LONG-TERM TOTAL CONTAINMENT VS CONTROLLED RELEASE: AN EVALUATION FOR THE YUCCA MOUNTAIN ENVIRONMENT

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ABSTRACT

BNL has a contractual obligation with the OCRWM to

"focus on the issue of waste package containment lifetime. In particular, we would like an assessment conducted that examines various lifetimes, including times beyond the 300-1000 year performance objective of 10 CFR 60, and evaluates methods (both physical tests and analytical approaches, to be performed by the projects) to assess longevity. This assessment should provide the basis for or recommendation to OGR on waste package lifetime."

Past and present NNWSI strategies for compliance with 10 CFR 60 rely heavily on controlling releases from spent fuel for approximately 10,000 years.

Spent fuel is thermodynamically unstable in all environments. The number of factors contributing to the degree of instability are greatest in oxidizing environments. Both theory and existing experiments show that neither solubility limited concepts nor matrix dissolution concepts can be justified for long-term prediction of radionuclide release rates in an environment containing oxygen and water. No predictive models exist for releases from spent fuel under such conditions. The physical processes involved in the observed releases fall into at least three categories. A limited number of the physical processes are understood and might be approximated by modeling. Some physical processes are recognized but modeling cannot be defended because values or acceptable bounding estimates of critical parameters are not yet available, (powdering during oxidation, grain boundary development, redistribution of radionuclides, UO₂ breakup, chemical species produced by alpha radiolysis, etc.). In some cases reactions involve processes that are poorly understood with little chance of elucidation in the near future, (changes in metastable species to unknown stable species, formation and removal of colloids and particulates in alpha radiolysis fronts, migration and reaction of excess oxygen produced by the fission process, etc.).

No models exist for predicting the chemical reactions in non-equilibrium waste waters. Although measurements of concentrations, activities, pH, gradients, etc, have meanings in non-equilibrium systems, the concept of a measured Eh value is only valid when the redox ions are in equilibrium and the measurements can be shown to be reversible. Models dependent upon Eh, are not likely to be credible.

No theory exists that allows estimates of the times involved in converting from thermodynamically unstable states to thermodynamically stable states. Many of the species observed in long-term spent fuel dissolution experiments are known to be unstable.

This paper emphasizes literature related to problems in demonstrating compliance with long-term controlled release. Past experience in license hearings has shown that regulatory agencies focus on literature which emphasizes problems in demonstrating required performance. The existence of such literature also minimizes the significance of literature in which the absence of adverse effects from short-term experiments are interpreted optimistically.

Evaluation of the literature cited here, indicates that the information needed to acceptably predict long-term radionuclide releases from the Engineered Barrier System (EBS), includes determining the minimum number of factors related to defending an upper bound on the maximum quantity of radioactive material (dissolved, suspended, i.e., soluble, colloidal or particulate) that can be transported from the EBS by a unit volume of liquid at all appropriate temperatures. The upper bound over the required 10,000year time period must be determined for each pertinent radionuclide, and it must be defended. In addition, the total quantity of water containing the upper bounded radionuclide inventory leaving the EBS on an annual basis and how it varies over 10,000 years needs to be predicted or upper bounded for the appropriate temperatures. Evidence will be required showing that both upper bounds are time stable or decrease with time.

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Since theoretical upper bounds for possible radionuclide masses that can be transported in water are likely to be relatively high, successful defense of long-term controlled release will be tied intrinsically to successful defense of limited and upper bounded quantities of water that can leave the EBS on an annual basis over a 10,000-year period. At the present time, the DOE has not been able to defend claims on upper bounds for the water leaving the EBS on an annual basis, nor has the DOE been able to develop acceptable models that can predict how such an upper bound would vary annually over the required 9000-9700 years.

For these reasons, it appears that there is sufficient justification to consider 10,000-year waste package lifetimes for the Yucca Mountain environment.

I. INTRODUCTION

BNL has a contractual obligation with the OCRWM to

"focus on the issue of waste package containment lifetime. In particular, we would like an assessment conducted that examines various lifetimes, including times beyond the 300-1000 year performance objective of 10 CFR 60, and evaluates methods (both physical tests and analytical approaches, to be performed by the projects) to assess longevity. This assessment should provide the basis for or recommendation to OGR on waste package lifetime."

