INTRODUCTION

The U.S. Department of Energy (DOE) has committed to prepare a series of Process Model Reports (PMRs) and supporting Analysis and Model Reports (AMRs) as the technical bases for the Total System Performance Assessment (TSPA) for the Site Recommendation (SR). The purpose of this deliverable is to update the Issue Resolution Status Report (IRSR) of the Evolution of the Near-Field Environment (ENFE) Key Technical Issue (KTI) to reflect the resolution status of the subissue on the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release based on a review of the information presented in the PMRs and AMRs. The following AMRs are a subset of those that have been identified from the DOE AMR/PMR schedule as being relevant to the ENFE subissue on chemical environment for radionuclide release: E0065–AMR on In-drift Thermal-Hydrologic-Chemical Analysis; F0055–AMR on Commercial Spent Nuclear Fuel (CSNF) Degradation Model; F0095–AMR on Dissolved Concentration Limits; F0130–AMR on In-Waste Package Chemistry Summary; and F0170–AMR on In-Waste Package Chemistry Abstraction. The relevant AMRs on features, events, and processes (FEPs) include: N0080–FEPs for the Near-Field Environment; F0050–FEP Screen Cladding; F0185–In-Waste Package FEPs Screening; E0015–EBS FEPs Degradation Modes Analysis; and E0110–EBS Degradation Modes and FEPs Abstraction.

Most of these AMRs and the relevant PMRs are not available for review as of this writing. In the following sections, the resolution status based on the Viability Assessment (VA) design and TSPA-VA are considered to be current. As appropriate, status based on information contained in the License Application Design Selection (LADS) report (CRWMS M&O, 1999a), Revision 3 of the Repository Safety Strategy (CRWMS M&O, 2000a), and the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) has been included where the approaches differ from those used in the TSPA-VA. It is important to note the TSPA-SR methods and assumptions report does not contain details on how the different modeling approaches will be implemented. It is anticipated that the resolution status of this subissue will be updated further as the more detailed AMRs and PMRs become available for review. In addition, during DOE quality assurance (QA) audits, information may become available which will be incorporated as appropriate.

4.3 THE EFFECTS OF COUPLED THERMAL-HYDROLOGIC-CHEMICAL PROCESSES ON THE CHEMICAL ENVIRONMENT FOR RADIONUCLIDE RELEASE

In Revision 2 of its Repository Safety Strategy (U.S. Department of Energy, 1998a), the DOE has identified slow rate of release of radionuclides from the waste form as a key attribute of the repository system that would help its objective of acceptably low annual doses to a person living near the site (U.S. Department of Energy, 1998a). In Revision 3 of the Repository Safety Strategy (CRWMS M&O, 2000a), the DOE considered solubility limits of dissolved radionuclides as one of the seven principal factors of the postclosure safety case. Other factors identified by the DOE for the postclosure safety case, though given lower importance, include (i) performance of CSNF waste form; (ii) performance of DOE-owned spent nuclear fuel (DSNF), Navy fuel, and plutonium disposition waste form; and (iii) performance of defense high-level waste (DHLW) form. The Nuclear Regulatory Commission (NRC) considers there are 14 integrated subissues (ISIs)—the integrated processes, features, and events that could impact system performance—that need to be abstracted into a TSPA. Two of these ISIs are

(i) quantity and chemistry of water contacting waste packages and waste forms, and (ii) radionuclide release rates and solubility limits. Radionuclide release from waste forms and from the engineered barrier system will depend on the chemical environment, which will be conditioned by coupled thermal-hydrologic-chemical processes. The abstraction of the quantity and chemistry of water contacting waste packages and waste form incorporate thermal-hydrologic-chemical processes that will determine the chemical environment for radionuclide release. Contributions from the Container Life and Source Term (CLST), Thermal Effects on Flow (TEF), Unsaturated and Saturated Flow Under Isothermal Conditions (USFIC), and Total System Performance Assessment and Integration (TSPAI) KTIs also will be required to resolve this subissue. The DOE must adequately evaluate the chemical environment for radionuclide release and appropriately consider coupled thermal-hydrologic-chemical processes affecting this chemical environment in its assessment of repository performance.

4.3.1 Review Methods and Acceptance Criteria

The DOE approach to evaluate and abstract coupled thermal-hydrologic-chemical processes affecting the chemical environment for radionuclide release in a TSPA for the proposed repository at Yucca Mountain is satisfactory if specific acceptance criteria are met. With this revision (Revision 3) and update of the ENFE IRSR, the acceptance criteria and review methods for the DOE approach to evaluate and abstract coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release have been moved to the appropriate ISI sections of the Yucca Mountain Review Plan (YMRP), Revision 0 (U.S. Nuclear Regulatory Commission, 2000a).

4.3.2 Technical Bases for Review Methods and Acceptance Criteria for Effects of Coupled Thermal-Hydrologic-Chemical Processes on the Chemical Environment for Radionuclide Release

The bases are primarily focused on explaining why the effects of coupled thermal-hydrologic-chemical processes may be important to the chemical environment controlling radionuclide release from the waste form and engineered barrier system. As mentioned in Section 3, limited analyses in past DOE performance assessments on the effects of coupled thermal-hydrologic-chemical processes on radionuclide release have been completed. In addition, the relevance to performance of a particular coupled thermal-hydrologic-chemical process is highly dependent on repository design (e.g., thermal loading strategy, waste package material, etc.). For these reasons, the acceptance criteria primarily focus on ensuring that analyses of thermal-hydrologic-chemical effects are completed. The sophistication of the analysis of the effect of coupled processes on the chemical environment for release that could be conducted and found acceptable by staff depends on the information available at the present, any plans to obtain additional information before the license application and as part of the long-term testing program, and the ability of codes to adequately model coupled processes and determine their impact on repository performance.

Previous versions of the ENFE IRSR (U.S. Nuclear Regulatory Commission, 1999a) have reviewed the technical bases for earlier versions of the DOE TSPA analysis of Yucca Mountain. With this revision of the ENFE IRSR, the focus is on preserving the previous evaluations and updating the technical bases for the YMRP review methods and acceptance criteria (U.S. Nuclear Regulatory Commission, 2000a), taking account of current repository design features and their effects on the chemical environment for radionuclide release. For example, the Enhanced Design Alternative-II (EDA-II) selected by the DOE during the LADS process (CRWMS M&O, 1999a) for TSPA-SR (CRWMS M&O, 1999b) calls for the use of backfill (optional), a titanium drip shield, a steel invert with granular ballast, steel ground support, and a waste package with an outer corrosion-resistant material (Alloy 22) and an inner stainless steel structural material. Interaction of fluids with these engineered materials or their degradation products could substantially affect the chemical environment for radionuclide release. For instance, acidic pH solutions may result from oxidation and hydrolysis of chromium contained in stainless steel, or high pH solutions may be generated due to interaction of water with cementitious grout material used to anchor the rock bolts of the ground support system. The altered pH may significantly increase the solubility and the rate of release of radionuclides. The DOE assessment of this impact would be acceptable if it demonstrated, using geochemical equilibrium modeling codes such as EQ3 (Wolery, 1992) or others, that the solubility range chosen for its reference case performance assessment was conservative relative to the results of the equilibrium calculations.

4.3.2.1 Coupled Thermal-Hydrologic-Chemical Processes Affecting Spent Fuel, Cladding, and Borosilicate Glass Degradation

Near-field environmental factors, including Eh, pH, temperature, Cl^-, NO_3^-, and HCO_3^-, and F^-, are governed by near-field thermal-hydrologic-chemical processes. These factors affect degradation modes of spent fuel and its Zircaloy cladding. Zirconium alloys are susceptible to a form of hydrogen embrittlement called delayed hydride cracking. This phenomenon is promoted by the precipitation of brittle zirconium hydrides (ZrH_{2-x}) in areas of stress concentrations upon cooling from high temperature (Cox, 1990). Slow cooling may induce reorientation of plate-like hydrides into an axial rather than circumferential distribution, facilitating failure (Chan, 1996). Although cladding creep at moderate temperatures is not dependent on environmental factors, it is considered a plausible mode of failure (Santanan, Raghavan, and Chin, 1992). Above a certain critical potential, Zircaloy is susceptible to pitting corrosion in chloride-containing environments (Cragnolino and Galvele, 1978). Such a potential can be attained naturally under slightly oxidizing conditions (i.e., in the presence of Fe^{3+}). Under the environmental and potential conditions leading to pitting, stress-corrosion cracking of zirconium and Zircaloy occurs in the presence of an applied stress (Cox, 1990). Whereas a decrease in Eh protects the fuel cladding from localized corrosion and stress-corrosion cracking, it can promote failure by delayed hydride cracking. Despite its relatively low concentration, the presence of the fluoride anion in the environment may increase the uniform dissolution of zirconium alloy. The increase in dissolution is the result of the greater stability of the ZrF_6^{2-} complexes compared to that of the passive ZrO_2 film.

Corrosion of spent fuel (predominantly UO_2) by contact with the groundwater is the most important process affecting the long-term performance of this waste form. The groundwater will be modified by chemical and physical interactions in the near field. A major factor determined by the near-field environment is the redox potential or Eh. Eh generally increases by gamma- or alpha-radiolysis. The corrosion rate of spent fuel is determined by the corrosion potential E_{corr}. UO_{2+x} is a relatively good electronic conductor because of its deviation from stoichiometry. As a result, E_{corr} is a well-defined electrochemical parameter for spent fuel immersed in an aqueous environment. The rates of reduction of species, such as O_2 and H_2O_2, are coupled to the rate of oxidation of UO_{2+x}, establishing E_{corr} as a mixed potential on the interface between the oxide and solution (Shoesmith, et al., 1989). The effect of the potential is important due to the oxidative nature of the dissolution of UO_2.

The effect of pH on the rate of dissolution of spent fuel depends on the pH range. Under oxidizing conditions, only a slight dependence of corrosion rate on pH has been observed at pH values lower than 4. At pH values between 4 and 8, the rate of dissolution decreases linearly with pH (Grambow, 1989). At higher pH values, the rate of dissolution seems to be unaffected by pH changes. As in the case of other metals, valuable information can be compiled in terms of Eh-pH diagrams for the U-H_2O system in the presence of certain anions (Paquette and Lemire, 1981). Specific domains for the dominant degradation modes can be superimposed onto the Eh-pH diagrams. Temperature increases the rate of dissolution of UO_2, although the functional dependence is not well established over a wide range of temperatures.

The nature of the anionic species present in the groundwater and their concentrations are extremely important in determining the rate of corrosion of spent fuel. Anions such as CO_3^{2-}, that form stable soluble complexes with U^{6+} cations, substantially increase the rate of oxidative dissolution (Blesa, Morando, and Regazzoni, 1994). At low CO_3^{2-} concentrations (0.001 M), the rate of dissolution is proportional to the total concentration (Blesa, Morando, and Regazzoni, 1994). At intermediate concentrations of CO_3^{2-} (0.5 M), the dissolution rate depends on the square root of the total concentration (Grambow, 1989). At a higher CO_3^{2-} concentration (1.0 M at 100 °C), the corrosion rate reaches a constant value. Finally, at even higher concentrations, the corrosion rate decreases, probably due to the formation of surface films (Needes, Nicol, and Finkelstein, 1975). These concentrations, while high for the nominal water composition, may occur due to evaporative processes in the near field. Corrosion is accelerated by anions in the sequence $Cl^- < PO_4^{3-} < SO_4^{2-} < F^- < CO_3^{2-}$. In the case of PO_4^{3-} and SO_4^{2-}, a maximum in the corrosion rate is observed at intermediate concentrations (about 1.5×10^{-2} M) (Blesa, Morando, and Regazzoni, 1994).

Other species, such as $SiO_2(aq)$, $H_3SiO_4^-$, and $H_2SiO_4^{2-}$, can react with U(VI) to precipitate complex uranyl silicates. These secondary minerals may tend to reduce the corrosion rates and exposure of fresh surface by forming a protective layer over the spent fuel. Under certain circumstances, acceleration of spent fuel dissolution can occur as a result of spallation of the alteration layers.

Rapid increases in the concentration of spent fuel dissolution products may lead to saturation of the medium with secondary alteration products. This accelerated precipitation of secondary phases could eventually preferentially release certain radionuclides. Bates, et al. (1995) found that intermittent additions of controlled amounts of groundwater to spent fuel led to precipitation of most of the transuranic elements (americium, curium, and plutonium). Neptunium was not precipitated and remained in solution. Wilson (1990) used semi-static experiments (i.e., involving periodic removal of a leachant aliquot and replacement with fresh solution). He observed that actinide (uranium, plutonium, americium, curium, and neptunium) concentrations reached constant values rapidly. This observation suggests that steady-state conditions between spent fuel dissolution and secondary-phase formation are established. Formation of U^{6+} secondary phases, such as uranophane, was confirmed. Actinide concentrations, with the exception of neptunium, measured at 85 °C were lower than at 25 °C, which suggests that the solubility limiting phases are formed more rapidly at the higher temperature. Alternatively, this effect could be the consequence of the retrograde solubility of secondary products. The presence of plutonium, americium, and curium as colloids in the leachates was reported, but the formation of precipitated secondary phases predominated at 85 °C.

Under oxidizing conditions and in the presence of carbonate anions, there is a large driving force for the dissolution of the UO_2 matrix. Soluble radionuclides, such as ^{137}Cs, ^{90}Sr, and ^{125}Sb, exhibited congruent dissolution from spent fuel in flow-through tests. The release rate of these fission products decreased with time to a steady-state value similar to the release rate of uranium from the UO_2 matrix (Gray, Leider, and Steward, 1992). In semi-static tests, the fractional release of ^{90}Sr, ^{137}Cs, ^{129}I, and ^{99}Tc increased with temperature, and almost linearly with time. Species such as Ca^{2+}, Mg^{2+}, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, and CO_3^{2-} precipitated from solution in tests conducted at higher temperatures. Bates, et al. (1995) suggested that the corrosion rate of the matrix and release of radionuclides are accelerated in unsaturated tests compared to those under semi-static conditions. This situation leads to incongruent release of individual fission products and actinides, probably controlled by the formation of particulates in solution. In addition, the corrosion rate, and especially the rate of radionuclide release, depend on the characteristics of the spent fuel (e.g., composition, degree of burnup). Pre-oxidation of the fuel was not thought to be a factor in the acceleration of the dissolution rate (Bates, et al., 1995). However, the modification of the pH of the leachate attributed to the formation of HNO_3 by alpha-radiolysis of humid air, as well as the generation of formate and oxalate from inorganic C, may raise the solubility of actinides (Finn, et al., 1994). All these effects are postulated to become even more important at relatively large surface area-to-groundwater volume ratios such as may be expected in the unsaturated zone at Yucca Mountain. However, acid generating processes may be counteracted by alkalinity deriving from cement-water interactions.

