U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

NUREG-1914

Dissolution Kinetics of Commercial Spent Nuclear Fuels in the Potential Yucca Mountain Repository Environment

Office of Nuclear Material Safety and Safeguards

AVAILABILITY OF REFERENCE MATERIALS IN NRC PUBLICATIONS

NRC Reference Material

As of November 1999, you may electronically access NUREG-series publications and other NRC records at NRC's Public Electronic Reading Room at http://www.nrc.gov/reading-rm.html.
Publicly released records include, to name a few, NUREG-series publications; *Federal Register* notices; applicant, licensee, and vendor documents and correspondence; NRC correspondence and internal memoranda; bulletins and information notices; inspection and investigative reports; licensee event reports; and Commission papers and their attachments.

NRC publications in the NUREG series, NRC regulations, and *Title 10, Energy*, in the Code of *Federal Regulations* may also be purchased from one of these two sources.

1. The Superintendent of Documents
   U.S. Government Printing Office
   Mail Stop SSOP
   Washington, DC 20402–0001
   Internet: bookstore.gpo.gov
   Telephone: 202-512-1800
   Fax: 202-512-2250
2. The National Technical Information Service
   Springfield, VA 22161–0002
   www.ntis.gov
   1–800–553–6847 or, locally, 703–605–6000

A single copy of each NRC draft report for comment is available free, to the extent of supply, upon written request as follows:

Address: U.S. Nuclear Regulatory Commission
Office of Administration
Mail, Distribution and Messenger Team
Washington, DC 20555-0001
E-mail: DISTRIBUTION@nrc.gov
Facsimile: 301–415–2289

Some publications in the NUREG series that are posted at NRC's Web site address http://www.nrc.gov/reading-rm/doc-collections/nuregs are updated periodically and may differ from the last printed version. Although references to material found on a Web site bear the date the material was accessed, the material available on the date cited may subsequently be removed from the site.

Non-NRC Reference Material

Documents available from public and special technical libraries include all open literature items, such as books, journal articles, and transactions, *Federal Register* notices, Federal and State legislation, and congressional reports. Such documents as theses, dissertations, foreign reports and translations, and non-NRC conference proceedings may be purchased from their sponsoring organization.

Copies of industry codes and standards used in a substantive manner in the NRC regulatory process are maintained at—

The NRC Technical Library
Two White Flint North
11545 Rockville Pike
Rockville, MD 20852–2738

These standards are available in the library for reference use by the public. Codes and standards are usually copyrighted and may be purchased from the originating organization or, if they are American National Standards, from—

American National Standards Institute
11 West 42nd Street
New York, NY 10036–8002
www.ansi.org
212–642–4900

Legally binding regulatory requirements are stated only in laws; NRC regulations; licenses, including technical specifications; or orders, not in NUREG-series publications. The views expressed in contractor-prepared publications in this series are not necessarily those of the NRC.

The NUREG series comprises (1) technical and administrative reports and books prepared by the staff (NUREG–XXXX) or agency contractors (NUREG/CR–XXXX), (2) proceedings of conferences (NUREG/CP–XXXX), (3) reports resulting from international agreements (NUREG/IA–XXXX), (4) brochures (NUREG/BR–XXXX), and (5) compilations of legal decisions and orders of the Commission and Atomic and Safety Licensing Boards and of Directors' decisions under Section 2.206 of NRC's regulations (NUREG–0750).

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

NUREG-1914

Dissolution Kinetics of Commercial Spent Nuclear Fuels in the Potential Yucca Mountain Repository Environment

Manuscript Completed: December 2007
Date Published: October 2008

Prepared by
T.M. Ahn[1]
S. Mohanty[2]

[1]U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

[2]Center for Nuclear Waste Regulatory Analyses
San Antonio, TX 78238-5166

Office of Nuclear Material Safety and Safeguards

Abstract

This report provides a summary of a literature survey and an independent analysis of relevant experimental data on the dissolution rate of commercial spent nuclear fuel (CSNF) for disposal at the potential high-level waste repository at Yucca Mountain, Nevada. This analysis was carried out to identify models and parameters for the CSNF dissolution rate, for use in performance assessment (PA) models. The survey and analysis focused on three key areas that potentially control the CSNF dissolution rate: (I) in-package water chemistry; (ii) CSNF conditions before aqueous dissolution; and (iii) the modes of groundwater contact with CSNF from the failure of the drip shield and the waste package components. Based on the key findings, two models and their parameters for the CSNF dissolution rates are presented to be used in PA. Two models and their parameters for determining the exposed CSNF surface area for water contact are also presented. These models and parameters are used for determining the rate of radionuclide transfer from CSNF into the contacting water in the WP. PA was conducted to assess the sensitivities of the identified models and parameter values, and the associated uncertainties in radionuclide release.

Contents

List of Figures

Executive Summary

This report provides a summary of a literature survey and an independent analysis of relevant experimental data on the dissolution rate of commercial spent nuclear fuel (CSNF) for disposal at the potential high-level waste repository at Yucca Mountain, Nevada. This analysis was carried out to identify models and parameters for the CSNF dissolution rate for use in performance assessment (PA) models. The survey and analysis focused on three key areas that potentially control the CSNF dissolution rate: (I) in-package water chemistry; (ii) CSNF conditions before aqueous dissolution; and (iii) the modes of groundwater contact with CSNF from the failure of the drip shield and the waste package components. PA was conducted to assess the sensitivities of the identified models and parameter values, and the associated uncertainties.

A literature review of the in-package water chemistry suggests that the factors controlling the CSNF dissolution rate are primarily: (I) carbonate concentration, (ii) cation availability in the contacting water, (iii) pH, (iv) oxygen concentration, (v) iron concentration, and (vi) temperature. The carbonate concentration alone linearly increases the CSNF dissolution rate. The carbonate concentration effect is not discussed extensively in this report because the CSNF dissolution rate determined in pure carbonate solution is conservative and, therefore, easily adopted in PA. Calcium and silica cations (Ca^{2+} and SiO_4^{4-}) in an amount to be present in the potential in-package water tend to decrease the CSNF dissolution rate by as much as, or more than, 2 orders of magnitude, at 25 °C [77 °F] compared to those in pure carbonate solutions of 2×10^{-4} - 2×10^{-2} M. As the pH decreases below ~ 5 under oxidizing conditions, the CSNF dissolution rate increases (e.g., a factor of 10 - 20 increase at pH ~ 3). In the carbonate solution, the increasing factor was extended to a factor of 10–20. In the presence of steel components (i.e., introducing dissolved iron ions in the groundwater), local oxygen concentration may decrease, which in turn could decrease the CSNF dissolution rate. Decrease in the CSNF dissolution rate by more than an order of magnitude was observed from the tests when iron was present in sodium chloride (NaCl) solutions at 25 °C [77 °F] in a German analog repository environment. The CSNF dissolution rate varies with temperature, by a combination of temperature itself and the activation energy in a rate equation of Arrhenius type. The activation energies extracted from appropriate literature test date to the in-package water vary depending on measurement conditions such as solution chemistry. The values extracted are 24–33 kJ/mol [6–8 kcal/mol].