This report has been developed under conditions of conflicting guidance from senior staff of the OCRWM. In spite of the above task and NRC staff claims that 10,000-year containment is acceptable, some OCRWM staff still believe that 10,000-year containment is inconsistent with 10 CFR 60. For example, in the attachment to a letter⁽¹⁾ from the OCRWM to BNL dated April 19, 1988, the conclusion states,

"In addition, the NRC 10 CFR 60.113 states that the containment period shall be not less than 300 years nor more than 1000 years after permanent closure of the geologic repository; and the release of any radionuclide from the engineered barrier system following the containment period shall not exceed specific release limits. A 10,000-year containment by the EBS will put an unnecessary burden on the EBS and is inconsistent with the NRC's multiple barrier approach. In explaining the concept of multiple barriers, 10 CFR 60.102 states, "Following the containment period, special emphasis is placed upon the ability to achieve isolation of the wastes by virtue of the characteristics of the geologic repository." This is consistent with the NRC staff position (NUREG-0804) that the performance of the engineered and natural barriers must each make a definite contribution. The NRC 10 CFR 60.101(a)(2) also states, "While these performance objectives and criteria are generally stated in unqualified terms, it is not expected that complete assurance can be presented. A reasonable assurance... is the general standard that is required." In view of the fact that the NNWSI Project strategy is based on our current understanding of the anticipated behavior of the site, the 10,000 year containment that is recommended by the BNL is neither necessary nor beneficial, and is inconsistent with 10 CFR Part 60.113."

It is common knowledge that the NRC statement in 10 CFR 60 on the 300-1000 year containment period is to be considered as defining a minimal containment period. The generally accepted interpretation of the rule is that the NRC will not <u>require</u> more than 1000 years for the containment period, i.e., containment periods in excess of the 300-1000 year minimum are optional.

Total containment is a logical and consistent extrapolation of the controlled release requirement. The release requirement of a part in 10^5 per year is a maximum permissible release rate. If the DOE submits evidence for a release rate of one part in 10^6 , or one part in 10^7 , the NRC cannot, with credibility, reject the application on the grounds that such release rates are too low. Similarly, they could not reject a release rate of a part in 10^{50} (essentially total containment), if it were defensible.

Believing the above arguments to be valid, this report has been written in response to the task requiring BNL to provide a *"recommendation to* OGR on waste package lifetime."

Difficulties in obtaining consistent guidance in this area, and premature termination of the program, have not permitted the BNL staff to complete the work we started on evaluation of methods for "physical tests and analytical approaches to be performed by the projects to assess longevity." In addition, we were not able to do as extensive an evaluation on the overall comparison of total containment vs controlled release as we feel is necessary⁽²⁾. Nevertheless, we believe that the work reported here, however incomplete, will serve a useful purpose in pointing out problems associated with demonstrating controlled release from spent fuel in oxidizing environments. Based on draft SCPs and the DOE literature that was available at the time of this writing, these problems do not appear to have been fully recognized by the OCRWM and its contractors.

A great deal of literature exists on radionuclide releases from spent fuel under conditions pertinent to the Yucca Mountain environment. Much of the literature is consistent in recognizing what type of information is needed to predict long-term radionuclide releases. There appears to be general agreement on the types of problems that exist in obtaining this information. Analysis of the literature shows that there are a very limited number of alternative approaches that might allow acceptable defense of models for predicting long-term radionuclide releases from spent fuel in oxidizing environments.

Compliance with the existing regulations for the isolation of high level radioactive waste requires prediction, with reasonable assurance, of the releases of radionuclides from the EBS and from irradiated UO_2 in anticipated repository environments for thousands of years.

Under assumptions of significant quantities of water in an unsaturated environment, releases have been considered through rate controlling concepts involving leaching, diffusion, and/or matrix dissolution. Under assumptions of limited quantities and limited movement of water, solubility limits and colloid and particulate formation have been considered to play important roles.

A great deal of data on dissolution of spent fuel under oxidizing conditions has been generated in the past. The results involve large uncertainties, in some cases many orders of magnitude. The uncertainties occur with respect to reproducibility in a given experiment and in comparing what should be equivalent results from different experiments. The literature recognizes the large number of internal and external uncontrollable variables that can affect releases from spent fuel.

They include, but are not restricted to, type of reactor exposure, crud contamination, decontamination history if any, manufacturing variations, fuel pool histories, oxygen activity, pH, carbonate activity, alpha radiolysis fronts, etc. In several cases in the literature, it is explicitly recognized that large uncertainties are expected and have been intrinsic to the attempts of predicting and modeling long-term spent fuel releases.

There are many properties of spent fuel that intrinsically limit the validity of predictive radionuclide release models. Chief among these are thermodynamic instability and chemical instability in oxidizing environments.

II. OXIDATION AND THERMODYNAMIC STABILITY

Nuclides formed by fission are held in the UO_2 lattice by a combination of chemical and physical forces. Small amounts of the oxides of some fission products may form solid solutions with the UO_2 matrix. Small amounts of some radionuclide oxides may be held by polar forces and oxide bridges. Most of the fission products are expected to be held in unstable stressed sites because of the energetics and disruption of the lattice resulting from quenching of thermal spikes.

Release of radionuclides from such lattices depends upon many microscopic and macroscopic properties of the lattice such as distribution of the fission tracks and stresses, distribution and migration of the excess oxygen caused by the fission process, crystallite size, surface area, etc. Some of these factors, in turn, depend upon degree of burnup and others depend upon manufacturing variables affecting the original UO_2 .