Through interactions with oxidizing components, including radiolytic products, spent fuel will eventually oxidize and form a large quantity of UO_2^{2+}-bearing solids. Natural analog (Pearcy, et al., 1994) and experimental studies (Wronkiewicz, et al., 1992) indicate that schoepite, soddyite, and uranophane are among the secondary minerals likely to form from spent-fuel oxidation. Furthermore, these studies indicate that rates of oxidation of reduced uraninite and unirradiated fuel (both analogs of spent fuel) are rapid relative to transport of uranium away from the natural geologic setting or the experimentally simulated waste package, respectively. Therefore, secondary oxidation products will accumulate and uranyl minerals will have a large effect on near-field physical and chemical conditions.

Secondary uranium phases are likely to have several important effects on the near-field environment. First, physical disruption of structural components (e.g., cladding or degraded containers), due to the large volume increase accompanying oxidation and hydration of UO_2, may occur. Second, both porosity and permeability could be reduced because of the volume expansion. Third, neptunium, plutonium, and other radioactive waste species may be incorporated into secondary uranium phases by coprecipitation. Fourth, the secondary uranium phases may limit ingress of water and oxidants to unaltered wastes. Finally, the secondary uranium phases may control the solubility or dissolution rate of spent fuel. Thus, secondary uranium phases may control the source term for radionuclide (not just U) releases from the breached waste packages. With regard to long-term performance of the proposed repository, secondary alteration products resulting from interactions of spent fuel with the near-field environment, rather than unaltered spent fuel, will likely control releases of many radionuclides from the engineered barrier system.

Experimental (Holland and Brush, 1979) and theoretical (Murphy, 1997) studies indicate that the solubilities of uranyl minerals, such as schoepite and uranophane, are retrograde with temperature. The emplacement horizon will reach its maximum temperature shortly after waste emplacement (e.g., within tens or hundreds of years). Thereafter, it will experience an environment of continuously decreasing temperature. Consequently, the solubilities of alteration products of spent fuel will tend to increase with time. In contrast, through a process of Ostwald ripening, increasingly stable secondary phases, with lower solubilities, will crystallize. With the EDA-II design, the maximum temperature is expected to be shorter and the duration of elevated temperatures is expected to be shorter compared to the TSPA-VA design.

In DOE and NRC performance assessments, solubility is invoked as a conservative upper limit to the radionuclide concentration in aqueous solution. In principle, mineral solubilities and radionuclide concentrations can be calculated based on thermodynamic data and the chemical characteristics of the system, i.e., temperature, pressure, and composition. In practice, estimation of maximum radionuclide concentrations are further complicated by metastability of solid phases, metastable supersaturation, solid solution (coprecipitation), colloid stability, oxidation-reduction disequilibria, disequilibrium dissolution of source material, sorption, etc. The gross disequilibrium between spent nuclear fuel and the Yucca Mountain geochemical environment creates a strong potential to generate metastable conditions including solution concentrations in excess of minimum equilibrium solubilities. Consequently, radionuclide solubilities used in performance assessments have tended to be uncertain (i.e., sampled over a large range) and conservative (i.e., high relative to the most thermodynamically stable possibilities).

One approach to foster conservatism in experimental determination of radionuclide solubilities for performance assessment is to approach steady-state concentrations from a state of supersaturation (as well as from undersaturation). This approach was advocated in the NRC position paper on solubilities (U.S. Nuclear Regulatory Commission, 1984) and followed in experimental studies conducted by Nitsche, et al. (1993, 1994) for neptunium solubilities. Resulting neptunium solubilities are high and contribute to high neptunium contributions in estimated doses in performance assessments conducted in TSPA-93 and TSPA-95.

For TSPA-VA, the range of solubility values for neptunium species was about two orders of magnitude lower than that used in the DOE TSPA-1993 and TSPA-1995. It was argued that the solubility values used in the earlier performance assessments were based on experiments that used solutions supersaturated with NpO_2, possibly with metastable phases present in solution, and did not adequately represent the conditions in the spent nuclear fuel dissolution experiments or for fluid compositions similar to J-13 water anticipated in the WP. Reducing the values of neptunium solubility in performance assessments from the empirical values used in previous performance assessment iterations requires substantial justification. The solid phase proposed to control lower solubilities should be shown by empirical and theoretical means to form and to remain stable, e.g., by reversal of the stability of this solid phase from undersaturated and supersaturated conditions and by thermodynamic calculations of its stability for expected environmental conditions. Also, measurements of the distribution of the radionuclide between the solid phase and the aqueous phase should be made and used together with an evaluation of anticipated aqueous speciation to determine radionuclide concentrations. Empirical measurements of concentrations under a particular set of experimental conditions provide weak justification for maximum concentration limits in performance assessments because relevant repository conditions will be different and will vary due to the effects of coupled thermal-hydrologic-chemical processes. The solubility limits need to be reevaluated by the DOE as the water chemistry inside the waste package becomes better known.

Coprecipitation of a minor species in a phase composed predominantly of other species does not lead to maximum concentration limits in the same sense that solubility of a stoichiometric phase limits the concentrations of species in solution. A strong potential exists for a small amount of substitution of a minor or trace species. This potential may be reduced as the amount of substitution increases for thermodynamic reasons (entropy and enthalpy of mixing) related to structural (crystallographic) effects. Nevertheless, concentrations of trace elements may be severely limited by coprecipitation. Concentrations of many trace constituents in natural environmental waters are limited by sorption and coprecipitation (solid solution) phenomena.

The likelihood of limitation of radionuclide concentrations by coprecipitation with uranyl phases in a Yucca Mountain repository is indicated by several lines of evidence: (i) the abundance of uranium in the spent nuclear fuel waste form; (ii) the wealth of experimental, theoretical, and natural analog data indicating that relatively stable uranyl minerals will form on oxidation of uranium in the Yucca Mountain environment; and (iii) experimental and theoretical crystallographic indications of coprecipitation of minor radionuclides in secondary uranyl minerals.

However, data for the equilibrium solubilities (thermodynamic properties) of uranyl hydrate-silicate solid phases are uncertain, and experimental data for the distribution of radionuclides between aqueous solution and the structures of these phases are sparse. Experimental examination of this issue should be a high priority for contributions to evaluations of performance assessments for Yucca Mountain.

The second main waste form planned for the proposed repository at Yucca Mountain is borosilicate glass. Environmental factors affecting the general or localized dissolution rate of borosilicate glasses include Eh, pH, temperature, Cl^-, HCO_3^-, $H_3SiO_4^-$, F^-, and Fe^{2+}. As in the case of metals, the interrelationship of Eh and pH on the dissolution of waste glass can be displayed in a potential-versus-pH diagram (Jantzen, 1992). In general, Eh has practically no effect on the dissolution of the glass matrix. Silicon, boron, and aluminum, which are the principal network formers of borosilicate glasses, do not undergo changes in oxidation state within the range of Eh values expected under repository conditions. The effect of pH is far more important. The rate of dissolution is strongly accelerated at alkaline pH due to matrix dissolution. At pH lower than 4, the rate is accelerated by diffusion-controlled hydrogen ion exchange for alkali ions. Many anions have a minor effect on the solubility and rate of dissolution of borosilicate glasses. However, fluoride accelerates the dissolution substantially through the formation of SiF_6^{2-} complexes. The value of relative humidity is important in the durability of glasses in humid air. Glasses also are susceptible to environmentally assisted cracking in aqueous environments (McCauley, 1995). The effect of this phenomenon on radionuclide releases may be far less important than that associated with generalized dissolution.

Alteration of glass depends primarily on the activity of aqueous silica. In the ambient geochemical environment, and for predicted geochemical conditions in the host rock, the aqueous silica concentration is large (Yang, 1992; Yang, Rattray, and Yu, 1996). A glass waste form would be expected to be fairly unreactive for these conditions. Other components of the glass (e.g., B) will also affect the stability of the glass. Alkalinity will be produced by interactions of water with cementitious materials. Also lower silica activity, as a consequence of precipitation of silicates by interactions of groundwater and unstable engineered materials, could enhance the alteration of glass waste forms. Ultimate glass waste form alteration products are likely to be clay or zeolite minerals. These are analogous to alteration products of the natural volcanic glasses existing at Yucca Mountain. Both the clay and zeolite minerals are likely to incorporate augmented quantities of components of the engineered barrier system, such as Fe and Ca. Clay minerals generally have low solubilities. Some quantity of radioactive waste species is likely to be incorporated in mineral alteration products of glass waste forms.

4.3.2.2 Effects of Engineered Materials on the Chemical Environment for Radionuclide Release

The effects of engineered materials are likely to be important to the chemical environment for radionuclide release. Several metal alloys that are thermodynamically unstable in contact with oxidizing water are being considered as container materials for the Yucca Mountain repository. In addition, if carbon steel is used as structural support for the drifts, then reactions affecting the containers would also affect the structural supports. Although corrosion of these materials may be slow, it would consume oxidants in the near-field environment and, thus, could affect the continued corrosion of the spent fuel. Therefore, corrosion of container materials may lead to locally reducing conditions in the near field and strong gradients in oxidation potential, despite the prevailing oxidizing nature of the geologic setting (Murphy and Pabalan, 1994). Reducing conditions will likely have a limited effect on radionuclide release, except for redox-sensitive radioelements such as technetium that form relatively insoluble solid phases under reducing conditions. Depending on the geometry of the flow path of water through the engineered barrier system, the flux of oxygen, and the mass and rate of oxidation of easily oxidizable metals along the transport path, local conditions could be chemically reducing.

Corrosion products from metallic components, mostly in the form of metal cations, can affect corrosion rates of spent fuel directly through precipitation reactions forming secondary minerals that may slow the rate of dissolution. Conversely, corrosion rates can be increased by indirect action of corrosion products that may change the redox potential and the pH of the environment. The redox potential can increase by the action of reducible cations, such as Fe^{3+}. The pH can decrease by oxidation of Cr, present in stainless steel, to Cr^{3+}, or by hydrolysis of highly-charged cations, such as Fe^{2+} and Cr^{3+}, among others. Low-molecular-weight organic compounds, including carboxylic acids, can be produced by degradation of fuel, lubricants, or other organic materials, either by chemical or biochemical mediated processes. These compounds may accelerate the rate of corrosion of spent fuel due to the formation of complexing species and chelating species. In addition, published literature (McVay and Buckwalter, 1983; Barkatt et al., 1989; Bourcier, et al., 1992) indicate, under some conditions, dissolution rates of silicate glasses are strongly enhanced by dissolved Fe. Thus, waste package corrosion products such as Fe^{3+} could be important in determining the dissolution rate of the glass waste form.

Although no longer considered in the EDA-II repository design, the use of cementitious materials, in the form of concrete inverts and linings, was considered in the TSPA-VA design for the estimated 179 km of emplacement drifts of the proposed Yucca Mountain high-level waste (HLW) repository, in addition to the planned use of cement in roadways for construction, and emplacement ramps and service mains. Cement is used primarily for its structural (e.g., high compressive strength) and physical (e.g., low permeability) properties. However, its effect on the near-field chemical environment of a repository could be pronounced. Cements are extremely fine-grained, high-surface area materials containing somewhat soluble and thermodynamically metastable phases (e.g., a gel-like phase designated CSH because it contains Ca, Si, and H_2O) that are unstable with respect to crystalline cement phases. These properties and the partially interconnected pore network of the solids make these materials potentially reactive with the near-field environment and the engineered barrier system.

Interactions between cementitious materials and the near-field system can be potentially beneficial for mitigating release of radionuclides. The persistent alkaline pH (>10) characteristic of pore fluids in contact with hydrated cement phases favors precipitation of a wide variety of radionuclides, including transuranics (Glasser, et al., 1985; Atkins, et al., 1990). For example, interaction of cement with aqueous U^{6+} can result in the formation of Ca-bearing phases uranophane or becquerelite, a poorly-crystallized Ca-uranyl hydrate (Atkins, Beckley, and Glasser, 1988; Atkins, et al., 1990). On the other hand, alkaline conditions can be detrimental to the stability of nuclear waste glass. For example, experiments by Heimann (1988) indicated that cement-glass interaction leads to accelerated dissolution or alteration of the nuclear waste glass compared to a system without cement present. The degree to which cementitious materials can affect the chemical environment for radionuclide release will depend to a large part on its inventory and on the reactivity with groundwater of the specific cement material formulation used.

In the TSPA-SR design, cementitious materials are not planned to be used for ground support, except in the form of grout to anchor the rock bolts of the ground support system. The potential effect of cementitious materials on the chemical environment for radionuclide release in the TSPA-SR design is expected to be substantially reduced compared to the TSPA-VA design.

4.3.2.3 Radiolysis Effects on Radionuclide Release

Radiolysis has complex effects on aqueous oxidation-reduction conditions. According to Dubessy, et al., (1988), the dose of absorbed γ rays is only 0.02 times the dose of absorbed α particles in a given time. Also, according to Spinks and Woods (1976) (cited in Dubessy, et al., 1988), a single 1 MeV α particle can ionize 10^5 molecules as it loses energy. Therefore, the primary cause of water radiolysis is α-particle radiation. Radiolysis occurs close to the site of radioactive decay and can affect wetted surfaces of radioactive waste forms.

Radiolytic oxidizing species, such as $OH^\bullet$, where "$^\bullet$" denotes a free radical, H_2O_2, $HO_2^\bullet$, and O^{2-} (Spinks and Woods, 1976), could oxidize reduced species (e.g., Fe^0 in the waste package to Fe^{2+} and Fe^{3+}, $N_2(aq)$ to NO_2^- or NO_3^-, and U^{4+} to U^{6+}). Molecular hydrogen (H_2) produced as the result of the combination of two $H^\bullet$, in contrast, is relatively non-reactive. H_2 is likely to diffuse away from the site of radiolysis. Various experimental studies using gamma radiation suggest that radiolysis will promote waste form (both spent fuel and glass) instability and radionuclide mobility through enhancement of oxidative processes and lowering of pH (Wronkiewicz, Young, and Bates, 1991; Wronkiewicz, et al., 1993; Sunder, et al., 1992; Sunder and Christensen, 1993). As pointed out by Van Konynenburg (1986), such processes are enhanced by unsaturated conditions expected in the proposed Yucca Mountain repository. On the other hand, bicarbonate could limit the radiolytic pH lowering (Van Konynenburg, 1986), as could cement-water interactions.

4.3.2.4 Microbial Effects on the Chemical Environment for Radionuclide Release

The potential importance of microbial processes to affect the chemical environment for radionuclide release from nuclear waste repositories has been recognized in Europe (Pedersen and Karlsson, 1995; Lessart, et al., 1997; Christofi and Philp, 1997). Metabolic byproducts of microorganisms may lead to solubilization and increased mobility of radionuclides (Christofi and Philp, 1997). Complexation of actinides (e.g., uranium and neptunium) by organic acids could increase their solubilities by about two orders of magnitude (McKinley, West, and Grogan, 1985).

