate to demonstrate that corrosive conditions will be present only briefly. The DOE has not established whether nitrate will inhibit localized corrosion over the entire range of temperatures in which brines could exist. Furthermore, based on the DOE's estimates, the Board believes that there is ample chloride to cause a significant amount of localized corrosion. Thus, the Board believes that deliquescence-induced localized corrosion is likely to be initiated during the thermal pulse in the DOE's high-temperature repository design. Localized corrosion is likely to propagate during the remainder of the thermal pulse and is likely to continue even after the thermal pulse at temperatures below 95°C. Because of the high temperatures of the current repository design and operation, this localized corrosion will result in the perforation of the waste packages.

Seepage-induced corrosion. Making any definitive statement about whether seepage during the thermal pulse will lead to degradation of the waste packages is very difficult. The Board believes that the possibility of seepage where the rocks are above boiling cannot be excluded but that seepage most likely would be limited. The DOE's analyses of water chemistries and their corrosive potential are extremely complex and suffer from empirical and theoretical weaknesses. Thus, the Board does not have a high degree of confidence in the DOE's conclusion that any seepage water would be dilute or noncorrosive, because the methods used in the DOE's analyses have significant technical uncertainties. Although the drip shields may act to protect waste packages from dripping water, the titanium of which they are constructed may itself be susceptible to corrosion during and after the thermal pulse.

Factors that might exacerbate corrosion. The Board believes that the current waste package design, which adds two circumferential welds to hold the trunnion collar sleeve and a long, tight crevice between the two welds, could exacerbate any corrosion that might be initiated. The Board also believes that phase instabilities in the metal or near extended welds, created by high temperatures used in fabricating the waste packages, could exacerbate corrosion during the thermal pulse.

Implications

During the several thousand years after the thermal pulse, the DOE maintains that a capillary barrier will be established that prevents almost all the water that percolates down to the drifts from actually entering them. The DOE points to modeling results, observations within Yucca Mountain, and natural and man-made analogues to support its position. The Board believes that the capillary barrier could weaken because of drift degradation brought on by thermal stresses and seismic events. This weakening, coupled with the disappearance of any vaporization barrier and the postulated increase in percolation arising from climate changes, could allow liquid water to seep into the drift. If the water contacts the waste package, which might have been corroded during the thermal pulse by the localized corrosion processes described in this paper, more radionuclides could be mobilized and transported outside the drifts than the DOE now estimates.

Board conclusions

Corrosion. Based on the DOE's calculations of temperature and relative humidity in its currently proposed high-temperature design, all the conditions necessary to initiate localized corrosion of the waste packages will likely be present during the thermal pulse because of the deliquescence of salts on waste package surfaces, and thus it is likely that deliquescence-induced localized corrosion will be initiated during the thermal pulse. Furthermore, in the Board's opinion, the DOE has not firmly established its conclusion that corrosion would not be caused by water seeping into drifts during the thermal pulse. Localized corrosion is likely to propagate during the remainder of the thermal pulse and is likely to continue even after the thermal pulse at temperatures below 95°C. As a result of the high temperatures of the current repository design and operation, this process will result in the perforation of the waste packages. The data currently available to the Board indicate that perforation caused by localized corrosion is unlikely if waste-package surface temperatures are kept below 95ºC.

Multiple barriers and defense-in-depth. If the Board's interpretation of the data and analyses presented by the DOE is correct, an important engineered element of the DOE's current repository design, the waste package, will be susceptible to corrosion during and following the thermal pulse. There also may be more seepage, and thus potentially more and earlier transport of at least some radionuclides, than the DOE now projects. The contribution of the other natural barriers to radionuclide isolation depends on complex modeling calculations whose uncertainties are high and will remain high for many years. Therefore, although some combination of multiple barriers will be operating at various times in the repository, the capability of those barriers to provide meaningful defense-in-depth—that is, redundancy—in isolating and containing radionuclides, is unclear with the DOE's high-temperature design.

Do the Board's technical conclusions have significant effect on performance calculations for the repository system *as a whole*? Although a precise statement about whether, or how much, dose might be increased or the safety margin decreased cannot be made given the existing uncertainties, the Board believes that the implications of the Board's conclusions for repository system performance could be substantial. Therefore, it is incumbent on the DOE to demonstrate unambiguously the reliability and safety of any design concept for Yucca Mountain.

I. Introduction and Background

Over the last 20 years, the U. S. Department of Energy (DOE) has been developing a set of arguments about how a repository system constructed at Yucca Mountain in Nevada might isolate and contain high-level radioactive waste and spent nuclear fuel for many thousands of years.[1] To support the arguments, the DOE has collected data from extensive site investigations that have lasted more than a decade and from laboratory experiments of somewhat shorter duration. It also has used natural and man-made analogues to gain insights into processes and phenomena that may affect repository performance over long time frames or large distances.

At meetings of the U. S. Nuclear Waste Technical Review Board held in May and September 2003, the DOE synthesized some of these site investigations and laboratory studies and described in considerable detail how two elements of its proposed system, the environment associated with the underground tunnels and the waste package, would work together to prevent the release of radioactive waste.[2] In this paper, the Board evaluates the DOE's technical arguments for these elements and some other related ones. The primary focus of its evaluation is the circumstances under which localized corrosion of the waste packages might be initiated. Because the conditions to which the packages are exposed affect the likelihood of corrosion, the Board's evaluation will necessarily touch on the question of whether the environment is likely to behave as the DOE claims. Finally, the Board discusses some implications of its evaluation and presents its major conclusions.

This paper is not designed to provide an exhaustive analysis of the entire repository system as proposed by the DOE. Some elements of that system are not addressed at all, such as the role the waste form might play in inhibiting mobilization of radionuclides or the roles the unsaturated zone below the repository horizon and the saturated zone might play in delaying transport of radionuclides.

II. Brief Description of the Proposed Repository System

A. Location and Design

The site of the proposed Yucca Mountain repository is on federal government land in the Mojave Desert in Nye County in southern Nevada, approximately 160 kilometers northwest of Las Vegas. The area surrounding the site receives an average of about 170 millimeters (mm) of precipitation per year.[3]

Yucca Mountain is composed of layers of volcanic rock (tuff) laid down approximately 12 to 13 million years ago. The underground part of the repository would be composed of a series of drifts (tunnels) located about 300 meters below the surface of Yucca Mountain and about 300 meters above the present water table. Thus, the drifts would lie in the unsaturated hydrogeologic zone. About one-fifth or less of the drifts would be in the middle nonlithophysal unit; the rest would be below in the lower lithophysal unit.[4] In the current DOE design, the drifts would be approximately 600 meters long and 5.5 meters in diameter, and their centers would be 81 meters apart. On average, only a small fraction of the precipitation that falls on the crest of the mountain percolates down to the level where the DOE proposes to construct the drifts.

The current design calls for the radioactive waste to be placed in large packages composed of two metallic shells. The outer shell is 20 mm thick and is made of a nickel-based material, Alloy 22.[5] The inner shell is 50 mm thick and is made of stainless steel. Alloy 22 is generally very corrosion resistant. This metal has been in commercial use for about 25 years, although it is an evolutionary improvement over other alloys with high nickel-chromium-molybdenum contents that have been available longer. Various types of stainless steels have been in general use for approximately a century. In addition, overlapping, interlocking segments, approximately 5.8 meters long and made of 15-mm-thick titanium grade 7, would be placed over the waste packages just before the repository is closed to form a continuous drip shield in each drift. Ideally, the shields would divert any dripping water from the waste packages.

The DOE's proposed repository system contains other natural and engineered barriers that would contribute to waste isolation and containment. For example, the waste form and fuel cladding make mobilizing the radioactive waste more difficult. The invert on which the waste package rests could retard radionuclide transport either in liquid or solid form (colloids). Both the unsaturated zone beneath the drifts and the saturated zone beneath Yucca Mountain could slow the movement of the radioactive waste.

B. Drift Conditions During the Thermal Pulse

Temperature

Radioactive waste generates heat as it decays. The heat will be transferred to the waste packages, to the air and other materials surrounding the packages, and to the rocks (and the water in the rocks) that form the drift walls, thereby increasing their temperatures. By adjusting the amount of waste in a package, the distance separating the packages, the volume and duration of forced ventilation, and the time of emplacement, among other things, repository designers can influence to some extent how high temperatures eventually will rise. The DOE has chosen a repository design in which waste package temperatures are calculated to peak somewhere between 160°C and 180°C several decades after the proposed repository is closed. (Waste packages at the ends of emplacement drifts, however, would be unlikely to exceed the boiling point of water.[6]) The average temperature is calculated to fall below 96°C (the boiling point of pure water at the elevation of the drifts at Yucca Mountain) approximately 1,000 years after the proposed repository is closed. The period during which temperatures would be above boiling is called the "thermal pulse."

