



UNITED STATES
NUCLEAR REGULATORY COMMISSION

ADVISORY COMMITTEE ON NUCLEAR WASTE
WASHINGTON, D.C. 20555-0001

January 11, 2000

The Honorable Richard A. Meserve
Chairman
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555-0001

Dear Chairman Meserve:

**SUBJECT: COMMENTS ON THE IMPORTANCE OF CHEMISTRY IN THE NEAR FIELD
TO DOE's YUCCA MOUNTAIN REPOSITORY LICENSE APPLICATION**

This letter provides comments and recommendations on the importance of chemical phenomena in the near field to the U.S. Department of Energy's (DOE's) Yucca Mountain Repository proposed License Application (LA). This letter also transmits the attached "white paper" by Raymond Wymer titled "Chemistry in the Proposed Yucca Mountain Repository Near Field." In his paper Dr. Wymer examines some chemical aspects of the near field of the Yucca Mountain repository with particular reference to chemical effects in engineered barriers, to the formation and dissolution of solids, and to corrosion. The potential contributions of intentionally added chemical materials to the near field for the control of radionuclide release and transport from the waste forms are discussed, along with the implications for possible NRC studies.

The recommendations are based on briefings by both NRC staff and DOE on DOE's Viability Assessment; on a working group meeting on the Near Field Environment and Performance of Engineered Barriers in the Yucca Mountain Repository held June 10-11, 1998, by Advisory Committee on Nuclear Waste (ACNW); and on discussions during a visit to the Center for Nuclear Waste Regulatory Analyses (CNWRA) June 28-30, 1999.

White Paper on Chemistry in the Proposed Yucca Mountain Repository Near Field

In the attached paper, Dr. Wymer discusses the potential advantages of using backfill in the drifts and in waste packages as a means of significantly retarding radionuclide transport by sorption and precipitation reactions. He reviews the status of chemical studies on the formation and dissolution of secondary phases at the waste form-water interface and discusses the potential importance of secondary phases in limiting release of radionuclides from the waste. The paper discusses the reliance by DOE on use of corrosion-resistant metals for drip shields, waste packages, and the zircaloy cladding of the spent fuel for preventing premature release of radionuclides from the repository.

DOE may use backfill or take credit for certain chemical processes in its analysis for its LA. Consequently, NRC should be prepared to analyze those aspects of an LA.

The problem of extrapolating corrosion data to the 10,000-year horizon makes it important to have as complete an understanding as possible of the important phenomena. For example, there is a temperature regime where corrosion of the metals of interest is much more severe

RSO2

than at temperatures anywhere outside that regime. NRC and CNWRA are at the forefront of corrosion studies related to the repository. This activity should continue.

Recommendations

Recommendation 1

The NRC staff should conduct scoping calculations of the importance of backfill to modify the chemical environment and to act as an attenuating agent for released radionuclides. If it is determined from these calculations that the use of backfill or the effects of corrosion products can have an important effect on performance, then more detailed analyses should be requested of the applicant.

Recommendation 2

The NRC staff should continue to work on the role of secondary phases in attenuating radionuclide releases. In particular, we recommend continued work on natural analogs, such as the Peña Blanca site.

Recommendation 3

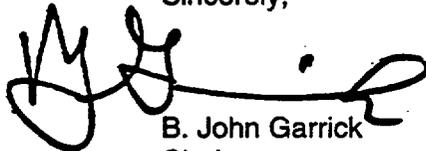
The NRC staff should continue to collect as much confirmatory data as possible on the corrosion rates and mechanisms of corrosion of the drip shield, the waste packages, and the zircaloy cladding of the spent fuel under the range of expected conditions.

Recommendation 4

The NRC staff needs to continue and refine careful analysis of the role of coupled processes in repository performance as part of its development of review capabilities. Because of the complexity of the models and the abstraction of these models into the Total System Performance Assessment, the key focus is to ensure that an important coupled process is not left out of the performance assessment. The effects of temperature will be of particular importance.

ACNW will continue to follow developments in near-field chemistry of the proposed Yucca Mountain Repository.

Sincerely,

A handwritten signature in black ink, appearing to read 'B. John Garrick', written over a horizontal line.

B. John Garrick
Chairman

Attachment:

R. G. Wymer, Member, Advisory Committee on Nuclear Waste and Andrew C. Campbell, Advisory Committee on Nuclear Waste, Senior Staff Scientist, "Chemistry in the Proposed Yucca Mountain Repository Near Field," dated January 11, 2000.

January 11, 2000

CHEMISTRY IN THE PROPOSED YUCCA MOUNTAIN REPOSITORY NEAR FIELD

R.G. Wymer, ACNW Member

Andrew C. Campbell, ACNW Senior Staff Scientist

Executive Summary

This paper focuses on select aspects of the near-field chemistry in the proposed Yucca Mountain high-level waste (HLW) repository. The goal is to identify areas where additional studies could help the Nuclear Regulatory Commission (NRC) position itself better to respond to changes in repository design. In this paper we focus on the portion of the near field within the confines of the drift walls. The near-field chemistry can be altered by chemical reactions that could occur by the interaction of percolating water with materials contained within the repository (e.g., backfill in the proposed) Enhanced Design Alternative II (EDA-II) design or concrete in drift liners that had been proposed as part of the Viability Assessment (VA) design. These chemical reactions can have an important effect on the potential release of radionuclides from the repository and ultimately its performance. A key area that the paper will consider is the possible use of chemically engineered backfills to alter near-field chemical properties to minimize the potential release of radionuclides and reduce long-term uncertainties in performance. Water composition, air composition and circulation, and temperature are discussed in the context of their effects on chemistry and on coupled effects in the repository near field. The importance of modeling to the license application and the influence of chemistry of the drift environment on modeling are also discussed.

The Role of Chemistry in Repository Licensing

The key issue from a regulatory perspective is the adequacy of information and models to make decisions about the safety of the repository. There will never be a complete knowledge base that covers all near-field chemistry issues. Because there are many deficiencies both in the availability of relevant information and in incorporating available information from the literature on chemistry, natural analogs, and experimental studies into databases, NRC will have to decide what information is essential for making regulatory decisions about the Site Recommendation and License Application. In particular, NRC will need to specify what information is critical for making a determination of reasonable assurance as it develops the Yucca Mountain Review Plan for the HLW repository.

The Near-Field Environment and Coupled Processes

Water is the *sine qua non* of chemical reactions in the near field, including interactions with engineered barriers, corrosion, solids dissolution, and radionuclide transport. There may be little that can be done in a practical way about controlling the long-term uncertainties in the amount of water that contacts the repository, although some possible solutions to this problem were examined in the white paper on Engineered Barriers at Yucca Mountain by Charles Fairhurst (1999). The chemical conditions of water reacting with materials in the near field may also be amenable to some control. For example, backfill, which is proposed in U. S. Department of Energy's most recent design, could be engineered to have certain chemical properties that can influence the near-field chemical environment in a positive way. From another perspective, engineering of the near-field environment should be done so as to avoid placing materials in the repository that could lead to increased uncertainties for radionuclide releases. An example is the use of large amounts of concrete as drift liners in the VA design.

Air, which is about 21 percent oxygen, plays a major role in promoting degradation processes that can release radionuclides from the repository. Because the proposed HLW repository at Yucca Mountain is in the unsaturated zone, the availability of significant air trapped in rock pores and fractures and the fluxes of air through fractures in the mountain (e.g., from barometric pumping) help to maintain an oxidizing environment.¹ This plays a dominant role in dissolving uranium dioxide in spent fuel and releasing fission products and actinide elements contained in the matrix. Radiolysis also may play a significant role in maintaining oxidizing conditions inside the waste package. In this environment, two of the important radionuclides (technetium and neptunium) exist in a more mobile state than if reducing conditions prevailed. In addition, the presence of carbon dioxide may lead to the formation of actinide carbonate complexes, especially uranium, that are also more amenable to transport with water. Various proposals for an open or closed repository after it has been filled with waste may also have a powerful influence on the potential for oxidation reactions in the repository near field.

Temperature in the repository, or more precisely the high temperature thermal pulse generated in the near-field environment by radioactive decay heat, is affected by the placement and areal extent of the waste packages in the repository. The thermal pulse can be greatly moderated by forced circulation of air at relatively high volumes during the open period of the repository, since a significant portion of the heat-producing decay reactions take place during the first few hundred years. Although the primary function of increased air circulation in the new DOE EDA-II design concept is to remove heat, some water will also be removed by evaporation. There is an important coupling of the effects of waterflow, airflow, and temperature with the near-field chemistry of the repository (i.e., coupled Thermal Hydrological Chemical [THC] processes); these effects are bound up inextricably with the repository design. Because reaction rates are controlled to a significant degree by temperature, a major goal of engineering to control the thermal loading of the repository is to reduce the uncertainties of coupled THC processes, which could result in changes in permeability in the near field and enhanced corrosion of the waste packages.

The Effects of Repository Materials on Near-Field Chemistry

Engineered barriers in the near field may be used to help control radionuclide release and transport and to limit degradation of waste packages, spent fuel cladding, and waste forms. Of particular chemical interest are drift backfill materials (and possibly materials introduced into the waste package) that could be used to buffer the near-field chemistry and constrain the formation of secondary phases so as to limit the release rate of radionuclides. There is a large range of potential backfill materials, each having advantages and disadvantages. The materials may include a variety of compounds that may act as reducing agents, precipitating agents, or scavengers for important radionuclides, such as technetium and neptunium. Backfill materials that have been proposed for nuclear waste repositories include crushed tuff, calcite, and quartzite sands (Yucca Mountain); various types of clays including bentonite and zeolites (saturated zone repositories proposed worldwide); and magnesium oxide (MgO) in the Waste Isolation Pilot Plant (WIPP). Depleted uranium has also been proposed as a backfill to help limit the dissolution of the uranium dioxide (UO₂) in the fuel and ensure that any mobilization of fissile material cannot form a critical mass (Forsberg,

¹ The Yucca Mountain environment has a relatively high "redox potential." The redox potential of a system refers to its tendency to oxidize or reduce chemical species. Many important chemical processes in the repository will occur due to changes in redox potential. Uranium dioxide (UO₂) in spent fuel exists in the +4 valence state as it comes out of the reactor. Over time, as it is exposed to air and water containing oxygen and other oxidizing chemical species generated by radiolysis, the UO₂ becomes "oxidized" to the +6 valence state, which forms more soluble chemical compounds than the reduced form does. Hence oxidation of spent fuel results in the dissolution of the uranium matrix and the release of radionuclides.

(UO_2) in the fuel and ensure that any mobilization of fissile material cannot form a critical mass (Forsberg, 1997). Addition of backfill to the waste package could put material in the immediate vicinity of the waste form and thus increase the efficacy of chemical actions; however, the thermal impact on cladding due to the insulating effect would have to be considered.