The potential for enhanced HLW glass dissolution and the production of chelating and complexing ligands as a result of microbial activity has also been recognized by the DOE as potentially important to radionuclide release. These topics are addressed in the CLST IRSR (U.S. Nuclear Regulatory Commission, 1999c). Horn and Meike (1995) concluded that microbial activity may promote dissolution of glass by producing acidic conditions, and may increase the solubility of metals via chelation. Investigations of Yucca Mountain indigenous microbes, documented in Hersman (1996), suggested that they are capable of producing enough chelating agents (e.g., siderophores) to chelate 0.2 g L^{-1} of ^{239}Pu in the subsurface pore water. Corrosion of natural basaltic glass (Thorseth, Furnes, and Tumyr, 1995) and simulated nuclear-waste glass (Staudigel, et al., 1995) by biologically mediated dissolution has been demonstrated. Despite these studies, the DOE did not consider microbial effects on radionuclide release in its TSPA-VA (TRW Environmental Safety Systems, Inc., 1997).

It will not be necessary to address microbial effects on radionuclide release in its performance assessments if the DOE demonstrates, through the use of a mass balance of nutrients and energy-producing reactions approach (McKinley, et al., 1997), that microbial activity within the engineered barrier system is unlikely to be of significance. This approach has been discussed in detail in Section 4.2.2.3 and a detailed discussion of the limitations for microbial activity has been presented in Section 4.1.2.3. While microbial activity in the volcanic tuffs will be limited by a lack of nutrients, additional nutrients may be available within the engineered barrier system. Thus, an analysis of the supply nutrients and energy-producing reactions, which would consume the nutrients, should be conducted. The DOE stated that they will use this type of approach to evaluate the potential for microbiological processes in the near-field geochemical environment (TRW Environmental Safety Systems, Inc., 1997).

5.4.3 Subissue 3: Effects of Coupled Thermal-Hydrologic-Chemical Processes on the Chemical Environment for Radionuclide Release

In the YMRP (U.S. Nuclear Regulatory Commission, 2000a), the DOE approach to assess the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release must meet the following generic acceptance criteria for each relevant ISI: (i) integration; (ii) data and model justification; (iii) data uncertainty and verification; (iv) model uncertainty; and (v) model verification. QA is handled in a separate section of the YMRP.

Two model abstraction ISIs are influenced by the ENFE within the scope of the chemical environment for radionuclide release subissue. The ISIs are (i) Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms and (ii) Radionuclide Release Rates and Solubility Limits (U.S. Nuclear Regulatory Commission, 2000a). The NRC Total-system Performance Assessment (TPA) abstraction of radionuclide release requires input from the two abstractions in this subissue (U.S. Nuclear Regulatory Commission, 2000a,b). The effects of coupled thermal-hydrologic-chemical processes need to be considered in the evaluation of each abstraction. As part of this evaluation, the acceptance criteria and review methods in the YMRP for the two ISIs will be used to review the DOE PMRs and the supporting AMRs as they become available. This evaluation will also include a review of the relevant FEPs included/excluded from the DOE TSPA.

The review will focus on the DOE Waste Form Degradation PMR. This PMR describes the models, abstractions, and analyses that address the following major topics related to waste form degradation: (i) inventory; (ii) CSNF cladding degradation; (iii) CSNF waste form degradation; (iv) DSNF, Navy fuel, plutonium disposition wastes degradation; (v) HLW glass degradation; (vi) dissolved radionuclide concentration limits; (vii) colloid-assisted radionuclide concentration limits; (viii) in-package chemistry; and (ix) in-package source term and radionuclide transport abstraction. An evaluation of the DOE abstraction of radionuclide inventory [topic (i)] is presented in the TSPAI IRSR (U.S. Nuclear Regulatory Commission, 1999b); an evaluation of the DOE abstraction of in-package source term and radionuclide transport [topic (ix)] will be presented in Section 5.4.4 of Revision 3 of the ENFE IRSR.

The information provided in the Waste Form Degradation PMR and in the supporting AMRs is expected to encompass the information required to assess the effects of coupled thermal-hydrologic-chemical processes on radionuclide release. For this revision of the ENFE IRSR (Revision 3), the review will focus on the DOE models, abstractions, and analyses for topics (ii) to (viii), and on the following subset of AMRs relevant to the ENFE subissue on the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release: E0065–AMR on In-drift Thermal-Hydrologic-Chemical Analysis; F0055–AMR on CSNF Degradation Model; F0095–AMR on Dissolved Concentration Limits; F0105–AMR on Colloid Source Term, Los Alamos National Laboratory; F0110–AMR on Colloid Source Term, Argonne National Laboratory; F0155–AMR on Colloid Source Term Abstraction; F0065–AMR on Other Waste Form Abstraction; F0130–AMR on In-Waste Package Chemistry Summary; and F0170–AMR on In-Waste Package Chemistry Abstraction. Also included in the review are the following AMRs on FEPs: N0080–FEPs for the Near-Field Environment; F0050–FEP Screen Cladding; F0185–In-Waste Package FEPs Screening; E0015–Engineered Barrier System FEPs Degradation Modes Analysis; and E0110–Engineered Barrier System Degradation Modes and FEPs Abstractions.

Most of these AMRs and the PMR on Waste Form Degradation are not available for review as of this writing. In the following sections, the resolution status based on the VA design and TSPA-VA are considered to be current, except where the relevant AMR is available. As appropriate, resolution status based on information contained in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) and in Revision 3 of the Repository Safety Strategy (CRWMS M&O, 2000a) has been included where the approaches differ from that used in TSPA-VA. It is important to note that the TSPA-SR methods and assumptions report and the Repository Safety Strategy report do not contain details on how the different modeling approaches will be implemented. It is anticipated that this section will be further updated as the AMRs and PMRs become available. Information that may become available during DOE QA audits will be incorporated as appropriate.

To facilitate the discussion of resolution status with respect to the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release, the acceptance criteria for the ISIs on (i) radionuclide release rates and solubility limits and (ii) quantity and chemistry of water contacting waste packages and waste forms are listed in Section 5.4.3.1. Note that the wording of these generic acceptance criteria is similar in both ISIs. A summary of the DOE models, abstractions, and analyses for the seven waste form degradation topics is presented in Section 5.4.3.2, and staff analyses of the DOE models, abstractions, and analyses are presented in Section 5.4.3.3.

5.4.3.1 Acceptance Criteria

For subissue 3 of the ENFE IRSR, the DOE approach to abstract coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release in a TSPA for the proposed repository at Yucca Mountain will be acceptable if each of the acceptance criteria for the ISIs on radionuclide release rates and solubility limits (Section 4.2.1.3.4.3 of the YMRP) and quantity and chemistry of water contacting waste packages and waste forms (Section 4.2.1.3.3.3 of the YMRP) is met. These acceptance criteria pertain to (i) integration; (ii) data and model justification; (iii) data uncertainty and verification; (iv) model uncertainty; and (v) model verification. Descriptions of these acceptance criteria, taken from the pertinent sections of the YMRP, are given in this section.

Criterion 1: Integration

Integrated Subissue on Radionuclide Release Rates and Solubility Limits

Important design features, physical phenomena and couplings, and consistent and appropriate assumptions have been identified and described sufficiently for incorporation into the abstraction of radionuclide release rates and solubility limits in the TSPA, and the technical bases are provided. The features, phenomena and couplings, and assumptions used to abstract release of radionuclides from waste forms inside the waste package and the transport and release of radionuclides from the engineered barrier system should be provided. The TSPA abstraction is consistent with the identification and description of those aspects of radionuclide release rates and solubility limits that are important to waste isolation. The TSPA abstraction is also consistent with the technical bases for these descriptions of barriers important to waste isolation.

Integrated Subissue on Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms

Important design features, physical phenomena and couplings, and consistent and appropriate assumptions have been identified and described sufficiently for incorporation into the abstraction of the quantity and chemistry of water contacting waste packages and waste forms in the performance assessment and other related abstractions in the TSPA, and the technical bases are provided. The TSPA abstraction in the DOE license application (LA) identifies and describes aspects of the quantity and chemistry of water contacting waste packages and waste forms that are important to waste isolation and includes the technical bases for these descriptions.

Criterion 2: Data and Model Justification

Integrated Subissue on Radionuclide Release Rates and Solubility Limits

Sufficient data on design features (including Ti drip shield, backfill, waste packages, waste forms, other engineered barrier system components, and thermal loading), geology, hydrology, and geochemistry of the unsaturated zone (UZ) and drift environment (e.g., field, laboratory, and natural analog data) are available to adequately define relevant parameters and conceptual models necessary for developing the abstraction of radionuclide release rates and solubility limits used in the TSPA. The data are also sufficient to assess the degree to which FEPs related to radionuclide release rates and solubility limits, and which affect compliance with 10 CFR 63.113(b), have been characterized, and to determine whether the technical bases provided for inclusion or exclusion of these FEPs are adequate. Where adequate data do not exist, other information sources such as expert elicitation have been appropriately incorporated.

Integrated Subissue on Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms

Sufficient data on design features (including drip shield, backfill, waste packages, cladding, other engineered barrier components, and thermal loading), geology, hydrology, geochemistry, and geomechanics of the UZ and drift environment (e.g., field, laboratory, and natural analog data) are available to adequately define relevant parameters and conceptual models necessary for developing the abstraction of the quantity and chemistry of water contacting waste packages and waste forms in the TSPA. The data are also sufficient to assess the degree to which FEPs related to the quantity and chemistry of water contacting waste packages and waste forms, and which affect compliance with 10 CFR 63.113(b), have been characterized, and to determine whether the technical bases provided for inclusion or exclusion of these FEPs are adequate. Where adequate data do not exist, other information sources such as expert elicitation have been appropriately incorporated into the abstraction process.

Criterion 3: Data Uncertainty and Verification

Integrated Subissue on Radionuclide Release Rates and Solubility Limits

Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the TSPA abstraction of radionuclide release rates and solubility limits are consistent with site characterization, design data, laboratory experiments, field measurements, and natural analog data.

Integrated Subissue on Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms

Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the TSPA abstraction of quantity and chemistry of water contacting waste packages and waste forms, such as the pH, chloride concentration, and amount of water flowing into and out of the breached waste package, are consistent with site characterization data, design data, laboratory experiments, field measurements, and natural analog data, are technically defensible, and reasonably account for uncertainties and variabilities. The technical bases for the parameter values used in the TSPA abstraction are provided.

Criterion 4: Model Uncertainty

Integrated Subissue on Radionuclide Release Rates and Solubility Limits

Alternative modeling approaches consistent with available data and current scientific understanding are investigated and results and limitations are appropriately factored into the abstraction of radionuclide release rates and solubility limits. In its technical bases, the DOE has provided sufficient evidence that alternative conceptual models of features and processes have been considered, that the models are consistent with available data (e.g., design features, field, laboratory, and natural analog) and current scientific understanding, and that the effect of these alternative conceptual models on TSPA has been evaluated.

Integrated Subissue on Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms

Alternative modeling approaches consistent with available data (e.g., design features, field, laboratory, and natural analog) and current scientific understanding are investigated and results and limitations are appropriately factored into the abstraction of quantity and chemistry of water contacting waste packages and waste forms. The DOE has provided sufficient evidence that alternative conceptual models (ACMs) of features and processes have been considered, that the models are consistent with available data and current scientific understanding, and that the effect of these ACMs on TSPA has been evaluated.

Criterion 5: Model Verification

Integrated Subissue on Radionuclide Release Rates and Solubility Limits

Outputs from the TSPA abstraction of radionuclide release rates and solubility limits is justified through comparison with output from detailed process-level models and empirical observations (e.g., laboratory testing, field measurements, natural analogs).

Integrated Subissue on Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms

Output from the TSPA abstraction of quantity and chemistry of water contacting waste packages and waste forms is justified through comparison with output from detailed process-level models and/or empirical observations (e.g., laboratory testing, field measurements, natural analogs).

5.4.3.2 Description of the U.S. Department of Energy Models, Abstractions, and Analyses

For the TSPA-VA, the DOE model of waste form degradation was based on the assumption that the waste packages were breached. After the waste packages are breached, radionuclides are not available for release and transport until: (i) failure of the fuel cladding or HLW canister; (ii) degradation of the solid waste form; and (iii) mobilization of radionuclides into aqueous solution or an aqueous colloidal suspension. Mobile radionuclides are transported out of the degraded waste package and through the engineered barrier system to the geosphere via one of two mechanisms: (i) movement of dissolved or colloidal material via diffusion or (ii) movement of dissolved or colloidal material via advection (U.S. Department of Energy, 1998b). The components of the waste form degradation model used by the DOE include the initial inventory, degradation of the cladding on CSNF, dissolution rates from the waste forms, solubility constraints on radionuclide mobilization, and formation of colloids and secondary mineral phases.

The important input into the waste form degradation model in the TSPA-VA included the inventory of radionuclides. In addition, the temperature at the waste package surface, RH at the waste package surface, and liquid saturation in the invert beneath the waste package, all derived from thermal-hydrologic modeling results, were inputs to the models. Results from waste package degradation, cladding degradation, water ingress into waste packages, the amount of exposed fuel surface caused by cladding degradation, and the near-field geochemical conditions were also used as input to the waste form degradation model.

Based on information provided in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b), the general approach to be used by the DOE for the TSPA-SR and for the LA will remain the same as the TSPA-VA approach, although the analyses will take into account the potential effects of the new repository design and a more elaborate evaluation of the in-drift geochemical environment will be done. Most of the AMRs that provide the details on DOE models, abstractions, and analyses are not available as of this writing, thus the summary of the DOE approach given in the following sections is mostly based on the TSPA-VA (U.S. Department of Energy, 1998b) and the supporting technical basis document (CRWMS M&O, 1998).

5.4.3.2.1 Commercial Spent Nuclear Fuel Clad Degradation

A review of the DOE models and abstractions regarding the behavior of CSNF is presented in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c). An important component of these models is the degradation of the Zircaloy cladding used in commercial water-cooled nuclear reactors. The cladding can act as a barrier to the release of radionuclides. For the TSPA-VA, the DOE included the consideration of cladding as an additional metallic barrier (U.S. Department of Energy, 1998b). Cladding will be included also as a barrier in the process models of TSPA-SR (CRWMS M&O, 1999b). Several potential degradation mechanisms of Zircaloy cladding, such as uniform and localized corrosion, creep, delayed hydride cracking, hydrogen embrittlement, mechanical failure owing to rock fall, stress corrosion cracking, and fuel and cladding oxidation, can impair that beneficial action, as discussed in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c) and in more detail elsewhere (Cragnolino et al., 1999). The DOE has evaluated these possible failure modes, but neglected most of them as a cause of cladding failure under disposal conditions on the basis of auxiliary analyses (CRWMS M&O, 1998). The exceptions are uniform corrosion and mechanical failure as a result of rockfall once the waste package has lost structural integrity. In addition, it is assumed that a small fraction, equal to 0.1 percent of the CSNF rods, have failed during reactor operations. This type of failure is classified as "juvenile" cladding failure (U.S. Department of Energy, 1998b) Also, the small percentage (about 1.5 percent) of the CSNF fabricated with stainless steel cladding are considered to fail as soon as the waste package fails because it is assumed that the rate of corrosion of stainless steel is comparatively rapid with respect to that of Zircaloy cladding.