Important processes related to the conditions of CSNF before aqueous dissolution begins include the opening up of grain-boundary internal surface areas to solution due to dry oxidation and hydration prior to the dissolution, leading to the formation of grain-size or sub-grain-size powders. These processes could effectively increase the surface area of CSNF for water contact, thus increase the release of radionuclides (RN) from the CSNF to the contacting water. Given the same exposed surface area, the oxidized matrix (i.e., $UO_{2.4}$ or U_3O_8) and unoxidized matrix (i.e., UO_2) show similar dissolution rates. Hydrated UO_3 xH_2O ($x = 0.8, 2$) dissolves at 10 - 20 times higher rates than the unhydrated UO_2 matrix. However, hydration rates forming UO_3 xH_2O are slower than the aqueous dissolution rates. $UO_{2.4}$ tends to open up more grain boundaries, increasing the RN release rate by a factor of ~10 in 2×10^{-2} M of total carbonate anions, pH of 8, and temperature of 25 °C [77 °F], and no increase in 2×10^{-3} M of total carbonate anions, pH of 9, and temperature of 50 °C [122 °F]. U_3O_8 or UO_3 xH_2O tends to become sub-grain-sized powder, increasing the exposed surface area by as much as 2 to 3 orders of magnitude, compared to the geometric surface area of the CSNF fragment. Prolonged oxidation or hydration may weaken deeper more grain boundaries. Mechanical impact would result in powdering of the fragment into grains. However, such mechanical impacts depend on the magnitude of the event. Available data on the CSNF dissolution rate indicate that the RN release from the grain boundary and gap inventory can be substantial along with the true long-term matrix dissolution rate. Therefore, the true long-term matrix dissolution rate could be lower than the measured (i.e., apparent) dissolution rate by as much as an order of magnitude. This indication is obtained by a detailed analysis of (I) RN inventory of the grain boundary, (ii) the observed apparent CSNF dissolution rate, and (iii) the dissolution rate of the unirradiated UO_2 matrix or CSNF grains which exclude the grain boundary RN inventory.

For groundwater to contact CSNF, the drip shield and the waste package (WP) components (i.e., the WP inner and outer overpack containers and the CSNF cladding) must fail. Depending on the failure modes of these components (e.g., overpack containers) and the flow rate of groundwater into the WP, the groundwater contact modes for CSNF will vary. Dissolution rates for CSNF are significantly influenced by immersion versus drip condition for CSNF, the flow rate of groundwater into the WP, and the degree of partial protection by failed cladding. Immersion tests show lower CSNF dissolution rate than high-drip rate tests, in J-13 well water obtained near Yucca Mountain. However, under low-drip rate conditions which appear more representative of repository conditions, the CSNF dissolution rate could be lower than the immersion tests. In the presence of partial protection by failed cladding, the RN release decreases significantly. Slit- or hole-defected CSNF rods under immersion conditions in J-13 well water at 85 °C [185 °F], showed RN release rates that decreased by a factor of ~140 for Tc-99, $\sim 7 \times 10^5$ for I-129, and ~ 65 for Sr-90, compared to bare CSNF. Partially clad rod segments under drip conditions also showed decreased Tc-99 release rates, to a factor of 10–100.

The rate of RN transfer from CSNF into groundwater in a WP is modeled as a function of the flow rate of groundwater contacting CSNF, water chemistry, and the RN solubility in this water. Fission- and activation-product RN normally have high-solubility limits that do not limit the release of these RN from a WP. These RN include Tc-99, I-129, Cs-135, C-14, and Cl-36. Np-237 may belong to this category also at high flow rates. These RN are considered to be released congruently with the dissolving CSNF matrix. Np-237 at low flow rates and other actinides such Pu-(239+240) are considered to be released at rates determined by solubility limits and groundwater flow rates. Two specific models for the CSNF dissolution are presented. The first model from the literature is based on an enhanced CSNF dissolution rate derived from tests in pure carbonate solutions. In this model, the dissolution rate is a function of carbonate concnetration, pH, oxygen fugacity, and temperature. The second model is based on a CSNF dissolution rate considering all the above: (I) in-package water chemistry; (ii) CSNF conditions before aqueous dissolution; and (iii) the modes of groundwater contact with CSNF from the failure of the drip shield and the WP components. In this model, the dissolution rate is an Arrehnius form with a pre-exponential term incorporating other factors included in (I) to (iii).

The RN release is proportional to the surface area of CSNF exposed to groundwater because the CSNF dissolution rate is defined per unit exposed surface area. Two models for determining the CSNF surface area are presented in this report. The first model represents surface area, using fragmented pellets (i.e., particles), and the second model uses CSNF grain-size criteria. The particle model assumes that CSNF in a WP is fragmented into small spherical particles. The grain model assumes that smaller individual grains in particles are exposed. The effects of alpha-, beta-, and gamma-ray radiolysis were not considered. In the oxygen-buffered solution at the potential Yucca Mountain repository, radiolysis effects are offset by the oxygen effects within the uncertainty range. Ongoing work in Europe does not suggest the long-term alteration of crystal structure/integrity or radionuclide redistribution. Nevertheless, PA models consider these uncertainties too.

To include the CSNF dissolution models in PA, various parameter values used in the model are considered and the associated ranges of the parameter values are presented to evaluate uncertainties in RN release. These models and parameters are used for determining the rate of radionuclide transfer from CSNF into the contacting water in the WP. PA was conducted to assess the sensitivities of the identified models and parameter values, and the associated uncertainties.

Acknowledgments

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of a license application for a geological repository at Yucca Mountain. The paper was prepared to document work performed by CNWRA for NRC under Contract No. NRC–02–02–012. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety. This report is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

The authors are thankful for the NRC management's support for this work. The manuscript was reviewed by staff of the NRC. The content of this report was also presented or discussed for external reviews at Materials Research Society Meeting and foreign research institutes.

Abbreviations

ANL	Argonne National Laboratory
CSNF	commercial spent nuclear fuel
DOE	U.S. Department of Energy
DS	drip shield
NRC	U.S. Nuclear Regulatory Commission
PA	performance assessment
RH	relative humidity
RN	radionuclides
U.S.	United States
WP	waste package
YM	Yucca Mountain

1. Introduction

Current plans for commercial spent nuclear fuel (CSNF) in the United States (U.S.) call for disposal in waste packages (WP), in drifts excavated nearly 300 meters (m) (984 feet, ft) below the ground surface, at the potential Yucca Mountain (YM) repository in Nevada. If the WP container, cladding, and other engineered barrier system components such as the drip shield (DS) fail, radionuclides (RN) such as technetium-99 (Tc-99), iodine-129 (I-129), and neptunium-237 (Np-237) could be mobilized upon the CSNF contact with groundwater and the subsequent dissolution of CSNF. The high solubility RN —Tc-99 and I-129—are released from the WP at the dissolution rate of the CSNF UO_2 matrix (i.e., dissolution rate). Under high-flow-rate conditions, Np-237 is also released from the WP at the dissolution rate. Np-237 at low flow rates and other actinides such Pu-(239+240) of low solubility are considered to be released by solubility limits and groundwater flow rates, after the continuous matrix dissolution and its subsequent precipitation back. The dissolution rate is a function of the evolved physico-chemical environment inside the WP, especially water chemistry inside a failed WP (i.e., in-package water chemistry) such as: (I) concentration of carbonate/bicarbonate (i.e., carbonate) anions; (ii) concentration of calcium (Ca) or silica (Si oxide) cations; (iii) pH; (iv) concentration of oxygen and iron; and (v) temperature. Further modifications of the in-package water chemistry may occur by groundwater interaction with materials inside the WP such as neutron poison materials. CSNF conditions before aqueous dissolution are also important to the dissolution process. Such conditions include the pre-hydration/oxidation of the CSNF UO_2 matrix (i.e., the matrix) prior to the dissolution, and the RN inventory of the grain boundaries. The dissolution rate is also a function of the mode in which groundwater contacts CSNF. The water contact mode influences the RN release primarily through the surface area and duration of contact between groundwater and CSNF. The mode of groundwater contact (immersion versus drip), the flow rate of groundwater past the CSNF, and partial protection by failed cladding influence the area and period of groundwater contact. The immersion test uses a small amount of CSNF sample in a batch of solution. The drip test uses a small volume of solution dripping onto the CSNF sample. The RN release is also proportional to the surface area of CSNF exposed to groundwater because the CSNF dissolution rate is defined per unit exposed surface area. The effects of alpha-, beta-, and gamma-ray radiolysis were not considered. In the oxygen-buffered solution at the potential YM repository, radiolysis effects are offset by the oxygen effects within the uncertainty range (Ferry, et al., 2005a,b; Poinssot, et al., 2005; Bechtel SAIC Company, 2004; Poinssot, 2001; Shoesmith, 2000). Ongoing work in Europe does not suggest the long-term alteration of crystal structure/integrity or radionuclide redistribution. Nevertheless, PA models consider these uncertainties too.