Realistic calculations of tunnel and waste package temperatures are necessary for understanding the environment to which waste packages would be exposed after a repository is closed. In addition to the design variables mentioned above that are under the control of the repository designer, the calculated temperature will depend on the values and variances of three critical variables associated with the geologic regime in which the repository would be constructed.[7]

- *Rock-mass thermal conductivity.* This is a measure of the rate of heat flow by conduction from an area of higher temperature to an area of lower temperature. Thermal conductivity is a function of temperature and moisture content in the rock. The lower the conductivity, the hotter the rock near the tunnel wall will get and vice versa. Spatial and temporal variances will cause localized spots to heat either more or less than the average.

- *Drift degradation and rockfall.* Over time, it is likely that some rock will spall off from drift walls and ceilings and land on the drip shields. If the drip shields have degraded or shifted, the rocks could land directly on the waste packages. In either case, the rocks could form an insulating blanket. The greater the drift degradation, the hotter the waste packages and the drip shields will get and vice versa.

- *Amount of natural ventilation and air circulation.* After the repository is closed, air will continue to move within the drifts, driven by differences in air density caused by the heat generated by the waste packages. When the flow includes a path to the surface through, for example, fractures and faults, it is called "natural ventilation." When the flow is confined to a closed path within the drifts and fractures, it is called "natural air circulation."[8] In general, the greater the natural ventilation and air circulation, the cooler the rock typically will get and vice versa.

The Board believes that the DOE's temperature calculations may be inaccurate because the DOE's estimates of rock-mass thermal conductivity may be too high. Recently reported field testing, laboratory testing, and statistical analyses all point to a lower mean value for rock-mass thermal conductivity than the one used in the DOE's latest published temperature projections.[9] If a lower mean value and revised distributions of thermal conductivity are adopted, the predicted maximum drift wall and waste package temperatures may increase.

The Board believes that the DOE's temperature calculations also may be inaccurate because they do not include the effects of drift degradation and rockfall. On the basis of large-scale fracture mapping and analysis principally of the middle nonlithophysal unit, the DOE concluded that the effects of drift degradation on performance are limited, and therefore additional sensitivity and uncertainty analyses are not necessary.[10] It is unclear, however, whether that conclusion holds for rocks in the lower lithophysal unit.[11]

The Board also believes that the model relied on by the DOE does not realistically represent the processes that cause heat to be removed from the repository because of natural ventilation and air circulation.[12] If these effects were fully accounted for, repository temperatures could be lower than now estimated.

Relative Humidity

Although the proposed underground facility at Yucca Mountain would be constructed in formations located in the unsaturated zone, a substantial amount of water is found in the pores of the nonlithophysal and lithophysal units.[13] Consequently, water vapor continuously migrates into the drifts. The amount present would be determined, in part, by how much is carried off both by forced ventilation (before repository closure), natural fluctuations in barometric pressure, and buoyancy-driven flow induced by the elevated temperature of the waste package.

From the standpoint of corrosion, the key parameter relating to water vapor present in the drift atmosphere is the relative humidity during the thermal pulse. The hotter the conditions are, the lower the relative humidity. The bulk humidity of the air inside the drifts can be estimated readily from first principles of chemistry and physics for a particular air temperature. According to the DOE, relative humidity would reach a minimum of 10-20 percent during the first 100 years after the repository is closed and then would rise to above 80 percent by the time the thermal pulse ends.[14] However, because the DOE's temperature calculations may be inaccurate and because natural ventilation and air circulation are not accounted for in the DOE's projections, the bulk relative humidity in the drift at a given time may be higher or lower than the DOE now estimates.

The DOE's views and the Board's evaluation of those views are summarized in Table 1.[15]

Table 1: Drift Conditions During the Thermal Pulse

Technical Item	*DOE Views*	*Board Evaluation*
Temperature	Temperature is adequately or conservatively modeled.	1. The values that the DOE uses for thermal conductivity of the lower lithophysal rock may be too high. Thus, temperature calculations may be underestimated. 2. The DOE does not account for the insulating effect of rockfall due to drift degradation on waste package surface temperatures. Thus, temperature calculations may be underestimated. 3. The DOE does not take into account the effects of in-drift and natural ventilation and air circulation after the repository is closed. Thus, temperature calculations may be overestimated.
Relative humidity	Relative humidity is adequately or conservatively modeled.	1. Because the DOE's temperature calculations may be inaccurate, the DOE's relatively humidity calculations also are likely to be inaccurate. 2. The DOE does not take into account the effects of natural ventilation and air circulation after the repository is closed. Thus, the relative humidity calculations may be inaccurate.

In general, the Board believes that there are significant parametric and conceptual uncertainties associated with the DOE's representation of repository tunnel environments during the period after the repository is closed. For example, if the thermal conductivity of the rock has been overestimated, the temperatures in the DOE's repository design may be higher than the DOE currently predicts. If the effects of natural ventilation and air circulation on the highly fractured rock at Yucca Mountain were fully taken into account, temperatures might be lower (and relative humidity higher) during the thermal pulse than estimated in the DOE's repository design. Because the sources of inaccuracy act in opposing directions, determining whether the DOE's calculations of temperature and relative humidity are too high, too low, or just about correct is difficult. In the analyses that follow in this paper, however, the Board uses the DOE's calculations of temperature and relative humidity as presented at the May 2003 meeting.

III. Technical Issues Related to Waste Package Corrosion During the Thermal Pulse

In its *Yucca Mountain Site Suitability Evaluation*, the DOE made the following assertion in early 2002: "…the engineered barriers would primarily degrade because of very slow processes, such as aqueous general corrosion. Consequently, the lifetimes of the…waste package[s] are very long."[16] Since then, the DOE and others have obtained a great deal of new experimental data and other information on conditions during the thermal pulse and on possible corrosion during the thermal pulse. Essentially all of the new data and information were discussed at the Board's January and May 2003 meetings.

This section discusses what is known about the waste package's outer shell material (Alloy 22), the environments that might be found around the outer shell at Yucca Mountain, and corrosion in those environments. The discussion concentrates on the thermal pulse period, roughly the 1,000 years after repository closure. This section also describes the DOE's views on conditions[17] and resultant possible corrosion and the Board's evaluation of those views.

Over the last few years, the Board has followed closely the DOE's analyses of how Alloy 22 might behave when exposed to temperatures significantly higher than the boiling point of water. The Board previously expressed concern about the potentially large corrosion uncertainties. Data collected relatively recently heighten those concerns.

There are many forms of corrosion: for example, general corrosion, localized corrosion, and environmentally assisted cracking. General corrosion occurs more or less uniformly over the entire surface of a metal and usually results in wastage of the metal surface. Depending on the environment in which general corrosion occurs, it may progress at a constant rate, at a rate that decreases with time, or at a rate that increases with time. Localized corrosion occurs in specific areas on the surface of a metal, often widely spaced, but it may proceed very rapidly and often increases with elapsed time. The ratio of the depth of corrosion penetration to the nominal diameter of the area affected is generally high for localized corrosion. Localized corrosion processes are particularly insidious because initiation is difficult to predict and propagation rates can be very rapid.

Two closely related forms of localized corrosion are crevice corrosion and pitting corrosion. Crevice corrosion generally requires some occluded regions where access by the bulk environment is restricted, often by diffusional processes. Examples of regions susceptible to crevice corrosion are gasketed surfaces, mating surfaces, joints, and solid precipitates deposited on metal surfaces either through evaporation of near-saturated solutions or through physical deposition, e.g., dust or debris in contact with metal surfaces. The environment inside of crevices is generally quite different from bulk environments and is most often more chemically aggressive. Pitting corrosion begins on free surfaces. However, once a pit begins to propagate, the environment inside of the pit essentially approaches that of crevices. Environmentally assisted cracking, such as stress-corrosion cracking, generally is caused by a combination of corrosive chemical environments, often specific to metal or alloy families, and static or cyclic tensile stresses.

The rate of corrosion of a metal depends on the characteristics of the metal and the environments (pressures, temperatures, phases, and chemical compositions) to which the surfaces of the metal are exposed. In theory, if the characteristics of a metal and the environments to which it is exposed over its lifetime are known and if sufficient experimental data exist for the corrosion performance of the metal in those environments, then the corrosion lifetime of the metal can be predicted with accuracy and confidence. In practice, not everything is known about the characteristics of the metal or about the environment to which it would be exposed, there are never enough data, and the data do not replicate or even approximate all of the conditions under which the metal will be used. These circumstances clearly hold with respect to an Alloy 22 waste package that might be emplaced in Yucca Mountain.

A corrosion engineer's first line of inquiry in choosing candidate materials of construction is the general corrosion rate. If the general corrosion rate is known with confidence, one may determine from first principles the thickness of material required to perform for the life of the system. Conversely, for a given thickness of material, one may determine how long the material will survive until the remaining thickness becomes unacceptable. In the case of the Yucca Mountain Project, one needs corrosion-rate information in representative repository environments. To date, most corrosion data and all long-term (multiyear) corrosion data are at 95ºC (the approximate boiling point of pure water at the altitude of the repository) or lower. These data may constitute an adequate technical basis for predicting general corrosion behavior if the waste package surface temperatures never exceed 95ºC, although the range of chemical environments that may exist on waste package surfaces at or below 95ºC has not been explored entirely.