Corrosion of Zircaloy cladding was modeled in TSPA-VA using the WAPDEG code and assuming that general corrosion of Zircaloy can occur inside the waste packages according to the model used for alloy 22 as inner waste package container material (CRWMS M&O, 1998). Three general corrosion rate cumulative distribution functions for alloy 22, applicable to three different temperatures (20, 50 and 100 °C), were used with two bounded conditions. For one of them, it was assumed the rate of corrosion of Zircaloy was 10 times slower than that of alloy 22, whereas the rate was considered to be 1,000 times slower in the other one. This range of relative corrosion rates was selected on the basis of literature data (Yau and Webster, 1987) for Zr_7O_2 (commercially pure zirconium) and alloy C-276 (an alloy similar but less corrosion-resistant than alloy 22) in environments typical of the chemical process industries (concentrated solutions of H_2SO_4, HNO_3, H_3PO_4, and HCl acids at temperatures ranging from 100 to 230 °C), which are more aggressive environments than those expected at Yucca Mountain. Rates of corrosion of alloy C-276 were reported to range from 10 to 83,000 times higher than those of Zr_70_2 in the concentrated acid solutions (CRWMS M&O, 1998).

Mechanical failure of cladding through rockfall is considered in TSPA-VA (CRWMS M&O, 1998) by assuming the following sequence of events (i) rocks fall and lie on top of the waste package; (ii) waste package containers corrode, become mechanically weak, and fail; (iii) inner components of the waste package fail and fuel assemblies fall to the bottom of the waste package; and (iv) rocks fall from the container top and damage the fuel assemblies inside. Mechanical failure is treated by considering the cladding (thin-walled tube) as a simple elastic-plastic beam with clamped ends subjected to an external load resulting from the rock fall. The elastic-plastic behavior of the fuel rod is described by a piecewise linear stress-strain curve. The model takes into account the block size, block geometry, drop height, stack arrangement of the fuel assemblies, fracture geometry of the fuel rods and assemblies, and the load-displacement response of the fuel rod and assemblies and the failure criterion is based on the uniform elongation of the fuel rod.

5.4.3.2.2 Commercial Spent Nuclear Fuel Waste Form Degradation

A review of DOE models and abstractions of waste form degradation can be found in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c). A key hypothesis of TSPA-VA (TRW Environmental Safety Systems, Inc., 1997) is that the CSNF intrinsic dissolution rate will determine the aqueous release of soluble radionuclides that are contained within the CSNF matrix. The same hypothesis will be used for the TSPA-SR (CRWMS M&O, 1999b). The product of the intrinsic dissolution rate and the wetted surface area provides the source term for radionuclide transport through the unsaturated zone. High-solubility radionuclides, such as ^{99}Tc or ^{129}I, are assumed to be released congruently with the dissolution of the matrix, whereas uranium and low-solubility radionuclides, such as ^{239}Pu or ^{241}Am, are assumed to be reprecipitated on the surface of the irradiated UO_2 as secondary minerals. Consequently, the release of low-solubility radionuclides from the engineered barrier system is constrained by the solubility limit of the solid phase containing the radionuclide. In addition, sensitivity analyses are performed to determine the effect of retention of radionuclides (^{237}Np) by secondary minerals formed subsequent to dissolution of the CSNF. The drip test results from Argonne National Laboratory, along with reactive transport modeling, are used to estimate the retention of these radionuclides in the secondary minerals. The DOE abstraction of dissolved radionuclide concentration limit is discussed in Section 5.4.3.2.5.

The intrinsic dissolution rates derived from flow-through tests are used by the DOE as input to the release of highly soluble radionuclides in the base-case analyses of TSPA-VA (CRWMS M&O, 1998). The intrinsic dissolution rate is a function of temperature, pH, and total carbonate concentration (Gray, et al., 1992; Steward and Weed, 1994; Gray and Wilson, 1995). In DOE tests in sodium carbonate solutions, pH, carbonate concentration, oxygen fugacity, and temperature were varied to obtain a parametric equation for the rate of dissolution. However, the flow-through test data (Gray and Wilson, 1995) used by the DOE in deriving the dissolution rate expression for TSPA-VA were obtained for a relatively narrow range of environmental conditions, e.g., pH from 8 to 10.

5.4.3.2.3 U.S. Department of Energy-Owned Spent Nuclear Fuel, Navy Fuel, and Plutonium Disposition Wastes Degradation

The DSNF has over 250 potential waste form types for disposal. These were grouped into 16 categories based on similar performance characteristics (CRWMS M&O, 1998). Performance analyses of the first 13 categories conducted in 1997 (CRWMS M&O, 1997) indicated only Categories 1, 4, 5, 6, 8, and 11 contributed significantly to dose, and the dose from a composite of 13 categories was about two orders of magnitude below that of the CSNF in the repository. Based on the 1997 analyses, the TSPA-VA analyses used a surrogate DSNF with a radionuclide inventory based on a weighted average of the inventories of Categories 1, 4, 5, 6, 8, and 11. A conservative assumption was built into the surrogate model by using a dissolution rate based on the uranium metal fuel dissolution model. The metallic spent fuel dissolution rate is faster than the rate for the nonmetallic fuels.

For the TSPA-VA, the model for the degradation of metallic fuel was an Arrhenius kinetic equation using parameters derived from assessments of spent nuclear fuel and HLW (Rechard, 1995). The model is based on the equation

$$M = Ae^{-B/T}(t_2^C - t_1^C)D\cdot E\cdot SA \tag{5-1}$$

where

M = mass of layer corroded in a time step (kg)
A = Arrhenius-type pre-exponential term (kg/m^2s)
B = Arrhenius-type activation energy term (K)
T = temperature (K)
t_2 and t1 = time at the beginning and end of the time step in seconds
C = time dependence term
E = oxygen concentration dependence term
SA = surface area of the layer (m^2)
D = saturation dependence term, which is 0, 1, or $1 - e^{-\alpha(Sat-TS)}$

where

α = $\ln(0.01)/(S_{99} - TS)$
Sat = fracture water saturation
TS = threshold fracture saturation below which wet corrosion does not occur
S_{99} = fracture saturation where the wet corrosion rate is 99 percent of the corrosion rate at 100 percent saturation

When the temperature in the repository is below 100 °C, water was assumed to be present on the waste form (wet oxidizing conditions), and humid air conditions are assumed at all other times. The DOE notes in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) that there were little applicable experimental data to substantiate the parameter values selected for the TSPA-VA, and that the TSPA-SR will use a degradation rate and a corresponding effective surface area that bounds the experimental data on N-Reactor fuel collected by the DOE over a range of conditions in the last few years.

Two other DOE-owned materials were considered in the TSPA-VA analyses. These waste forms include spent Navy reactor fuel and plutonium disposition wastes. The source term for Navy fuel was provided in the form of a look-up table of mass release rate from a waste package for each radionuclide as a function of time (CRWMS M&O, 1998). For plutonium disposition wastes, two waste forms—a mixed uranium-plutonium oxide (MOX) fuel and a plutonium-bearing ceramic form—were considered. The MOX fuel was assumed to have the same physical characteristics as CSNF and the same degradation models were used for MOX fuel as for CSNF. Degradation models for the plutonium ceramic form were those for ceramic DOE fuel and HLW glass. There is no mention of MOX fuel and plutonium disposition wastes in the DOE TSPA-SR methods and assumptions report (CRWMS M&O, 1999b), and it is possible the DOE will not consider these wastes in its TSPA for the site recommendation and license application.

5.4.3.2.4 High-Level Waste Glass Degradation

The DOE recognizes that glass waste forms are thermodynamically unstable over long time periods, and will alter on contact with water. Radionuclides can be mobilized from the glass waste by a variety of processes, including degradation and alteration of the glass, phase separation, congruent dissolution, precipitation of silicates, coprecipitation of other minerals including iron corrosion products, and selective leaching. Not all these processes are incorporated into the DOE abstraction of glass degradation. The DOE states in the VA technical basis document (CRWMS M&O, 1998) that the entire phenomenology of the glass alteration process cannot be incorporated directly into a performance assessment model because it would necessitate tracking too many system variables and because several of the relationships between glass reaction rate and solution chemistry cannot be quantified with available experimental data.

Instead, the DOE generated a simplified glass model amenable for incorporation into performance assessment calculations. This model incorporates the parameters the DOE believed most important for controlling the rate of glass reaction: (i) temperature, (ii) fluid pH, (iii) fluid silica concentration, and (iv) reactive glass surface. In the TSPA-VA, the DOE used a simplified rate equation for waste glass dissolution, expressed (in mass units of grams) as

$$R = s\left[k\left(1 - \frac{Q}{K}\right) + k_{long}\right] \tag{5-2}$$

where

R = alteration rate of glass (g/yr)
s = surface area (m^2)
k = glass surface alteration rate constant ($g/m^2/y$), a function of temperature and pH of the solution
Q = concentration of dissolved silica (g/m^3/water)
K = a quasi-thermodynamic parameter for glass equal to the silica saturation value for the glass (g/m^3/water)
k_{long} = long-term dissolution rate determined from test data

The values of k and k_{long} are determined from experimental data. For the TSPA-VA, an expression for k as a function of pH and temperature was derived by fitting experimental data for a simplified glass composition (SRL-165), which had the most complete set of data at the time of the TSPA-VA. However, it was stated in the TSPA-VA technical basis document (CRWMS M&O, 1998) that data for the SRL-202 glass will be used in abstracting glass dissolution rate for the TSPA-LA. The value of k_{long} is based on glass corrosion tests at 90 °C, and is given the same temperature dependency as k (CRWMS M&O, 1998). The value of K, the silica saturation for waste glass, is assumed equal to the equilibrium constant for amorphous silica. This assumption was made by the DOE in the absence of a mechanistic quantitative understanding of how K varies with glass composition and experimental test conditions.

The TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) states that the model to be developed for aqueous degradation of HLW in TSPA-SR will be similar to that in TSPA-VA, but will use updated rate parameters based on additional experimental data.

5.4.3.2.5 Dissolved Radionuclide Concentration Limits

For the TSPA-VA, and also for the TSPA-SR, the DOE approach to calculate bounds on the aqueous concentration of radionuclides in groundwater that has reacted with the waste form is to initially derive the concentrations from the waste form dissolution model. Subsequently, a comparison is made between the waste form dissolution-based aqueous radionuclide concentration and a value determined thermodynamically by the solubility limit for each radionuclide considered. If the solubility-limited value is lower for a given radionuclide than its concentration derived from the waste form dissolution, then the aqueous concentration is set to the solubility-limited value and the difference in mass is assumed to precipitate out of solution. The solubility-limited values place constraints on the aqueous concentration of the particular radionuclide element considered, with each isotope of that element present in proportion to its isotopic abundance (CRWMS M&O, 1998).

The concentration limit usually is the solubility limit of the solid phases that contain the radioisotopes (either solid phases with the radioisotope as the dominant element or solid phases with trace amounts of the radionuclide, as in coprecipitated species). For one radioelement (neptunium), the DOE claims that experiments have shown much lower concentrations in solution compared to the thermodynamically calculated value. In this case, the DOE may use a lower solubility limit to bound the aqueous concentration of neptunium. The solid phases that form depend on the temperature, redox conditions, and chemical composition of the groundwater. Because of uncertainty in the precise values for these variables in the waste package and near-field environment, there is a wide range of possible radionuclide concentration limits.

For TSPA-VA, the distribution of each radioisotope transported was primarily based on an elicitation of experts both inside and outside the Yucca Mountain Project conducted in 1993 (Wilson, et al., 1994; CRWMS M&O, 1998). The assumptions behind the expert panel's development of the distributions are (i) the unsaturated zone water composition is bounded by the composition of J-13 well water and that of UE-25p#1, (ii) the solubility limits will be determined by the far-field groundwater environment, (iii) the environment is oxidizing, and (iv) future climate changes will cause groundwater compositional changes. A number of additional sources were used to further constrain distributions of solubility limits for the radionuclides used in the TSPA-VA analysis. Also, the solubility-limited concentration distribution for neptunium used in previous TSPA calculations was revised based on an analysis by Sassani and Siegmann (1998).

For TSPA-SR, the methods and assumptions report (CRWMS M&O, 1999b) states a reevaluation of radioisotope solubility is planned. A distribution of concentration limits for important radioisotopes will first be based on a wide variety of chemical conditions. Using assumed solubility controlling solid phases and range of water chemistry, the range of the distribution of radionuclide concentration limits will be facilitated using the chemical equilibrium code EQ3NR, based either on thermodynamic data or on literature data (CRWMS M&O, 1999b). The distribution later will be refined and narrowed as information becomes available on the design of the engineered barrier, fluid flow rates, and thermal history. The concentration limits for each radioisotope will be expressed as a distribution of values in the TSPA-SR. However, the concentration limit for uranium and neptunium, for which more data are available, will probably be expressed as a function of water chemistry (pH, Eh, and carbonate concentration).

5.4.3.2.6 Colloid-Assisted Radionuclide Concentration Limits

The DOE abstraction of colloidal radionuclide release, as reported in a preliminary version of AMR F0115 (Colloid Source Term Abstraction) (CRWMS M&O, 2000b), uses empirical data on release and colloid stability to formulate a dependence of colloidal radionuclide release on in-package ionic strength and pH. The report uses literature and Yucca Mountain Project data to support its construction of an algorithm for calculating colloid-associated radionuclide concentrations in solutions leaving the waste package. No credit is taken for colloid retardation within the waste package. Direct inputs for conceptual models and parameters were obtained from two supporting AMRs (F0105–Colloid Source Term, Los Alamos National Laboratory; F0110–Colloid Source Term, Argonne National Laboratory), as well as from a small number of literature sources. The abstraction takes output from in-package geochemical models and uses pH, ionic strength, and dissolved radionuclide concentration to calculate colloid concentrations, irreversibly colloid-bound radionuclide concentrations, and reversible colloid binding of radionuclides. The results are combined to provide a total colloid-associated source term for a given radionuclide. Presently, the abstraction is applied only to plutonium and americium, although the americium abstraction is incomplete. The abstraction classifies colloids as waste form, groundwater (pre-existing), or iron oxyhydroxide (from corrosion). Note that the following discussion was based on a preliminary version of the AMR. Details may change before final release of Revision 00.