Pure UO_2 is not stable in air or in water containing dissolved oxygen. Spent fuel, because of the extra energy of the defects, is even more unstable.

At ambient temperatures UO_2 oxidizes and goes through a series of intermediate solid state phases. Some of these change in specific volume causing changes in the matrix structure and redistributing the retained fission products. Such changes are known to affect release rates. The details of how the UO_2 matrix changes and how the release rates are affected depend upon the original state of the material prior to oxidation, whether or not the material was irradiated, the degree of burnup, the rate of the oxidation at a given temperature, the temperature, (equal degrees of oxidation or equal oxidation rates at two different temperatures may result in different release rates), the presence or absence of impurities or fission products that can catalyze or inhibit oxidation or can catalyze or inhibit release, etc.

No theory can relate the time dependence of the release of inclusions in a matrix solely to the chemical composition of the matrix. The physical properties that vary with the microstructure and with the macrostructure of the solid can significantly affect releases of retained materials. Depending upon origin and history, different samples of spent fuel vary both in chemical composition and in physical structure. With respect to the spent fuel to be disposed of as high level waste, these factors are uncontrollable and the uncertainties associated with them are unavoidable.

It is well known that, at a given temperature, it is not possible for an unirradiated thermodynamically stable single crystal of UO_2 to be in equilibrium with more than single oxygen activity. Above that activity the UO_2 oxidizes, and below that activity it decomposes. It is not possible for irradiated UO_2 to be in equilibrium with any environment.

Solids such as spent fuel that have been irradiated by neutrons at temperatures at which defects produced by the irradiation do not anneal, are thermodynamically unstable for several reasons. The defects produced by neutron irradiation (interstitials, vacancies, fission products, transmutation species, etc.) increase the internal energy, the enthalpy and the Gibbs free energy of the materials through lattice stresses, chemical potential increases and surface and interface energy increases.

Spent fuel is thermodynamically unstable with respect to both internal changes and changes in any environment. In contrast to a single crystal of UO_2 which can be in equilibrium with one value of oxygen activity at a given temperature, spent fuel consists of a range of stoichiometric and non-stoichiometric uranium oxides so that it is not possible, in principle, for spent fuel to be in equilibrium with any external environment.

Only solids that are thermodynamically stable in their appropriate vapor pressures are forbidden from undergoing internal changes.

Systems in equilibrium with their environments do not undergo kinetic reactions other than the requisite equilibrium exchange reactions of the same component in different phases. If a material reacts with its environment, the system (material + environment) is, by definition, thermodynamically unstable while it is reacting. Alternatively, if the system is unstable it will react until it becomes stable. Spent fuel should react in all conceivable Yucca Mountain environments, wet or dry.

It has been known for decades that

"In air at room temperature, the most thermodynamically stable uranium oxide is UO_{γ} "

and that

"Under some conditions, UO₂ powders may even burn in contact with air."

[M.J. Bannister, J. Nucl. Mater., Vol. 26, 174-184, (1968)]

(Also see [J. Belle (Ed.), "Uranium Dioxide: Properties and Nuclear Applications" (Naval Reactors, Division of Reactor Development, USAEC, 1961)]).

In the case of spent fuel reactions in oxidizing environments, the literature recognizes that many traditional equilibrium approximations and kinetic extrapolations are known to be invalid. A number of basic concepts suggest that there are unavoidable uncertainties associated with modeling long-term predictions of releases from spent fuel.

Kinetic reactions yield products that are more stable than the reactants. Kinetic reactions stop when one or more of the reactants have been depleted or when the total system is in equilibrium. Spent fuel reactions that are slow and can be ignored in the laboratory or in spent fuel pools over several years, may be important over thousands of years. Low temperature spent fuel reactions in air will cease when all the fission products are released and when the UO_2 has converted to a thermodynamically stable form of UO_3 or hydrated UO_3 .

Existing literature cannot be used to claim that either spent fuel reactions go to completion at the end of 10,000 years, or that adverse hypothetical reactions that are not observed in short-term experiments will not occur during the 10,000-year performance period.

Any long-term prediction based on kinetics has severe theoretical limitations. Although the science of chemical kinetics can be used, in special circumstances, to predict non-equilibrium changes that tend to approach equilibrium final states, there is no valid method for long-term prediction of non-equilibrium systems evolving towards ill-defined end states.

In the absence of the theoretical test of substituting equilibrium concentrations to check the validity of an isothermal rate expression at long times, a great deal of highly precise work is necessary to identify and defend an isothermal rate law for a multi-component heterogeneous system. For such systems, the overall reaction rate at any given temperature is a composite from many processes only one of which is generally rate determining. In principle, each process has its own temperature dependence, making it unlikely that the same process is rate determining at all temperatures. In practice, the energy barrier that prevents the unstable reactants from instantaneously forming more stable products is estimated from treatment of precise isothermal rate expressions over narrow temperature ranges through Arrhenius' concepts. Since different processes may have similar barriers, justification of the use of these techniques over large temperature ranges, requires that all the factors affecting the isothermal rate at any one temperature also appear in the same mathematical form at every other temperature. No such set of spent fuel dissolution rates exists. Experience has shown that for the dissolution phenomena involved in waste isolation, the uncertainties associated with the data necessary for chemical kinetics and the uncertainties in the kinetic expressions themselves, will very likely preclude successful justification for kinetic predictions of this type.