Formation and Dissolution of Secondary Solid Phases

The formation and dissolution of secondary radionuclide compounds that can form as spent fuel and other waste forms dissolve and reprecipitate as solid compounds are likely to be major determinants in the rate of radionuclide release from the proposed repository. In addition, radionuclide transport will be strongly affected by chemical species formed at the waste form-aqueous phase interface. Analyses made to date of both solids formation and radionuclide dissolution are limited because of the complexity of the chemical systems involved and the deficiencies of thermodynamic and kinetic databases used in the calculations for chemical reactions, solubilities, and new phase formation. Lack of specific chemical knowledge is sometimes treated in the modeling studies by making bounding-case assumptions. For example, the dissolution model that DOE used in the Total System Performance Assessment Viability Assessment is based on laboratory experiments using water with a more aggressive chemical composition than is realistic for Yucca Mountain. This approach results in radionuclides dissolving completely and quickly from the spent fuel (~ 400 years) and being released at a relatively high rate from the repository. The conservatism resulting from this approach leads to reliance on the waste package to limit any releases and has the potential to cause problems if unexpected phenomena occur or if changes in regulations require or permit changes in the amount or rate of radionuclides transported. A more definitive approach based on more complete knowledge could help reduce the conservatism.

Corrosion

Corrosion of the drip shield, the waste package, the spent fuel cladding, and drift structural materials such as the invert are key issues in evaluating radionuclide releases and determining chemical species produced. The fundamental mechanisms of specific corrosion processes that could adversely affect the lifetime of barrier materials must be better understood. The goal would be to enhance confidence (i.e., reduce uncertainty) in the required, very long-term extrapolations of corrosion data, which of necessity must be made from data taken over a much shorter time period.

Modeling

Elaborate and flexible models have been developed by DOE and NRC to analyze repository performance. These models are capable of handling a very wide range of chemical and other processes because of their modular nature and their built-in capability to incorporate new processes, new physical characteristics, and new data. However, the lack of some key supporting chemical data and of a firm understanding of some key chemical mechanisms may lead to questions about the adequacy and validity of the chemistry model calculations. This lack of key information in some areas can lead to the use of overly conservative assumptions and overly conservative results.

“Expert elicitation” (Kotra, et al., 1996), a highly structured and well-documented process whereby expert judgments are obtained, has been used to obtain values for use in the models where solid data are lacking, uncertainties are large, technical judgments are required about the conservative nature of bounding assumptions, or more than one conceptual model is consistent with available data. It is recognized that this

approach, although valuable when lack of time and experimental difficulties preclude obtaining the necessary data, should not be used when it is practical to obtain the necessary data experimentally (NUREG-1563).

The complexity and sophistication of the process level models require that they be abstracted into the TSPA model. Abstraction² of the models further complicates treatment and may inhibit full incorporation of important coupled effects. Consequently, there may be a loss of detail in the model calculations for the approximations of radionuclide releases from the repository, thus adding to the uncertainty in the resultant doses calculated for the critical group. Coupled processes are difficult to model and should receive careful attention in the abstraction process. The chemical processes in particular are difficult to model because of interactions of the many chemicals present and because of the influences of water composition, air, and temperature. Similar comments apply to both the NRC models and the DOE models.

Conclusions

Chemistry plays a critical role in the near-field performance of the repository. There is an important and unavoidable coupling of the effects of water, air, and temperature with the near-field chemistry of the repository; these effects are inextricably bound up with repository design. The present DOE repository design of the near field relies on corrosion resistance of the waste package and drip shield as major contributors to the multiple-barriers concept for in-depth defense. The case for meeting the multiple-barriers licensing requirement, which is a major element of the defense-in-depth licensing philosophy, may be improved by the deliberate introduction of certain chemical features in the repository near field. In particular, carefully chosen backfill materials and materials to fill the void space in the waste packages can chemically alter radionuclides such as ⁹⁹Tc and ²³⁷Np such that they are transported much less rapidly out of the near field through sorption or precipitation reactions. In this way the contributions of ⁹⁹Tc and ²³⁷Np to the radiation dose over the time of interest for licensing may be substantially reduced. Because of the potential significant contributions of deliberately added chemical features to the repository, NRC should anticipate their inclusion and be prepared to evaluate them.

Specific activities that staff may undertake or should continue include:

- Staff should conduct scoping calculations of the importance of backfill to modify the chemical environment and to act as an attenuating agent for released radionuclides. If it is determined from these calculations that the use of backfill or the effects of corrosion products can have an important effect on performance then more realistic analysis would be required by the applicant.
- Staff's analysis of the potential importance of secondary uranium phases show significant reductions in calculated dose: therefore continued work on the role of secondary phases is essential to be prepared for possible inclusion of this phenomena in DOE's safety case. This work should not only include secondary uranium phases, but also other secondary phases (e.g., iron oxyhydroxide corrosion products if DOE decides to include this as an important element in its safety case) that are likely to form and may sequester or attenuate key radionuclides.

² Abstraction is a process whereby computer models are simplified to make calculations less time consuming and less expensive, or in some instances even possible. Model detail is lost in the process of abstraction. This loss may be compensated for by doing "off-line" calculations that support and justify the simplifications.

- Staff needs to continue its work on understanding the rates and especially the mechanisms of corrosion of the drip shields, the waste packages, and the spent fuel cladding.
- Staff needs to continue and refine careful analysis of the role of coupled processes in repository performance as part of its development of review capabilities. Because of the complexity of the models and the abstraction of these models into the TSPA the key focus is to ensure that an important coupled process is not left out of the performance assessment.

Introduction

This paper presents and discusses selected aspects of the near-field chemistry in the proposed Yucca Mountain high-level waste (HLW) repository. Based on this discussion, key chemistry areas are identified, about which additional studies would help the Nuclear Regulatory Commission position itself better to evaluate the U.S. Department of Energy's (DOE's) license application (LA) and to respond to changes in repository design. Three important chemistry areas are focused on for possible additional study in the technical literature, in the laboratory, and in modeling. The three areas are: *chemical reactions in engineered barriers, solids formation and dissolution, and corrosion*. Water composition, air composition and circulation, and temperature are discussed in the context of their effects on chemistry and on coupled effects in the repository near field. The importance of process-level modeling of the three chemistry areas and the impact of the drift environment on modeling is discussed in terms of needs that should be addressed in the abstraction of process modeling into Total System Performance Assessment (TSPA) models.

This paper highlights and discusses what the author views as the most important chemistry study areas in the "near field"³ that merit increased attention by NRC staff. A more thorough analysis of these areas could help NRC position itself better to evaluate DOE's TSPA for the site recommendation (SR) and LA for the repository. Such analyses would also help position NRC to accommodate future changes in DOE's design assumptions for the repository in a timely way. The discussion in this paper is restricted to chemistry in the near field because it is there that the greatest possibility exists for changes in materials and engineering features of the repository and, consequently, for reductions in uncertainty in repository performance. A number of excellent reviews of the literature on the near-field environment and the geochemistry of the proposed Yucca Mountain HLW repository are available (Angell, et al., 1996; Murphy and Pabalan, 1994).

Chemical reactions in engineered barriers can have a significant effect on the rate of release and transport of radionuclides in the near field. Three types of chemical reactions have the potential to be of importance, namely co-precipitation reactions that can incorporate important radionuclides into the crystal structure of other solid chemical phases, oxidation/reduction (redox) reactions that could lead to less mobile forms of key radionuclides such as technetium and neptunium, and radionuclide sorption-desorption reactions that could attenuate possible releases of key radionuclides. Taken together these processes could be used to reduce the uncertainties associated with the mobilization and transport of important radionuclides such as ⁹⁹Tc, ¹²⁹I, and ²³⁷Np. For example, oxidative dissolution of spent fuel and the subsequent formation of secondary solid phases (e.g., higher valent uranium oxides) at the spent fuel-water interface could have a profound effect on the rate of release of radionuclides from the spent fuel by producing solids that can co-precipitate and/or adsorb radionuclides or by possibly limiting further oxidation of the fuel. This is an important area for further study (Pearcy, et.al., 1994).

³ In this report, definition of the "near field" is limited to the contents of the drift, including features such as drift supports and other construction materials, drift backfill, drip shields, waste packages and internals, cladding, spent fuel, and the water and air that enters the drift. Broader definitions of the near field often include the zone of rock affected by the thermal pulse from the waste.

The Role of Chemistry in Repository Licensing

Chemistry plays a critical role in both the near-field performance of the repository and the performance of the natural (geologic) barrier (Simmons, et al., 1995). As reported by the TSPA Peer Review Panel (1999), "the near-field geochemical environment is an important and complex part of the performance assessment." Both DOE and NRC recognize that, because of the complexity of this environment, performance assessments of the proposed repository at Yucca Mountain will always rely on many assumptions and abstractions about near-field chemistry in making the case for licensing the repository for high-level radioactive waste disposal. This includes assumed and/or calculated near-field chemistry parameters in computer modeling of processes that affect corrosion, radionuclide dissolution, and radionuclide transport. The NRC staff will need to be in a position to evaluate DOE's assumptions and abstractions when it considers the SR and LA.

The most important chemical processes in the near field are corrosion (of drip shields, waste packages and their supports, and spent fuel cladding), radionuclide dissolution (especially of irradiated uranium dioxide, which contains the transuranium elements and fission products of interest), secondary chemical phase formation, and radionuclide transport (especially of neptunium, technetium, and iodine) through backfill material that may be present. The NRC must understand these processes sufficiently to be able to evaluate the validity and relevance of chemical information and the analyses of the chemical processes DOE provides in support of its LA. DOE must make supportable arguments about the chemical processes to defend the reliance of its LA on the presence of multiple barriers in the repository, which is a major component of the defense-in depth philosophy required by NRC. It is also important for NRC to be able to analyze the implications (especially the degree of conservatism) of the reliance DOE has placed on "bounding cases"⁴ in its analysis.

The continuing changes that DOE is making in repository design substantially complicate NRC's task of preparing to evaluate the repository LA. Some of these design changes could have a profound effect on the chemistry and performance of the repository, and these changes in the design may lead to considerable additional work on the part of NRC and the Center for Nuclear Waste Regulatory Analyses (CNWRA) in experimental programs and modeling studies. Furthermore, additional changes to the proposed design are anticipated prior to the LA. A key issue is how NRC should focus its resources to have sufficient depth and breadth to review the final LA with whatever new design features and enhancements that DOE may choose to include.

Computer modeling plays a central role in predicting repository performance. The success of the models (including process-level modeling and total systems performance modeling⁵) rests, in part, on a thorough

⁴ The term "bounding cases" is used to denote instances in which the largest or smallest value believed to be realizable is used to provide an upper or lower limit to a calculated value. This is a useful approach when a more realistic value cannot be calculated, but it can lead to excessive conservatism and tends to compromise the concept of defense in depth by obscuring the true contributions of individual barriers.