The following key inputs are used in the colloid release abstraction (CRWMS M&O, 2000b):

- solution ionic strength, pH, and radionuclide concentration, from separate TSPA in-package geochemical calculations

- effect of ionic strength on water concentration of waste-form colloidal plutonium, including a maximum colloidal plutonium concentration of 6×10^{-8} mol/L at ionic strength < 0.01 mol/L, and a minimum of 1×10^{-11} mol/L at ionic strength > 0.05 mol/L; from data in AMR F0110 (Colloid Source Term, Argonne National Laboratory) (CRWMS M&O, 2000c)

- maximum ionic strength stability limits for waste-form colloids as a function of pH, ranging from 0.01 mol/L at pH 2 to 0.05 mol/L at pH ≥ 6; based on montmorillonite data from Tombacz, et al. (1990) and on AMR F0110 (Colloid Source Term, Argonne National Laboratory) (CRWMS M&O, 2000c)

- maximum ionic strength stability limits for iron oxyhydroxide colloids as a function of pH, ranging from 0.05 mol/L at $6 > \text{pH} > 11$ to a minimum of 0.01 mol/L at pH 8–9; from Liang and Morgan (1990)

- relationship between ionic strength and mass of groundwater colloids, ranging between a minimum of 3×10^{-6} mg/L and a maximum of 3×10^{-2} mg/L; from TSPA-VA Technical Basis Document (CRWMS M&O, 1998; Figure 4-30)

- range of distribution coefficients for reversible plutonium sorption onto colloids, with a geometric mean of 1×10^{4} mL/g; based on data in AMR F0105 (Colloid Source Term, Los Alamos National Laboratory) (CRWMS M&O, 2000d).

The order of calculation is as follows:

(1) water concentration of radionuclide irreversibly sorbed to waste-form colloids, using ionic strength and pH,

(2) mass concentration of waste-form colloids, using experimental relationship between concentrations of colloids and radionuclide irreversibly sorbed to them,

(3) radionuclide reversibly sorbed to waste-form colloids, using distribution coefficient,

(4) mass concentration of iron oxyhydroxide colloids, using ionic strength and pH,

(5) radionuclide reversibly sorbed to iron oxyhydroxide colloids, using distribution coefficient,

(6) mass concentration of groundwater colloids, using ionic strength,

(7) radionuclide reversibly sorbed to groundwater colloids, using distribution coefficient, and

(8) summed colloidal radionuclide concentration and summed colloid mass concentration output to exterior of waste package.

The portion of the abstraction dealing with irreversible attachment to waste-form colloids is based on tests on HLW glasses (CRWMS M&O, 2000c), but is applied to all waste forms. This appears to be conservative in that HLW glass tests produce higher colloid concentrations than spent nuclear fuel tests (CRWMS M&O, 2000b).

5.4.3.2.7 In-Package Chemistry

For the TSPA-VA, the DOE developed a set of five models to represent the near-field geochemical environment (U.S. Department of Energy, 1998b): (i) a description of the gas, water, and colloid composition coming into the drift; (ii) the composition of gas phase relative to the major gas sinks in the drift; (iii) the evolution of water composition reacting with major materials within the drift and the drift gas phase; (iv) a description of the stability and quantity of clay and iron-oxide colloids in the drift; and (v) the in-drift microbial communities. With the exception of the microbial communities and colloid model, these models were used to predict the chemistry of water contacting the waste package and waste forms. Reaction of in-drift water and gas was calculated for different points along the flow-path of water. As a result, calculations of water and gas reacting with the concrete drift liner (not present in the EDA-II design), iron corrosion products, and spent nuclear fuel were completed. Calculation of the water composition was completed as a function of time, using six discrete periods: three during the boiling regime (0–2,000 years) and three periods that extend beyond to 100,000 years. Based on the different degradation rates of the different engineered materials in the VA design (concrete, waste package, and spent nuclear fuel), different sequential reactions (e.g., incoming water, concrete, waste package, and then waste form) were used in the different time periods (U.S. Department of Energy, 1998b). The two-dimensional thermal-hydrologic model at the mountain-scale provided both the air mass fraction and gas fluxes through the drift as a function of time. These results included the effects of boiling and gas flow on the mix of air and steam in the gas phase, but none of the chemical interactions with the host rock. While 15 geochemical parameters describing the chemistry of water were calculated at various locations and at several different time periods, only the pH, ionic strength, and total carbonate concentrations were used in performance assessment calculations. The chemistry of water contacting the waste package calculated in these models was not used in the waste package degradation model (U.S. Department of Energy, 1998b). In addition, the chemistry of water expected inside the waste package was not used in the cladding degradation models.

For the TSPA-SR, the DOE methods and assumptions report (CRWMS M&O, 1999b) indicates that an in-drift geochemical environment model will be developed for the TSPA that will provide a quantitative description of the changing compositional conditions under which waste forms degrade and precipitate as secondary phases and radionuclides mobilize from the waste form. The objective of the in-drift geochemical model is to determine the changes in water chemistry resulting from the interaction of engineered barrier materials with water seeping into the drift and to provide this information to TSPA analyses. The model takes into account the variation in seepage and drainage fluxes, the effects of temperature changes on chemical equilibria, and physical processes such as evaporation and condensation.

The TSPA-SR in-drift geochemical environment model separates the major potential contributors to water compositional changes into nine subsystem models. The separate models will be used to assess the relative capacities of the different processes to alter compositions of various chemical phases at various times. The nine subsystem models are: (i) seepage/backfill interactions; (ii) precipitates/salts analysis; (iii) corrosion products; (iv) seepage/invert interactions; (v) seepage/cement interactions; (vi) in-package chemistry; (vii) in-drift gas flux and composition; (viii) microbial communities; and (ix) in-drift colloids and concentrations. The relationships between the submodels, their coupling, and spatial locations of potential importance are described in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b).

Of particular interest for this review is the submodel on in-package chemistry. This submodel provides a quantitative description of the combined effects of important chemical interactions that can occur between aqueous seepage entering the waste package and materials in the package. Materials in the package to be considered include the waste package, the waste package internals, corrosion products from waste package internals, and the waste form. This submodel provides the compositions of water and gas that may react with the waste forms. The major chemical constituents of the waste form will also be evaluated for their potential to change the water chemistry from its initial composition. Staff will review the DOE abstraction and analyses of in-package chemistry when the AMR on In-Waste Package Chemistry Abstraction (F0170) becomes available.

An approach that has been used by the DOE to calculate the chemistry of water inside waste packages was published by Zhang and Stockman (1999). In the model, the effect of internal components on the environment contacting the waste forms was considered and was applied in evaluating the potential for criticality of DSNF and plutonium-ceramic waste forms that will be co-disposed with HLW glass (Zhang and Stockman, 1999; Stockman, 1999; Massari, 1999). The conceptual model for in-package environment proposed by Zhang and Stockman (1999) makes the following assumptions:

- The waste package deterioration is considered to be essentially a chemical process with the use of reaction rate terms in the EQ6 code that are independent of redox potential.
- A solid-centered flow-through model is used where a volume of incoming fluid replaces an equal volume of exiting fluid.
- The solutions that drip into the waste package will have a composition approximating J-13 water. Implicit in this assumption are assumptions that thermal and vapor pressure gradients and waste package degradation have no effect on the incoming water composition. In particular, the alloy 22 barrier is assumed to react minimally or not at all with the incoming water.
- All the dissolved species in the waste package are in chemical equilibrium with each other and bound by one redox system of the water contacting all the solids.
- The chromium and molybdenum in the stainless steels are fully converted to Cr(VI) and Mo(VI) species. The basis for this assumption is the equilibrium code, EQ3, which suggests that dissolved Cr and Mo in equilibrium with air will be converted to their hexavalent state.
- The average rate of dissolution assumed for type 304L stainless steel pour canister was 0.1 μm/yr, whereas the average rate assumed for the A516 basket material was 35 μm/yr.

Staff comments on Zhang and Stockman's (1999) approach are given in Section 5.4.3.3.8.

5.4.3.3 Analysis of the U.S. Department of Energy Models, Abstractions, and Analyses

Staff analysis of DOE models, abstractions, and analyses pertinent to the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release is presented in this section. For this revision of the ENFE IRSR, staff analysis centered on using the acceptance criterion on integration in reviewing The DOE work. Staff analysis using all five acceptance criteria will be done as the DOE AMRs and PMRs become available. An analysis of the FEPs relevant to subissue 3 of the ENFE IRSR is presented in the first part of this section, followed by discussions specific to the seven DOE abstractions.

5.4.3.3.1 FEPs Screening

The approach the DOE used for the VA did not include a formal screening process for FEPs. As a result, many important design features, physical phenomena, and couplings that cause temporal and spatial variations in conditions were not evaluated in a performance assessment framework. Thus, the TSPA-VA models neglect without explanation known temporal and spatial variations in conditions affecting coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release.

Recently, the DOE has developed a more formal documentation of the FEPs identification and screening process for the TSPA-SR (Swift, et al., 1999). The contents of the DOE FEPs database (U.S. Department of Energy, 1999) have been screened and those related to the ENFE subissue on effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release have been identified (Pickett and Leslie, 1999; U.S. Nuclear Regulatory Commission, 2000b). The results of the screening by Pickett and Leslie (1999) are presented in the first three columns of Table 5-1.

The audit review of Pickett and Leslie (1999) indicated that 80 primary FEPs are relevant to this ENFE subissue. Of these 80, 28 are excluded by the DOE screening process. For two design related FEPs (1.1.07.00.00–Repository design; 1.1.08.00.00–Quality control), deviations from design are excluded and, for one FEP (2.1.13.02.00–Radiation damage in waste and engineered barrier system), the FEP component related to backfills, seals, and rock is excluded. Two additional FEPs (2.1.06.06.00–Effects of degradation of drip shield; 2.2.07.06.00–Episodic/pulse release from repository) have no screening status given in the DOE database. A review of the 28 FEPs that are excluded by the DOE screening process indicated that eight of those (FEPs 2.1.02.05.00, 2.1.02.13.00, 2.1.02.15.00, 2.1.09.02.00, 2.1.09.07.00, 2.1.11.08.00, 2.1.12.01.00, and 2.1.12.03.00) should not have been excluded. Of the two FEPs without screening status, staff believes one (FEP 2.1.06.06.00) should be included. The bases for the determination that these FEPs should not be excluded are discussed in the following paragraphs.

2.1.02.05.00 Glass cracking and surface area

This FEP concerns possible effects on HLW glass alteration and radionuclide dissolution as a result of surface area increase due to glass cooling and handling. The screening argument states that "The robust container used at Yucca Mountain means that the concerns about fragmentation (and increased leach rate) of vitrified wastes are secondary" (U.S. Department of Energy, 1999). However, as in TSPA-VA (U.S. Department of Energy, 1998b), planned DOE modeling of HLW glass degradation for TSPA-SR does include a surface area term (CRWMS M&O, 1999b). In addition, greater glass surface area may also enhance the chemical effect on water contacting the glass. Development of the surface area term in the HLW glass degradation abstraction should include allowance for cooling and handling effects, unless the DOE provides a technical basis for neglecting them. Staff expects this FEP to be addressed in the FEPs screening AMR F0185. Also, staff considers this FEP relevant to the DOE abstractions of (i) dissolved radionuclide concentration limits, (ii) colloid-assisted radionuclide concentration, and (iii) in-package chemistry.

2.1.02.13.00 General corrosion of cladding

As stated in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b), "because Zircaloy provides such excellent protective properties on average, characterization of the uncertainty in its performance is important." Zirconium oxidation is presented in this database entry as a mechanism for cladding degradation. The screening argument in the preliminary

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction.

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
1.1.02.03.00	Undesirable materials left	Exclude							
1.1.07.00.00	Repository design	Include (exclude deviations from design)	X	X	X	X	X	X	X
1.1.08.00.00	Quality control	Include (exclude defects and deviations)							
1.1.12.01.00	Accidents and unplanned events during operation	Exclude							
1.1.13.00.00	Retrievability	Include							
1.2.06.00.00	Hydrothermal activity	Exclude							
2.1.01.02.00	Codisposal/colocation of waste	Include	X	X	X	X	X	X	X
2.1.01.03.00	Heterogeneity of waste forms	Include	X	X	X	X	X	X	X
2.1.02.01.00	DSNF degradation, alteration, and dissolution	Include	X		X	X	X	X	X
2.1.02.02.00	CSNF alteration, dissolution, and radionuclide release	Include	X	X			X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.02.03.00	Glass degradation, alteration, and dissolution	Include			X	X		X	X
2.1.02.04.00	Alpha recoil enhances dissolution	Exclude							
2.1.02.05.00	Glass cracking and surface area	Exclude				X	X	X	X
2.1.02.06.00	Glass recrystallization	Exclude							
2.1.02.07.00	Gap and grain release of Cs, I	Include		X	X				X
2.1.02.08.00	Pyrophoricity	Exclude							
2.1.02.09.00	Void space (in glass container)	Exclude							
2.1.02.13.00	General corrosion of cladding	Exclude	X	X	X		X	X	X
2.1.02.14.00	MIC of cladding	Exclude							
2.1.02.15.00	Acid corrosion of cladding from radiolysis	Exclude (?)	X	X	X		X	X	X
2.1.02.16.00	Localized corrosion (pitting) of cladding	Include	X	X	X		X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.02.17.00	Localized corrosion (crevice corrosion) of cladding	Include	X	X	X		X	X	X
2.1.02.18.00	High dissolved silica content of waters enhances corrosion of cladding	Include	X	X	X		X	X	X
2.1.02.19.00	Creep rupture of cladding	Exclude							
2.1.02.20.00	Pressurization from He production causes cladding failure	Exclude							
2.1.02.21.00	Stress corrosion cracking of cladding	Include	X	X	X		X	X	X
2.1.02.22.00	Hydride embrittlement of cladding	Include	X	X	X		X	X	X
2.1.02.23.00	Cladding unzipping	Include	X	X	X		X	X	X
2.1.02.24.00	Mechanical failure of cladding	Include	X	X	X		X	X	X
2.1.02.25.00	DSNF cladding degradation	Include	X	X	X	X	X	X	X
2.1.03.06.00	Internal corrosion of waste container	Include	X	X	X	X	X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.03.11.00	Container form	Include	X	X	X	X	X	X	X
2.1.03.12.00	Container failure (long term)	Include	X	X	X	X	X	X	X
2.1.04.01.00	Preferential pathways in the backfill	Include	X	X	X	X	X	X	X
2.1.04.02.00	Physical and chemical properties of backfill	Include	X	X	X	X	X	X	X
2.1.04.03.00	Erosion or dissolution of backfill	Exclude							
2.1.04.05.00	Backfill evolution	Include	X	X	X	X	X	X	X
2.1.06.01.00	Degradation of cementitious materials in drift	Include	X	X	X	X	X	X	X
2.1.06.03.00	Degradation of the liner	Include	X	X	X	X	X	X	X
2.1.06.04.00	Flow through the liner	Exclude							
2.1.06.06.00	Effects and degradation of drip shield		X	X	X	X	X	X	X
2.1.06.07.00	Effects at material interfaces	Include	X	X	X	X	X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.08.07.00	Pathways for unsaturated flow and transport in the waste and EBS	Include(?)	X	X	X	X	X	X	X
2.1.08.08.00	Induced hydrological changes in the waste and EBS	Include	X	X	X	X	X	X	X
2.1.08.11.00	Resaturation of repository	Include	X	X	X	X	X	X	X
2.1.09.01.00	Properties of the potential carrier plume in the waste and EBS	Include	X	X	X	X	X	X	X
2.1.09.02.00	Interaction with corrosion products	Exclude(?)	X	X	X	X	X	X	X
2.1.09.04.00	Radionuclide solubility, solubility limits, and speciation in the waste form and EBS	Include					X	X	X
2.1.09.06.00	Reduction-oxidation potential in waste and EBS	Include	X	X	X	X	X	X	X
2.1.09.07.00	Reaction kinetics in waste and EBS	Exclude	X	X	X	X	X	X	X
2.1.09.08.00	Chemical gradients/enhanced diffusion in waste and EBS	Include	X	X	X	X	X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.09.10.00	Secondary phase effects on dissolved radionuclide concentrations at the waste form	Include		X	X	X	X	X	X
2.1.09.11.00	Waste-rock contact	Exclude							
2.1.09.12.00	Rind (altered zone) formation in waste, EBS, and adjacent rock	Include		X	X	X	X	X	X
2.1.09.13.00	Complexation by organics in waste and EBS	Include	X	X	X	X	X	X	X
2.1.09.14.00	Colloid formation in waste and EBS	Include		X	X	X		X	X
2.1.09.15.00	Formation of true colloids in waste and EBS	Include		X	X	X		X	X
2.1.09.16.00	Formation of pseudo-colloids (natural) in waste and EBS	Include		X	X	X		X	X
2.1.09.17.00	Formation of pseudo-colloids (corrosion products) in waste and EBS	Include		X	X	X		X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.09.18.00	Microbial colloid transport in the waste and EBS	Include		X	X	X		X	X
2.1.10.01.00	Biological activity in waste and EBS	Include ?	X	X	X	X	X	X	X
2.1.11.01.00	Heat output/temperature in waste and EBS	Include	X	X	X	X	X	X	X
2.1.11.02.00	Nonuniform heat distribution/edge effects in repository	Include	X	X	X	X	X	X	X
2.1.11.03.00	Exothermic reactions in waste and EBS	Exclude							
2.1.11.04.00	Temperature effects/coupled processes in waste and EBS	Include	X	X	X	X	X	X	X
2.1.11.08.00	Thermal effects: chemical and microbiological changes in the waste and EBS	Exclude	X	X	X	X	X	X	X
2.1.11.09.00	Thermal effects on liquid or two-phase fluid flow in the waste and EBS	Include	X	X	X	X	X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.1.11.10.00	Thermal effects on diffusion (Soret effect) in waste and EBS	Exclude							
2.1.12.01.00	Gas generation	Exclude	X	X	X	X	X	X	X
2.1.12.02.00	Gas generation (He) from fuel decay	Exclude							
2.1.12.03.00	Gas generation (H_2) from metal corrosion	Exclude	X	X	X	X	X	X	X
2.1.12.04.00	Gas generation (CO_2, CH_4, H_2S) from microbial degradation	Exclude							
2.1.12.06.00	Gas transport in waste and EBS	Exclude							
2.1.12.07.00	Radioactive gases in waste and EBS	Exclude							
2.1.12.08.00	Gas explosions	Exclude							
2.1.13.01.00	Radiolysis	Include	X	X	X	X	X	X	X
2.1.13.02.00	Radiation damage in waste and EBS	Include, Exclude (backfill, seals, rock)	X	X	X	X	X	X	X