Few data exist, however, at the higher temperatures of the thermal pulse period. Moreover, the nature of the aqueous environments in contact with the waste packages (or drip shields) is not very well known under such conditions. Concentration and nonequilibrium processes of various kinds may lead to aggressive chemistries. Thus, the uncertainties surrounding general corrosion during the thermal pulse remain a concern of the Board.

Data recently developed by the DOE indicate that aqueous localized corrosion during the thermal pulse is highly probable. The paragraphs that follow examine how this type of corrosion may initiate in the presence of brines formed through deliquescence processes and consider the many uncertainties about the amount and nature of water seeping into drifts during the thermal pulse. In addition, the consequences for corrosion of waste package design and exposure of the alloy to very high temperatures during manufacturing (from, for example, welding) are addressed.

A. Deliquescence-Induced Localized Corrosion

Deliquescence is the absorption of atmospheric water vapor by a solid salt to the point where the salt dissolves into a saturated solution. All salts that are soluble in water exhibit the property of deliquescence to some degree. Certain salts are more deliquescent than others; that is, they deliquesce at lower relative humidities (and thus higher temperatures) than other salts.[18] Calcium chloride, magnesium chloride, and salt mixtures containing one or both of these salts are highly deliquescent, for example. Deliquescence is important because it is a mechanism by which liquid water could exist on waste package surfaces during the thermal pulse.

Are the conditions necessary for deliquescence present at Yucca Mountain?

Two conditions are required for deliquescence on waste package surfaces: (1) the proper combination of temperature and relative humidity[19] and (2) the presence of salts. As noted above, according to the DOE, peak temperatures in places other than the ends of drifts would range from 160°C to 180°C within decades after the repository is closed and subsequently would fall below boiling. Furthermore, according to the DOE, when the temperature is 160°C, the relative humidity would be approximately 20 percent. Highly deliquescent salts will deliquesce to form very concentrated brines under these conditions. At higher temperatures, however, relative humidity may be too low to support deliquescence. At lower temperatures, relative humidities will be higher, which will cause not only highly deliquescent salts to deliquesce but also some moderately deliquescent ones.

Dust will accumulate on waste packages during the period that the repository is open, which may extend for 50 years or longer. The dust will derive primarily from two sources: the rock walls of the emplacement drifts resulting from construction and degradation and the outside air used for ventilation. Recent studies indicate that the dust from the rock walls contains, among other chemicals, some water-soluble chloride-containing salts of calcium and magnesium.[20] Dust also could be deposited as a result of drift degradation. Because of temperature differences along the drifts, convective air currents will exist inside emplacement drifts and under drip shields during the period after the repository is closed. Therefore, dust will continue to accumulate on waste package surfaces after closure.

The DOE has carried out a very limited number of deliquescence experiments using metallic coupons coated with solid calcium chloride or magnesium chloride in a thermogravimetric apparatus. The experiments, which were conducted at 150°C and 22.5 percent relative humidity, confirm that deliquescence can and will occur under these conditions. The DOE's current temperature and relative humidity calculations indicate that almost all the waste packages in the proposed repository at Yucca Mountain will be subjected to not only the specific conditions of 150°C and 22.5 percent relative humidity but also a wide range of temperature and relative humidity conditions under which deliquescence would occur.[21]

It is clear to the Board that all conditions (appropriate levels of temperature and relative humidity together with appropriate amounts of salt or salts present) necessary for deliquescence will be present during the thermal pulse for nearly all waste packages. In fact, these conditions will be present for almost the entire thermal pulse period except when temperatures are rapidly increasing in the few decades immediately following repository closure and the subsequent few decades when temperatures are above 160°C.

Will corrosion of the waste packages be initiated as a result of deliquescence on their surfaces?

Recent data developed by the DOE indicate that crevice corrosion of Alloy 22 is virtually certain to begin if the waste package surface temperature is above a certain value and if concentrated calcium chloride brines—such as would be formed by the deliquescence of pure calcium chloride or calcium chloride in salt mixtures—are present.[22] The exact value of the minimum temperature necessary for crevice corrosion is uncertain, but current data indicate that it may be lower than 120°C and is certainly no higher than about 140°C.[23] This finding is important because brines containing calcium chloride (or magnesium chloride, which is likely to be as corrosive as calcium chloride) can form by deliquescence at temperatures up to about 160°C. Thus, the temperature range within which corrosive brines could exist is at least 20°C wide and may be 40°C or wider. The duration of this temperature range during the cooling phase of the thermal pulse is approximately 100 years if the range is 20°C and approximately 200 years or more if the range is 40°C or wider.[24]

Current data also indicate that the presence of nitrate ions in the calcium chloride-rich brine would have a beneficial effect, that is, an effect that inhibits crevice corrosion, if the molar ratio of nitrate to chloride ions in the brine is higher than approximately 0.1-0.2.[25] The beneficial effect seems to drop as temperatures increase, however, and may not exist at temperatures above about 140°C.[26] Finally, current data indicate that welded samples of Alloy 22 are more susceptible to localized corrosion than are mill-annealed samples.[27]

The DOE's views on deliquescence-induced corrosion. The DOE believes that when the temperature is higher than 160°C, the relative humidity in the drifts would be too low to support deliquescence. Typically, as the temperature decreases, the relative humidity will increase, and deliquescence will occur. The DOE, however, believes that localized corrosion of Alloy 22 in high-temperature brines formed by deliquescence will *not* occur for the following two reasons. First, the period of existence of conditions necessary for crevice corrosion would be too brief for measurable corrosion to occur. This conclusion is based on observations during the thermogravimetric experiments cited above. In those investigations, the dissolved salts in the brines reacted over a period of about 20 hours with the water in the brines to form gaseous hydrochloric acid, which dissipated quickly and harmlessly, and a noncorrosive solid precipitate. Second, the DOE maintains that there always will be sufficient amounts of nitrate present to exceed the molar ratio of nitrate to chloride ions in the brine needed to inhibit localized corrosion.

In addition, the DOE has carried out a preliminary bounding calculation on the effect of chloride on waste package corrosion.[28] According to the DOE, the calculation shows that the maximum possible effect on a waste package of the hydrogen chloride formed by the decomposition of calcium chloride deliquescence brines is limited by the availability of chloride to loss of a uniform layer of less than 5 percent (1 mm) of the wall thickness of the waste package. The DOE believes that the assumptions underlying the preliminary calculation are extremely conservative. Some of the assumptions are that several million moles of chloride would enter each mile of drift over a 4,000-year period and be deposited on waste package surfaces but that all of the chloride would convert to hydrochloric acid and that all of the hydrochloric acid would react with the waste package surface.

The Board's evaluation of the DOE's views on deliquescence-induced corrosion. First, the Board does not believe that the experiments relied on by the DOE to conclude that the period when conditions necessary for crevice corrosion would be too brief for measurable corrosion to occur are adequate for reaching that conclusion for several reasons:

1. The experiments use pure magnesium chloride or calcium chloride brines rather than brines of compositions approximating what actually would exist at Yucca Mountain. Furthermore, the DOE has not shown that magnesium chloride or calcium chloride brines are "worst case" brines. (For example, mixtures of salts will deliquesce at lower relative humidities, and thus higher temperatures, than the pure salts making up the mixtures.)

2. The experiments have been performed only over a very narrow part of the temperature and relative humidity range at which deliquescence could occur.

3. The experiments are run in a thermogravimetric apparatus (TGA) that is an "open system," where gaseous reaction products are immediately swept away. However, whether the drift environment in Yucca Mountain would behave as an open system over short time periods has not been established. Moreover, even if the bulk drift environment behaves as an open system on some time scale, whether small areas on waste package surfaces behave as open systems on the same time scale also has not been established. Thus, whether the TGA appropriately simulates the microenvironments associated with crevices is not known. In particular, no explanation has been furnished of why gaseous hydrochloric acid would dissipate so rapidly that it would not cause harm.

4. Samples used in the TGA experiments did not contain crevices, a necessary precursor to crevice corrosion.

5. The DOE has not explained seemingly contradictory results between TGA experiments, potentiodynamic experiments, and "dip-and-dunk" experiments.[29]

Second, although the Board agrees that nitrate will inhibit localized corrosion in some circumstances, the DOE has not established whether nitrate will inhibit localized corrosion over the entire range of temperatures in which brines could exist. In particular, the data furnished by the DOE indicate that nitrate may not inhibit localized corrosion in the upper temperature range of the thermal pulse (i.e., for temperatures higher than about 140°C). Furthermore, insufficient amounts of nitrate may be available at various repository locations, and natural precipitation/dissolution processes and gravitational forces could separate nitrate and chloride ions. Finally, it is not clear whether the nitrate will be depleted by microbial activity within the host rock.[30]

In addition, the Board notes that the DOE has assumed general corrosion in its preliminary bounding calculation. The Board believes that there is no reason to assume that the chloride will be uniformly distributed or that general corrosion will be the dominant mode of corrosive attack. In fact, recent experimental data appear to show that localized corrosion is the form of corrosion to be most concerned about during the thermal pulse. Localized corrosion, by definition, happens in small local areas. Using the DOE's assumed numbers for the amount of chloride available and its other assumptions (except the assumption of general corrosion), the Board concludes that there would be ample chloride to support penetration of almost all the waste packages.