This report attempts to summarize the relevant key information, pertinent to the potential repository at YM, available in the literature on CSNF dissolution. This initial study is based on an acceptable “baseline-event sequence,” regarding the most abundant type of CSNF. This work helps inform NRC’s independent model for CSNF dissolution, potentially used in performance assessment. In the following sections, key findings are presented for: (I) the in-package water chemistry (ii) CSNF conditions before aqueous dissolution; and (iii) groundwater contact modes with CSNF from the failure of the DS and WP components. Based on the key findings, models and parameters for the CSNF dissolution rates are presented to be used in PA. Two models for determining the CSNF surface area are also presented. The first model determines surface area, using fragmented pellets (i.e., particles), and the second model uses CSNF grain-size criteria.

To include the CSNF dissolution models in PA, various parameter values and ranges used in the model are presented to treat uncertainties. These models and parameters are used for determining the rate of radionuclide transfer from CSNF into the contacting water in the WP. PA was conducted to assess the sensitivities of the identified models and parameter values, and the associated uncertainties.

2. Literature Survey

2.1 In-Package Water Chemistry

A literature review of the physico-chemical environment inside a failed WP suggests that the primary controlling parameters in the dissolution rate are: (I) concentration of carbonate anions; (ii) concentration of calcium (Ca) or silica (Si oxide) cations; (iii) pH; (iv) concentration of oxygen and iron; and (v) temperature [Shoesmith, 2000; Bechtel SAIC Company, 2004]. Table 1 summarizes CSNF dissolution rates from laboratory studies, selected from the literature, on the basis of their relevance to YM. Oversby and VMO Konsult [1999] indicate that the dissolution rate at the room temperature varies over a range of more than 2 orders of magnitude, mostly in the pH range of 5 – 10. The dissolution rate will vary by a factor of 10 – 20, if pH decreases to ~ 3, from the near neutral values. Discussions about the effects of important environmental variables that were noted, follow.

2.1.1 Carbonate Effects

The carbonate concentration alone linearly increases the dissolution rate [Mohanty, et al., 2002]. The carbonate concentration effect is not discussed extensively in this report because the dissolution rates determined in pure carbonate solutions are generally higher than those in realistic groundwater containing magnesium, calcium, fluoride, nitrate, sulfate and silica ions, in addition to carbonate anions. Therefore, they are conservatively used in many performance assessment models. The discussion in this report focuses on more realistic dissolution rates considering various environmental and SNF conditions.

2.1.2 Cation Effects

Solutions with calcium and silica cations (Ca^{2+} and SiO_4^{4-}) in an amount potentially present at the YM repository tend to decrease the dissolution rate by more than 2 orders of magnitude, at 25 °Centigrade (C) [77 °Farenheit (F)] compared to the pure carbonate solutions of 2×10^{-4} – 2×10^{-2} M [Shoesmith, 2000; Gray, 1997; Gray, 1992] (Figure 1). These tests were conducted at very high flow rates of a large volume of solution (i.e., flow-through tests). These decreased dissolution rates partly support the lower end of the distribution of the CSNF dissolution rates in PA. In the drip tests, these cations are consumed by forming uranosilicates. Consequently, reactions without cations are likely to form hydrated or dehydrated schoepite in drip tests. On the other hand, under a static immersion condition, the cations are expected to be available, although details of the localized chemistry between the uranium alteration (i.e., precipitation of continuously dissolved uranium) layer and the bare CSNF surface are not very well-known. Although the carbonate anions are known to ease the inhibition effect of these cations in the dissolution, the carbonate anions present in immersion tests or flow-through tests do not appear to be concentrated enough to affect the cation effect, as shown in Table 1. Additionally, the presence of schoepite formed without the cations is also considered to decrease the dissolution rates by impeding the transport of oxygen to the bare CSNF surface, possibly forming less oxidizing local conditions between the schoepite and the bare CSNF surface.

Table 1. Relevant CSNF Dissolution Rates in the Potential YM Repository

Dissolution Rate, (mg/m^2-d)	Sample Tested	Solution Chemistry	pH	T (°C)	Surface Area*	Test Method	Reference
0.2 - 1.0**	CSNF	J-13	8.4	25	1	I	Wilson, 1990
0.2	Archived CSNF	J-13	8.4	22	1	FT	Gray, 1992 Gray and Wilson, 1995
3 x (10^{-2} - 1)	UO_2	$NaHCO_3$ +$CaCl_2$ +Silicic Acid	8.4	25	2	FT	Gray and Wilson, 1995
(0.8 - 2.5) x 10^{-2}	UO_2	Silicate Solution	near neutral	25	1	FT	Tait and Luht, 1997
0.07 (X 5 at pH=3.2)	CSNF	Allard Synthetic Ground Water	8.1 (3.2)	20 - 25	1	I	Forsyth, 1997 Forsyth and Wermer 1985
4.2 - 8.0	CSNF	J-13	8.4	90	vary	Drip	Finn et al., 2002
x (10 - 20) at pH=3	UO_2	Dilute KCl or KOH $NaClO_4$	~ 3 w.r.t neutral	25	1	FT	Torrero, et al., 1997
			~ 3 w.r.t neutral	20 - 30	2	FT	Thomas and Till, 1984
25	CSNF	2 x 10^{-2} M total carbonate	8	25	1	FT	Gray, 1997
2 - 12	UO_2, CSNF	5 x (10^{-4} - 10^{-2}) M total carbonate	8 - 10	25	1	FT	Bechtel SAIC Company, 2004
0.023 - 0.165	SIMFUEL	Allard and Granite Groundwater	near-neutral	25	2 (1.52x 10^{-3} m^2/ pellet)	***	Oversby and VMO Konsult, 1999
3.7x10^{-2}	CSNF (Segment)	Carbonate Groundwater with Ca and Si	7.2	25	1	I	Jégu, et al., 2004, 2001
0.19 - 0.57	CSNF	Clay, Granite Groundwater	near-neutral	25	2	I	Grambow, et al., 2000

I= Immersion, FT= Flow-through; CSNF=Commercial Spent Nuclear Fuel;
Tc (Sr if Tc is unavailable) was used as a marker; all under oxidizing conditions otherwise specified

* Two surface areas were used. The specific surface area (e.g., Brunauer, Emmett, and Teller, BET, measurement) considering the surface roughness is presented by 1 (normally ~ 7.2 cm^2/g for CSNF fragments). The simple geometric surface area is presented by 2 and it is normally smaller by a factor of 3 for CSNF fragments. Except for flow-through tests, it is unlikely to have a roughness factor as the alteration phase masks the surface. It is user's choice in the performance assessment.