The problem is made even more difficult by the fact that the spent fuel matrix is subject to complex slow long-term internal changes that affect the spent fuel reactions with external environments.

Even for single crystals of UO_2 , existing literature shows that the factors determining the mechanisms and rates of dissolution of single crystals of unirradiated UO_2 in groundwaters include redox conditions, pH, chemical composition of the groundwater, temperature and pressure. For spent fuel the factors also include the physical and chemical properties of the irradiated UO_2 including the excess oxygen which results from the fission process and which depends upon the degree of burnup. Both the kinetic releases and the long-term "solubilities" resulting from reactions of spent fuel can be significantly different from those observed in unirradiated UO_2 experiments.

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Oxidation or reduction of polycrystalline solids can result in "powdering" or gross physical changes. In the conversion of UO_2 to U_2O_3 and UO₃, significant changes in specific volume occur. Impurities trapped in the original matrix can be released to new surfaces and new grain boundaries generated by the physical changes accompanying the chemical transformations. If the oxidation involves a sequence of intermediate compounds or complexes, such as those involved in the conversion of UO_2 through U_3O_7 to U_3O_8 to UO_3 , the rates of conversion from one state to another are neither intrinsic nor monotonic. The individual rates can differ in their dependences upon the surface areas and physical properties of the solid reactants, the oxygen and moisture concentrations, and the temperatures at which the oxidations occur. The fission process produces excess oxygen in the UO_2 matrix which depends upon the degree of burnup, age of the fuel and other factors. Details of how the excess oxygen diffuses and reacts are not known. These poorly understood relationships, all of which can play roles in determining how long it takes to oxidize a given species, make acceleration techniques unreliable. Properties such as rates of release and rates of redistribution of species retained in the matrix also can be non-monotonic and dependent upon details of how the oxidations occur. The radionuclide release rates that can increase and decrease over the 10,000-year period because of internal properties of the UO_2 , also are known to depend upon an additional number of external variables that are poorly understood and uncontrollable. These include, but are not restricted to, surface films formed after removal of the fuel from the reactor, carbonate activity in the water, oxygen activity in the water, the development of alpha radiolysis fronts and production of H_2O_2 , the presence of reducing or oxidizing impurities in the water, etc.

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Non-monotonic release rates (i.e., rates exhibiting maxima and minima), over the required 10,000-year performance period can cause unavoidable uncertainties in demonstrating compliance. Unequal release rates allow for unequal radionuclide exposures to different generations. The NRC has already stated that releases that can vary over long times from below the regulatory limit to above the regulatory limit, lead to different exposures to different generations and cannot be defended. Early estimates claiming that UO_2 may not convert to UO_3 during the times and temperatures required for performance are not supported by literature.

In agreement with theory, several experimenters have found that UO_3 forms from UO_2 at room temperatures in moist air and in water containing dissolved oxygen.

Aronson, in 1958, studied the reactions of UO_2 powder in water containing oxygen at temperatures of 87 to $177^{\circ}C$.

[S. Aronson, "Oxidation of UO₂ in Water Containing Oxygen," Bettis Technical Review, WAPD-BT-10, October 1958].

Oxidation of UO₂ at 87° C in water containing oxygen was readily detectable after several days. X-ray analyses of the partially oxidized samples showed the formation of UO₃•O•8H₂O which increased with oxidation.

Hoekstra, et al., in 1961, stated

"Evidence is given to show that the oxidized surface layer which forms on UO_2 at $25^{\circ}C$ is amorphous UO_3 ."

[H.R. Hoekstra, A. Santoro and S. Siegal, J. Inorg. Nucl. Chem, Vol. 18, pp. 166 -178, (1961)].

Small amounts of a hydrated form of UO_3 have been determined to form from unirradiated uranium dioxide in a closed plastic tube over a 15-year period at room temperature.

[T. Wadsten, "The Oxidation Of Polycrystalline Uranium Dioxide In Air At Room Temperature," J. Nuc. Mater. 64, 315, (1977)].

"When dissolution is occurring into a medium in which $U^{(VI)}$ has a low solubility (i.e., low carbonate), a surface film of $UO_3 \circ xH_2O$ is formed."