Thus, the Board believes that deliquescence-induced localized corrosion is likely to be initiated during the thermal pulse.

The DOE's views and the Board's evaluation of those views are summarized in Table 2.

Table 2: Initiation of Localized Corrosion Due to Deliquescence During the Thermal Pulse

Technical Item	*DOE Views*	*Board Evaluation*
Duration of conditions that could cause localized corrosion	Water and salt components of the brines react quickly to form gaseous hydrogen chloride, which dissipates rapidly, and a harmless solid precipitate. The duration of conditions necessary for localized corrosion is too short for measurable corrosion to occur.	Experimental results to date form an insufficient basis for the DOE's conclusion for the following reasons: 1. Brines tested so far may not be representative or bounding of actual brines that would exist in the repository. 2. Experiments to date have been run only over a narrow part of the temperature and relative humidity range over which deliquescence can occur. 3. Experimental apparatus is an "open" system, which may not approximate short-term repository behavior. 4. Samples used in experiments did not have crevices. 5. No explanation has been offered for seemingly contradictory results from other experiments.
Inhibition of localized corrosion	There will always be sufficient amounts of nitrate present to inhibit localized corrosion.	1. The DOE has not established that nitrate would inhibit localized corrosion over the entire range of temperatures in which brines could exist, particularly for temperatures higher than about 140°C. 2. The DOE has not demonstrated the ubiquitous presence of nitrate in the unsaturated zone pore water above the repository footprint. 3. Natural processes could separate nitrate and chloride ions. 4. The DOE has not demonstrated whether nitrates will be consumed by microbes before seepage into the drifts.
Amount of chloride contacting the waste package	Even when using highly conservative assumptions about the amount of chloride that would contact and react with waste packages, less than a 1-mm layer of Alloy 22 would be lost to general corrosion.	The amount of chloride contacting and reacting with waste packages assumed by the DOE would be ample for many penetrations of almost all waste packages to occur through localized corrosion.[31] The DOE's assumption of general corrosion is unjustified.

If initiated, how rapidly will the corrosion proceed? How pervasive could it be?

Localized corrosion will affect the isolation and containment of radioactive waste if it proceeds rapidly and if it is pervasive. The Board is not aware of any studies conducted by the DOE to determine the rate or extent of localized corrosion.

Yet, a great deal is known about localized corrosion in general. For example, localized corrosion of any metal, once initiated, can propagate rapidly. Once initiated, localized corrosion will continue under less severe temperature and relative humidity conditions than necessary for its initiation. That is, crevice corrosion initiated during the thermal pulse is likely to propagate during the remainder of the thermal pulse and even at temperatures below the thermal pulse. Even if conditions become so benign that localized corrosion cannot initiate, the acidic concentrated solutions inside a crevice or pit will remain sufficiently aggressive to continue propagation of corrosion damage. The Board is aware of data and inferences that waste packages could be penetrated in less than 100 years under certain conditions that could occur at Yucca Mountain during the thermal pulse.[32] If localized corrosion is initiated, penetration of most of the waste packages during and after the thermal pulse becomes quite probable.

Board findings and conclusions about deliquescence-induced corrosion

If the DOE's current temperature and relative humidity calculations approximate, underestimate, or only slightly overestimate the actual temperatures and humidities that would exist in a repository at Yucca Mountain, then the conditions necessary to initiate deliquescence-induced localized corrosion of the waste packages will likely be present during the thermal pulse. Thus, in the Board's view, deliquescence-induced localized corrosion will likely be initiated during the thermal pulse. Localized corrosion is likely to propagate during the remainder of the thermal pulse and is likely to continue even after the thermal pulse at temperatures below 95°C. Because of the high temperatures of the current repository design and operation, this process will result in the perforation of the waste packages. The data currently available to the Board indicate that perforation caused by localized corrosion is unlikely if waste-package surface temperatures are kept below 95ºC.

B. Seepage-Induced Localized Corrosion

The DOE's environmental investigations have focused primarily on whether water seeping into the drifts might contain chemicals that could cause the waste package to corrode. The DOE has developed complex and detailed arguments, many of which were presented at the Board's May 2003 meeting, about why it believes that such corrosion would not happen. In the sections below, the Board evaluates the technical basis for the DOE's beliefs.

Will liquid water seep into the drifts?

In the *Yucca Mountain Site Suitability Evaluation*, the DOE also asserts: "Seepage into the drifts in unsaturated formations is less than local percolation flux. This is mainly the result of capillary forces holding water in the formation, diverting the water around repository openings [drifts], and preventing the water from entering."[33] At the May 2003 Board meeting, the DOE also indicated that hot repository rocks would prevent liquid water from entering the drifts during the thermal pulse.

Several processes significantly affect seepage in the fractured unsaturated rocks where the DOE proposes to put thermally hot radioactive waste. As water percolates downward through these porous rocks, an appreciable fraction of it will flow nonuniformly along preferential channels in the rock fractures. The DOE calls that phenomenon "flow focusing."

Where water drains into rock heated to temperatures above the boiling point of water, it will tend to vaporize into steam. When the vapor enters rocks that are at temperatures below the boiling point of water, it will condense and drain downward under the force of gravity.

Anywhere that the rocks are not completely saturated with water, capillary suction will act against the downward drainage of water. The magnitude of capillary suction decreases with increasing saturation. With saturated rock, seepage will occur. During the thermal period, superheated rock around the repository drifts may form a boiling zone within the area affected by capillary suction.

The DOE's views on seepage into the drifts. The DOE uses a numerical technique called the "active fracture model" to predict the spacing of rock fractures that contain flowing water.[34] This technique has been used to make predictions that are reasonably consistent with observed data at Yucca Mountain.

In above-boiling repository rocks, the DOE maintains that vaporization will form a pervasive barrier to seepage of water into the repository drifts. The DOE uses numerical models to demonstrate the existence of this zone of vaporization above and around the drifts in rocks that are at above-boiling temperatures. In those models, water boils in the hot rocks surrounding the heated drifts, rises as steam, and then condenses and drains into cooler rocks between the drifts. The DOE refers to this phenomenon as a "vaporization barrier." According to the DOE, its drift-scale test was an experimental demonstration of the character of the boiling front.

The DOE also argues that capillary diversion will be an important phenomenon in the rocks above repository drifts that are not saturated with water. The DOE uses numerical models, which incorporate variability in rock hydraulic properties (heterogeneity), to infer the existence of a zone around the drifts where capillary suction limits seepage of water into the repository drifts. The DOE calls this zone a "capillary barrier." There are theoretical and empirical reasons for believing that a capillary barrier will form under certain conditions.[35] For rocks of a given permeability and capillarity, there is an amount of percolation flux below which no seepage will occur. The DOE calls this the "seepage threshold."

At the May 2003 Board meeting, the DOE identified three primary variables that control seepage: water percolation, rock permeability, and rock capillary suction strength. Several field tests, according to the DOE, have demonstrated experimentally that seepage is reduced or eliminated because of capillary diversion. The tests led the DOE to conclude that the seepage threshold in Yucca Mountain rocks will be as much as 1000 mm/year.[36] The DOE also points to man-made and natural analogues, such as the underground cities in Cappadocia, Turkey, Egyptian tombs, and Buddhist temples, to support its claim that capillary barriers function for extended periods.

The Board's evaluation of the DOE's view on seepage into the drifts. The phenomenon of some fractures conducting flowing water while other nearby fractures do not conduct such water has been widely observed and reported. However, the active fracture model never has been tested to demonstrate that it reliably predicts preferential seepage in rocks. Further, the key parameter describing fracture "activity" of the active fracture model is not measurable by any presently known technique. Consequently, the Board views predictions based on the active fracture model with caution.

The vaporization barrier will exist where the conditions necessary to create and maintain it are present. However, currently, the DOE's analysis is not sufficient to demonstrate that the necessary conditions will persist continuously along all sections of the repository drifts predicted to be above boiling. The formation of the vaporization barrier depends heavily on repository temperatures. The Board's concerns about the DOE's repository temperature calculations are discussed in Section II.B. The drift-scale test did demonstrate the movement of water and water vapor in rocks subjected to large influxes of heat. However, the drift-scale study an imperfect test of the DOE's ability to predict the pervasiveness of a vaporization barrier at Yucca Mountain for two reasons. First, the experiment was not conducted in the lower lithophysal unit where roughly 80 percent of the drifts would be located. Second, the bulkheads, that should have been tight, leaked.

Furthermore, studies have shown that the vaporization barrier might be penetrated by seeping water.[37] Those studies cannot be dismissed at this time.[38] Finally, the two-dimensional models used by the DOE are not likely to capture the displacement and movement of moisture and heat that take place in a three-dimensional world. In short, because its data, conceptual models, and numerical analyses may be inadequate, the DOE has not predicted convincingly the movement of water or the state of saturation in the rock-mass due to thermohydrologic processes.