⁵ Process-level models are chemical and physical models and associated codes of the basic phenomena and processes that are thought to be important to repository performance. Total systems models are abstracted from the process-level models to represent these key processes in a simplified manner so that the analyst can evaluate the overall functioning of the system and identify the aspects and features of the system that are most important to overall performance. Although in principle one could simply combine all the process models into a

understanding of the physical and chemical mechanisms and processes that control the degradation of engineered barriers (including spent fuel and other waste forms) and the mobilization and transport of radionuclides. Chemistry of the near field is a key factor in the models used to analyze repository performance. Several computer codes are used in the models⁶ to calculate phase equilibria and the distribution of species. Current generation models are constructed in such a way that they are capable of handling greater sophistication and breadth in describing the chemical processes for Yucca Mountain than has been required of them to date. The models, however, do not include databases for some of the more complicated coupled chemical processes⁷ involved in solids formation and in chemical reactions in the backfill. This absence is due, in part, to the lack of data required for analyses of these potentially important chemical reactions and their kinetics, and to the fact that backfill has not been considered seriously by DOE until recent design changes. It is also due to the difficulty of carrying out the modeling. A particularly important modeling area is model abstraction, wherein the simplifications inherent in the abstraction process may leave out or overly simplify important coupled chemical processes.

The Near-Field Environment and Coupled Processes

It is useful to consider the essential features of the major environmental contributors to the chemistry of the near field. In this way a context is provided to think about the chemical considerations related to chemical reactions in engineered barriers and solids formation and dissolution. The key components that control chemistry in the near field are water, materials that react with it, and gases. The temperature of the system plays a major role in determining the rates and extent of reactions that take place between the aqueous and gaseous phases in the near field and support materials, backfill, container materials, spent fuel cladding, and the waste forms. These reactions are highly coupled as thermal-hydrological chemical (THC) processes and cannot be properly treated as individual processes.

Water composition and reactions in the proposed repository drifts will have a major effect on the chemical processes involved in radionuclide dissolution and transport, engineered barriers, and corrosion. Yucca Mountain tuff contains about 10 percent water by volume and the current percolation of water (from surficial processes) into the repository is estimated to be from 1 to 10 millimeters per year. The water contains minor but important constituents such as dissolved oxygen; calcium, carbonate, bicarbonate, silicate and chloride ions; and others. Chloride ions could be very important in corrosion. Carbonate and silicate ions are likely components of interfacial solids that may form. Chemically reactive materials may also be added to the water through reactions of the water with backfill. The added reactive materials could affect either the formation of solids or the transport of radionuclides such as technetium and neptunium by changing their valence. They could also change the pH of the water. The pH and the oxidizing or reducing

single total systems model, the resulting model and code would be too cumbersome to operate efficiently and the amount of time required to conduct calculations would be excessive. Many aspects of the process-level models are not important to repository performance (though they may play some role) and therefore the approach that both NRC and DOE have taken is to abstract and represent key processes within the total system model.

⁶ Examples of such codes are EQ3/6, PHREEQE, SOLMINEQ.88, SOLVEQ, MINEQL, MINTEQ, and ECHEM.

⁷ Coupled processes are those processes wherein two or more processes are interrelated and interact in a manner such that a change in one process causes changes in the others.

nature of the water and its solutes will greatly influence the chemistry of primary reactions such as corrosion and of secondary reactions such as formation of solid mineral phases and redox reactions.

Radiolysis of water will form hydroperoxide radicals, hydrogen peroxide, and other oxidizing (as well as reducing) species, all of which have the potential to change the valences of important radionuclides, e.g., Np and Tc, thereby radically changing their chemistries. Radiolysis is unlikely to have a major effect on overall repository performance at any significant distance from the waste form because gamma rays will be the main source of radiolysis, and the gamma dose will decrease rapidly (being due largely to ¹³⁷Cs decay) relative to the 10,000-year licensing period of the repository. The effect of radiolysis at the surface of the spent fuel or vitrified waste could, however, be of some importance because of the presence of alpha-induced chemical species. The formation of nitrate and nitrite ions by radiolysis of nitrogen in the presence of water could produce the respective acids (nitric and nitrous) which, if formed in sufficient amounts, could affect the rate of dissolution of the waste form.

Table 1 presents information on the J-13 well-water composition commonly used to represent the water that will enter the drifts. The appropriateness of this composition as representative of water in the near field will need to be confirmed.

Table 1. Approximate Composition of J-13 Well Water (DOE, 1998)
(pH = 6.8 - 8.3)

Chemical Species	Molality x 10 ⁴
SiO ₂ (aq.)	95.00 - 11.40
Na ⁺	18.30 - 21.70
Ca ²⁺	2.90 - 3.70
HCO ₃ ⁻	1.93 - 2.34
Cl ⁻	1.78 - 2.37
K ⁺	1.00 - 1.40

Air entering and circulating in the repository will have a major influence on the humidity and overall oxidizing conditions of the near field. As long as air is circulating through the repository, and in the absence of a reducing backfill, it will be impractical to establish a near-field environment that is, on average, reducing. Oxygen in the air will have a great influence on the chemistry of the radionuclides of greatest interest (e.g., Np, Tc, I, and U), and will play a major role both in providing an oxidizing environment to corrode the drip shield, the waste canisters, and the spent fuel cladding and in oxidizing constituents of the spent fuel and vitrified waste. It could also react with chemically reactive backfill materials. The oxidizing effects will be due largely to oxygen in the air and dissolved in the water, but could also be due to radiolysis in the short term. Radiolysis of nitrogen from the air will produce oxides of nitrogen that may ultimately form nitric and nitrous acids by reaction with water. The higher valence states of uranium (+6 versus +4) are more stable and form complexes more soluble than the reduced form of uranium. The oxidizing environment also determines the valence states of radionuclides such as

technetium and neptunium by oxidizing them to species (TcO_4^- and NpO_2^+) that form more soluble complexes with water and are more readily transported by water than the reduced species. However, even though the overall repository conditions are oxidizing while air is being circulated, there will be local regions that are chemically reducing in nature. This would be the case, for example, in the immediate vicinity of the inner stainless steel waste package container for spent fuel and the steel containers for the vitrified waste when they are corroding and producing ferrous ions, which are moderately strong reducing agents under some conditions.

Other constituents of air (e.g., carbon dioxide and water) will play a role in chemical reactions of the fuel material when fuel cladding fails, and could potentially have a role in bacterially produced phenomena. The carbon dioxide in the air is a potential reactant for the formation of soluble carbonate complexes of several actinide elements, notably uranium and neptunium. Uranyl ions, formed by oxidation of uranium dioxide to UO_3 followed by reaction with water, can react with carbonate ions to form the very stable and highly soluble uranyl tricarbonate complex ions, (Grenthe, et al., 1992) providing an excellent example of this type of complexation reaction. Neptunyl ions also form stable carbonate complex ions. Such ions would be soluble in and readily transported by water. However, maximum amounts of carbonate complexes are formed at pHs somewhat above the expected pH of the water in the repository.

Temperature has a dominant influence on the relative humidity and the presence or absence of liquid water in the repository. Temperature also greatly affects the mechanisms and kinetics of corrosion and dissolution, the transport of radionuclides, solid phase solubilities, and chemical equilibria throughout the repository. In general, both thermodynamic free energy (which quantifies chemical equilibria) and reaction rates are related in a positive and exponential way to temperature, which contributes to the great importance of temperature to chemistry.

DOE proposes in its EDA-II design concept to control the temperature of the repository in such a way that water is driven away from the drifts, condenses in the areas between the drifts, and percolates into rock layers below the waste. During the time of the thermal pulse, the temperature also has a major effect on the corrosion potential of the new waste package design.⁸ If spent fuel is exposed to the circulating water and air under these conditions, chemical reaction rates and equilibria, solubilities of solid phases, and possibly sorption-desorption reactions in the backfill could be adversely affected. Inclusion of backfill in the drifts will also have an important effect on the temperature of the near field by insulating the waste packages. Placement of specific materials in the near field in conjunction with control of the thermal loading of the repository thus can have an important influence on the expected water composition and amount, and, consequently, the chemical reactions that take place.

Because of the strong influence of temperature on chemical (and other) aspects of the repository, it makes a major difference whether the repository is cooled or not. Even in a cooled repository, the temperatures inside the waste packages will be much higher than the temperatures in the walls of the drift. An unventilated repository will reach a temperature dictated by radioactive decay, repository design, waste package loading, areal loading of the repository, and time. If backfill is introduced, repository temperatures will rise because of the insulating effect of the backfill, as noted earlier. Data on the effects

⁸ In a limited temperature regime between about 85 and 100° C, the outer waste package layer (alloy-22) is more susceptible to localized (crevice) corrosion than at either higher or lower temperatures.

of temperature on solubilities and equilibria and on the kinetics of corrosion are needed for the model calculations of the chemistry of the near field. In some cases such data have been obtained and incorporated into the models, but in some potentially important cases, for example for silicates, such data are lacking.

The Effects of Repository Materials on Near-Field Chemistry

DOE has gone through a succession of major and minor repository design changes during and following the period of preparation of the TSPA-VA. These design changes have resulted in major changes in repository materials and consequently in the anticipated repository chemistry and its modeling. For example, DOE's most recent design calls for the emplacement of backfill around the waste canisters (Barrett, 1999). Although the primary motivating factors appear to be preventing rock-fall damage to the drip shields and physically diverting moisture away from the waste packages, backfill could be engineered to have chemical properties that can influence the near-field chemical environment in a positive way. From another perspective, engineering of the near-field environment should be done to avoid placing materials in the repository that could lead to enhanced uncertainties for radionuclide releases. For example, in the most recent DOE design, the use of concrete as a major support material in the drifts is largely eliminated. The goal is to reduce the uncertainties associated with high pH fluids that could result from water reacting with concrete, possibly leading to higher solubilities and lower sorption of some radionuclides in the near field. Changing placement of waste packages has a major effect on repository temperature profiles. Changing the proposed materials of construction of the drip shield and the location of materials of construction of the waste packages has had a major effect on the model predictions of rates and amounts of radionuclide releases for a 10,000-year period. So too has the change from an uncooled to a cooled (using forced circulation of air) repository for the 50 (or more) years prior to closing. Continuing changes in design make NRC's job of preparing to review the expected DOE repository LA more difficult. If the LA is to be addressed in a timely way, NRC either needs reliable advance information on the repository design so it can be prepared to make an independent assessment of the results of DOE's analysis of the Yucca Mountain repository and of the LA, or it needs to be prepared in a general way to accommodate to possible future changes in the repository design. The NRC staff has developed a flexible model and code (TPA) to deal with the changing DOE designs, but needs to anticipate increased DOE reliance on near-field chemistry in its long-term safety case.