**(~ x 1/140, partially cladded);

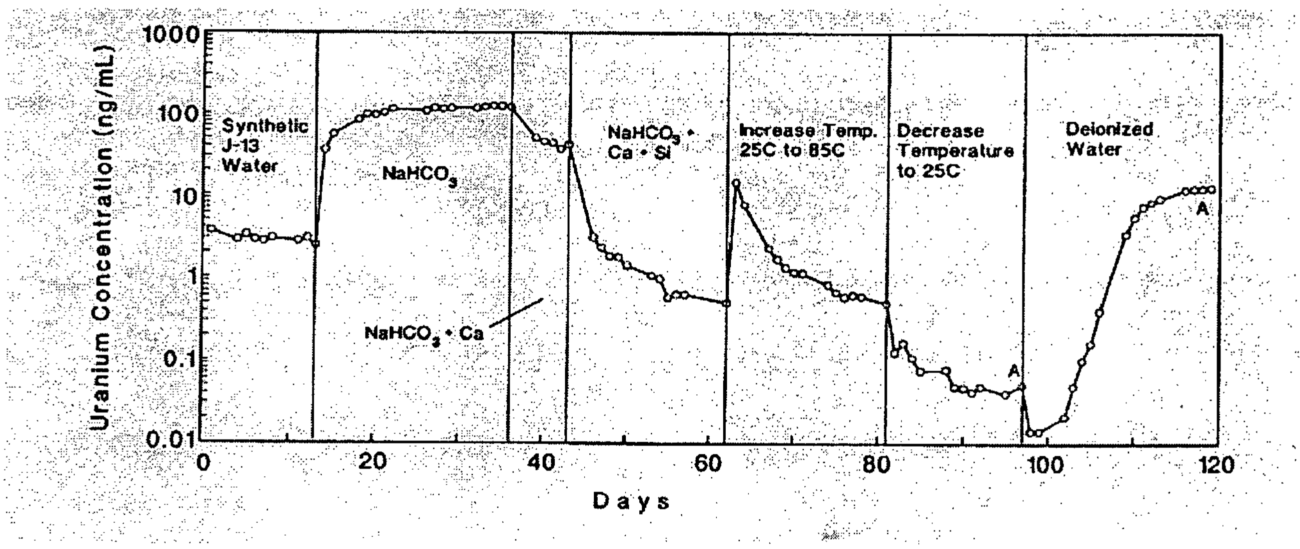
*** static tests, increase ~ x2.5 in flow-through tests;

$mg\ m^{-2}\ d^{-1} = 1.42 \times 10^{-9}\ lb/in^2\text{-}d$

$°F = °C \times 9/5 + 32$

(This information on page 4)

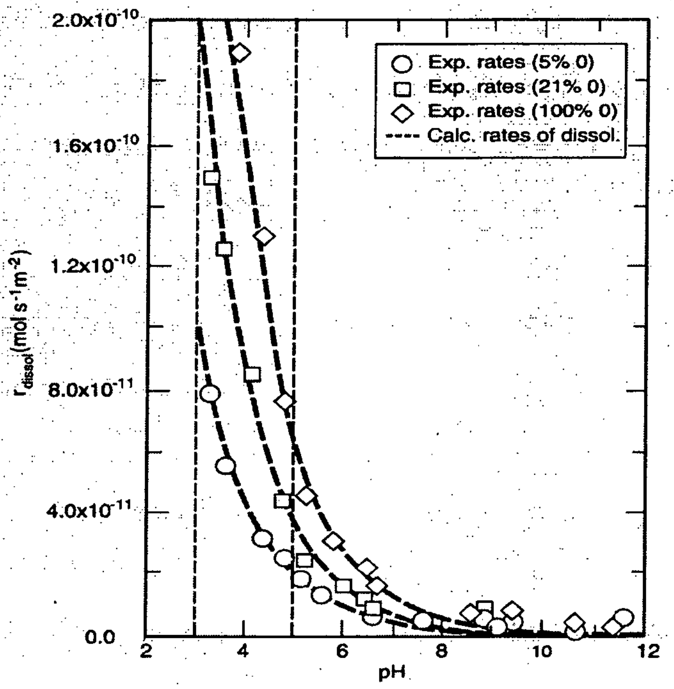
Figure 1. Uranium Concentration Measured in Flow-Through Tests with UO_2, Where Water Chemistry and Temperature Were Periodically Adjusted [Wilson and Gray, 1990; C. N. Wilson and W. J. Gray, Measurement of Soluble Nuclide Dissolution Rates from Spent Fuel, Mat. Res. Soc. Symp. Proc., Vol. 176, p. 489, 1990, p. 494, Reprinted with Permission of Materials Research Society]



2.1.3 pH Effects

Data on the pH dependence of the CSNF dissolution rates are not sufficient to cover a full range of the pH in the expected repository environment. Nevertheless, an estimate of the pH effect can be made, based on data from Torrero, et al. [1997] and Thomas and Till [1984], under oxidizing conditions relevant to the potential YM environment. As the pH decreases below ~ 5, the dissolution rate increases by a factor of 10-20 at pH ~ 3, as shown in Table 1 and Figure 2. In the carbonate solution, the increasing factor was somewhat larger than 10-20, depending on the choice of the reference pH above 6 [Röllin, et al., 2001]. The potential YM repository may have low pH, because the reaction of WP components with limited amounts of groundwater may result in forming stagnant groundwater films. These increased dissolution rates partly support the higher end of the distribution of the CSNF dissolution rates in PA. The WP components such as internal steel structure or WP itself include metallic ions, such as chromium (Cr) ions, responsible for lowering pH. At low pH, cations such as calcium and silica ions are theoretically known to be ineffective in lowering the dissolution rate [Shoesmith, 2000]. However, as shown in Table 1 [Forsyth, 1997; Forsyth and Wermer, 1985], Swedish tests in Allard synthetic groundwater containing calcium and silica ions did not indicate any drastic change of the dissolution rate resulting from ineffective cation effects at low pH.

Figure 2. Rates of UO_2 Dissolution as a Function of pH and Oxygen Concentration [after M. E. Torrero, E. Baraj, J. De Pablo, J. Giménéz, and I. Casas, Kinetics of Corrosion and Dissolution of Uranium Dioxide as a Function of pH, Int. J. Chemical Kinetics, Vol. 29, 1997, p. 263; Copyright, 1997, John Wiley and Sons, Inc.; Reprinted with Permission of John Wiley & Sons, Inc.]



2.1.4 Effects of Oxygen and Iron Concentration

Iron ions from the steel components into the in-package water may decrease local oxygen concentration forming reducing environments, which in turn could decrease the dissolution rate. The presence of iron in sodium chloride (NaCl) based groundwater and NaCl solution at ambient temperature decreased the dissolution rates by more than an order of magnitude [Quiñones, et al., 2001]. These decreased dissolution rates partly support the lower end of the distribution of the CSNF dissolution rates in PA. However, the decreased dissolution rates in the presence of iron may be localized and transitory. The production of oxidants from radiolysis and abundant air inflow may buffer the reducing environment formed by iron. It is necessary to understand better the iron effects with respect to the radiolysis and the air buffering. For example, after 100-1000 years, gamma and beta radiation fields will decay away substantially, whereas alpha fields will remain strong [Shoesmith, 2000].

2.1.5 Temperature Effects

The CSNF dissolution rate varies with temperature, by a combination of temperature itself and the activation energy in a rate equation of Arrhenius type. The activation energies vary depending on measurement conditions such as solution chemistry or CSNF conditions. Literature data show activation energies of: (I) over 29-34 kilo-joule per mole (kJ/mol) [7-8 kilo-calorie (kcal)/mol] in non-complexing neutral solutions; (ii) 47 kJ/mol [11 kcal/mol] in aerated carbonate solutions; (iii) 20 kJ/mol [5 kcal/mol] in distilled water; and (iv) 26-31 kJ/mol [6-7 kcal/mol], in borate-buffered granite groundwater. In some experiments a decrease in the dissolution rates was also observed with temperature; and insensitivity to temperatures was additionally observed at low pH [Shoesmith, 2000]. The lower dissolution rate is obtained from mineral deposits resulting in negative activation energies for strontium-90 (Sr-90) release and very low activation energy values, 10-18 kJ/mol [2-4 kcal/mol]) for cesium-137 (Cs-137) release. The release rates of these RN are used as markers for the CSNF dissolution, because they are not precipitated back to CNSF as uranium ions. The present work adopts activation energies obtained from the immersion tests of CSNF in J-13 well water (YM area groundwater), because this system is considered close to the potential YM environment. The obtained values are 24-33 k./mol [6-8 kcal/mol] for Tc-99 and I-129 releases. These values are within the range published in the other literature. The in-package chemistry inside failed waste package may have variation in pH and limited availability of cations. Currently, data at different temperatures under these conditions are not available.