Consistent with theory, capillary diversion will exist where the prerequisite conditions required to create it exist. At the present time, however, the DOE's analyses are not sufficient to demonstrate that the necessary conditions will persist continuously along all sections of the repository drifts. Drifts are not likely to have either a regular curvature or a profile. According to observations in the lower lithophysal unit and expected excavation-induced effects, surface roughness features would most likely exceed the capillary layer of a few centimeters of thickness necessary for the formation of a capillary barrier. In the seepage experiments performed in the middle nonlithophysal unit, the DOE has had trouble accounting for much of the applied water. No seepage experiments have been carried out in the formation where most of the drifts would be constructed, the lower lithophysal unit. The voids found there may disrupt any capillary barrier that otherwise might form. The Board notes that the 1,000 mm/year seepage threshold is substantially higher than any used in the past and may be an artifact arising from the experimental difficulties inherent in challenging field experiments.[39] The DOE's interpretation of what it claims to be analogues also is not without its own problems. Although no evidence was found that water dripped into some analogue openings, some traces of water were found as films, which flowed on the surface of these openings. Moreover, because each analogue was naturally ventilated, some unknown amount of water could have been removed as vapor.

For these reasons, the Board believes that the DOE has not demonstrated definitively that water will not seep into the drifts during the thermal pulse. For example, refluxing, which is "fast" water flow through a large-aperture fracture(s) that connects the saturated part of the boiling front and the drift boundary, could result in the dripping of water into the drift before it evaporates.[40] In sections of drifts subject to edge-cooling, water also could seep in if the capillary barrier is degraded.

The DOE's views and the Board's evaluation of those views are summarized in Table 3.

Table 3: Seepage Into Drifts During the Thermal Pulse

DOE Views	*Board Evaluation*
The active fracture model reliably predicts which fractures will conduct flowing water.	The active fracture model may be a reasonable approach to this very challenging problem, but it has never been tested adequately, and the key controlling active fracture geometric parameter is not measurable using any presently known technique.
Temperatures above boiling in rocks around repository drifts will vaporize liquid water, forming a pervasive vaporization barrier that prevents seepage of water into drifts.	Vaporization will occur above and around the drifts during the thermal pulse, but the DOE has not demonstrated that the conditions required for a pervasive vaporization barrier to form will occur everywhere. The DOE's view is based on an insufficient analysis. Future testing under *in situ* conditions in Yucca Mountain may improve the technical defensibility of any claim about the effectiveness, or lack of effectiveness, of a vaporization barrier.
The suction of water into small void spaces and fractures in the rock will be strong enough to form a pervasive capillary barrier along the length of 100 kilometers of drifts that limits seepage into drifts.	Capillarity is a well-recognized phenomenon in unsaturated rocks, but the DOE has not demonstrated that the conditions required for a capillary barrier to form are satisfied throughout the drifts. The DOE's view is based on insufficient data and modeling.

Will water seeping into drifts be corrosive?

Whether seepage waters are corrosive depends on the composition of the salts and other materials dissolved in the water as well as on the temperature when the water comes in contact with either the drip shield or the waste package. The DOE's positions on the composition and corrosive properties of seepage waters during the thermal pulse are given below together with the Board's evaluation of the DOE's basis for its positions.

The DOE's view on the corrosive properties of any water dripping into the drift during the thermal pulse. On the basis of the results of its models, the DOE has concluded that only a very small fraction (about 1 percent) of any water that might seep into the drift during the thermal pulse will be corrosive. The DOE's analysis uses measurements of water chemistry and rock properties in Yucca Mountain. The model, TOUGHREACT, then simulates the evolution of the water chemistry. The calculated chemistries are next grouped together according to their geochemical characteristics in a process that the DOE calls "binning." Finally, the DOE uses a second model, EQ3/6, to evaporate the "binned" solutions to dryness.

The Board's evaluation of the DOE's view on the corrosive properties of any water dripping into the drift during the thermal pulse. The Board believes that the DOE has not fully acknowledged the limits and assumptions underlying their models. Thus, it is unclear how conducive to corrosion the chemistry of the water will be during the thermal pulse.

In particular, prediction of the chemistry of the seepage waters using TOUGHREACT requires specification of initial water chemistry and rock mineralogy. The modeling is sensitive to small variations in those initial conditions. Problems with specification of initial conditions could produce results that are inaccurate for some chemicals. The DOE's EQ3/6 evaporation calculations do not simulate water or steam flow, which can be important processes in areas of strong thermal perturbation.[41] Although solutions will approach that limit, we do not know whether they will exceed it. During the evaporation process, the ionic strengths will likely exceed 100 molal. Finally, the DOE's position appears to be based on the argument that only waters containing magnesium chloride or calcium chloride can be corrosive. This may be true, but the corrosion resistance of Alloy 22 and titanium in other waters that could exist during the thermal pulse, particularly the higher-temperature part of the thermal pulse, has not been tested.

Will the drip shield prevent corrosion by diverting seepage water?

Drip shields may play an important role in preventing seepage-induced corrosion by preventing those waters from contacting the waste package. The DOE's apparent position is that drip shields *will* prevent any seeping water from falling on the waste package during the thermal pulse and that therefore there will be no waste package corrosion during this period.

The Board believes that the DOE's position is based mostly on assumptions that could be unrealistic and overly optimistic. First, no prototype drip shield has ever been built, and the concept of a long-lasting drip shield in an underground application has never been applied elsewhere. Thus, the DOE's projections of how this structure will perform for thousands of years are speculative. The DOE assumes, for example, that the joints between drip shield segments will remain leakproof during the thermal pulse despite the fact that only limited paper studies of the joints have been done. Furthermore, the DOE assumes that drip shields will not corrode to the point of leaking during the thermal pulse despite the fact that there are very little, if any, corrosion data supporting this assumption and despite the fact that titanium, the drip shield material of construction, is known to be susceptible to fluoride-based corrosion and hydrogen embrittlement, as well as to crevice corrosion in elevated-temperature, high-chloride environments.[42]

Board findings and conclusions about seepage-induced corrosion

Making any definitive statement about whether seepage during the thermal pulse will lead to degradation of the waste packages is very difficult. The Board believes that the possibility of seepage during that time cannot be excluded but that it most likely would be limited. The DOE's analyses of water chemistries and their corrosive potential are extremely complex and suffer from empirical and theoretical weaknesses. Thus, the Board does not have a high degree of confidence in the DOE's conclusion that any seepage water would be dilute or non-corrosive because the methods the DOE used have significant technical uncertainties. The drip shields may act to protect waste packages from dripping water, but the titanium from which they are constructed may itself be susceptible to corrosion during and after the thermal pulse.

C. The Effects of Waste Package Design and Fabrication on Alloy 22 Corrosion Behavior

Regardless of whether the localized corrosion is induced by deliquescence or seepage, characteristics of waste package fabrication and design also could affect the ability of the waste package to contain the radioactive waste.

How might waste package design affect the likelihood of localized corrosion resistance?

Waste package design can affect corrosion resistance. Welds, for example, are generally more susceptible to corrosion than base metal is. This problem could be reduced if waste packages were designed to minimize welds, particularly welds that will not be solution-annealed and quenched. Welds often are sites where crevices have an increased propensity to form. The DOE believes that its current waste package design is satisfactory for corrosion resistance. The Board is less sanguine because the current waste package design adds two circumferential welds to hold the trunnion collar sleeve and a long, tight crevice between the two welds. Such a design could exacerbate any corrosion that might be initiated.

Will very high manufacturing temperatures affect Alloy 22 corrosion behavior?

Very high temperatures (higher than 500°C) will be reached during heat treating and welding of the waste package while it is being manufactured and during welding of the final closure welds. Certain deleterious phases can precipitate during the high temperatures, affecting the corrosion resistance of the metal. Uneven cooling after welding can leave residual stresses, which can affect corrosion, particularly stress-corrosion cracking.

The DOE takes the position that solution-annealing and quenching the waste package before loading it will remove all precipitated phases and residual stresses except those associated with the final closure weld. The DOE also takes the position that laser peening or burnishing would mitigate residual tensile stresses in or near final closure welds, although localized corrosion at weldments is likely to expose the residual tensile stresses that must exist below compressive stresses imposed by peening or burnishing.

The Board believes that testing and experimentation to date are not sufficient to justify the DOE's positions for three reasons. First, solution-annealing and quenching (which are well-established commercial practices) have not been performed on a prototype waste package similar to waste packages proposed for Yucca Mountain. Second, commercial experience in laser peening and burnishing is very limited, and there is no experience in applying these technologies in a high-radiation environment. Third, although laser peening or burnishing may mitigate residual tensile stresses, the welds and nearby heat-affected zones of the final closure welds will still show increased susceptibility to localized corrosion and will be exposed to possibly large residual tensile stresses under the applied-surface compressive stresses. Thus, the possibility remains that phase instabilities in the metal or near extended welds could increase susceptibility to corrosion during the thermal pulse.