Table 5-1. U.S. Department of Energy (DOE) features, events, and processes (FEP) database (Revision 00b) (U.S. Department of Energy, 1999) entries relevant to subissue 3 of the Evolution of the Near-Field Environment Key Technical Issue. X indicates the FEP is considered relevant to the specific DOE abstraction (cont'd).

DOE Features, Events, and Processes Number	Features, Events, and Processes Name	Screening	DOE Abstraction						
			Clad Degrad.	CSNF Degrad.	DSNF Degrad.	HLW Glass Degrad.	Solubility Limits	Colloids	In-Package Chem.
2.2.07.06.00	Episodic/pulse release from repository								
2.2.08.01.00	Groundwater chemistry/composition in UZ and SZ	Include	X	X	X	X	X	X	X
3.1.01.01.00	Radioactive decay and ingrowth	Include	X	X	X	X	X	X	X
		Total Number	46	53	54	45	50	56	57

database (U.S. Department of Energy, 1999) provides a description of the process, rather than a rationale for its exclusion. This FEP is unresolved until the DOE provides a technical basis for exclusion. Staff expects this FEP to be addressed in the FEPs screening AMR F0050. Also, staff considers this FEP relevant to six of the seven DOE abstractions covered in this review.

2.1.02.15.00 Acid corrosion of cladding from radiolysis

The database screening of this FEP is tentative; the TSPA disposition field states, "Not a major issue, could use analysis at later time" (U.S. Department of Energy, 1999). Otherwise, there is no screening argument for a process that is potentially significant (Cragnolino, et al., 1999) and this specific mechanism is not addressed in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b). This FEP is unresolved until the DOE provides a technical basis for exclusion. Staff expects this FEP to be addressed in the FEPs screening AMR F0050. Also, staff considers this FEP relevant to six of the seven DOE abstractions covered in this review.

2.1.06.06.00 Effects and degradation of drip shield

No screening status was given for this FEP in the DOE database (U.S. Department of Energy, 1999). However, staff believes the drip shield and its degradation could potentially affect the flow and chemistry of water contacting the waste forms. Staff expects this FEP to be addressed in the FEPs screening AMR F0185. Staff also considers this FEP to be relevant to all seven DOE abstractions covered in this review.

2.1.09.02.00 Interaction with corrosion products

This FEP is concerned with effects on radionuclide mobility of corrosion products of metallic components. The database specifically refers to sorption, desorption, coprecipitation, and dissolution processes. The database screening of this FEP is tentative; the TSPA disposition field states that this effect will be "included only in the integrated source term and associated sorption parameters" (U.S. Department of Energy, 1999). In addition, the screening argument states that "Interaction of contaminants with corrosion products is expected to control mobilization and speciation of the contaminants." Finally, the TSPA-SR methods and assumptions report states that "changes to water chemistry due to corrosion products will be provided as input to the TSPA drip shield, waste package, and waste form degradation models" (CRWMS M&O, 1999b, Section 3.3.2). It is apparent that this FEP will not be excluded, and staff expects this to be reported in the FEPs screening AMR F0185. In addition, staff considers this FEP relevant to all seven DOE abstractions covered in this review.

2.1.09.07.00 Reaction kinetics in waste and engineered barrier system

The FEP description reads, "Chemical reactions, such as radionuclide dissolution/precipitation reactions and reactions controlling the reduction-oxidation state, may not be in equilibrium in the drift and waste environment" (U.S. Department of Energy, 1999). However, the screening argument addresses only redox. The DOE is relying on "experimentally derived K_ds" to include these effects. "Specific effects of redox kinetics are therefore excluded from the TSPA on the basis of low consequence" (U.S. Department of Energy, 1999). Reliance on experimental K_ds and discussion of kinetics only in the context of redox may constitute an oversimplification of chemical processes in the waste and engineered barrier system. In addition, the sole secondary entry—2.1.09.07.01—is "included" and the argument says that kinetics "...are to be included in detailed modeling of chemical interactions using EQ3/6." In discussing the implementation in TSPA-SR of the in-drift geochemical environment model, the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b, Sections 3.3.5 and 3.3.7) refers to the use of kinetic rate constants. Therefore, it appears that this FEP will not be excluded, and staff expects this to be reported in the FEPs screening AMR F0185. In addition, staff considers this FEP relevant to all seven DOE abstractions covered in this review.

2.1.11.08.00 Thermal effects: chemical and microbiological changes in the waste and engineered barrier system

This FEP is very broadly defined as follows: "Temperature changes may affect chemical and microbial processes in the waste and engineered barrier system" (U.S. Department of Energy, 1999). The screening argument refers to other entries—2.1.10.01.00 and subentries under 2.1.09.00.00—but does not provide a rationale for exclusion. None of the primary entries cited in the screening argument deal specifically with thermal effects. The discussions of in-drift geochemical environment models in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b, Section 3.3) make it clear that temperature effects on chemical processes affecting radionuclide release will be implemented in TSPA-SR. It, therefore, appears that this FEP will not be excluded, and staff expects this FEP to be considered in the DOE screening of FEPs with respect to radionuclide release in AMR F0185. In addition, staff considers this FEP relevant to all seven DOE abstractions covered in this review.

2.1.12.01.00 Gas generation

The FEP description states, in part, "Gas generation might lead to pressurization of the repository, produce multiphase flow, and affect radionuclide transport. This FEP aggregates all types of gas generation into a single category" (U.S. Department of Energy, 1999). The screening argument states that "Since the repository would be in the UZ, which is well-connected to the surface, gas produced by whatever reaction is expected to escape or at least be only temporarily confined beneath the condensate zone above the drifts." Exclusion of this FEP implies that gases generated in the near field will have no impact on the chemical environment for radionuclide release. Clearly, gases can affect water chemistry, in turn affecting release processes. The conclusion that gas will escape with no effect on the near-field chemical environment needs a technical basis, particularly since the possibility of temporary confinement is acknowledged. With respect to FEP screening related to radionuclide release, staff expects this FEP to be addressed in AMR F0185. The staff also considers this FEP relevant to all seven DOE abstractions covered in this review.

2.1.12.03.00 Gas generation (H_2) from metal corrosion

Although this FEP is included under the broadly defined 2.1.12.01.00, it is presented as a separate primary entry in the database. The description specifically includes effects on chemical conditions and transport. The screening argument states that "Gas generated by metal corrosion will interact with the containers or escape from the drifts," but does not argue against any effects. Exclusion of this FEP implies that H_2 gas generated in the near field will have no chemical impact. The conclusion that gas will escape with no effect on the near-field chemical environment needs a technical basis. With respect to FEP screening related to radionuclide release, this FEP may be addressed in AMR F0185, but staff also considers this FEP relevant to all seven DOE abstractions covered in this review.

The status of the remaining 20 FEPs excluded by the DOE screening process, the three partially excluded FEPs, and the second FEP with no given screening status, is considered resolved. The bases for this determination are discussed in the following paragraphs.

1.1.02.03.00 Undesirable materials left

As noted by Pickett and Leslie (1999), NRC inspectors should take care of this FEP. Operational errors, however, cannot be excluded without quality control procedures. Review of the DOE QA program will be addressed in Section 4.3.1 of the YMRP (U.S. Nuclear Regulatory Commission, 2000a). Also, the DOE states that thermal and radiolytic degradation of decontamination solvents may reduce the consequence of these materials, but that this will require a technical basis. The DOE references this FEP with regard to the operational period; preclosure aspects of the proposed repository are reviewed under Section 4.1 of the YMRP (U.S. Nuclear Regulatory Commission, 2000a) and not in the postclosure model abstraction section that pertains to this review.

1.1.07.00.00 Repository design and 1.1.08.00.00 Quality control (deviations from design)

These two FEPs are included in the DOE screening, but deviations from design and operational error are excluded. Knowledge of quality control procedures (Section 4.3.1 of the YMRP) and operational procedures under normal and accident conditions are reviewed in Sections 4.3.6 and 4.3.7 of the YMRP (U.S. Nuclear Regulatory Commission, 2000a). Also, the DOE references these FEPs with regard to the operational period; preclosure aspects of the proposed repository are reviewed under Section 4.1 of the YMRP and not in the postclosure model abstraction section that pertains to this review.

1.1.12.01.00 Accidents and unplanned events during operation

Knowledge of quality control procedures (Section 4.3.1 of the YMRP) and operational procedures under normal and accident conditions are reviewed in Sections 4.3.6 and 4.3.7 of the YMRP (U.S. Nuclear Regulatory Commission, 2000a). Also, the DOE references these FEPs with regard to the operational period; preclosure aspects of the proposed repository are reviewed under Section 4.1 of the YMRP and not in the postclosure model abstraction section that pertains to this review.

1.2.06.00.00 Hydrothermal activity

This FEP refers to natural hydrothermal activity. The staff considers exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.04.00 Alpha recoil enhances dissolution

The staff considers the DOE screening argument for excluding this FEP appropriate. The staff believes the potential effect of alpha recoil on dissolution negligible compared to other thermal-hydrologic-chemical processes. Exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.06.00 Glass recrystallization

The DOE excluded this FEP on the basis that (i) glass recrystallization is a very slow process, (ii) glass recrystallization is only possible if high glass temperature is maintained over a prolonged period, (iii) glass recrystallization is unlikely to occur below 400 °C, and (iv) the waste glass at a Yucca Mountain repository will not be exposed to temperatures of 400 °C. The staff considers the DOE rationale appropriate and exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.08.00 Pyrophoricity

The DOE excluded this FEP on the basis of low consequence. The staff considers the DOE screening argument for this FEP appropriate and exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.09.00 Void space (in glass container)

The staff considers this FEP will not significantly influence the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release. Exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.14.00 Microbially induced corrosion of cladding

The staff considers this FEP will not significantly influence the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release. Staff considers the DOE screening argument for this FEP appropriate and exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.19.00 Creep rupture of cladding

The staff considers this FEP will not significantly influence the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release. Exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.02.20.00 Pressurization from He production causes cladding failure

The staff considers this FEP will not significantly influence the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release. Staff considers the DOE screening argument for this FEP is appropriate and exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.04.03.00 Erosion or dissolution of backfill

The FEP description in the DOE database (U.S. Department of Energy, 1999) states, "Solid material in buffer or backfill is carried away by flowing groundwater, either by erosion of particulate matter or by dissolution." Although the DOE has not defined the backfill material as yet, the staff considers the potential effect of solid material from the backfill on the chemical environment for radionuclide release will be negligible. Thus, staff considers exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.06.04.00 Flow through the liner

DOE excludes this FEP because the EDA-II design eliminates concrete liner that was included in the TSPA-VA design. At this time, staff considers excluding this FEP in the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.09.11.00 Waste-rock contact

The staff considers this FEP will not significantly influence the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release. Staff considers the DOE screening argument for this FEP is appropriate and exclusion of this FEP from the DOE evaluation of coupled thermal-hydrologic-chemical effects on the chemical environment for radionuclide release is acceptable.

2.1.11.03.00 Exothermic reactions in waste and engineered barrier system

Staff considers the effects of exothermic reactions in the waste and engineered barrier system on the chemical environment for radionuclide release negligible compared to the effects of other coupled thermal-hydrologic-chemical processes. Staff considers the DOE screening argument for this FEP appropriate and exclusion of this FEP from the DOE analyses of radionuclide release is acceptable.