The repository will contain both spent Light Water Reactor fuel and DOE high-level waste in the weight ratio of about nine to one. There will be relatively small amounts of miscellaneous DOE spent fuel derived from a variety of experimental studies over many years. Appendix A presents the proposed allocation of repository space to types of waste and the principal proposed Yucca Mountain repository design features at the time of writing this paper. Once the waste package and fuel cladding (or the canister holding the vitrified waste) have been breached, the spent fuel material or vitrified waste will be exposed to chemical attack by the water that reaches them. The composition of the water reaching the waste forms will not be the same as that of the water that entered the drift because of the chemical reactions the water will have undergone by corroding the waste packages and by reaction with other materials (e.g., backfill) it has contacted. The water will also have been altered in composition by evaporative concentration of dissolved constituents such as calcium, carbonate (and bicarbonate), silicate, and chloride ions. Other chemical species will be formed by radiolysis. These changes, depending on how extensive they are, have the potential of having a profound effect on the dissolution reactions of the water with the waste form and the vitrified defense high-level waste. Appendix B shows representative physical and chemical characteristics of Pressure Water Reactor (PWR) and Boiling Water Reactor (BWR) spent fuels and the effects of burnup

on the composition of the fuel material. A listing of the radionuclides and curie content in typical PWR and BWR fuel assemblies is given in Appendix C. A more detailed discussion of the radionuclide attributes is presented in Appendix D.

The degraded repository materials through which radionuclide transport takes place can have a major influence on the mechanisms and rates of transport by retarding the movement of contaminants.⁹ The most likely and most abundant corrosion products in the near field will be those from the iron in the repository. Because the five-centimeter-thick stainless steel inner shell of the waste package will be very close to the waste form and external to it, there is a very good possibility that any actinides and fission products leaving the spent fuel or vitrified waste will come into contact with ionic ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions or with solid oxides or hydrated oxides of iron, which will tend to bind the actinides and fission products in their structures. However, because of the insolubility of iron hydroxides, the concentrations of ferrous and ferric ions will be low, and redox reactions will be limited. The NRC staff will need to determine the importance of this process if DOE decides to include retardation in corrosion products as an important element in its safety case.

The presently proposed Yucca Mountain repository design calls for the inclusion of backfill in the drifts, which could act as an engineered barrier. The term "backfill" is generally interpreted to mean any material other than waste packages and structural materials that is placed in the repository drifts such that it partially fills the drift. Currently DOE is primarily considering relatively unreactive materials such as sand or crushed tuff as backfill. The use of chemically active backfill materials could be a major simplifying factor in modeling, for example by effectively removing reactants such as carbonate and bicarbonate ions, by controlling pH, and by removing oxygen. A realistic analysis of the use and amount of backfill material required to remove the above reactants would aid in determining the practicality of the use of backfill in this way. Backfill material in the drifts offers the following important potential chemical advantages:

- The rate and extent of transport of radionuclides, especially of technetium, neptunium, and iodine, could be greatly reduced by introducing chemical backfill systems in which chemical sorption is strong, that is, in which the K_d ¹⁰ is large. In the cases of some radionuclides (e.g., technetium and neptunium) it might be necessary to change the chemical species, such as by changing the valence, to enable effective sorption. Both sorption and chemical change might be accomplished by reaction with the same backfill material, or a mixture of backfill materials might be used to obtain the desired chemical conditions.

⁹ The term "retarded transport" means that the rate and extent of radionuclide transport are diminished by some mechanism. Retarded transport may be facilitated by engineered barriers or possibly through the formation of corrosion products or secondary solid phases as the waste degrades.

¹⁰ " K_d " is a term that gives a quantitative measure of the retention of a dissolved chemical species on a solid sorbing medium. It is usually defined as the ratio at equilibrium of the mass of the sorbed species per gram of a solid sorbing phase divided by the mass of dissolved species per milliliter of aqueous solution (e.g., milliliters/gram). K_d is thus a measure of the fraction of a chemical species sorbed onto a solid phase. Other measures of sorption have also been introduced that evaluate the fraction of a dissolved species sorbed per unit surface area of a sorbing medium. By introducing a measure of the rate of movement of water through the sorbing medium, the retarded rate of movement of the chemical species through the sorbing medium may be calculated.

- The dissolution rates of waste-related materials in the drifts (e.g., waste containers, spent fuel cladding, spent fuel material, and vitrified defense high-level waste and its containers) could be substantially slowed by saturating the dissolvent (the incident aqueous solutions) with the chemical species being dissolved, e.g., the uranium in the spent fuel.
- Solids formation could be enhanced by addition of chemical species that form interfacial solids to inhibit dissolution and release of radionuclides from the waste form. For example, calcium and silicate ions that could react with uranium to form analogs of natural insoluble minerals such as uranophane could be added.

A large number of potential backfill materials might be considered and studied for use in the repository drifts to control radionuclide transport. Some of these have already been considered by both DOE and NRC, as noted earlier. In the presence of oxidizable materials (i.e., reducing agents) in the backfill, water and air entering the drifts could be depleted in oxygen before they reach the waste package. If desired, carbon dioxide could also be removed by an appropriately chosen backfill material. The exiting solutions of radionuclides produced by water contacting the waste form could react with carefully chosen backfill material, or with material added to the invert structure beneath the waste packages, to slow the passage of the radionuclides out of the drift. Some possible backfill materials that have been proposed for waste repositories are listed in Appendix E. The list of backfill materials in Appendix E is meant to be suggestive of the large number of potential backfill materials that might be considered, some of which might have very beneficial effects on repository performance. Because pertechnetate, neptunyl, and iodine ions are among the most difficult in the repository to control chemically, and because they are also among the principal long-term contributors to health concerns at the Yucca Mountain repository boundary (currently 20 kilometers south of the repository itself), these elements are discussed below.

Formation and Dissolution of Secondary Solid Phases

The potential importance of the formation of solid phases at the interface between water and the spent fuel has been pointed out by Murphy and Codell (1998). Nonetheless, to date there has been limited effort spent by DOE or NRC either experimentally or in modeling studies to elucidate the chemical reactions leading to solids formation and their ability to limit the release of fission products and actinide elements from the waste form (i.e., spent fuel and vitrified DOE high-level waste) or to bind them in the solid phases (Buck et al., 1998; Burns, Ewing, and Miller, 1997; Wronkiewicz et al., 1992). The great complexity of the chemical system, the effects of aging on the physical nature of the solids formed (e.g., many precipitates become more crystalline and their crystals grow and even change composition with the passage of time), and the kinetics of the solids formation processes pose formidable challenges to the experimentalist. These may be some of the reasons that little has been done in this area compared with the time and effort spent in other areas of repository performance.

One approach taken to addressing interfacial solids formation is to assume that naturally occurring uranium minerals will form or can be used as surrogates for interfacial solids that are likely to form (Apps, et al., 1993). This assumption is based on the fact that geological sites similar to the Yucca Mountain site have natural uranium minerals (e.g., uranophane, soddyite, and schoepite) that exhibit long-term stability. One such site that has been closely studied is the Peña Blanca site in Chihuahua, Mexico (Percy, et al., 1994). This site is in an arid and oxidizing environment with siliceous tuffaceous rock, much like Yucca Mountain. The presence of uranophane at this site suggests that uranophane is a mineral likely to form at the water-spent fuel interface in the proposed Yucca Mountain repository. The presence of calcium and

silicate ions in the water in Yucca Mountain support this suggestion.¹¹ Even if uranophane is not formed, it is suggested that uranophane is similar enough to other minerals that might form that uranophane is a reasonable surrogate for those other minerals. This assumption, while reasonable, should be confirmed by experimental studies under conditions that duplicate as nearly as possible those at Yucca Mountain.

As the radionuclides in the waste packages are released, they will not necessarily be made available for immediate transport out of the near field. It is likely that some constituents of the water, such as silicate and calcium ions or carbonate ions, will react to produce solid phases of which the radionuclides are an essential part or in which they are bound up by processes such as sorption or inclusion. These reactions, perhaps augmented by other species (e.g., K and Na), will likely lead to precipitation of solid phases in the immediate vicinity of the waste form. As noted earlier, the solid phases could substantially impede the release of waste materials such as Np, Tc, Pu, and, possibly, I if those elements are present as suitable chemical species. The vitrified defense HLW waste is likely to form insoluble silicates with the incorporated waste materials because of the high silicate ion content. Better and more extensive experimental data on uranium solids formation and on the solubilities of solid species formed in the repository environment, especially of silicates, are needed. The NRC staff's analysis of the potential importance of secondary uranium phases shows significant reductions in calculated dose; therefore, continued work in this area is essential to be prepared for possible inclusion of this phenomena in DOE's safety analysis.

Corrosion

An understanding of the rates, and especially of the mechanisms, of corrosion of the drip shields, the waste packages, the spent fuel cladding, and the materials of construction of the drifts themselves (e.g., the waste package supports and the invert) is fundamental to predicting the chemical behavior of the repository in both the short and long terms, and thus to determining the suitability of the repository for disposing of spent LWR fuel and DOE defense HLW and reactor fuels. The composition of the water, especially of the pH, incident on the drip shields and waste packages; the presence or absence of continuously replenished air; and the temperature of the repository are major determinants of corrosion rates, as are the materials of construction of the drip shields, waste packages, spent fuel cladding, and canisters of vitrified waste. The minor constituents of the water—especially chloride ions, but also other ions of a corrosive nature—that contact the waste packages and their contents will be important, especially if they are concentrated by evaporation of the water.

The effects of radiolysis and of microbial action on corrosion may be important and should continue to be studied to the point where their relative importance may be assessed. Radiolysis is likely to be more important to corrosion that takes place very near the waste form where alpha-particle-induced reactions are most likely. Microbiological processes (Pope et al., 1988), if significant, will be most prominent on the outer areas of the waste packages, where nutritional sources are most likely to be available for the bacteria.

Confidence in extrapolations of corrosion data to the very long times of applicability of the LA depends on an understanding of the mechanisms of corrosion. A great deal is known about the phenomenological nature of corrosion of the various materials in the drifts, but much less is known about the basic

¹¹ Uranophane has the chemical composition $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5 \text{H}_2\text{O}$. All of the chemical species necessary to form uranophane are likely to be present at the water-spent fuel interface.

mechanisms of corrosion. It is likely, of course, that it will not be possible to fully elucidate the mechanisms of some of the most important kinds of corrosion (e.g., of crevice corrosion and stress corrosion cracking of alloy C-22) by the time of the LA. Some of these types of corrosion have been studied for many years by many investigators with no consensus on their mechanisms. Nonetheless it is essential to obtain as much basic understanding as possible. It is especially important to learn as much as is practicable about *critical corrosion temperature regimes* for the materials of construction, the temperature range where corrosion is likely to be most severe. Additional confidence in the corrosion data may be obtained by adherence to American Society for Testing and Materials standards.

Materials of construction

Table 2 presents the amounts of metals per waste package in the present repository design concept. The values are very approximate and are presented to give an idea of the amounts of metals available for chemical reactions. They do not include things such as inverts, whose design is still uncertain.

Table 2. Approximate Average Kilograms of Metal per Waste Package Containing Spent Nuclear Fuel, Including Drip Shield*

Stainless Steel	Titanium	C-22 Alloy	Zirconium
10,000 kg	3,390 kg	2,390 kg	3,570 kg

* The values in the table are approximate. There are several sizes of waste packages and several possible waste package designs depending on the type of waste contained.