IV. Implications

Although the DOE's presentations at the May and September 2003 Board meetings did not touch on matters such as the transport of radionuclides from the waste package through the engineered barrier system, the Board's evaluations made earlier in this paper, which are based on the DOE's data and results, may have important implications for that issue. In its *Yucca Mountain Science and Engineering Report*, the DOE holds, "Transport [of radionuclides] from breached waste packages into the unsaturated zone could occur either through advection, which is the flow of liquid water, or by diffusion. The scarcity of water [in the drift] makes advective transport unlikely, but diffusive transport through thin films…is possible."[43] The Board does not believe that there is a strong technical basis for the DOE's claim of scarcity of water in the drift over the long term.

Even if a capillary barrier had been established, it is by no means clear that it could be maintained for several thousand years after the repository is closed. After the thermal pulse ends, thermal stresses and seismic events, which have occurred up to that time, are likely to result in significant drift degradation.[44] Degradation will destroy the drift profile and degrade the ability of the drift to divert seepage because of capillarity. The products of drift degradation will create substantial piles of debris around and over the drip shield and the waste package. Although the maximum extent of drift degradation can be reasonably estimated, the rate of drift degradation is difficult to predict accurately at this time. However, given the DOE's current mode of ground support, the ability of some sections of the drifts to divert seepage water via capillarity may not exist by the time the repository is closed, which may be as long as 300 years from now.

Thus, when repository temperatures drop below the boiling point of water after the thermal pulse, water seepage into the drifts could increase because of the disappearance of the vaporization barrier, the degradation of the capillary barrier, and an increase in percolation brought on by postulated climate changes. If the drip shield is no longer intact or is rendered nonfunctional, the water could directly contact the corroded waste package. The water then could mobilize at least some of the radionuclides and transport them outside the drifts. Even if the drip shield is intact and functional, some radionuclide transport could still take place. Because the drip shields will be cooler than waste package surfaces, condensation on the undersides of drip shields would be expected. This condensation then could fall onto the potentially perforated waste packages. By this mechanism, the use of drip shields could lead to dripping on the waste packages rather than preventing it.

Other barriers are incorporated in the entire repository system that the DOE is proposing. They include the cladding of the spent fuel, the waste form, the invert on which the package is placed, and the saturated zone beneath the underground facility. Each of these barriers, or a combination of them, will likely play some role in isolating and containing the radioactive waste. Nevertheless, the Board believes that two of the primary barriers, the waste package and the unsaturated zone above the repository horizon, could be less effective than indicated by the DOE's analyses.

V. Overall Board Conclusions

Conclusions regarding the likelihood and extent of localized corrosion

On the basis of the DOE's temperature and relative humidity calculations and salts in dust deposited on waste package surfaces, all the conditions necessary to initiate localized corrosion of the waste packages will likely be present during the thermal pulse because of the deliquescence of salts on waste package surfaces, and thus it is likely that deliquescence-induced localized corrosion will be initiated during the thermal pulse. Furthermore, in the Board's opinion, the DOE has not firmly established its conclusion that corrosion would not be caused by water seeping into drifts during the thermal pulse. Localized corrosion is likely to propagate during the remainder of the thermal pulse and is likely to continue even after the thermal pulse at temperatures below 95°C. Because of the high temperatures of the current repository design and operation, this localized corrosion will result in the perforation of the waste packages. The data currently available to the Board indicate that perforation caused by localized corrosion is unlikely if waste-package surface temperatures are kept below 95ºC.

Conclusions regarding the existence of multiple barriers and defense-in-depth

If the Board's interpretation of the data and analyses presented by the DOE is correct, an important engineered element of the DOE's current repository design, the waste package, will be susceptible to corrosion during and following the thermal pulse. There also may be more seepage, and thus potentially more and earlier transport of at least some radionuclides, than the DOE now projects. The contribution of the other natural barriers to radionuclide isolation depends on complex modeling calculations whose uncertainties are high and will remain high for many years. Therefore, although some combination of multiple barriers will be operating at various times in the repository, the capability of those barriers to provide meaningful defense-in-depth—that is, redundancy—in isolating and containing radionuclides is unclear with the DOE's high-temperature design.

Do the Board's technical conclusions have significant effect on performance calculations for the repository system *as a whole*? Although a precise statement about whether, or how much, dose might be increased or the safety margin decreased cannot be made given the existing uncertainties, the Board believes that the implications of the Board's conclusions for repository system performance could be substantial.[45] Therefore, it is incumbent on the DOE to demonstrate unambiguously the reliability and safety of any design concept for Yucca Mountain.

ENDNOTES

[1] See, for example, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Environmental Assessment: Yucca Mountain Site, Nevada Research and Development Area, Nevada*, DOE/RW-0073, May 1986; and U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Repository Safety Strategy: U.S. Department of Energy's Strategy to Protect Public Health and Safety After Closure of a Yucca Mountain Repository*, YMP/96-01 Rev. 01, January 1998.

[2] The term "radioactive waste" as used in this paper denotes both solidified high-level waste from reprocessing operations and spent nuclear fuel derived from both defense and civilian activities.

[3] Climate states are known to have shifted dramatically in the past, as evidenced by pluvial climates recorded at Devil's Hole.

[4] Lithophysae are voids in the rock.

[5] The specification for Alloy 22 (wt%) is carbon, .015 max; manganese, 0.5 max; phosphorous, .02 max; sulfur, .02 max; silicon, .08 max; chromium, 20.0-22.5; molybdenum, 12.5-14.5; iron, 2.0-6.0; cobalt, 2.5 max; tungsten, 2.5-3.5, vanadium; 0.35 max; nickel, balance. From *Standard Specification for Low-Carbon Nickel-Molybdenum-Chromium, Low-Carbon Nickel-Chromium-Molybdenum, Low-Carbon Nickel-Chromium-Molybdenum-Copper, Low-Carbon Nickel-Chromium-Molybdenum-Tantalum, and Low-Carbon Nickel-Chromium-Molybdenum-Tungsten Alloy Plate, Sheet, and Strip,* ASTM standard specification B575-99a, ASTM International; West Conshohocken, Pennsylvania; November, 1999.

[6] See C. Manepally and R. W. Fedors, "Edge-Cooling Effect on the Potential Thermohydrologic Conditions at Yucca Mountain," in *Proceedings of the 10th International High-Level Radioactive Waste Management Conference* (IHLRWMC) March 30 – April 2, 2003; Las Vegas, Nevada; American Nuclear Society. La Grange, Illinois.

[7] The situation is complicated further as a result of edge and cold-trap effects. Alternative in-drift thermal analyses indicate a significant difference between the temperatures of waste packages at the center and those at the edge of subsurface repository layout. Large thermal gradients will exist along the axes of the emplacement drifts. Variabilities in temperatures and relative humidity make waste package corrosion assessments more difficult. Waste packages at the center of emplacement drifts could be exposed to 160°C –180°C temperatures and minimum of 20 percent relative humidity associated with deliquescence and localized corrosion; waste packages located closer to the edge of the repository could be at lower temperatures and higher relative humidity. See Manepally and Fedors. See also M .T. Itamura , N. D. Francis, and S. N. Webb, "In-Drift Convection Analysis of the Low Temperature Operating Mode (LTOM) Design," IHLRWMC; 2003.

[8] U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Supplemental Science and Performance Assessment (SSPA)*, Volume 1, TDR-MGR-MD-0000007 Rev. 00; June 2001, p. 5-55.

[9] The DOE used a mean value of 1.27 W/mK (dry thermal conductivity) and 1.87 W/mK (wet thermal conductivity). See Table 5.3.1.4.8-1 in the SSPA. See also the charts presented by the DOE at the May 2003 Board meeting. Because three-quarters of the emplacement area would be located in the lower lithophysal unit of the Topopah Spring Tuff, temperature predictions would be sensitive to the thermal conductivities of the rock in this unit. Recently, 60 samples from this zone were distributed among three laboratories for measurement of dry thermal conductivity. (See N. S. Brodsky, D. R. Bronowski, and C. L. Howard, "Laboratory Thermal Conductivity Testing for the Tptpll Lithostratigraphic Unit," IHLRWMC; 2003.) Dry thermal conductivity is particularly important during the thermal pulse period. Although most measurements of dry thermal conductivity were close to 1.7 W/mK, they varied widely, from 0.8 to 2.5 W/mk. The measurements also confirmed that thermal conductivity of the lithophysal rock decreases strongly with increasing porosity. The lithophysal units contain many lithophysae, some of which are quite large (more than 50 mm in diameter, even up to 1.25 m in diameter). Because almost all of the 60 samples are 50mm or less in diameter, it is unlikely they could be representative of the bulk thermal conductivity of the parts of the zone

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that contain large lithophysae. See also N. S. Brodsky, C. L. Howard, R. S. Taylor, and J. T. George, “Field Thermal Conductivity Measurements in the Tonopah Spring Lower Lithophysal Unit,” IHLRWMC; 2003; N. S. Brodsky, C. L. Howard, R. S. Taylor, and J. T. George, “Thermal Conductivity Measurements in the Topopah Spring Lower Lithophysal Unit,” IHLRWMC,;2003; and G. Danko, N. Shah, D. Bahrani, and S. Lanka, “Monte Carlo Analysis of In Situ REKA Lithophysal Properties Identifications,” IHLRWMC; 2003. Inconsistencies in the range and mean percentage lithophysal porosity as reported in U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Thermal Conductivity of the Potential Repository Horizon Model Report*, MDL-NBS-GS-000005 Rev. 00; September 2002, and significant increases in lithophysal porosity estimates based on recent panel mapping activities as reported in RDTME DOE-NRC technical exchanges need to be resolved.