2.2 Condition of CSNF before Water Contact

Important processes related to the conditions of CSNF before aqueous dissolution begins include the opening up of grain-boundary surface area due to dry oxidation and hydration prior to the dissolution, leading to the formation of grain-size or sub-grain-size powders [Shoesmith, 2000; Gray, 1997; Gray and Wilson, 1995]. These could effectively increase the surface area of CSNF for water contact, thus increase the release of RN from the CSNF to the contacting water.

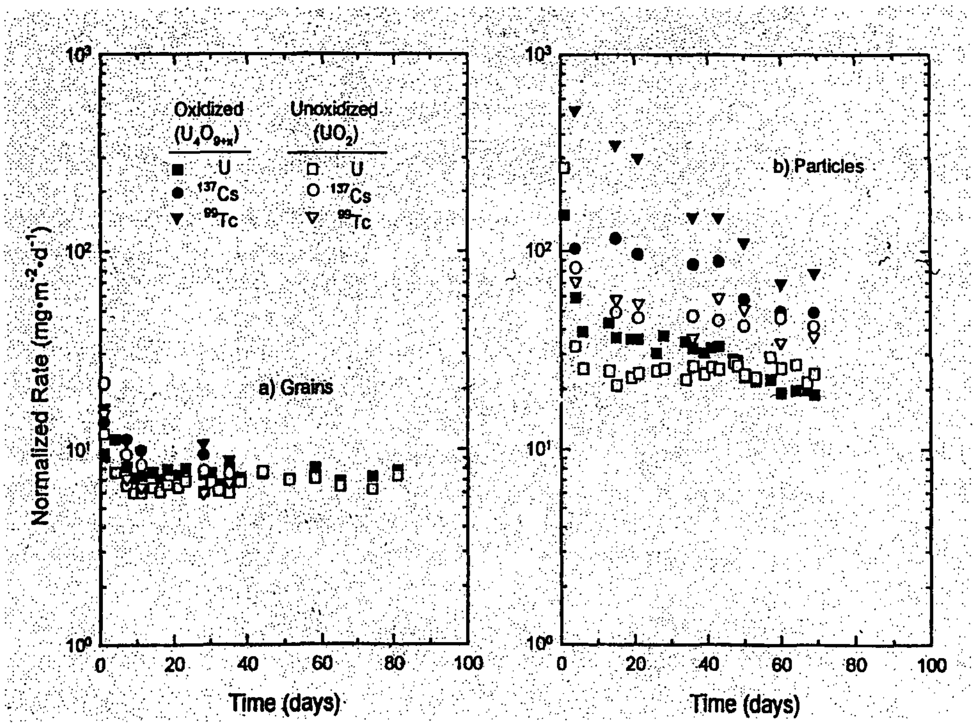
2.2.1 Pre-Oxidation/Hydration

Higher uranium oxides ($UO_{2.4}$ or U_3O_8) that form by oxidization of the uranium matirx dissolve at a rate similar to the unoxidized UO_2 matrix. Hydrated $UO_3\,xH_2O$ (x = 0.8, 2) dissolves 10-20 times faster than unhydrated oxides [TRW, 1997; Casas, et al., 1993]. However, the rate of hydration (i.e., the formation rate of $UO_3\,xH_2O$) is slower than the aqueous dissolution rate [Finn, et al., 1998, 1996].

Tc-99 is used as a dissolution marker (including Tc-99 bounded in an ε-phase particle) because Tc-99 has high solubility and does not precipitate back to CSNF. Also, Tc-99 dissolves oxidatively in the higher ionic valence state, regardless of the pre-oxidation. These two characteristics show that Tc-99 is a good marker for the dissolution. Although $UO_{2.4}$ dissolves similarly to UO_2 per unit surface area, $UO_{2.4}$ tends to have more grain boundaries (i.e., greater surface area) in flow-through tests. This increases the release rate by a factor of ~10 in a solution at 25 °C [77 °F] with 2×10^{-2} M total carbonate concentration and at pH of 8 (Figure 3). No such increase was observed in 2×10^{-3} M of total carbonate concentration at pH of 9 and temperature of 50 °C [122 °F] [Gray, 1997]. Tests at 50 °C [122 °F] could have alteration products that prevent grain boundary opening. Unlike flow-through tests at 25 °C [77 °F], it is generally understood that grain boundary openings are masked with alteration products in drip or immersion tests. U_3O_8 or $UO_3\,xH_2O$ tends to become sub-grain-sized powder, increasing the exposed surface area by as much as 2 to 3 orders of magnitude, compared to the geometric surface area of the CSNF pellet fragments. In addition to $UO_3\,xH_2O$ formation on the surface, extended vapor hydration or aqueous dissolution may weaken the grain boundaries by deeper preferential attacks along grain boundaries. Under the conditions of $UO_{2.4}$ formation or hydration, mechanical impact such as seismically initiated mechanical impact would result in powdering of the matrices into grains. With the current WP design being considered for the potential YM repository, dry oxidation or hydration of CSNF could occur prior to the dissolution in initially failed WP soon after the repository closure when the temperature peaks, especially if drift degradation would occur. There is a limited likelihood that the WP temperature would exceed 250 °C [482 °F] [Manepally, et al., 2003], which is necessary for U_3O_8 to form. $UO_{2.4}$ is likely to form below 250 °C [482 °F] during the early period in an initially failed WP. Typically, $UO_{2.4}$ would form at relative humidity (RH) less than ~ 50, above which hydration would occur [Ahn, 1996].

Grain boundary attacks by hydration and aqueous dissolution would occur up to a depth of 20-30 grains [Finch, et al., 1999]. However, mechanical impacts depending on the magnitude of the event such as seismicity can break the fragment into grains. In PA, the large exposed surface area caused by oxidation or hydration may be exercised by sensitivity analyses, observing changes in the peak expected dose with respect to a base case.

Figure 3. Dissolution Rates of ATM-105 Spent Fuel in 2 x 10^{-3} M $NaHCO_3/Na_2CO_3$, pH = 9, O2 = 0.2 atm, 50°C [Gray and Wilson, 1995]



2.2.2 Grain-Boundary Effects

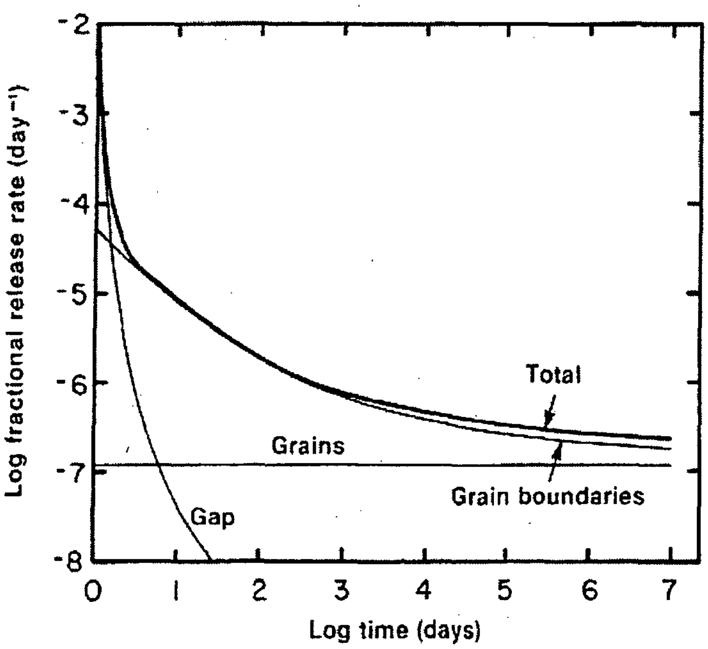
In the current U. S. Department of Energy (DOE) [OCRWM, 2006; Bechtel SAIC Company, 2004] or NRC [Mohanty, et al., 2004] performance assessment models, the release of RN from its inventory at grain boundaries is conservatively assumed to be instantaneous. Because most measured RN releases include grain boundary inventory, it is necessary to determine the dissolution rate of the matrix alone to be used in long-term PA. With unirradiated UO_2, the true matrix dissolution rates are obtained by the uranium mass dissolved in flow-through test. In CSNF tests, powdered grains are used from which the grain boundary inventories are removed by pre-washing. Tests with fragments under all conditions of immersion, drip, or flow-through tests appear to measure a substantial amount of grain boundary RN inventory in determining the measured (i.e., apparent) dissolution rates, which are based on the release of Tc-99, I-129, Cs-137, or Sr-90 as markers for the matrix dissolution. A significant portion of the released RN could be from grain boundaries.[1] The true matrix dissolution could be lower, compared to CSNF fragments, by at least an order of magnitude. This was indicated in the flow-through tests of unirradiated UO_2 grains, with/without addition of calcium/silica ions [Gray and Wilson, 1995; Gray, 1992; Wilson and Gray, 1990]. Unirradiated UO_2 grains do not contain RN in the matrix or grain boundaries. The true matrix dissolution rates partly support the lower end of the distribution of the CSNF dissolution rates in PA.