Corrosion may be either "dry" or "wet," depending on whether or not water is present. Water may be present either as bulk water or as a film of water caused by condensation of humidity in the air.

Reaction of oxygenated water with iron to produce, first, ferrous ions, and then, after oxidation of the metallic iron is complete, ferric ions, will add these ions to the water while removing oxygen from the water and the air until the iron is completely oxidized. The presence of this reducing environment will be both local and time-dependent. As already noted, the length of time reducing conditions can exist will depend on the amount and location of reducing agent in the drift (in this case, iron) and on the rate at which oxygen enters the drift in air and/or water.

The iron in the waste packages will not be effective in changing the chemistry of corrosion of the drip shields, except perhaps at the point of contact of the drip shield with the support, because the dissolved iron will leave the repository without contacting the drip shields. Transport of the radionuclides could, however, be affected because presumably they will leave the repository by the same route as the iron-containing water, and will contact it. Thus the radionuclides could in some cases be reduced, or react in other ways with the iron to form chemical compounds or other species with it. In any case there will probably not be enough iron in the drift from materials of construction to maintain a reducing environment over the 10,000-year licensing period. If a reducing environment can be maintained, it must be done by adding reducing material to the drift, presumably in backfill.

Drip shields

The drip shield, which is currently planned to be made of grade 7 titanium 1.5 centimeters thick, is subject to corrosion, as are the waste package and the fuel cladding. The drip shield will be effective in diverting bulk (liquid) water away from the waste package only as long as it remains intact. As the drip shield corrodes, it will introduce titanium ions into the water incident on the waste packages. Tri-valent titanium ions are good reducing agents. The drip shield may rest on the iron waste package support and thus be subject to enhanced corrosion. An ionic path could be established between the drip shield and the iron in the waste package supports. It is also possible that the reverse will happen. That is, corrosion of iron in the drift could produce ferrous and/or ferric ions that could provide an ionic path from the waste package to the titanium drip shield. It is not known whether either process will be of importance to the chemistry of the radionuclides, but it may affect the corrosion of the drip shield. The times involved are so long that these processes (the mechanisms) and their effects may be important and should be considered.

Waste packages

The current waste package design is shown in cross section Figure 1. The outer container has a 2 centimeter-thick wall of alloy C-22, whose composition is given in table 3. The inner container has a 5 centimeter-thick wall of stainless steel. It is expected that the stainless steel will corrode much faster than the C-22 once water breaches the C-22, and that in times far shorter than the repository licensing period it will be completely oxidized provided that the C-22 is in fact breached. As noted above, this steel could produce locally reducing conditions in the waste package or drift, and if oxidized, will add to the ionic iron content of the water. (Iron corrosion products would occupy more volume than the stainless steel from which they come, leading to potential adverse mechanical and structural effects. However, these effects are not considered here.) Unlike the steel in the waste package support and the steel invert, the iron ions from the stainless steel in the waste package container will be available for chemical reactions with the waste form itself at the water-waste interface.

There are extensive sources of information and data on the corrosion of high-nickel alloys, some of which are similar to C-22 (Betteridge, 1984; Schweitzer, 1996; INCO Inc., 1969 and 1995), but none for anything approaching the lengths of time being considered for the lifetime of the waste packages. The corrosion data that do exist for C-22 are very encouraging. However, pit, crevice, and stress corrosion are still matters of concern, and a better understanding of the mechanisms involved in these corrosion processes is needed before credit can be taken for the very long-term protection that DOE may postulate in its LA.

Figure 1. Waste Package and Drift Design Cross Section

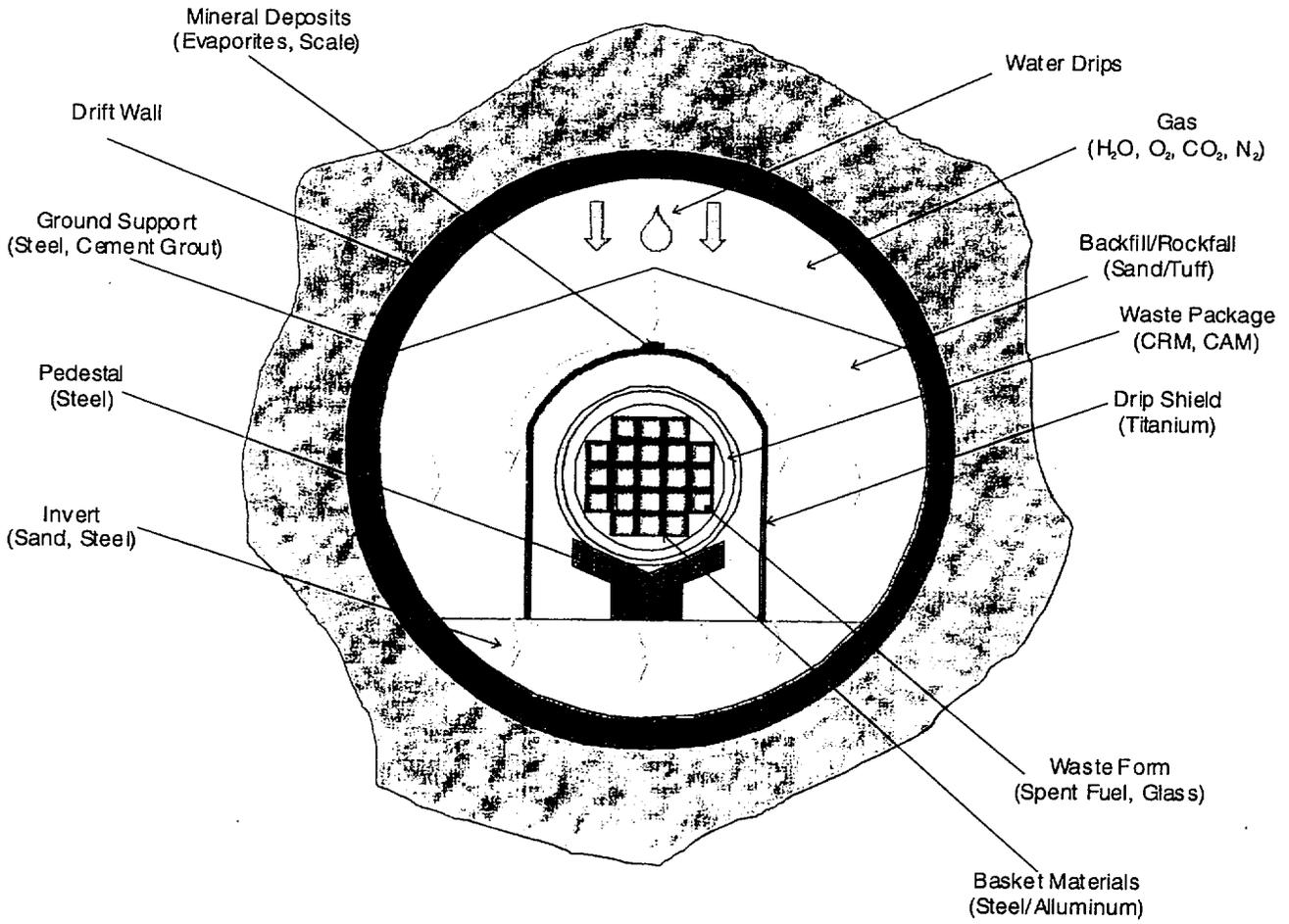


Table 3. Composition of Alloy C-22

Alloying Element	Weight Percent
Nickel	57.8
Chromium	21.4
Molybdenum	13.6
Iron	3.80
Tungsten	3.0
Vanadium	0.15
Manganese	0.12
Silicon	0.03
Carbon	0.004
Sulfur	0.002

The influence of temperature, and the possible existence of a temperature regime where corrosion is expected to be greatest, must be investigated. It is hypothesized, for example, that at temperatures above about 100° C, water will be driven away from the drift, thereby eliminating corrosion of C-22 for many hundreds or thousands of years. At temperatures below about 80° C, it is hypothesized that the rate of corrosion of C-22 will be so slow as to virtually eliminate corrosion. This hypothesis of a *critical temperature regime* illustrates the important role temperature plays in the chemistry of the repository. It also stresses the importance of repository design in determining temperatures, and thus chemistries, of important chemical processes such as corrosion.

Spent fuel cladding

Calculations based on corrosion data for the contribution of the Zircaloy cladding on commercial spent nuclear fuel to the prevention of the release of radionuclides from the fuel indicate a beneficial contribution by the cladding. (About 1.15 percent of the expected inventory of spent fuel in the repository is clad with stainless steel (DOE, 1998). All of this fuel is assumed in DOE's analysis to fail immediately.) A major question is how well the very good, but relatively short-term, corrosion data on Zircaloy can be extrapolated to the very long times (i.e., 10,000 years) required for the data to be valid for use in repository licensing. This is another example of the need for more understanding of the mechanisms of corrosion. The better the mechanisms are understood, the greater the confidence in both the data extrapolations and the multiple barrier arguments made in the LA. A potentially important factor that must be considered very carefully is the number of spent fuel elements that either already have failed before being put into the repository or are damaged during handling at the repository.

Vitrified defense high-level waste canisters

The canisters used for containing vitrified DOE defense HLW are made of steel. Once the waste package has failed, corrosion of the steel is expected to be relatively rapid as noted above for the stainless steel inner waste package container for the spent fuel. Like the iron from the stainless steel inner waste package container, the iron from the vitrified waste canister will be available for chemical reactions, primarily those involving chemical reduction (see Appendix F). In addition to the chemical reduction reactions caused by iron, iron oxides and hydrous iron oxides will sorb some chemical species. Such sorption may be an important factor in retarding radionuclide transport. The reactions of plutonium to form polymers are also addressed in Appendix F. These reactions, like the reduction of NpO_2^+ by iron, are also very dependent on pH.

Modeling

Quantitative evaluation of the ability of the Yucca Mountain repository to isolate radioactive wastes from the biosphere is a key component of the demonstration of the ability of the repository to meet the licensing requirements. This quantitative evaluation is achieved through the use of complex computer models with extensive databases.

Computer models exist that directly or indirectly minimize the free energy of a large number of interacting chemical systems. In this way the dominant chemical reactions in a suite of reactions are singled out. However, these models depend on databases that include all of the chemical important reactions, and are likely to be inadequate in some important aspects, for example, in solids forming reactions. The chemical processes that occur in the repository near field are extremely complex and are coupled, sometimes leading the modelers to take the conservative approach of assuming bounding cases.

Because of the complexity of the chemical nature of the repository and its contents, it is by no means certain that the bounding cases chosen are an adequate or reliable representation of the true situation. In fact, because of simplifying assumptions or inadequate or erroneous information, the bounding cases may not properly represent the facts, even in a conservative sense. Therefore, experimental verification of some of the results of computer analyses is necessary.