[10] See U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Supplemental Science and Performance Assessment (SSPA),* Volume 2, TDR-MGR-MD-0000007 Rev. 00; July 2001; p. 3-15.

[11] Current assessments of drift degradation in the lower lithophysal unit (Tptpll) using small-scale fracture data and laboratory and field-test geomechanics data show that the rock mass around emplacement drifts when subject to a combination of thermomechanical processes, seismic events, and the effects of static fatigue produce extensive drift degradation. See D. Kicker, *Drift Degradation Analysis*, ANL-EBS-MD-000027 Rev 02; May 2003. The Project has yet to fully assess the performance-related implications of drift degradation on the near-field and in-drift environments. Similar estimates of drift degradation have been developed independently in *Mechfail: A Total-System Performance Assessment Code Module for Evaluating Engineered Barrier Performance Under Mechanical Loading Conditions*, prepared for the U.S. Nuclear Regulatory Commission under Contract NRC-02-02-012 by the Center for Nuclear Waste Regulatory Analyses (CNWRA), May 2003.

[12] Convective heat-transfer processes have been observed in the field tests conducted in the ESF and the ECRB, and in laboratory experiments at the Atlas facility. See also E. Hardin, *Model Validation Status Report,* TDR-WIS-MD-000005 Rev. 00; November 2001; and J. S. Stuckless, “A Case for Long-term Passive Ventilation of the Proposed Repository at Yucca Mountain, Nevada – Evidence from Natural Analogues,” IHLRWMC; 2003.

[13] The estimate is that the pores are approximately 90 percent saturated.

[14] See *SSPA*, Volume 1, Figure 5.4.1-7, p. 5F-100.

[15] The DOE’s views have been expressed in published documents, technical analyses, and presentations to the Board. In addition, the DOE provided written answers to questions posed by the Board’s staff following the May 2003 meeting. The DOE’s views often are clearly stated. From time to time, however, there may be some ambiguity in those views. The Board has tried in this paper to describe, as accurately as it can, what those views are.

[16] U.S. Department of Energy, Office of Civilian Radioactive Waste Management*, Yucca Mountain Site Suitability Evaluation.* DOE/RW-0549, Washington, D.C.; February 2002; p. 3-10.

[17] In an October 10, 2003 letter responding to the Board’s written comments on the May 2003 meeting the DOE makes the following observations. “[O]ur technical basis continues to be based on : a) no significant corrosion above the boiling point of water because of the lack of seepage and the presence of primarily benign deliquescent brines; b) no significant corrosion at and near the boiling point of water because of the presence of the drip shield; c) no significant corrosion below the boiling point of water because of the presence of primarily benign seepage brines and the presence of the drip shield.” Letter from Dr. Margaret Chu, Director, Office of Civilian Radioactive Waste Management, to Dr. Michael Corradini, Chairman, Nuclear Waste Technical Review Board, p. 2.

[18] The lowest relative humidity at which a salt will deliquesce is known as its deliquescence point. The deliquescence point of a salt varies with temperature. The deliquescence point of a salt mixture is the same as or lower than the deliquescence point of the salt in the mixture having the lowest deliquescence point.

[19] Throughout Section III, unless stated differently, “temperatures” and “relative humidities” refer to temperatures on the outer surface of the waste package and relative humidities of the gas phase where it contacts the waste package

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surface. The average temperature of the bulk gas phase outside the waste package is always lower than the average temperature on the waste package surface, and therefore the average relative humidity in the bulk gas phase is correspondingly higher than the average relative humidity of the gas that is in contact with the waste package surface.

[20] Extensive sampling and analyses of the dust derived from the rock walls have been reported on recently, see Z. E. Peterman, J. B. Paces, L. A. Neymark, and D. Hudson, "Geochemistry of Dust in the Exploratory Studies Facility, Yucca Mountain, Nevada," IHLRWMC; 2003. Along with many other components, the dust contains water-soluble salts of magnesium, calcium, and chloride.

[21] J. C. Farmer presented results of these thermogravimetric experiments at the Board's January and May 2003 meetings. See also email of responses to staff questions, personal communication from Claudia Newbury to Carl Di Bella and Daniel Metlay, May 30, 2003.

[22] The data referred to are the data presented by J. C. Farmer at the Board's January and May 2003 meetings, particularly Farmer's cyclic polarization overheads 27 and 28 from the January meeting and overheads 35 and 36 on 'critical temperature for localized corrosion" from the May meeting. On overheads 35 and 36, the differences between the corrosion potential (green line) and the repassivation potential or breakdown potential is less than approximately 150mV or 300mV, respectively, for temperatures higher than 140°C. Particularly important on overheads 35 and 36 are the steady-state corrosion potentials of base metal and weld metal after 1 year of exposure. Apparently, the dashed-line boxes on these overheads are based on a single data point at 90°C. This data point showed an increase in corrosion potential of more than 400mV during the 1-year exposure period. In addition, Farmer's overhead 31 from the Spring meeting shows an increase in corrosion potential of approximately 200 mV after 1 year of exposure at 120°C. See also personal communication, 2003, particularly the response to question 2.

[23] The minimum temperature for localized corrosion is based on the apparent intersections of corrosion potentials and breakdown potentials or repassivation potentials. The intersections may be seen on the overheads cited in the previous footnote. The minimum temperature for localized corrosion is lower for weld metal than for base metal.

[24] These are average numbers. Because of the heterogeneities within Yucca Mountain and the variability of heat output among waste packages, the range could be larger.

[25] Overhead 37 of J. C. Farmer's presentation at the Board's May 2003 meeting illustrates the beneficial effect of nitrate well: The addition of 0.1 (molar) nitrate increases the repassivation potential approximately 300 millivolts. The minimum proportion of nitrate need to achieve protection against localized corrosion is not known and may b a function of many variables, including whether the alloy is base or weld metal. See also the presentation by G. A. Cragnolino at the May 2003 Board meeting, especially his overheads 11, 14, 16, 22.

[26] Data in J. C. Farmer's overheads 27 and 28 from the Board's May 2003 meeting appear to indicate that nitrate no longer has a beneficial effect at temperatures higher than approximately 140°C. The intersections of steady-state corrosion potentials with breakdown potentials or repassivation potentials on J. C. Farmer's overheads 35 and 36 from the Board's May 2003 meeting seem to indicate that nitrate no longer has a beneficial effect at even lower temperatures.

[27] See, for example, overheads 35 and 36 from J. C. Farmer's presentation at the Board's May 2003 meeting. Data on these overheads indicate a higher steady-state corrosion potential for weld metal Alloy 22 than for base metal Alloy 22. See also overhead 14 from G. A. Cragnolino's presentation at the same meeting. It shows lower repassivation potentials for aged or welded material than for mill-annealed material. In general, if material X shows higher corrosion potentials than material Y does under the same conditions or if material X shows lower repassivation potentials than material Y under the same conditions, then material X is likely to be more susceptible to localized corrosion than is material Y. That is, the conditions necessary for localized corrosion of material X are less severe (e.g., lower temperature, lower chloride concentration) than the conditions necessary for the localized corrosion of material Y.

[28] See personal communication, 2003, particularly the response to Question 10.

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[29] Sources for corrosion data of Alloy 22 at conditions that are similar to or related to conditions that might occur during the thermal pulse in a repository at Yucca Mountain include Lawrence Livermore National Laboratory (LLNL), CNWRA, and the Catholic University of America (CUA). Yucca Mountain-related corrosion work is sponsored at those institutions by the U.S. Department of Energy, the U.S. Nuclear Regulatory Commission, and the State of Nevada, respectively. There are seemingly contradictory results from some of the experiments conducted by these institutions, which the DOE has yet to explain. For example, both the thermogravimetric analysis (TGA) and cyclic polarization experiments have been run at LLNL in similar conditions. The TGA experiments show no detectable corrosion, but the cyclic polarization experiments indicate that corrosion is occurring. We suspect that the reason for the seeming contradiction has to do with the fact that the TGA system is an "open" system, while the cyclic polarization system may be a "less open" or even a "closed" system. The DOE needs to explain the reason(s) for the contradictions and, more important, relate the experiments to the type of systems that would occur at Yucca Mountain for both bulk and local scales. Recent CNWRA work indicates that the susceptibility of Alloy 22 in chloride-containing solutions increases with increasing temperature and increasing chloride concentration. No localized corrosion, however, was noted at or below 95°C in 0.5 molar chloride. See D. S. Dunn, L. Yang, Y-M. Pan, and G. A. Cragnolino, "Localized Corrosion Susceptibility of Alloy 22," in *Proceedings of Corrosion2003*; March 16-20, 2003; San Diego, California. In addition, two corrosion tests of Alloy 22 coupons by CUA researchers at 144ºC in low-pH, concentrated brines that could evolve at Yucca Mountain indicated general corrosion rates of 678 and 10943 µm/year, sufficient to penetrate the 20 mm Alloy 22 outer shell of the waste package in less than 30 years and 2 years, respectively. See the presentation by R. W. Staehle at the Board's January and May 2003 meetings.