[S. Sunder, D.W. Shoesmith, M.G. Bailey and G.J. Wallace, "Mechanism of Oxidative Dissolution of UO₂ Under Waste Disposal Vault Conditions," Canadian Nuclear Society, International Conference On Radioactive Waste Management (1982) CONF-820933-Sums, ISBN 0-919784-00-3]. In the report "Dissolution of Uranium Dioxide In Groundwater," [Kaija Ollila, Technical Research Centre of Finland, Report YJT-83-11, September 1983, Voimayhtioiden Ydinjatetoimikunta], the author states for single-crystal UO₂ exposed to water containing oxygen,

"In lower temperatures $(25^{\circ}C \text{ to } 75^{\circ}C)$ uranyl hydrates form as thin films consisting mainly of $UO_3 \cdot 2H_2O$ phases. At elevated temperatures $(150^{\circ}C)$, the deposition of large uranyl crystals of $UO_2(OH)_2$ occurs."

And,

"Continuous oxidation and dissolution of UO_2 surface after the formation of hydrates $[UO_3 \bullet 2H_2O, UO_2(OH)_2]$ depends also on the nature of the deposited film."

The author also notes from L.H. Johnson, et al., "The Dissolution of Irradiated UO₂ Fuel Under Hydrothermal Oxidizing Conditions," AECL-TR-128, p. 32, 1981,

"When an unirradiated UO_2 pellet was exposed to air-saturated granite groundwater, a yellow precipitate identified as a mixture of $UO_3 \cdot O \cdot 8H_2O$ and $UO_2(OH)_2$ formed on the surface."

More recently,

"Samples of used UO_2 fuel exposed to air saturated water at $25^{\circ}C$ for eight years have been examined using electron microscopy and X-ray diffraction techniques. The results, in conjunction with solution analysis data, show evidence for a $UO_3 \circ 2H_2O$ precipitate on the fuel surface."

[S. Stroes-Gascoyne, L.H. Johnson, P.A. Beely and D.M. Sellinger, "Dissolution Of Used Candu Fuel At Various Temperatures And Redox Conditions," Scientific Basis For Nuclear Waste Management, MRS, Vol. 50, p. 317, 1985]. It is also known that several phases of UO_3 form when UO_2 is oxidized by nitrogen dioxide at low temperatures.

[A.N. Tsvigunov and L.M. Kusnetsov, "Low Temperature Oxidation of UO₂, U₃O₈, and U₃O_(8-x) by Nitrogen Dioxide," Radiokhimiya (USSR), Vol. 18:3, pp. 411-413, (1976)].

Although much evidence exists that UO_2 converts to UO_3 at ambient temperatures, it is not possible, from any existing theory, to predict either the time dependence or the extent of such transformations in spent fuel because of the large number of ill-defined factors that can affect such changes. In chemically changing systems where the final products are both totally defined and thermodynamically stable, the validity of the rate expression can be tested by inserting the expected final stable values obtained from thermodynamic data bases and showing that the rate equals zero. There is no known method to check the long-time validity of rate expressions in systems where the postulated final products are not totally defined and/or are not thermodynamically stable. For chemically reacting irradiated UO_2 containing appreciable but varying amounts of fission products, the information needed to define the final stable states is not known under any repository conditions.

Attempts have been made to avoid some of the uncertainties and problems in measuring and extrapolating individual radionuclide release rates through two limiting assumptions. In the first it is assumed that the radionuclide release rates are all equal and determined by the dissolution rate of the matrix. In the second, it is assumed that the radionuclide release rates are fast relative to release from the engineered barrier system so that the water is saturated.

III. MATRIX DISSOLUTION AND SOLUBILITY LIMITED APPROACHES: PREDICTIVE MODELING

Under conditions where thermodynamically unstable spent fuel reacts with water to release radionuclides in oxidizing environments, literature exists addressing problems in attempts to treat releases through matrix dissolution concepts and solubility limited concepts.

A. MATRIX DISSOLUTION

Difficulties in modeling matrix dissolution of spent fuel have been recognized for many years. In [S. Sunder, D.W. Shoesmith, M.G. Bailey and G.J. Wallace, "Mechanism of Oxidative Dissolution of UO₂ Under Waste Disposal Vault Conditions," Canadian Nuclear Society, International Conference On Radioactive Waste Management (1982) CONF-820933-Sums, ISBN 0-919784-00-3], the authors state,

"When dissolution is occurring into a medium in which $U^{(VI)}$ has a low solubility (i.e., low carbonate), a surface film of $UO_3 \circ xH_2O$ is formed. When dissolution is occurring into a high solubility medium, (i.e., high carbonate), then the UO_2 surface is severely attacked leading to the etching out of the individual particles in the pellet and to erosion of UO_2 particles from the surface. These results indicate that under oxidative dissolution conditions, pellet break-up is a possibility."

And,

"Radionuclides are not homogeneously distributed throughout the fuel, and consequently, radionuclide release will be very dependent on physical as well as chemical, aspects of the dissolution process. For instance, if dissolution occurs preferentially at grain or particle boundaries, then radionuclides that have concentrated at these sites could be released more quickly than radionuclides homogeneously distributed throughout the fuel. If such preferential processes do occur, then fuel failure cannot simply be described by a straight-forward matrix dissolution model, and the rate of radionuclide release will not be directly proportional to the amount of uranium dissolved." [Ibid].