Model structure

The Yucca Mountain repository design is so complex that no one model is used to represent it. Rather, it is modeled through the use of multiple, interacting models. The Center for Nuclear Waste Regulatory Analysis has provided a literature review of coupled processes in the proposed repository (Manterfel, et al., 1993). DOE plans to synthesize technical and supporting information for its models through Process Model Reports (PMRs). At present the following nine PMRs are planned:

- Integrated site model.
- Unsaturated zone flow and transport model.
- Saturated zone flow and transport model.
- Near-field environment.
- Waste package degradation.
- Waste form degradation.
- Engineered Barrier System degradation and flow/transport model.

- Biosphere.
- Tectonics.

The models themselves are subdivided into components. Thus, the EBS PMR will be composed of:

- The physical and chemical environment model.
- The water distribution and removal model.
- The radionuclide transport model.
- The degradation mode analysis.

The physical and chemical environment model will have seven abstraction models. The chemical models are among the most complex and the most interactive (that is, coupled). It is these complexities that lead to the conservatism in the chemical aspects employed in the model analyses.

Model abstraction

In order to make practical calculations, it is necessary to "abstract" the complex models into a simplified form as noted above. This abstraction necessarily omits details of the repository near-field chemistry that have been judged by calculations, literature information, or technical judgment to be non-essential to obtaining valid results. In certain cases supplemental calculations are made to provide modeling information for the abstraction process. It is necessary to ensure that the various approaches to abstraction are indeed valid and that the omissions they entail are justifiable. This is especially true where technical judgment is the principal basis for the omissions or approximations.

Coupled effects

Water, air, and temperature govern chemistry in the near field. They can be controlled up to a point by the engineered barrier system; however, they are coupled and they cannot be controlled independently. Water in the drifts may be controlled, at least in part, by air flow and temperature. Control of water contacting the waste packages may also be achieved or attempted by diverting it from the waste package either by use of a drip shield or by backfill, for example by use of a "Richard's Barrier (Conca, et al., 1998). Primary control of air volume may be obtained by having the repository open or closed. If it is open, air volume control may be either by natural or forced air circulation in the short term or by natural circulation in the long term. Temperature is controlled by repository design, that is, by arrangement and spacing of the drifts, waste package spacing in the drifts, design and content of waste packages, controlling circulation of air, and backfill. If backfill were not introduced for 300 years after closure of the repository (one scenario suggested by DOE) and the repository had been cooled until that time, then radioactive decay of the wastes would have reduced the production of decay heat to the point that the repository maximum temperature may not rise to levels that drive water from the drifts. Lowered maximum temperatures may permit consideration of a group of backfill materials (e.g., clays) that might otherwise be excluded because of alteration of their chemical and physical properties at higher temperatures.

Chemical effects are also coupled, both to each other and to water, air, and temperature. For example, solids formation at the waste form-water interface depends on presence of corrosion products, dissolution of the fuel form, constituents such as silicates dissolved in the water, the oxidation states of elements (as determined by oxygen in the air), and the temperature (which will determine the solubility). The

interdependence and interactions of all these couplings lead to an extraordinarily complicated system that must be described, understood, and modeled.

Databases

Incompleteness of the thermodynamic and kinetic databases is a significant shortcoming of the chemistry models used to date for second-phase and mixed-phase formation, especially at the surface of the waste forms. The near-field chemistry, especially at the interface of water and fuel material or of water and vitrified waste, which is where second phases are most likely to form, is very complex. Many phases are possible in principle, and several are known to be likely under the Yucca Mountain repository conditions. Not only may their formation be slow, but the composition of the phases may change over time due to the well-known process of Ostwald ripening. Nonetheless, it is likely to be important to understand what phases do form, how soluble they are (especially as a function of temperature), and what their long-term behavior is. That is, how do they change with time? Do they become more refractory; do crystals grow larger; are additional elements incorporated into their structures over long time periods? Not all such data can be obtained before licensing the repository, but many can, and they are likely to be important in the licensing process.

Relatively little consideration is given in the databases to the possibility of valence changes or of new species formation brought about either by deliberate action or as a natural consequence of repository design. This is especially true in the cases of technetium, neptunium, and iodine. The paucity of data has been addressed in some instances by "expert elicitation." Expert elicitation is an accepted practice and must be resorted to when experimental data are not available and cannot be obtained in a practical sense (Kotra, et al., 1996). However, the divergence of opinions sometimes encountered among the experts of values to be assigned to chemical parameters attests to the uncertainties attending this approach. It is apparent that quality assurance of data in the usual sense cannot be obtained from expert elicitations.

Conclusion

Chemistry plays a critical role in the near-field performance of the repository. There is an important and unavoidable coupling of the effects of water, air, and temperature with the near-field chemistry of the repository; these effects are inextricably bound up with repository design. The present DOE repository design of the near field relies on corrosion resistance of the waste package and drip shield as major contributors to the multiple-barriers concept for defense in-depth. The case for meeting the multiple-barriers licensing requirement, which is a major element of the defense in-depth licensing philosophy, may be improved by the deliberate introduction of certain chemical features in the repository near field. In particular, carefully chosen backfill materials and materials to fill the void space in the waste packages can chemically alter radionuclides such as ^{99}Tc and ^{237}Np such that they are transported much less rapidly out of the near field through the action of sorption or precipitation reactions. In this way the contribution of ^{99}Tc and ^{237}Np to the radiation dose at the repository site boundary over the time of interest for licensing may be substantially reduced. Because of the potential significant contributions of deliberately added chemical features to the repository, the NRC should anticipate their inclusion and be prepared to evaluate them.

Specific activities that staff may undertake or should continue include:

- Staff should conduct scoping calculations of the importance of backfill to modify the chemical environment and to act as an attenuating agent for released radionuclides. If it is determined from these calculations that the use of backfill can have an important effect on performance, then more realistic analysis would be required by the applicant.
- Staff's analysis of the potential importance of secondary uranium phases shows significant reductions in calculated dose; therefore, continued work in the area of the role of secondary phases is essential to be prepared for possible inclusion of this phenomena in DOE's safety case. This work should not only include secondary uranium phases, but also other secondary phases (e.g., iron oxyhydroxide corrosion products if DOE decides to include this as an important element in its safety case) that are likely to form and may sequester or attenuate key radionuclides.
- Staff needs to continue their work on understanding the rates and, especially, the mechanisms of corrosion of the drip shields, the waste packages, and the spent fuel cladding.
- Staff needs to continue careful analysis of the role of coupled processes in repository performance as part of its development of review capabilities. Because of the complexity of the models and the abstraction of these models into the TSPA the key focus is to ensure that an important coupled process is not left out of the performance assessment.

Appendices

Appendix A. Repository Design Features

The repository is statutorily limited to 70,000 metric tonnes of uranium in nuclear fuel and other high-level waste expressed in terms of uranium and uranium equivalents¹² until a second repository is in operation. The proposed distribution of the uranium among the repository waste types is given in the following table .

Allocation of Repository Space to Types of Wastes

Waste type	Radioactivity, MCi	Metric tonnes U or U equivalent
Commercial spent nuclear fuel	19,000	63,000
Equivalent defense high-level waste	200	4,027
DOE-owned spent nuclear fuel	100	2,333
Equivalent commercial fuel	-	640

The present plan is that DOE-owned spent nuclear fuel will be placed in stainless steel canisters. The canisters will be placed in the center of waste packages surrounded by either 3 or 5 canisters of vitrified high-level waste. Some waste will be placed in small, high-integrity cans made of C-22 alloy prior to placement in the stainless steel canisters.

The details of the current repository design differ in significant ways from the design presented in the Viability Assessment (DOE, 1993). The following table gives a comparison of recent information on design features of the proposed repository with the VA reference design. This recent design is referred to as the Enhanced Design Alternative II (EDA-II).

¹² The amounts of wastes are expressed in terms of the amounts of uranium in the wastes. In the case of defense high-level waste, these amounts refer to the amounts of uranium that must have fissioned to produce the wastes, and are referred to as "equivalent" amounts of uranium.

Design Features of the EDA II Design

Criteria	EDA II	VA Reference
Repository area, acre	1060	740
Areal mass loading, MTU/acre	60	85
Drift spacing, meters	81	28
Drift diameter, meters	5.5	5.5
Emplacement drifts length, km	54	-
Access drift length, km	33.4	-
Ground support	Steel sets	Concrete lining
Invert	Steel with sand or gravel ballast	Concrete
Waste package materials	2 cm Alloy-22 over 5cm stainless steel	10 cm Carbon Steel under 2 cm alloy-22
Waste package capacity for PWR spent fuel assemblies	21	21
Waste package capacity for BWR spent fuel assemblies	44	44
Number of waste packages	10,039	-
Drip shield (placed at closure)	2 cm Ti-grade 7	None
Backfill (placed at closure)	Yes	No
Pre-closure period, years	50	50
Pre-closure ventilation rate, m ³ /s	2-5	0.1
Temperature		
Cladding	350° C	
Drift wall	200° C	
Pillar center	96° C	

Appendix B. Representative Characteristics of Spent LWR Fuels at Several Burnups

Attribute		PWR	BWR
Diameter/width	Fuel pellet	0.82 cm	1.06 cm
	Fuel rod	0.95 cm	1.25 cm
	Assembly	21.4 cm	13.9 cm
Fuel rods per assembly	Array	17X17	8X8
	Number	264	63
Height	Fuel stack	3.66 m	3.76 m
	Rod	3.85 m	4.06 m
	Assembly	4.06 m	4.47 m
Assembly weight		658 kg	320 kg
Fuel per assembly	Uranium metal	461 kg	183 kg
	Uranium dioxide	523 kg	208 kg
Metal hardware per assembly		135 kg	112 kg
Assembly volume		0.186 m ³	0.086 m ³
Avg. specific power, MW/Mg U		37.5	25.9
Burnup, Gwd/Mg U	Historical	33	27.5
	Future	60	46
Composition (historical burnup - future burnup)			
Initial ²³⁵ U enrichment, %		3.30 - 4.73	2.77 - 3.64
Final Uranium, kg/Mg initial U		955.4 - 922.2	962.5 - 937.1
Uranium enrichment, % ²³⁵ U		0.84 - 0.54	0.79 - 0.57
Plutonium, kg/Mg initial U		9.47 - 14.38	8.26 - 12.3
Other actinides, kg/Mg initial U		0.71 - 1.8	0.59 - 1.50
Fission products, kg/Mg initial U		34.4 - 61.6	28.6 - 49.1
Inventory (annual additions - cumulative), Mg initial U			
1994		1207 - 19,024	675 - 10,788
2000		1300 - 27,400	600 - 14,900
2010		1400 - 39,000	700 - 21,400
2020		700 - 50,200	400 - 26,900

Appendix C. Typical Radionuclide Activities per Assembly for PWRs and BRWs.

(Taken from Draft Environmental Impact Statement for the Disposal of Spent Nuclear Fuel and High-Level Radioactive Waste at Yucca Mountain, Nye County, Nevada, Volume II, Appendix A, page A-17.)