2.1.11.10.00 Thermal effects on diffusion (Soret effect) in waste and engineered barrier system

The contribution of the Soret effect to radionuclide transport through the engineered and natural barriers is likely to be small in comparison to other chemical processes such as sorption/desorption and has been excluded by the DOE. This is an appropriate screening argument, particularly given the relatively heavy radioelements and the lower thermal gradient attributed to the EDA-II design, and the staff has no further questions on this FEP.

2.1.12.02.00 Gas generation (He) from fuel decay

Staff considers the effects of this FEP on the chemical environment for radionuclide release negligible compared to the effects of other coupled thermal-hydrologic-chemical processes. Exclusion of this FEP from the DOE analyses of radionuclide release is acceptable.

2.1.12.04.00 Gas generation (CO_2, CH_4, H_2S) from microbial degradation

Staff considers the effects of this FEP on the chemical environment for radionuclide release negligible compared to the effects of other coupled thermal-hydrologic-chemical processes. Exclusion of this FEP from the DOE analyses of radionuclide release is acceptable.

2.1.12.06.00 Gas transport in waste and engineered barrier system and 2.1.12.07.00 Radioactive gases in waste and engineered barrier system

These two FEPs pertain to the transport of radioactive gases and their potential contribution to dose. Staff considers exclusion of this FEP from the DOE abstractions of the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release is acceptable.

2.1.12.08.00 Gas explosions

The DOE excludes this FEP largely because the repository will be located in the unsaturated zone and be well connected to the surface, thus minimizing the potential for postclosure gas buildup, and because there is a lack of an ignition source. Based on the information available at this time, this exclusion may be acceptable if the DOE provides a technical basis for the screening argument, particularly since the possibility exists for temporary confinement of gas. Technical support for the lack of an ignition source will be a key part of the basis for exclusion.

2.2.07.06.00 Episodic/pulse release from repository

Although no screening status (included or excluded) and no screening criteria are provided for this primary FEP in the DOE database (U.S. Department of Energy, 1999), staff considers exclusion of this FEP from the DOE abstractions of the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release is acceptable.

2.1.13.02.00 Radiation damage in waste and engineered barrier system

The DOE database (U.S. Department of Energy, 1999) indicates this FEP is included, except for radiation damage on backfill, seals, and rock. Staff considers the potential effects of radiation damage of backfill, seals, and rock on the chemical environment for radionuclide release will be negligible compared to the effects of other thermal-hydrologic-chemical processes. Staff considers acceptable excluding radiation damage on backfill, seals, and rock from the DOE analyses of radionuclide release.

The FEPs database developed by the DOE (U.S. Department of Energy, 1999) provides a more formalized documentation of the FEPs screening and identification process that will be used for the DOE site recommendation and license application. Pickett and Leslie (1999) provide an early audit review of the DOE treatment of FEPs. Future DOE analysis of FEPs should meet the acceptance criteria for scenario analysis in the TSPAI IRSR and in the YMRP (U.S. Nuclear Regulatory Commission, 2000a,b). The DOE must provide an adequate technical basis for omitting potentially important FEPs that may significantly affect the chemical environment for radionuclide release. This FEPs analysis will be an important action for the DOE to take to facilitate resolution of this subissue.

In the DOE TSPA abstractions, the FEPs are not dealt with on a one-by-one basis. To facilitate review of the DOE models, abstractions, and analyses, the FEPs considered by the staff relevant to the seven major topics in the DOE waste form degradation PMR of interest for this review are identified in Table 5-1. Staff will review the FEPs AMRs and the other AMRs relevant to these topics to determine if the relevant FEPs have been adequately incorporated into the DOE analyses.

5.4.3.3.2 Commercial Spent Nuclear Fuel Clad Degradation

Detailed analyses of the models for Zircaloy cladding degradation were not conducted for Revision 2 of the CLST IRSR, but will be provided in CLST IRSR Revision 3. In this section the adequacy of the DOE incorporation of the effects of coupled thermal-hydrologic-chemical processes on the chemical environment inside waste packages is evaluated, taking into consideration that these environmental conditions have a significant effect on the mode and rate of degradation of Zircaloy cladding.

The DOE model abstraction for cladding degradation is based on the questionable assumption that only uniform corrosion of Zircaloy would occur inside the breached waste packages. Corrosion rates are calculated assuming a correlation with the behavior of alloy C-276 (an alloy similar to alloy 22, but less resistant to localized corrosion) in environments such as hot concentrated solutions of H_2SO_4, HNO_3, H_3PO_4 and HCl acids, which are by no means representative of the expected in-package environment. These are very acidic solutions, encompassing a wide range of redox conditions, in which zirconium and its alloys exhibit a well known passive behavior with relatively low uniform corrosion rates. However, as discussed in detail elsewhere (Cragnolino, et al., 1999), zirconium and its alloys, including Zircaloy-2 and Zircaloy-4, are susceptible to both pitting corrosion and stress corrosion cracking in dilute chloride-containing solutions (at chloride concentrations greater that 0.01 M) above a pH-independent, critical pitting or repassivation potential. Chloride concentrations above 0.01 M can be attained in the water contacting waste packages and waste forms as a result of thermal-hydrologic-chemical processes. The critical potential can be reached in an oxidizing aqueous environment as that present in contact with irradiated pellets as a result of water radiolysis or in the presence of other easily reducible species, such as Fe^{3+} cations. In order to reach a corrosion potential higher than the repassivation potential, a sufficiently high Fe^{3+} concentration (probably around 5 mM in solutions containing 1 M Cl^-) should be attained. An important potential source of Fe^{3+} cations is the existence of steel baskets to support the fuel assemblies as internal components of the waste packages. It has been claimed (CRWMS M&O, 1998; U.S. Department of Energy, 1998b), however, that the calculated pH inside the waste packages is above 7.0; pH less than 3.0 is considered necessary to attain the $FeCl_3$ concentration levels required to induce pitting of Zircaloy. However, no detailed calculations or experimental data were presented in support of this argument. In fact, more recent calculations by Zhang and Stockman (1999) indicate the waste package internal environment can attain pH values in the range of 0.2 to 5 (see Section 5.4.3.3.3).

The possibility of accelerated corrosion of Zircaloy by the action of fluoride ions, although recognized by the DOE as a potential problem, has also been dismissed on the basis of concentration and pH arguments (CRWMS M&O, 1998; U.S. Department of Energy, 1998b). It is stated that, at pH above 8, the corrosion rate would be negligible, even in the presence of

100 ppm F^-. However, uncertainties still remain regarding F^- concentration and pH inside waste packages.

In summary, models currently used in TSPA-VA to assess the Zircaloy cladding corrosion are very simplistic in nature and do not take into consideration important environmental aspects. Assumptions in the models, arising from inappropriate consideration of in-package environment, lead to nonconservative estimates of cladding life extended to many thousands of years. The high uncertainty associated with the lack of relevant experimental data is magnified by the fact that corrosion failure modes, such as localized corrosion and stress corrosion cracking, that could have a significant effect on the life of the Zircaloy cladding as a result of the thin wall thickness (0.6–0.9 mm) are not included in the current analyses. An additional source of uncertainty associated with coupled thermal-hydrologic-chemical processes is related to the estimation of the maximum temperature that can be attained by the cladding, which has a significant effect in other failure modes, such as hydride reorientation and embrittlement (U.S. Nuclear Regulatory Commission, 1999c; Cragnolino, et al., 1999).

The chemical environment for cladding degradation can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that fourty-six are relevant to the DOE abstraction of cladding degradation. In the absence of the DOE AMR on FEP Screening–Cladding (F0050), it is not clear which FEPs the DOE has considered in its abstraction and analysis of cladding degradation. Staff will review the AMRs pertinent to cladding to determine which FEPs were included in the DOE abstraction of cladding degradation, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification for their exclusion.

5.4.3.3.3 Commercial Spent Nuclear Fuel Waste Form Degradation

Detailed analyses of the CSNF degradation models are provided in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c). Of relevance to the ENFE IRSR is the effect of coupled thermal-hydrologic-chemical processes on the chemical environment for waste form degradation. Staff analysis of the DOE abstractions, models, and analyses of the chemical environment for CSNF degradation is presented in the following paragraphs.

As mentioned in Section 5.4.3.2.2, the range of environmental conditions used in the DOE TSPA-VA to derive the parametric model for CSNF dissolution was narrow and did not consider the range of chemical conditions that could exist inside the waste package. For example, the environmental conditions used by the DOE in TSPA-VA do not consider the interactions of the waste package materials and the internal components with the water that drips into the waste package. Based on information given in the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b), it is not apparent that the DOE will consider such interactions in the TSPA-SR abstraction of CSNF waste form degradation. The DOE will need to provide data and analyses to support its assumption of chemical environments inside waste packages.

It should be noted that the effect of internal components on the environment contacting the waste forms was considered in modeling the potential for criticality of DSNF and plutonium-ceramic waste forms that will be co-disposed with HLW glass (Zhang and Stockman, 1999; Stockman, 1999; Massari, 1999). These models predict that the internal environment can attain pH values in the range of 0.2 to 5, depending on the oxygen fugacity and assumed rates of degradation of steel, glass, and plutonium-ceramic. These ranges of pH and oxygen fugacities are much broader than the ranges of pH and oxygen concentration considered in the TSPA-VA abstraction of CSNF degradation.

The broader range of pH in Zhang and Stockman's (1999) results is important because pH has a pronounced effect on both the dissolution rate of CSNF and the solubility of radionuclides. The dissolution rate of uraninite (UO_2) has a peak at a pH value of 2 and also at a pH of 10 (Nicol, et al., 1975; Needes et al., 1975). Grambow (1989) reviewed a number of experimental investigations of spent fuel and uraninite and showed that UO_2 dissolution rates increase by roughly three orders of magnitude when the pH decreases from 9 to about 3. Intermediate oxidation surface species, $UO_{2.5}/UO_{2.67}$, do not seem to control the dissolution below a pH of 5 and the oxidative dissolution rate increases significantly (Sunder and Shoesmith, 1991). The solubility of radionuclides has been calculated by the DOE using the geochemical code EQ3. However, it must be noted these calculations are accurate only below an ionic strength of about 1 molal, above which the thermodynamic model for calculating aqueous activities is not valid. The environment inside the waste package can be concentrated by evaporative effects (Rosenberg, et al., 1999) or by reaction with various waste package internals. The thermodynamic data needed to perform calculations beyond this ionic strength is unavailable.

Zhang and Stockman (1999) make several assumptions in calculating the internal environment of a waste package containing HLW glass and plutonium ceramic waste forms. While some of these assumptions (e.g., glass and pour canister dissolution) are specific to the HLW waste form, the overall approach is being considered for calculating the internal environment of waste package containing other waste forms (Stockman, 1999; Massari, 1999). The conceptual model for waste package internal environment proposed by Zhang and Stockman (1999) is discussed in Section 5.4.3.2.7.

The chemical environment for CSNF degradation can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that fifty-three are relevant to the DOE abstraction of CSNF degradation. In the absence of the DOE AMR on In-Waste Form FEPs Screening (F0185), it is not clear which FEPs the DOE has considered in its abstraction and analysis of CSNF degradation. Staff will review the AMRs pertinent to CSNF degradation to determine which FEPs were included in the DOE abstraction, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification for their exclusion.

5.4.3.3.4 U.S. Department of Energy-Owned Spent Nuclear Fuel, Navy Fuel, and Plutonium Disposition Wastes Degradation

In the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b), the DOE admits there was little applicable experimental data to substantiate the parameter values selected for the Arrhenius-type of equation used to model degradation of DSNF in the TSPA-VA. Thus, it is clear that the potential ranges in chemical environment inside waste packages have not been considered in the DOE abstractions of DSNF degradation. The DOE states that the TSPA-SR will use a degradation rate and a corresponding effective surface area that bounds the experimental data on N-Reactor fuel collected by the DOE over a range of conditions in the last few years. Staff expects the DOE will provide this information in the AMR on Other Waste Form Abstraction (F0085). As pointed out in Section 5.4.3.2.3, there is no mention of MOX fuel and plutonium-disposition wastes in the DOE TSPA-SR methods and assumptions report (CRWMS M&O, 1999b). The DOE will need to provide adequate justification if these wastes are not considered in its TSPA for the site recommendation and license application.

The chemical environment for DSNF degradation can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that fifty-four are relevant to the DOE abstraction of DSNF degradation. In the absence of the DOE AMR on In-Waste Form FEPs Screening (F0185), it is not clear which FEPs the DOE has considered in its abstraction and analysis of DSNF degradation. Staff will review the AMRs pertinent to DSNF degradation to determine which FEPs were included in the DOE abstraction, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification

5.4.3.3.5 High-Level Waste Glass Degradation

Staff analyses of the DOE abstraction of glass waste form degradation are discussed in detail in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c). The CLST IRSR discusses the status of resolution with respect to the adequacy of the DOE consideration of the effects of degradation of HLW glass on repository performance, taking into account the rate of degradation and its effect on the rate of radionuclide releases from the engineered barrier system. In this section, the discussion is focused on the adequacy of the DOE incorporation of the effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release from the glass waste form.

Based on analysis of the DOE abstraction of HLW glass degradation, staff believes the glass dissolution model used in the TSPA-VA is inadequate because it ignores the potential effects of various coupled thermal-hydrologic-chemical on the chemical environment for glass degradation. For example, as the DOE stated in the VA technical basis document, dissolution rates strongly decrease in the presence of dissolved Mg, Pb, and Zn, but are strongly enhanced under some conditions by Fe. The potential effect of dissolved Fe is particularly important because corrosion of the stainless steel inner barrier of the EDA-II design could provide significant quantities of dissolved Fe. The DOE recognizes that the glass model used for TSPA-VA ignores all solution chemistry other than pH and silica concentration and does not account for the effect of other dissolved species such as Mg and Fe, which can change glass dissolution rates by up to a few orders of magnitude. The DOE states that quantitative information needed to incorporate this effect is not available at the time of the TSPA-VA, although experiments are in progress to address this issue (CRWMS M&O, 1998). The DOE will need to demonstrate that these experiments considered the range of chemical compositions of water that could potentially contact the waste form inside breached waste packages.

The chemical environment for radionuclide release from glass waste forms can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database indicated that 45 FEPs are relevant to the DOE abstraction of glass degradation, as indicated in Table 5-1. Presently, it is not known which of the relevant FEPs will be included in the DOE glass degradation abstraction. Based on the description of the TSPA-VA glass degradation abstraction, it appears that most of the FEPs identified in Table 5-1 as relevant are not considered in the DOE abstraction. For example, as pointed out previously, interaction with corrosion products (FEP 2.1.09.02.00) such as dissolved Fe, which could enhance glass dissolution, is not considered in the DOE glass degradation model. Another example of a FEP that is not included in the analyses is FEP 2.1.09.10.00 (Secondary phase effects on dissolved radionuclide concentrations at the waste form), i.e., the DOE model does not consider the incorporation of radionuclides in the alteration phases that may result in episodic releases of radionuclides (U.S. Nuclear Regulatory Commission, 1999c).