B. SOLUBILITY LIMITED RELEASES

The "solubility limit" of a given species (expressed in activities) in equilibrium with a metastable solid must be higher than it is when the same dissolved species is in equilibrium with a thermodynamically stable solid phase. This well-known thermodynamic requirement can play a role in both matrix dissolution models and in solubility limited models for release. In matrix dissolution models the kinetics of a dissolving matrix can, in principle, be dependent on the value of the solubility limit. Some models for rates of solution assume that the rate is in some way dependent upon the difference between the instantaneous value of the material in solution and the solubility limit. If kinetic mechanisms remained equivalent, irradiated materials would react faster than unirradiated materials because of the free energy increases in the irradiated materials. For systems as complex as spent fuel, impurities or fission products can exert inhibiting or catalytic effects. Under such conditions, relative rate comparisons through free energy differences are unreliable and even crude approximations are questionable.

Solubility limited scenarios for thermodynamically unstable spent fuel cannot be justified and their validity has been questioned. In [L.H. Johnson, N.C. Garisto and S. Stroes-Gascoyne, "Used-Fuel Dissolution Studies In Canada," Waste Management '85: 479-482 CONF-850314-Vol. 1] the authors state,

"It should be emphasized that the release of radionuclides from used fuel may not be limited by uranium solubility if UO_2 is not a thermodynamically stable solid under vault (repository) conditions."

Even if solubility limited scenarios could be justified, and even if it were possible to ignore the potential formation of amorphous solids, colloids and particulates for the changing conditions occurring over thousands of years, developing the requisite thermodynamic data base for many of the thermodynamically stable radionuclide mineral species is recognized as a major problem. In many cases the thermodynamically stable solid species are not known.

"Thus, in most cases, it is not clear if these data bases are complete enough for detailed thermodynamic calculations for an element, or even whether the most important compounds and aqueous ions have been included."

[Joseph A. Rard, "Thermodynamic Data Bases For Multivalent Elements: An Example For Ruthenium," UCRL-96555, Rev. 1, (1987)].

In the few cases where fairly extensive thermodynamic data bases exist, large uncertainties exist because of the difficulties in achieving equilibrium in real systems.

C. PREDICTIVE MODELING

Existing literature indicates that the uncertainties involved in longterm release predictions can be considered in two main categories. Each category has both unavoidable uncertainties and uncertainties that can be reduced by accumulating appropriate information. Ignoring problems directly related to spent fuel, there are problems specific to predictive computer modeling of waste waters. These problems also have been emphasized in the literature. For example, a limitation in the predictive computer modeling of the chemistry of natural waters and waste waters was stressed by **R.D. Lindberg and D.D. Runnells, [Science, Vol. 225 (1984) pp. 925-927].** After analyses of several hundred water samples the authors stated:

"Our conclusions are most severe in the context of predictive computer modeling of the chemistry of natural waters and waste-waters. In order to provide meaningful redox input for such models, it may be necessary to analyze the samples for the dominant ions of every redox element of interest. Wolery [T.J. Wolery, UCRL-53414, Lawrence Livermore National Laboratory 1983] has suggested this approach for testing the state of redox equilibrium for his EQ3NR computer model. If any measured Eh is used as input for equilibrium calculations, the burden rests with the investigator to demonstrate the reversibility of the system."

The regulatory concept requiring demonstration of a maximum permissible controlled release over 10,000 years correctly assumes that whatever water is present, will continuously react with the engineered barrier system and with the spent fuel. If the water is reacting with the spent fuel or portions of the engineered barrier system, the water cannot, in principle, be in equilibrium. Measured Eh values will consequently involve unavoidable uncertainties.

IV. ACCELERATED TESTING

In the oxidation and conversion of UO_2 to U_3O_8 and UO_3 , the changes in specific volume that occur and the redistribution of the radionuclides in the matrix associated with the changes in volume, grain size, etc, are not predictable with time at low temperatures. Many factors related to fuel history and details of manufacturing of the reactor fuel can effect subsequent rates of oxidation of the spent fuel. Impurities trapped in the original matrix

can be released to new surfaces and new grain boundaries generated by the physical changes accompanying the chemical transformations. For chemical changes which involve a sequence of intermediate compounds or complexes, such as those involved in the conversion of UO_2 through U_3O_7 to U_3O_8 to UO_3 , the rates of conversion from one state to another are generally non-monotonic.

The individual rates can differ in their dependences upon the presence or absence of catalysts or inhibitors, the surface areas and physical properties of the solid reactants, the oxygen and moisture concentrations, and the temperatures at which the oxidations occur. The fission process produces excess oxygen in the UO_2 matrix which depends upon the degree of burnup, age of the fuel and other factors. Details of how the excess oxygen diffuses and reacts are not known. The composition of large crystallites of the fuel may not be homogeneous with respect to distribution of radionuclides. These poorly understood relationships, all of which can play roles in determining how long it takes to oxidize a given species, make acceleration techniques unreliable. Properties such as rates of release and rates of redistribution of species retained in the matrix also can be non-monotonic and dependent upon details of how the oxidations occur. The radionuclide release rates that can increase and decrease over the 10,000-year period because of internal properties of the UO_2 , also are known to depend upon an additional number of external variables that are poorly understood and uncontrollable.