[30] See B. J. Little, "A Perspective on the Use of Anion Ratios to Predict Corrosion in Yucca Mountain," *Corrosion*; 59:8, 701-704, (2003).

[31] The DOE takes the position that corrosion would occur uniformly, resulting in a uniform loss of 1 mm of waste package surface. The Board believes that it is more likely that corrosion would occur in a localized (nonuniform) fashion, resulting in deep crevices in some places and virtually no corrosion in others, depending on local conditions.

[32] See remarks on the CUA work in the previous note. At the Board's May 2003 meeting, a corrosion investigator at CNWRA implied that localized corrosion, if initiated, could penetrate the waste package in as few as 20 years. (See transcript for May 14, 2003; p. 438.)

[33] DOE/RW-0549, p. 3-10.

[34] H.H. Liu, C. Doughty, and G.S. Bodvarsson, "An active fracture model for unsaturated flow and transport in fractured rocks," *Water Resources Research*; 34:10, 2633-2646 (1998).

[35] J.R. Philip, "Some general results on the seepage exclusion problem," *Water Resources Research*, 26:3, 369-377, (1990).

[36] The DOE did present performance assessment analyses that showed how the inclusion of a fourth variable—flow focusing—could result in ambient-temperature seepage at percolation fluxes substantially less than 1,000 mm/year.

[37] J. Birkholzer, S. Mukhophadhyay, and Y. Tsang, "Analysis of the Vaporization Barrier above Waste Emplacement Drifts," IHLRWMC; 2003.

[38] D.L. Hughson, "Fingering Flow Through a Superheated Fracture: Hele-Shaw Experiment and Model Comparisons," Geological Society of America Abstracts with Programs, 32:7, A480 (2000) and O.M. Phillips, "Infiltration of a Liquid Finger Down a Fracture into Superheated Rock," *Water Resources Research*; 32:6, 1665-1670 (1996).

[39] However, the Board notes that the DOE's performance assessment incorporates flow focusing, allowing seepage to occur at lower seepage thresholds.

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[40] Phillips (endnote 38).

[41] P. Mariner *et al*., In-Drift Precipitate/Salt Model, ANL-EBS-MD-000045 Rev. 01A, March 2003, pps. 13, 86.

[42] See Waste Package Performance Peer Review Panel, *Final Report*, February 28, 2002, for a discussion of the potential for titanium to corrode.

[43] U.S. Department of Energy, Office of Civilian Radioactive Waste Management, *Yucca Mountain Science and Engineering Report*, DOE/RW-0539 Rev. 01; February 2002; p. xl.

[44] Kicker (endnote 11).

[45] At the September 2003 meeting, a DOE presenter from Sandia National Laboratories, R. J. MacKinnon, indicated that, if 1 percent of the waste packages failed because of deliquescence-induced localized corrosion, the dose received by the "reasonably maximally exposed individual" would increase by 0.2 millrem per year. If more packages are compromised the dose would go up linearly. He suggested, however, that those calculations were almost certainly conservative. See his overhead 20.

November 19, 2003

MEMORANDUM

To: Nuclear Waste Technical Review Board Members and Staff

From: Michael Corradini, NWTRB Chairman

Subject: Comments on YMP Thermal Phase and In-Drift Coupled Processes and the Board's technical report, *An Evaluation of Key Elements in the USDOE's Proposed System for Isolating and Containing Radioactive Waste*

Introduction

The NWTRB technical report, *An Evaluation of Key Elements in the USDOE's Proposed System for Isolating and Containing Radioactive Waste*, provides a relatively complete description of the physical processes that may be operative during the thermal phase. The Board members and staff conducted a detailed review of the in-drift conditions needed for localized corrosion during the thermal phase. I agree with most of the technical analyses. However, I have studied certain issues in depth over the last few months and regard particular conclusions as not accurate and nonphysical. The conclusions involve the physical processes of vapor transport, deliquescence, and diffusion transport of radionuclides. This memo discusses these issues.

Background

The current repository design is being finalized by the Department of Energy (DOE) and its contractors for license submittal. Current expectations are that the repository design will allow for a thermal phase with high temperatures in the drift and the waste package, transitioning to a lower-temperature long-term phase. This "thermal phase" is defined here as the condition, where the waste canister surface temperatures exceed the boiling point of water (> 96°C) for approximately 1,000 years. The longer-term phase would follow with lower temperatures (below 96°C), through the regulatory period (10,000 years).

In its role as an independent technical reviewer of the Yucca Mountain Project (YMP) repository design, the NWTRB has focused its efforts on this thermal phase of normal repository operation. Current corrosion data, presented by the DOE and its contractors as well as CNWRA, a Nuclear Regulatory Commission contractor, suggest the following:

> Localized corrosion would occur during the thermal phase of waste package isolation if:
>
> - the C-22 waste package surface temperature exceeds 100° C (for times >100 yrs),

- water exists during these time periods on the waste package from deliquescence or seepage,
- the water-solution chemistry is corrosive (e.g., high in chloride compounds), and
- there are C-22 surfaces with crevices, either welded or cold-worked without annealing,

The NWTRB stated the following opinion in its letter of October 21, 2003, to Dr. Margaret Chu, Director of OCRWM: given the conditions noted above, localized corrosion (e.g., crevice corrosion) could occur to such an extent that the waste package would be "breached" by small holes or perforations. The letter also noted that a detailed technical report would follow to present the technical bases for this opinion.

Relative Humidity and Vapor Mass Transport

The technical report states: *"From the standpoint of corrosion, the key parameter relating to water vapor present in the drift atmosphere is the relative humidity during the thermal pulse. The hotter the conditions are, the lower the relative humidity. The bulk humidity of the air inside the drifts can be estimated readily from first principles of chemistry and physics for a particular air temperature. According to the DOE, relative humidity would reach a minimum of 10-20 percent during the first 100 years after the repository is closed and then would rise to above 80 percent by the time the thermal pulse ends. However, because the DOE's temperature calculations may be inaccurate and because natural ventilation and air circulation are not accounted for in the DOE's projections, the bulk relative humidity in the drift at a given time may be higher or lower than the DOE now estimates."* The concern that I have with this statement (and it partly stems from the Board's not having the complete story from the DOE) is that bulk humidity is not readily estimated. Rather, it is a strong function of the air-vapor circulation and mass transport in the drift. My opinion is that air-vapor natural circulation will cause substantial mixing along the drift and the bulk relative humidity will be lower than current DOE estimates. Although, this may seem like a subtle point, it is quite important in predicting the in-drift conditions affecting the onset of deliquescence. This suggests that current DOE analyses overestimate the bulk relative humidity.

Deliquescence

The technical report states: *"All the conditions necessary for deliquescence will be present during the thermal pulse (phase) for nearly all waste packages."* This broad technical conclusion does not seem supportable by current data and its application to the waste package surface environment. Deliquescence is the absorption of atmospheric water vapor by a solid salt to the point where the salt dissolves into a saturated solution. The deliquescence point is defined as the set of temperature and humidity conditions at which the solution first appears. All the current deliquescence data, from DOE contractors and NRC contractors, have utilized an experimental approach where an isothermal surface with salt particles is immersed in a large homogeneous air-vapor mixture ("open system"). Such data would be applicable if the waste packages were not generating decay heat. However, heat is being produced (from 1.5kW/meter at emplacement to an order of magnitude less at 1,000 years), and this will produce a temperature difference from the surface to the bulk air-vapor mixture. Local mass-transport phenomena would cause the bulk relative humidity required for deliquescence to be higher than what current data suggest. Thus, the current data underestimates the deliquescence point, and this is incorrect. Deliquescence will likely occur late in the thermal phase, when relative humidity rises substantially, with only a small fraction of the waste packages being affected. Prototypic deliquescence data is needed for a heated surface. These data then can be used with natural-circulation analyses to predict the time and location of deliquescence in the drift.

Diffusion Transport in the Waste Package

The technical report also includes a caveat in its introduction: "*Some elements of that system are not addressed at all, such as the role the interior waste package and the design of the waste form might play in inhibiting the mobilization of radionuclides.*" This is an important point that I want to emphasize, particularly in regard to water diffusion transport in the waste package. DOE analysis currently assumes that any perforation of the waste package surface will directly lead to release of radionuclides. The release mechanism is by diffusion through a liquid water layer that is assumed to exist from the fuel rods to the drift floor. This assumption is not only bounding, it is also nonphysical; OECD/NEA-IAEA Peer Review of YMP (December 2001) came to the same conclusion. This nonphysical bounding assumption needs to be reexamined by the DOE and corrected appropriately.