Although the initial instant RN release from grain boundaries of several-grain depths could be excluded in determining the long-term dissolution rate, further continuous inward penetration of groundwater along grain boundaries could possibly release the grain boundary inventory continuously. The grain boundary inventory could be greater by 2 percent, as shown in the footnote 1. Some evidence is shown in Figure 3, where grain tests showed no discrepancy between RN release and uranium dissolution. However, fragment tests always show higher release rates (note the release in log scale) of RN, compared to uranium. These fragments were supposed not to have grain-boundary contributions, because the samples were tested after initial immersion tests during which time most grain boundary RN were considered released. Johnson, et al. (1985) assessed the dominance of the grain-boundary inventory by a factor of 2-10, in the observed RN releases, from the data of immersion tests longer than 8 years, in the Canadian repository system tests (Figure 4). Also, flow-through tests resulted in more RN release than immersion or drip tests. Flow-through tests are expected to have more aqueous penetration into grain boundaries. It is difficult to verify the true matrix dissolution rates from the micrographs of the altered layer of the fragments after dissolution tests. Determining a statistically averaged thickness of the altered layer over the entire sample requires an inordinate amount of time for the test and analysis.

---

[1] This is based on the calculation of the surface area associated with grain boundaries attacked during aqueous dissolution. For fragment size ~ 1 millimeter (mm) [0.04 in.], grain size ~ 10 micrometer (μm) [$4x10^{-4}$in.], and an average 5-grain penetration (a maximum 20 - 30), ~ 15 percent of the total surface area of grain boundaries are attacked. Assuming a grain- boundary RN inventory ~ 2 percent (0.3 - 26.8 percent [Poinssot, 2001; Bechtel SAIC Company, 2004]) as an example in a linear scale, the grain boundary contribution will be ~ 0.3 percent of the total RN inventory, from 15 percent of grain-boundary surfaces. In the drip tests, at an average 10^{-6}/day fractional release [OCRWM, 2003] the RN release from the matrix for 8.5 years would be 0.3 percent.

Figure 4. Schematic of Three Stages in Fission Product Release from Used Fuel [L. H. Johnson, N. C. Garisto and S. Stroess-Gascoyne, Used-Fuel Dissolution Studies in Canada, Waste Management '85, Waste Isolation in the U.S., Vol. 1, Waste Policies and Programs, High-Level Waste, Edited by Roy G. Post, Tucson, Arizona, March 24 - 28, 1985, Reprinted with Permission of Waste Management Symposia, Inc.]



2.3 Groundwater Contact Modes for CSNF

For groundwater to contact CSNF, the DS, the WP, and the cladding must fail. Depending on the failure modes of these components and the flow rate of groundwater, the groundwater contact modes for CSNF will vary. It is recognized that the immersion versus drip condition, the groundwater flow rate, and partial protection by failed cladding could significantly influence the CSNF dissolution rate.

2.3.1 Immersion versus Drip, and Flow Rate

The WP failure will form perforations and cracks on the WP surface. Depending on the location of the perforations or cracks, CSNF would be subject to immersion in groundwater or drips of groundwater.[2]

To provide a basis for models developed for representing the CSNF dissolution rate over a long period of time, the experiments conducted to date can be divided into two broad categories - immersion tests and drip tests. Immersion tests have been conducted in a variety of groundwater chemistries from different locales [Wilson, 1990; Forsyth, 1997], because most candidate repositories are saturated with groundwater. However, drip tests are unique to the U.S. YM Project, where only a small volume of groundwater is expected to drip in an unsaturated repository. Nevertheless, immersion tests are relevant to the U.S. YM Project too, because dripping groundwater could accumulate in a failed WP. The drip tests were mainly conducted at Argonne National Laboratory (ANL) [Bechtel SAIC Company, 2004], To understand mechanistically the results of immersion tests and drip tests, auxiliary flow-through tests are also used as laboratory-controlled (rather than repository-relevant) tests. Flow-through tests were designed to determine the true (i.e., intrinsic) dissolution rates on the surface of the CSNF, with an unlimited supply of reacting solutions. High flow rates were used, artificially, to remove any alteration-product deposits blocking the reacting surface.

Current ANL drip tests involve drips from 0.075 mL [$4.6\text{x}10^{-3}$ in.^{3}]/3.5 days to 0.75 mL [$4.6\text{x}10^{-2}$ in.^{3}]/3.5 days, over about 10 CSNF individual fragments, with each fragment 7.0 - 8.5 g [$(1.5 - 1.9)\text{x}10^{-2}$ lb] [Finn, et al., 1998]. Considering the initial geometric surface area of each fragment as ~ 2.1 cm^2/g [148 in.^{2}/lb] [Wilson, 1990] the drip rates per fragment area would be $1.3 \text{ x } (10^{-3}-10^{-2})$ mL/cm^2-day [$5.1\text{x}(10^{-4}-10^{-3})$ in.^{3}/in.^{2}-day].[3] On the other hand, the potential repository flow rate per unit CSNF surface area would be ~ $1.7 \text{ x } 10^{-4}$ mL/cm^2-day [$6.7\text{x}10^{-5}$ in.^{3}/in.^{2}-day] under conservative focused flow scenarios.[3] This is an order-of-magnitude lower value than the laboratory conditions. ANL data show several orders of magnitude decrease in the RN release rates when the drip rates are lowered by an order of magnitude, 0.75 mL [$4.6\text{x}10^{-2}$ in.^{3}] to 0.075 mL [$4.6\text{x}10^{-3}$ in.^{3}] for 3.5 days, as shown in Figure 6. This suggests that the RN release rates under the repository conditions would be even lower because the flow rates would be lower than even the lowest value of the ANL laboratory test drip rates. These lower CSNF dissolution rates partly support the lower end of the distribution of the CSNF dissolution rates in PA .

---

[2] NRC PA [Mohanty, et al., 2004] models the groundwater entry perforation on the WP crown and the groundwater exit perforation located at any place between the bottom and the crown of the WP. The distance between the entry and the exit is randomly sampled. A schematic of the process is in Figure 5.

[3] Under DOE's design for a potential repository, one WP would have 21 Pressurized Water Reactor (PWR) assemblies. Each assembly would have 264 rods of ~ 1.1 cm [0.43 in.] diameter and ~ 400 cm [157 in.] length. Considering an approximate average size of an individual CSNF pellet as ~ 0.2 cm × 0.2 cm × 0.2 cm [0.08 in. x 0.08 in. x 0.08 in.], one WP would have ~ 2.4×10^8 cm^2 [$3.7 \text{ x } 10^7$ in.^{2}] surface area. The modeled flow rate of groundwater is (1.5 - 150 L/year [$9.2 \text{ x } (10 - 10^3)$ in.^{3}/year [NRC, 2002]. Focused flow on a conservative basis would go up to 1.5×10^4 L/year [$9.2 \text{ x } 10^5$ in.^{3}/year] [Lin, 2003]. In the presence of focused flow, dry area without CSNF dissolution will be also present.