Predictive models require the information described above and will be limited by unavoidable uncertainties associated with many of the phenomena, and in some cases by uncertainties that can be reduced with additional testing.

In discussing the uncertainties in measurements of the oxidation of spent fuel [HEDL-SA-3627, "Predicting Spent Fuel Oxidation States In A Tuff Repository," R.E. Einziger and R.E. Woodley, "Workshop on Chemical Reactivity of Oxide Fuel and Fission Product Release, Berkeley, United Kingdom, April 1987"], the authors state in their introduction,

"Since leaching/dissolution of the fuel can be significantly affected by its oxidation state, it is important to know the actual phases present."

They offer the following conclusions in their report:

"When uncertainties are considered so that the highest values of the rate constants are used, complete conversion to U_3O_7 occurs in 30 to 1300 years after emplacement."

"Until uncertainties are reduced so that nearly nominal activation energies can be considered and the actual operative mechanism is determined, we will not be able to justify our ability to calculate lower amounts of U_3O_7 ."

"Even using reasonable temperature histories, the operative mechanism must be identified and the uncertainty in the activation energy for the mechanisms under consideration reduced in order to improve our predictions of the oxidation states of spent fuel in a repository."

With respect to accelerated tests for predicting release rates, leaching and matrix dissolution depend upon the oxidation state of the matrix, the microscopic crystalline surface areas and surface energies, the distribution of the radionuclides, the possible catalytic or inhibitive effects of impurities and/or excess oxygen, the grain boundary compositions etc. Extrapolation of high temperature oxidation rates to lower temperatures, even if they were valid, cannot be used to predict radionuclide specific release rates on an annual basis for long time periods. Complex redistribution of radionuclides can accompany the matrix changes during the oxidation of UO_2 . For such systems, predictions of changes in reaction rates are not equivalent to predictions of the changes in properties associated with the rates. Claims that there may be long periods of time where releases vary from below acceptable values to above acceptable values during the 10,000 years may be difficult to disprove when several different factors can lead to non-monotonic rates of release. The existing regulation requires compliance with release rates on an annual basis.

Accelerating tests for releases associated with the oxidation of spent fuel appear to involve unavoidable uncertainties. Review of the literature cited here indicates that accelerating techniques for estimating releases from spent fuel are not available.

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The literature reviewed consistently demonstrates that the oxidation and dissolution processes in spent fuel result from a series of complex changes with temperature from 25° C to 300° C. Many different temperature dependent products are formed during dissolution in oxidizing environments. In several cases the changes are related to uncontrollable variables associated with the history of the fuel. In other cases complex environmental interactions play roles.

"Calculations suggest that the production of hydrogen peroxide, due to alpha radiolysis of groundwater by used fuel, may occur at a rate sufficient to maintain oxidizing conditions at the fuel/water interface for thousands of years."

[L.H. Johnson, N.C. Garisto and S. Stroes-Gascoyne, "Used-Fuel Dissolution Studies In Canada," Waste Management '85: 479-482 CONF-850314-Vol. 1]

and

[H. Christensen and E. Bjergbakke, "Radiolysis of Groundwater From Spent Fuel," KBS TR 82-18, (1982)].

In addition,

"The oxidation of UO_2 in water is 200 times faster by H_2O_2 than by dissolved oxygen at the same concentration, and the mechanisms of oxidation change with pH."

[D.W. Shoesmith, S. Sunder, L.H. Johnson and M.G. Bailey, "Oxidation of Candu UO₂ Fuel By The Alpha Radiolysis Products Of Water," Scientific Basis For Nuclear Waste Management IX, MRS, Vol. 50, p. 309, 1985].

In some cases factors associated with the history of the fuel can be mistaken for factors associated with the complex environments. In considering differences between spent fuel and UO_2 releases in brine, W.J. Gray et al., state

"Not only release but also solution concentrations of uranium in the spent fuel tests were considerably higher (a factor of 100 or more) than those in the UO_2 tests. This could reflect a higher redox potential due to radiolysis."

[W.J. Gray, G.L. McVay, J.O. Barner, J.W. Shade and R.W. Cote, "Evaluation Of Spent Fuel As A Waste Form In A Salt Repository," Scientific Basis For Nuclear Waste Management VII, MRS, Vol. 26, p. 437, 1983].

In follow-up work, W.J. Gray states,

"Results from recently completed tests show that at least 90% of the reported difference between the dissolution behavior of spent fuel and UO_2 can be attributed to apparent surface oxidation of the spent fuel specimens after their discharge from the reactor."