The few FEPs that appear to have been considered are FEPs 2.1.02.03.00 (Glass degradation, alteration, and dissolution), 2.1.02.05.00 (Glass cracking and surface area), and 2.1.11.04.00 (Temperature effects/coupled processes in waste and engineered barrier system). The staff will review the AMRs pertinent to waste form degradation to determine which FEPs were included in the DOE abstraction, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction, the DOE will need to provide adequate justification for their exclusion.

5.4.3.3.6 Dissolved Radionuclide Concentration Limits

In its review of the DOE TSPA-VA, staff commented that the solubility limits need to be reevaluated by the DOE as the water chemistry inside the waste package becomes better known (U.S. Nuclear Regulatory Commission, 1999c; 2000b). For the TSPA-SR, the DOE plans to reevaluate the radioisotope solubility limits. The distribution of concentration limits will be based on a range of chemical conditions that takes into account the design of the engineered barrier system, fluid flow rates, and thermal history of the repository. Information presented in the DOE TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) indicates that an in-drift geochemical environment model is being developed to determine the changes in water chemistry resulting from the interaction of engineered barrier system materials with water seeping into the drift and to provide this information to TSPA analyses. Specifically, an in-package chemistry submodel is being developed that will provide a quantitative description of the combined effects of important chemical interactions that can occur between aqueous seepage entering the waste package and materials in the package, including waste package internals, corrosion products, and waste form. Staff agrees that the DOE should use the range of water chemistries calculated from the in-package chemistry model to determine the distribution of solubility limits for the important radionuclides.

The DOE stated in the TSPA-SR methods and assumptions report that the lower range of solubility limit probability distribution function for neptunium may be revised to incorporate the observation that ^{237}Np concentrations in spent nuclear fuel experiments are much lower than would be predicted through pure phase equilibrium calculations if the experimental evidence is sufficiently defensible. Staff previously noted (U.S. Nuclear Regulatory Commission, 1999c) that the DOE needs to provide experimental confirmation of the solid neptunium compounds assumed to be in equilibrium with the dissolved neptunium species in these experiments.

Radionuclide-bearing solid phase solubility depends on the chemical environment, which in turn can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that 50 are relevant to the DOE abstraction of dissolved radionuclide concentration limits. In the absence of the DOE AMRs on FEPs for Near

Field Environment (N0080) and In-Waste Form FEPs Screening (F0185), it is not clear which FEPs the DOE has considered in its abstraction and analysis of radionuclide concentration limits. Staff will review the AMRs pertinent to solubility and to dissolved concentration limits to determine which FEPs were included in the DOE abstraction of solubility limits, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification for their exclusion.

5.4.3.3.7 Colloid-Assisted Radionuclide Concentration Limits

The staff agrees with the general approach to modeling colloid release as described in AMR F0115 (Colloid Source Term Abstraction) (CRWMS M&O, 2000c). The abstraction attempts to quantify the effects of possibly changing in-package chemical conditions on colloidal radionuclide release using limited, site-specific data supplemented by literature review.

However, the abstraction AMR does not provide sufficient justification that the abstraction is unlikely to neglect effects that could increase the colloidal radionuclide concentration. For example, the corrosion test results discussed in AMR F0110 (Colloid Source Term, Argonne National Laboratory) (CRWMS M&O, 2000c) were conducted at 90°C and the colloid sorption tests in AMR F0105 (Colloid Source Term, Los Alamos National Laboratory) (CRWMS M&O, 2000d) at room temperature, but the abstraction AMR did not discuss possible temperature effects. In addition, the abstraction AMR did not critically assess the potential effects on colloid behavior of chemical parameters other than ionic strength and pH (e.g., oxidation potential and alkalinity) (U.S. Nuclear Regulatory Commission, 1999d). Notably, the abstraction adopted a maximum concentration of plutonium irreversibly attached to colloids of 6×10^{-8} mol/L, based on results of 15 Argonne National Laboratory HLW glass experiments (CRWMS M&O, 2000c). The literature on this topic is admittedly sparse, but the AMR did not make a strong case that this value is likely to bound plutonium concentrations under particular repository conditions. Another category of coupled thermal-hydrologic-chemical effect is water flow rate. While it may be acceptable that the abstraction does not incorporate effects of flow rate on colloid release, the DOE must provide a technical basis that this omission will not significantly underestimate release. In summary, the abstraction AMR (CRWMS M&O, 2000b) does not explicitly address a sufficient range of possible coupled thermal-hydrologic-chemical effects on colloid stability and radionuclide attachment to ensure that the abstraction is adequate for the range of possible repository conditions. In addition, no technical basis was provided for the inclusion of colloidal effects only on plutonium and americium release.

In order to address these comments, the DOE could either conduct further experiments or incorporate critical assessments of the effects on colloidal radionuclide release that are beyond the scope of applicable experimental work. Parameters that could be so addressed include: (i) temperature, (ii) oxidation potential, (iii) major cation and anion concentrations, and (iv) in package hydrologic conditions.

In addition, the DOE could more explicitly evaluate whether the experimental results are adopted in a manner that is conservative with respective to ionic strength and pH effects (e.g., on colloidal plutonium concentration). Finally, the DOE could extend the colloidal release abstraction to other radionuclides or provide a technical basis for exclusion of important radionuclides.

The chemical environment for colloid-assisted radionuclide release can be affected to varying degrees by numerous FEPs. Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that 56 are relevant to the DOE abstraction of colloid-assisted radionuclide concentration limits. Five FEPs specific to colloids are: (i) colloid formation in waste and engineered barrier system (FEP 2.1.09.14.00), (ii) formation of true colloids in waste (FEP 2.1.09.15.00), (iii) formation of pseudo-colloids (natural) in waste and engineered barrier system (FEP 2.1.09.16.00), (iv) formation of pseudo-colloids (corrosion products) in waste and engineered barrier system (FEP 2.1.09.17.00), and (v) microbial colloid transport in the waste and engineered barrier system (includes formation) (FEP 2.1.09.18.00). These FEPs are all listed as "included." In the case of the first four listed, inclusion is consistent with the model treatment described in Section 5.4.3.2.6, which includes the three categories of colloid listed in the database—true colloids (or waste form), natural pseudo-colloids (or groundwater), and corrosion product pseudo-colloids (or iron oxyhydroxide). With regard to FEP 2.1.09.18.00, the abstraction AMR (CRWMS M&O, 2000b) specifically excludes microbial colloid release, chiefly on the basis of lack of data and on the argument that such colloids tend to be large and thus easily filtered or settled out. The staff accepts the DOE treatment of these five FEPs related to colloid formation, but suggests that the FEPs database more accurately reflect the neglect of microbial colloid release.

In the absence of the DOE AMR on In-Waste Form FEPs screening, it is not clear whether the DOE has considered the remaining 51 FEPs in its abstraction and analysis of colloid-assisted radionuclide concentration limits. Staff will review the AMRs pertinent to colloids to determine which FEPs were included in the DOE abstraction, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification for their exclusion.

It should be noted that staff analysis of effects of colloids on radionuclide release documented in the CLST IRSR Revision 2 (U.S. Nuclear Regulatory Commission, 1999c) indicated that, based on the assumptions and calculations used in the analysis, the dose contribution from transport of colloidal material at Yucca Mountain is not expected to be significant. Therefore, staff concluded that further examinations of colloidal effects on transport and release are not considered necessary. However, the analysis neglected FEPs that could potentially enhance colloid-assisted radionuclide release. Staff will expect to see a more detailed analysis of the effects of colloids on repository performance in the DOE AMRs and PMRs.

5.4.3.3.8 In-Package Chemistry

In the TSPA-VA, the chemistry of water in the waste package is uncertain and the DOE treatment of this area is incomplete. The major limitation noted by the NRC and DOE staffs is that, although conceptually the complexity of coupled THC processes is recognized, many aspects of these processes are greatly simplified or omitted in the TSPA-VA analyses. For example, the effects of the alteration of cladding and basket materials on the chemistry in the waste packages controlling radionuclide releases were omitted (CRWMS M&O, 1998). These effects could be important because both basket and cladding materials may have different compositions than the waste packages. The additional materials could have a strong effect on corrosion products and associated water chemistry of the waste form environment. In addition, no process model exists for evolution of the gas phase chemistry within the drifts (CRWMS M&O, 1998). Neglect of these processes contributes to model uncertainty and should be justified or remedied. Other model inadequacies in the assessment of radionuclide release are noted, including limitations of J-13 well water as a starting composition in the models, effects of condensation, water-rock interactions, nonisothermal chemistry, and engineered materials (U.S. Nuclear Regulatory Commission, 1999d). Nevertheless, the DOE made considerable progress in addressing effects of coupled thermal-hydrologic-chemical processes on the chemical environment for radionuclide release in the TSPA-VA compared to prior TSPA activities. For example, the stepped temporal changes in the chemical composition of water entering and traversing the emplacement drift used in the TSPA-VA are a significant advance.

Based on more recent information provided in the TSPA-SR methods and assumptions report, the DOE is working towards addressing many of the limitations in its TSPA-VA modeling of in-package chemistry. However, the extent to which progress has been made by the DOE in correcting the limitations of its previous TSPA abstractions is not known because the AMR on In-Waste Package Chemistry Summary (F0130) is not yet available. Also, the extent to which calculations of in-package chemistry are integrated into the other abstractions are not known because the AMRs on specific abstractions are also not yet available. For example, the TSPA-SR methods and assumptions report (CRWMS M&O, 1999b) indicates that the rate of CSNF waste matrix degradation will be expressed as a classic kinetic equation, where the parameters have been evaluated through regression analysis of experimental data obtained over a range of temperatures, water chemistry (total carbonate concentration, pH), and oxygen concentration. It is not apparent whether changes in water chemistry arising from interactions with waste package materials will be considered in modeling CSNF waste form degradation.

As pointed out in Section 5.4.3.3.3, the effect of internal components on the environment contacting the waste forms was considered in the DOE modeling of the potential for criticality of DSNF and plutonium-ceramic waste forms that will be co-disposed with HLW glass (Zhang and Stockman, 1999; Stockman, 1999; Massari, 1999). Although the assumptions and results of Zhang and Stockman's (1999) calculations are specific to the HLW glass waste and plutonium ceramic waste forms, the overall approach is being considered for calculating the internal environment of waste packages containing other waste forms (Stockman, 1999; Massari, 1999). The conceptual model for waste package internal environment proposed by Zhang and Stockman (1999) is described in Section 5.4.3.2.7. Staff comments on Zhang and Stockman's conceptual model are presented in the following paragraphs.

There are several limitations to Zhang and Stockman's (1999) conceptual model that require further evaluation and construction of alternate conceptual models. The dissolution of the waste package components cannot be regarded as a purely chemical dissolution process. This means that anodic dissolution sites are supported by spatially separate cathodic reduction sites. The degree of spatial separation depends on the corrosion mode and environment conductivity. Under general corrosion the cathodic and anodic sites are not widely separated (and show an almost random location on the metallic surface), whereas, under localized corrosion, there is wide spatial separation between oxidation and reduction sites. The increased conductivity of the solution due to evaporative concentration as well as waste package degradation also favors wide spatial separation of the anodic and cathodic sites. The wide spatial separation of these sites will result in a greater acidification of the environment at certain locations than predicted by Zhang and Stockman. This difference arises because the anodic reactions generate cationic species (Fe^{2+}, Cr^{3+}, Ni^{2+}, etc.) that hydrolyze and decrease the pH. On the other hand, the cathodic reactions generate alkalinity.

The second assumption made by Zhang and Stockman is that waste package barrier material (alloy 22) does not contribute significantly to the alteration of the environment. If the only failure mode of waste package barriers is general dissolution, then this may be an adequate assumption. However, in the current waste package design, the alloy 22 outer barrier surrounds a type 316L Nuclear Grade stainless steel inner barrier. The galvanic contact between alloy 22 and 316L stainless steel will result in enhanced dissolution of the latter. Since even general dissolution is seldom completely uniform, where alloy 22 is breached first, localized corrosion of type 316L stainless steel will occur leading to extremely low pH values. For example, pH values as low as 3 have been reported in localized corrosion sites of Mo-containing alloy at 25°C (Sridhar and Dunn, 1994). The pH values may be lower for higher temperatures.

Zhang and Stockman also assume the average dissolution rate of type 304L stainless steel pour canister to be 0.1μm/yr and that this dissolution occurs in an uniform manner. The rates assumed correspond to passive dissolution behavior, controlled by a protective oxide film. Passive dissolution of type 304L and 316L stainless steels occurs only at sufficiently low potentials, low temperatures, and low chloride concentrations. For example, at an applied potential of 320 mV vs. Standard Hydrogen electrode (SHE), which can be considered to represent a moderately oxidizing environment, pitting in type 304 stainless steel has been shown to occur above 60°C at chloride concentrations greater than 3×10^{-4} M (Nakayama et al., 1993). The temperature decreases as the chloride concentration and potential increase. The literature data on types 304L and 316L stainless steels indicate that pitting is the most likely mode of corrosion under conditions anticipated to prevail in the waste package.

In contrast to low rates of passive dissolution, high rates of uniform dissolution of Fe-Ni-Cr-Mo alloys occur below a certain pH value called depassivation pH (pH_D). Under these conditions, the passive film is chemically destabilized. The pH_D at 25°C has been reported to be 1.3 to 1.5 irrespective of chloride concentration for type 316 stainless steel (Okayama et al., 1987). Under these conditions, the corrosion rate of the material will be very high (over 1 mm/yr).

These analyses indicate that

- Spatial variation in environmental condition within the waste package may dictate lower pH values than assumed by the DOE in their analysis of criticality. The DOE analysis may be conservative with respect to retention of fissile material for criticality, but nonconservative with respect to radionuclide release.
- The assumptions regarding the dissolution mode and rate of waste package internals are not consistent with literature on the corrosion behavior of these materials.

Detailed calculation of the evolution of the waste package internal environment is complicated by the number of interactions possible among a wide range of materials and the large number of FEPs that could potentially affect the in-package chemical environment. The bounding assumptions made by the DOE may not be conservative. On the other hand, alternative conceptual models of the evolution of environment due to the localized dissolution of waste package materials may lead to extremely high dissolution rates or solubilities. There is at present very little empirical experience with analogous engineering structures. Therefore, experiments to simulate leaking waste package barriers and internals may be needed to verify bounding assumptions used by the DOE.

Staff review of the FEPs database (U.S. Department of Energy, 1999) indicated that 57 are relevant to the DOE abstraction of in-package chemistry (Table 5-1). In the absence of the DOE AMR on FEPs for Near Field Environment (N0080), it is not clear which FEPs the DOE has considered in its abstraction and analysis of in-package chemistry. Staff will review the AMRs pertinent to in-package chemistry to determine which FEPs were included in the DOE abstraction, and if those FEPs have been incorporated adequately. For those FEPs that have not been included in the abstraction and analyses, the DOE will need to provide adequate justification for their exclusion.

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