Figure 5. Schematic of Bathtub Model with Incoming and Outgoing Water Conduits [Mohanty et al., 2002]

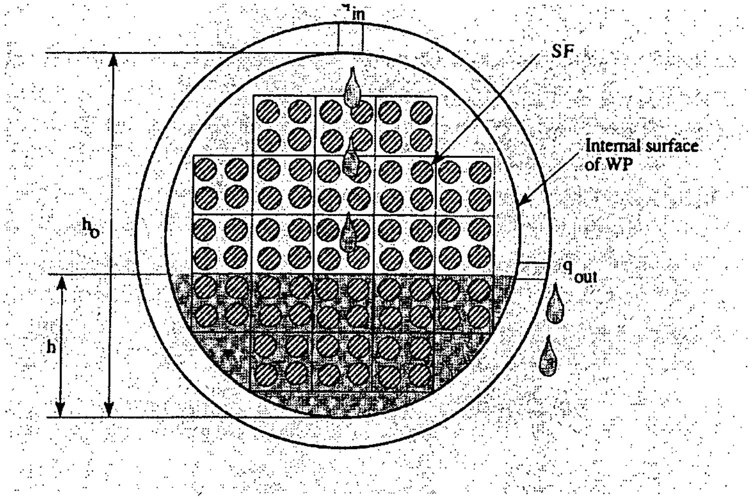
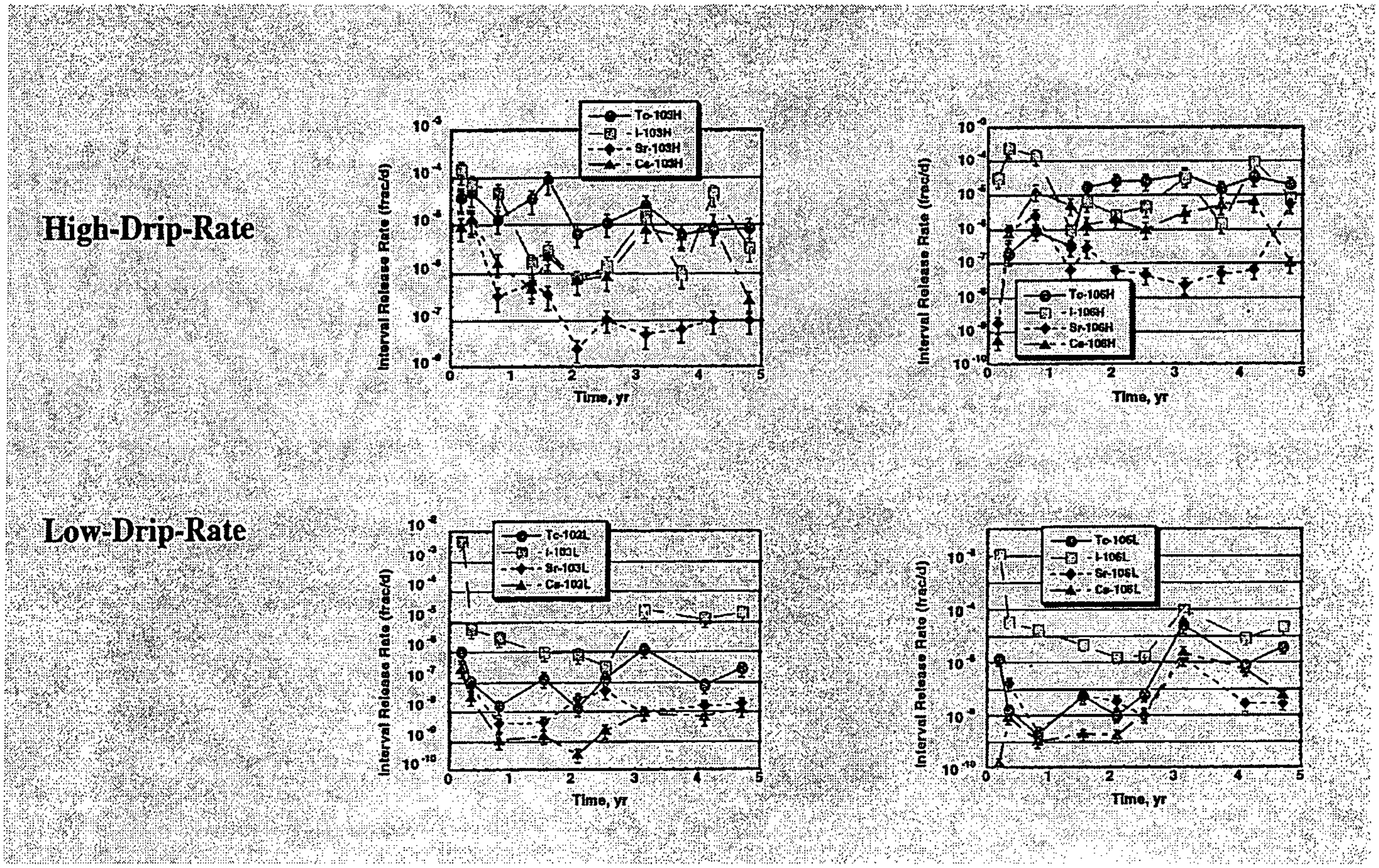


Table 1 includes relevant CSNF dissolution rates under different water contact modes. The water contact mode can be categorized as: (I) immersion; or (ii) dripping, of groundwater containing calcium/silica, expected at the potential YM repository. The data for drip contact were obtained at the higher drip rates (i.e., 0.75 mL [4.6×10^{-2} in.^{3}]/3.5 days). Immersion tests show lower dissolution rates than high-drip rate tests in J-13 well water. Data from the auxiliary flow-through tests were included to determine the true dissolution rates of bare CSNF by high-flow, eliminating deposits of alteration products.

Figure 6. CSNF Drip Test Results of ANL with J-13 Well at 90°C [high-drip-rate: 0.75 mL, low-drip-rate: 0.075 mL, for 3.5 days, Cunnane, 1999]



2.3.2 Partial Cladding Protection

In the presence of partial protection from failed cladding, the dissolution rate decreases significantly. Wilson [1990] conducted tests with slit (~0.015 cm [5.9×10^{-3} in.] diameter x ~ 2.54 cm [1 in.] length)- or hole (~ 0.02 cm [7.9×10^{-3} in.] diameter)-defected CSNF under immersion conditions in J-13 well water at 85 °C [185 °F]. The tests were intended to simulate cladding partially failed by localized corrosion or SCC. The RN release rates decreased by a factor of ~140 for Tc-99, ~7×10^{5} for I-129, and ~ 65 for Sr-90 [Wilson, 1990], compared to bare CSNF. Later ANL tests, with partially clad rod segments under drip conditions, also showed decreased Tc-99 release rates, to 2.6×10^{-8} f/d (~ 0.04 mg/m^2-d [5.7×10^{-11} lb/in.^{3}-d]) [OCRWM, 2003]. Such decreases in dissolution rates, compared to bare CSNF, partly support the lower end of the distribution of the CSNF dissolution rates in PA.