Especially important radionuclides from the point of view of repository safety are printed in bold face.

Radionuclide	PWR, curies/assembly*	BWR, curies/assembly**
Tritium	9.80e+01	3.4e+01
Carbon-14	6.4e-01	3.0e-01
Chlorine-36	5.4e-03	2.2e-03
Cobalt-60	1.5e+02	3.7e+01
Nickel-59	1.3e+00	3.5e-01
Nickel-63	1.8e+02	4.6e+01
Selenium-79	2.3e-01	7.9e-02
Krypton-85	9.3e+02	2.9e+02
Strontium-90	2.1e+04	7.1e+03
Zirconium-93	1.2e+00	4.8e-01
Niobium-93m	8.2e-01	3.5e-01
Niobium-94	5.8e-01	1.9e-02
Technetium-99	7.1e+00	2.5e+00
Rhodium-102	1.2e-03	2.8e-04
Ruthenium-106	4.8e-03	6.7e-04
Palladium-107	6.3e-02	2.4e-02
Tin-126	4.4e-01	1.5e-01
Iodine-129	1.8e-02	6.3e-03
Cesium-134	1.6e+01	3.4e+00
Cesium-135	2.5e-01	1.0e-01
Cesium-137	3.1e+04	1.1e+04
Samarium-151	1.9e+02	6.6e+01
Thorium-230	1.5e-04	5.8e-05

Uranium-232	1.9e-02	5.5e-03
Uranium-234	6.6e-01	2.4e-01
Uranium-235	8.4e-03	3.0e-03
Uranium-236	1.4e-01	4.8e-02
Uranium-238	1.5e-01	6.2e-02
Neptunium-237	2.3e-01	7.3e-02
Plutonium-238	1.7e+03	5.5e+02
Plutonium-239	1.8e+02	6.3e+01
Plutonium-240	2.7e+02	9.5e+01
Plutonium-241	2.0e+04	7.5e+03
Plutonium-242	9.9e-01	4.0e-01
Americium-241	1.7e+03	6.8e+02
Americium-242/242m	1.1e+01	4.6e+00
Americium-243	1.3e+01	4.9e+00
Curium-242	8.7e+00	3.8e+00
Curium-243	8.3e+00	3.1e+00
Curium-244	7.0e+02	2.5e+02
Curium-245	1.8e-01	6.3e-02
Curium-246	3.8e-02	1.3e-02

* Burnup: 39,560 MWd/MTHM; enrichment: 3.69 %; decay time: 25.9 yrs.

**Burnup: 32,240 MWd/MTHM; enrichment: 3.00 %; decay time: 27.2 yrs.

Appendix D - Radionuclide Attributes

Table 1. Radionuclides Important in the Repository

Radionuclide	Half life, yrs.	Type of radiation	Important oxidation states	Important chemical species
⁹⁹ Tc	2.13E05	β	+7	TcO ₄ ⁻ Tc ₂ O ₇ Tc ₂ S ₇
			+4	TcO ₂ TcO ₂ ·H ₂ O TcS ₂
			0	Tc ⁰
¹²⁹ I	1.57E07	β, e-, x-rays	+5	IO ₃ ⁻
			0	I ₂
			-1	I ⁻
^{238,235} U	4.468E09 (²³⁸ U)		+6	UO ₂ ²⁺ UO ₃ UO ₂ (OH) ₂ UO ₂ (CO ₃) ₃ ⁴⁺
			5 1/3	U ₃ O ₈
			+5	UO ₂ ⁺
			+4	UO ₂
²³⁷ Np	2.14E06	α	+6	NpO ₂ ²⁺
			+5	NpO ₂ ⁺ NpO ₂ OH NpO ₂ CO ₃ ⁻
			+4	NpO ₂ Np ⁴⁺
^{239, 240, 241} Pu	2.14E06 (²³⁹ Pu)	α	+6	PuO ₂ ²⁺
			+5	PuO ₂ ⁺
			+4	Pu ⁴⁺ Pu colloid (Pu polymer)
			+3	Pu ³⁺

Spent fuel

The radionuclides in the spent fuel waste packages usually considered most important, either from the point of view of radiologic hazards or of chemical effects, are listed in Table 1 along with some of their radioactive properties, important oxidation states, and important chemical species. The principal constituent of spent LWR fuel is UO_2 . It will have undergone physical and chemical changes due to fissioning. When LWR fuels are taken to the higher burnups (greater than 40,000 megawatt-days per ton) now being attained in some light water reactors these changes will become more extensive. (Manaktala, 1993) has provided a thorough discussion of the characteristics of spent nuclear fuel as the characteristics relate to source terms for radionuclides.

The early LWR spent fuel sent to storage will be the older fuel which has not experienced the high burnups expected for modern fuels. The Zircaloy-clad fuel rods are held together with Zircaloy tie rods attached to end pieces typically made of stainless steel. (Zircaloy is an alloy made of zirconium and small amounts of other metals). PWR fuel is expected to be the predominant fuel type in the repository. The weight ratio of PWR to BWR fuel assemblies in the repository is expected to be about 13 to 7. Each LWR spent fuel waste package will contain either 21 PWR or 44 BWR spent fuel assemblies. BWR fuel assemblies are Zircaloy-clad fuel rods enclosed in a sheet of Zircaloy channels along the length of the assembly. Therefore the ratio of the weight of metal hardware per assembly to the weight of fuel material per assembly is much higher for BWR fuel. The rods in both types of fuel are usually held in a square array by a Zircaloy grid spacer.

Vitrified defense high-level waste form

The principal constituent of the vitrified high-level defense waste is borosilicate glass which is used as an inert matrix to contain the defense high-level wastes. It typically holds about 25% by weight of the oxides of the waste. It is noteworthy that uranium and plutonium were removed to a large extent from this waste during the reprocessing operations, although neptunium was not. However, the very low burnup of the fuel in the reactor assures that the concentrations of actinide elements in the waste will be relatively low. The release of radionuclides from the glass is governed by the reactions of the glass itself. The temperature and composition of the water contacting the glass exert the major influence on the reactions that take place. The vitrified waste is a potential source of silicate ions in the repository. However, the already high SiO_2 content of the incident water should reduce the extent of attack on the waste glass. It is expected that a siliceous gel layer will form on the vitrified waste that becomes exposed to water, and that this layer will inhibit further attack of the glass and the concomitant release of radionuclides. However, it is not known how long this layer will last.

Transuranium elements

When a radionuclide has one or more of the following properties it becomes one of the important radionuclides in the repository: 1) high toxicity, 2) long half life, 3) facile transport through the environment, and 4) a high fission or neutron-capture yield. Because of the exceptional toxicity of the alpha-emitting actinides if they are taken internally, especially by breathing but also by ingestion, several of them, e.g., ^{237}Np and ^{239}Pu , are of primary importance from the point of view of health hazards.

Neptunium (^{237}Np) combines all four of the above properties and as a consequence is of importance in determining the licensability of the repository. The relative stability of the neptunyl ion (NpO_2^+) (except in redox reactions) is what permits its relatively rapid transport through media that retard many other ions. In the presence of oxygen or air, and in the absence of other reactants, neptunium is oxidized from lower

valence states to the stable pentavalent state. Similarly, neptunium is oxidized to the pentavalent NpO_2^+ ion by nitric acid and nitrogen oxides (such as might be produced by radiolysis) when other redox agents are absent. Thus, it is apparent that the mobile NpO_2^+ ion will be the predominant neptunium ion in the repository in the absence of reducing agents.

Plutonium (^{239}Pu) also combines the above four properties that make it important in determining the licensability of the repository. Plutonium has the same valence states as neptunium and uranium, and has analogous oxygenated ions. However, the chemical stabilities of these states are quite different from those of neptunium and uranium. The redox potentials of plutonium are such that it is possible to have all four valence states existing simultaneously in aqueous solution. Although its pentavalent oxygenated ions are considerably more prone to disproportionation into hexavalent and tetravalent ions than the pentavalent state of neptunium, it is possible to have appreciable concentrations of PuO_2^+ in solution at low concentrations and low acidities, conditions that exist in the repository.

A Plutonium "polymer" forms readily when Pu(IV) hydrolysis products are heated and/or aged. Plutonium polymers are a colloidal form of plutonium that becomes less readily soluble in mineral acids upon aging and/or heating. Pu(IV) will be the predominant plutonium species in the repository in the absence of intentional changes to its valence. The importance of plutonium polymer derives from the fact that it does not behave as an ion, but instead behaves as a relatively large, electrically charged suspended particle whose behavior depends upon the medium it is suspended in (primarily on the ionic strength, but also on the presence of ions such as fluoride) and the solid surrounding that medium. Thus, its behavior is very difficult to predict (and to model) in the absence of quite detailed and complete information about its surroundings.

Uranium, though not as toxic as plutonium and not as much of a radiation hazard as neptunium, is included here because of the large amount of it in the spent fuel (as the reduced species UO_2). This makes it potentially important because of chemical reactions it may undergo. Important changes occur in UO_2 during fissioning. Restructuring of the UO_2 in irradiated fuel pellets is brought about by the fission reactions and the concomitant high temperature. Restructuring results in shattering the UO_2 and producing fractures that facilitate movement of volatile elements such as iodine, cesium and noble gases, as well as providing pathways for movement and agglomeration of the noble metals to produce metallic particulates. The fission product oxides occupy more volume than the uranium dioxide from which they are produced and this too leads to changes in the structure of the UO_2 .

UO_2 in spent fuel will likely be attacked by water, as shown by the Nopal 1 deposit at Peña Blanca, Chihuahua, Mexico. If the uranium is oxidized to the hexavalent state, then carbon dioxide dissolved in the water will produce the highly soluble uranyl tricarbonate complex ion. As the uranyl tricarbonate complex ion is removed from the fuel material, the actinides and fission products will become accessible to chemical attack by the incident water and the dissolved constituents it contains, as well as by any radiolytically produced nitrogen-containing acids or other reactive radiolytic species. As already noted, uranium may react with ions such as silicate and calcium to form interfacial solids.

Fission products

Most of the fission products have half lives so short that they are of little consequence in the waste repository licensing analysis. In particular, ^{137}Cs and ^{90}Sr , which are the major contributors to radioactivity in the spent fuel and vitrified defense high-level waste during the first hundred years or so, will have radioactively decayed to negligible concentrations in much less than 10,000 years, although there will be

some residual cesium present as ^{135}Cs . The only circumstance in which cesium and strontium might be important health hazards is their early release through breaching of waste containers by accidental or very unlikely natural causes, e.g., volcanism. There are, however, several fission product radionuclides that remain of concern in the very long term. Unfortunately they are isotopes of elements whose chemistries are extremely complex, notably technetium (Puigdomenech and Bruno, 1995) and iodine. These elements pose difficult problems in their chemical modeling and in control of their transport.