[W.J. Gray, "Comparison Of Uranium Release From Spent Fuel And Unirradiated UO₂ In Salt Brine," Scientific Basis For Nuclear Waste Management X, MRS, Vol. 84, p. 141, 1987].

Generalized methods for accelerating chemical kinetic reactions involve utilizing known catalysts, increasing the temperatures, pressures, concentrations, surface areas, or any other parameter which is known to vary monotonically with the reaction rate. If an increase in the parameter causes a change in the mechanism of converting the reactants to products, then the original reaction is not involved and is therefore not accelerated.

With respect to accelerated testing of spent fuel releases, no known catalysts are recognized and existing literature shows that temperature increases are not valid methods of acceleration.

Radionuclide redistribution, grain boundary development and grain boundary changes, UO_2 breakup, chemical composition of surface films and their roles in changing release rates are all dependent on details of oxidation and reaction with water. They vary with the temperature of the reactions and the past history of the spent fuel. Consequently, increasing the fuel surface area is of limited value.

Existing literature indicates that, at present, there are no acceptable methods for predicting long-term releases from spent fuel in oxidizing environments by extrapolation of ambient measurements or by extrapolation of accelerated tests. There appear to be no useful acceleration techniques.

V. SUMMARY

Spent fuel is thermodynamically unstable in all environments. The number of factors contributing to the degree of instability are greatest in oxidizing environments. Both theory and existing experiments show that neither solubility limited concepts nor matrix dissolution concepts can be justified for long-term prediction of radionuclide release rates in an environment containing oxygen and water. No predictive models exist for releases from spent fuel under such conditions. The physical processes involved in the observed releases fall into at least three categories. A limited number of the physical processes are understood and might be approximated by modeling. Some physical processes are recognized but modeling cannot be defended because values or acceptable bounding estimates of critical parameters are not yet available, (powdering during oxidation, grain boundary development, redistribution of radionuclides, UO₂ breakup, chemical species produced by alpha radiolysis, etc.). In some cases reactions involve processes that are poorly understood with little chance of elucidation in the near future, (changes in metastable species to unknown stable species, formation and removal of colloids and particulates in alpha radiolysis fronts, migration and reaction of excess oxygen produced by the fission process, etc.).

No models exist for predicting the chemical reactions in non-equilibrium waste waters. Although measurements of concentrations, activities, pH, gradients, etc, have meanings in non-equilibrium systems, the concept of a measured Eh value is only valid when the redox ions are in equilibrium and the measurements can be shown to be reversible. Models dependent upon Eh, are not likely to be credible.

No theory exists that allows estimates of the times involved in converting from thermodynamically unstable states to thermodynamically stable states. Many of the species observed in long-term spent fuel dissolution experiments are known to be unstable.

This paper emphasizes literature related to problems in demonstrating compliance with long-term controlled release. Past experience in license hearings has shown that regulatory agencies focus on literature which emphasizes problems in demonstrating required performance. The existence of such literature also minimizes the significance of literature in which the absence of adverse effects from short-term experiments are interpreted optimistically.

VI. CONCLUSIONS

Evaluation of the literature cited here, indicates that the information needed to acceptably predict long-term radionuclide releases from the Engineered Barrier System, includes determining the minimum number of factors related to defending an upper bound on the maximum quantity of radioactive material (dissolved, suspended, i.e., soluble, colloidal or particulate) that can be transported from the EBS by a unit volume of liquid at all appropriate temperatures. The upper bound over the required 10,000-year time period must be determined for each pertinent radionuclide, and it must be defended. In addition, the total quantity of water containing the upper bounded radionuclide inventory leaving the EBS on an annual basis and how it varies over 10,000 years needs to be predicted or upper bounded for the appropriate temperatures. Evidence will be required showing that both upper bounds are time stable or decrease with time.

Since theoretical upper bounds for possible radionuclide masses that can be transported in water are likely to be relatively high, successful defense of long-term controlled release will be tied intrinsically to successful defense of limited and upper bounded quantities of water that can leave the EBS on an annual basis over a 10,000-year period. At the present time, the DOE has not been able to defend claims on upper bounds for the water leaving the EBS on an annual basis, nor has the DOE been able to develop acceptable models that can predict how such an upper bound would vary annually over the required 9000-9700 years. For these reasons, it appears that there is sufficient justification to consider 10,000-year waste package lifetimes for the Yucca Mountain environment.

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VII. ACKNOWLEDGEMENTS

This evaluation is based in part on numerous discussions held with all the BNL staff in the OCRWM support program.

VIII. REFERENCES

- 1. Response from Ralph Stein, Acting Associate Director for Systems Integration and Regulation, to a letter dated November 6, 1987 from D.G. Schweitzer expressing concern over claims made in the draft SCP on the NNWSI licensing strategy.
- 2. For example, we were not able to evaluate the potential of tailored backfills used in the EBS to control long-term releases.