Technetium (^{99}Tc) is a fission product and a beta particle emitter. It combines the same four properties as ^{237}Np and ^{239}Pu and is one of the principal radionuclides of concern in the repository. Because of technetium's tendency to be heptavalent in the presence of oxygen it can form the anionic pertechnetate ion TcO_4^- . This ion, like the closely similar perchlorate ion (ClO_4^-), reacts very little to form complex ions or precipitates, and is only slightly sorbed by normally sorptive media such as clays. Its extremely long half life makes it one of the few fission product radionuclides that might contribute to a potential health hazard more than 1000 years after repository closure. Technetium can have several valence states, as pointed out in Table 2. It is highly desirable to find a practical way to change the valence from +7 to a lower valence, probably +4, that is more tractable chemically.

It is known that in LWR fuel a significant fraction of the technetium as well as of other noble metal elements are present as finely divided metals or oxides that resist dissolution even under very vigorous chemical treatment (de Regge, et al., 1980). Table 2 shows typical data for the dissolution behavior of some noble metals in irradiated fast reactor fuels (in which their concentrations are typically higher than in spent LWR fuels) under treatment with concentrated nitric acid. Although the temperatures and fuel burnups in fast reactors are higher than in LWRs, and consequently the amounts and extent of migration of the noble metals are greater, there will be insoluble metallic inclusions of them in LWR fuels. This is especially true in light of the progress toward higher burnups in LWR fuels (burnups up to 60,000 Mwd/tonne are anticipated), and the fact that only about one-third of the spent fuel expected to be disposed of in the repository is in the present, lower burnup, inventory. It is to be expected that the much milder conditions in the repository will produce virtually no reaction with the very refractory residues in LWR fuels. An implication of this fact is that the technetium radiation dose at the site boundary (20 kilometers south of the repository) may be as much as one-third less than that calculated in the current modeling studies, even if no chemical reactions are invoked to change the chemical species of the technetium. A similar situation exists for technetium in vitrified defense high-level waste (Sombret, 1999).

Table 2. Insoluble Metallic Inclusions in Fast Reactor Fuel Dissolution Residues*, wt. %
(Average of 10 experiments)

Tc	Ru	Mo	Rh	Pd
33.7	37.1	18.9	7.6	2.7

* Dissolver solutions: 10M HNO_3 followed by 10M HNO_3 +0.1M HF

Iodine (^{129}I) also combines the four properties noted above, and is of potential concern because if ingested it concentrates in the human thyroid gland where it undergoes radioactive decay and is potentially harmful. The chemistry of iodine is very complex (Rudin and Garcia, 1992). It may exhibit all seven valence states, including the negatively charged iodide ion and elemental iodine. The fact that iodine is very volatile in its elemental state and that it forms few highly stable, refractory compounds makes its behavior particularly difficult to predict and to control and to model. In spent fuel it is usually found as the iodide ion, presumably in combination with cesium (with which it can combine because of the mobility of both iodine and cesium in the spent fuel). Because of the multiplicity of its valence states there are a number of

possibilities for iodine to react with elements in the spent fuel as well as with materials within the repository and beyond it. Consequently it is not unreasonable to expect iodine to be retarded somewhat in its transport. However, it is known to move readily through soil. Experiments under actual repository conditions are necessary to determine how much retardation might be expected to occur. It is not out of the question to consider reacting and thus immobilizing iodine with a backfill material (such as a copper compound), but a careful study would have to be made of the reactions of iodine (and of copper) with other chemical species present to see if adverse chemical reactions might take place.

Appendix E. Partial List of Potential Backfill Materials

Tuff

The simplest backfill material to obtain and use is probably the material Yucca Mountain is made of, namely tuff. Tuff exists in several major types and may have zeolitic clays in it. Studies suggest that plutonium sorbs strongly on tuffs, but that neptunium and uranium do not. Technetium is also poorly sorbed. Not much is known about either the species likely to be present or the sorption behavior of iodine in tuff (although iodide ion is probably the species most likely to be present).

UO₂

It has been suggested (Forsberg, 1999 and 1997), that the approximately 700,000 tonnes of depleted uranium stored as UF₆ at the uranium enrichment gaseous diffusion plants in the U.S. be converted to UO₂ and used as backfill in the drifts and/or waste packages as a way of disposing of the UF₆. Used in the drifts the UO₂ would saturate the water entering the drifts with uranium compounds, for example with uranyl tricarbonate after oxidation of the UO₂, thus potentially slowing dissolution of the spent fuel waste form, which is itself greater than 95 % UO₂. Adding uranium might also increase the rate and amount of secondary phase formation. It might also be advantageous to introduce the UO₂ around the spent fuel in the waste package. As mentioned earlier, in this way it could potentially react with the calcium and silicate ions in the water directly at the spent fuel-water interface to form a synthetic uranophane or similar natural uranium mineral analog and thus block the escape of radionuclides from the spent fuel. Although it may be premature for NRC to conduct an experimental program on UO₂ as a backfill in the absence of its study by DOE, it may be worthwhile to conduct a literature study of its potential use because of the advantages it appears to hold promise of offering.

MgO

Magnesia (MgO) has some potential advantages as a backfill material (Bynum, et.al., 1998). It could react with CO₂ entering the drift to form MgCO₃, thus removing or diminishing the possibility of carbonate and bicarbonate ion reactions with uranyl ions (and possibly with neptunyl ions) from the spent fuel to form highly soluble and mobile carbonate complexes. The rate and extent of dissolution of the spent fuel waste form through soluble carbonate complex ion formation would thus be reduced. The relatively small amount of CO₂ in the incoming air could be sorbed by MgO backfill.

Transition elements

There are several elements in the transition element series of the chemical periodic table that are potential drift backfill material or additions to backfill material. In general they are available as compounds in chemically reduced states that could react with oxygen entering the repository. In addition, they could react with the pertechnetate ions and neptunyl ions to produce lower-valent species that would be transported much less readily, either because of formation of precipitates or because of sorption-desorption reactions. Several such elements are discussed very briefly below.

Iron - The drifts already contain large amounts of iron in the form of materials of construction and in the waste packages. Therefore, iron is an obvious element to consider for inclusion in the backfill. Iron can form hematite which sorbs actinides strongly. In addition, iron hydroxides and oxyhydroxide (e.g.,

FeOOH), which would form under the repository conditions, are widely used as scavengers for a broad spectrum of ions in aqueous solutions.

However, the insolubility of Fe²⁺ hydroxide is so large that the reduced availability of ferrous ions and the problems of pH control are obstacles to its use for maintaining a reducing environment. Also, the importance of iron in bacterial processes introduces uncertainties into an already very complex chemical environment.

Manganese - Manganese is a potential reductant that might be added to the drift backfill. It has the advantages that the Mn²⁺ ion is a good reducing agent, and that Mn⁴⁺, the likely product of the oxidation reaction, forms solid MnO₂ which, like ferric hydroxide, is a good scavenger for ions in solution.

Copper - Copper is another illustration of a possible reducing and scavenging agent. If cuprous sulfide were used in the backfill material then the possibility exists that both technetium and iodine might be sequestered, technetium as the highly insoluble sulfide and iodine as insoluble copper iodide. Introduction of sulfur into the drifts is problematical because of the possibility of bacterial action on the sulfur. However, copper is a bactericide so the extent of the problem would depend on the specific bacteria present.

For a reducing material to be useful in slowing the movement of radionuclides by changing their valences, the ratio of oxygen entering the drift to reducing agent present would need to be small enough that the radionuclides would be chemically reduced over a long enough period to be effective.

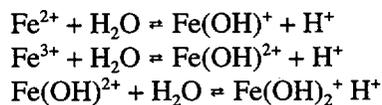
Potential waste package filler materials

Rather than leaving to chance the formation of interfacial solids such as uranophane by reaction of aqueous solutions of calcium and silicate ions in the incoming water with the UO₂ in the spent fuel, it is possible to place solids forming chemicals directly in the waste packages. This would increase the likelihood of solids formation, and would provide some control over the composition of the solids formed. It would also provide the possibility of adding chemical reactants such as reductants or precipitants for radionuclides such as technetium and neptunium. The reactants would be in the immediate vicinity of radionuclides as they left the spent fuel, and the likelihood of desired reactions taking place would be greatly increased. UO₂ is an example of a chemical that might be used to fill the void space around the spent fuel in the waste package. It could serve to saturate the water with uranium compounds and thus serve as a reactant to form a precipitate with ions such as silicate. It could also diminish the rate of dissolution of the spent fuel (which is largely UO₂) because the water would already be saturated with uranium. Similarly, reducing agents could be added to the waste package to reduce technetium and neptunium, and perhaps put iodine in an appropriate valence state for its controlled behavior.

Appendix F. Illustrative Chemical Reactions

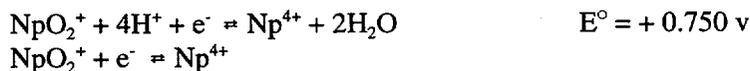
Iron

The presence of iron in the drifts, both as a material of construction and as a major constituent of the waste packages, makes a discussion of its reducing properties instructive. The reduction of neptunium is discussed below to illustrate some of the important aspects of the reactions of iron. Some of the redox and precipitation reactions of iron are given below to provide a basis for the discussion.

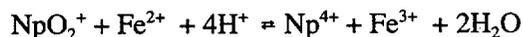


Neptunium Reduction

It is desirable to keep or to put neptunium in the tetravalent state in order to slow its transport to the Yucca Mountain site boundary. The following simplified analysis suggests that iron may not be an effective reducing agent for neptunium.



The reaction of iron with neptunium is given by the equilibrium equation



Using the values of standard potentials and solubility product constants given above, along with the usual relationship

$$\ln K = nFE^{\circ}/RT$$

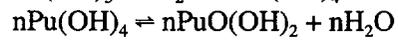
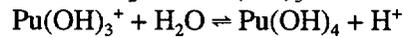
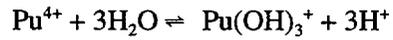
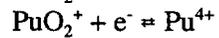
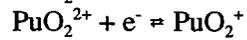
it is found that, very approximately, at 25 °C,

$$(\text{Np}^{4+})/(\text{NpO}_2^{+}) = 6.4 \times 10^7 (\text{H}^{+})^3$$

According to the above calculation until the pH reaches about 2 there will be essentially no reduction of neptunium. Admittedly this is a crude calculation, ignoring as it does possible competing reactions as well as equating chemical activities to concentrations and using a simplistic value for ferrous hydroxide solubility. Nonetheless, it does point out the strong influence that the acidity (pH) may have on the equilibrium and consequently on the fraction of the neptunium reduced.

Plutonium

Plutonium is likely to be of concern in the repository because of the considerable tendency of Pu^{4+} to form plutonium colloids (often referred to as plutonium polymer). It is generally accepted that Pu polymer can form under repository conditions. Plutonium will almost certainly be tetravalent, and will hydrolyze to form polymer. Pu polymer is formed by the elimination of water from the hydroxide of Pu^{4+} and the formation of oxygen bridges. The redox and polymer forming reactions are presented below in simplified form.



(Polymer)

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