However, in the segment tests of clad CSNF for light-water reactor CSNF immersed in Swedish Allard groundwater, the RN release rates did not decrease, compared to bare CSNF [Forsyth, 1997; Forsyth and Wermer, 1985]. In these tests, nearly half of the surface area was exposed. Similar conclusions can be drawn from tests with Canadian Deuterium-Natural Uranium Reactor CSNF, immersed in Canadian granitic groundwater [Stroes-Gascoyne, 1985]. These results suggest that cladding would not inhibit the dissolution rates if it fails catastrophically exposing a substantial surface area to the solution. In the most likely scenario, the unzipping is likely to occur in slit- or hole-defected cladding. Unzipping was observed in the ANL 1.5-year long tests, caused by stress generated by corrosion-product accumulation in the gap of cladding and the matrix from uniform corrosion of Zircaloy cladding at 175 °C [347 °F] [Bechtel SAIC Company, 2004]. The activation energy for Zircaloy uniform corrosion is large, ~93 k./mol [22 kcal/mol] [Wescott, 1995]. Thus, at lower repository temperatures, uniform corrosion would not be fast enough to build enough stress for cladding to unzip from the corrosion products. Below 100 °C [212 °F], estimated unzipping times based on this activation energy may exceed 10,000 years. Localized corrosion is likely to occur only at very low pH (less than 3) and temperatures below 95 °C [203 °F] [Brossia, 2002], which is needed to stabilize oxidants such as ferric ions. Such low pH conditions would occur with very low probabilities. In fact, in long-term CSNF storage facilities, cladding damage such as unzipping has not been identified even after 8 years, although inerting the environment inside the storage container may be contributing to cladding integrity [Wasywich and Frost, 1992].

3. Conceptual Models for CSNF Dissolution

The rate of RN transfer from CSNF into water in the WP is modeled as a function of the flow rate of water containing CSNF, the composition of water contacting CSNF, and the element solubility in that water. Fission- and activation-product RNs normally have high-solubility limits that do not limit the release of these RN from a WP. These RN include Tc-99, I-129, Cs-135, C-14, and Cl-36. Np-237 also may belong to this category of RN, depending on the chemistry and the flow rate of water in contact with CSNF. These RN are considered to be released congruently with the dissolving CSNF matrix in contact with groundwater. Np-237 at low flow rates and other actinides such Pu-(239+240) are considered to be released by solubility limits and groundwater flow rates, after the continuous matrix dissolution and its subsequent precipitation back. Gray and Wilson (1995) determined the dissolution rate of the CSNF matrix from flow-through tests. The flow-through tests use artificially high flow rates to eliminate the precipitation of alteration phases on the CSNF surface. Alteration phases may modify the dissolution rate of the CSNF matrix by altering the area of the reactive surface, or may otherwise affect radionuclide release by solubility limits of alteration phases/co-precipitation.

3.1 Specific Dissolution Models[4]

Two models are presented below for PA. The first model, referred to as Model 1, estimates the CSNF dissolution rates in solutions containing pure carbonate anions, which are conservative values. The pure carbonate solution is representative of altered in-package groundwaters. Model 1 was obtained from the DOE's CSNF dissolution model for Total System Performance Assessment [Gray and Wilson, 1995]. The CSNF dissolution rate in this model is a function of temperature, pH, total carbonate concentration, and oxygen fugacity. Gray and Wilson (1995) express this model as:

$$\begin{aligned}\log r &= 9.310 + 0.142 \log \left[\mathrm{CO}_3^{2-}\right] \\ &-16.7 \log \left(p_{\mathrm{O}_2}\right) + 0.140 \log \left[\mathrm{H}^+\right] - \frac{2130}{T} + 6.81 \log \left[T\right] \log \left(p_{\mathrm{O}_2}\right)\end{aligned} \tag{1}$$

where r is the dissolution rate [mg m^{-2} d^{-1}] [1.42 x 10^{-9} lb/in.^{3}-d], $\left[\mathrm{CO}_3^{2-}\right]$ is the total carbonate concentration [M], [Po_2] is the oxygen partial pressure [atm] [1 atm = 101 kPa], $\left[\mathrm{H}^+\right]$ is the concentration of hydrogen ions [M], and T is the temperature [K]. The second model (Model 2) is derived from the assessments presented previously in this report. In Model 2, the CSNF dissolution rate, r (mg/m^2-d) is represented by:

$$r = r_0 \exp\left[-\frac{E_a}{RT}\right] \tag{2}$$

---

[4] The models presented here are based on an NRC's PA (Mohanty, et al., 2002). Recently, updated formulae are being used, although the modifications are minor.

where E_a is the activation energy, 29 k./mol [7 kcal/mol], from immersion tests and r_o is the pre-exponential coefficient that varies between 1.2 x (10^3 - 10^6) mg/m^2-d [1.7 x (10^{-6} - 10^{-3}) lb/in.^{3}-d]. These values were selected to simulate the dissolution rates in the range 0.01 - 10 mg/m^2-d [1.4 x (10^{-11} - 10^{-8}) lb/in.^{3}-d] at room temperatures and in mineral waters extending to low pH. They are extracted from Table 1, considering cation effects, low pH effects, iron effects, the effects of grain boundary inventory, the effects of low-drip rates, and partial protection by failed cladding. In PA, r_o values have a log-uniform distribution and is sampled randomly.

3.2 CSNF Surface Area

Two models for determining the surface area are available in PA. The first model determines surface area, using fragmented pellets (i.e., particles), and the second model uses grain-size criteria. The particle model assumes that CSNF in a WP is fragmented into small spherical particles (~1 mm [0.04 in.] diameter), and the intergranular porosity does not contribute to the surface area. The total surface area for the particle model is then computed as:

$$A_p = \left(\frac{M_{SF}}{M_p} \times 4\pi\, r_{po}^2 \right) f_{\mathrm{wet}} \tag{3}$$

where $M_p = \frac{4}{3}\pi r_{po}^3\, \rho_{go}$ is particle mass [kg] [1 lb = 0.4536 kg], A_p is the particle surface area [m^2] [1 m = 39.4 in.], M_{SF} is the CSNF inventory/WP [kg], r_{po} is the particle radius [m], ρ_{go} is the density of oxidized CSNF [kg m^{-3}], and f_{wet} is the volume fraction of CSNF immersed in the WP water.

If subgranular fragmentation takes place through conversion from UO_2 to $UO_{2.4}$ and U_3O_8, a smaller particle size (i.e., equivalent) can be considered in the particle model, to represent additional exposed surface area. In the case of the second model, in which grains are exposed, the following expression is used to compute the total surface area:

$$A_g = 4x10^{-12}\pi \left(\frac{M_{SF}}{M_p} \right) \left[\left(r_g - w \right)^2 + \frac{3}{r_g} \left(3r_g^2 w - 3r_g w^2 + w^3 \right) \right] f_{\mathrm{wet}} \tag{4}$$

where A_g is the grain surface area [m^2], r_g is the grain radius [μm], and w is the width of the oxidized zone [μm].

The surface area available for dissolution is conservatively held constant throughout the dissolution period, even though the radius of the unoxidized grains or particles would decrease with time. This simplification is most likely to make a difference to peak dose. In addition, preferential attacks of grain boundaries in the particles were not considered, since the effect could be masked by the presence of alteration phases under the potential repository conditions of low flow rates.

3.3 Treatment of Uncertainty

Table 2 shows parameter values and ranges used in the models 1 and 2 for dissolution rate and surface area. Most parameters are assigned constant values, except three: (1) initial radius of UO_2 particle [normal distribution]; (2) subgrain fragment radius of UO_2 particle after transgranular fracture [normal distribution]; and (3) pre-exponential factor for CSNF dissolution rate from [log-uniform distribution]. Other parameters are fixed at constant values either because these are better determined (i.e., less uncertainty) or the model output is less sensitive to uncertainty.

Table 2. Parameter values selected for the TPA code based on literature survey (Mohanty et al., 2002)

Parameter Description	Distribution and Range	Rationale
Spent fuel density (kg/m^3)	Constant 10,600	Wilson (1990); based on UO_2
Oxygen partial pressure (over pressure) (atm)	Constant 0.21	Assumed in Mohanty, et al. (1996). Sensitivity Analysis indicates high sensitivity. Continue evaluating. Based on atmospheric composition. Stockman (1997).
Negative $\log_{10}$ of carbonate concentration in surrounding water (M)	Constant 3.71	Revised value that accounts for reinterpretation of literature data. Previous MULTIFLO runs based on only $[CO_3^{-2}]$; new MULTIFLO runs based on the total carbonate concentration.
Initial radius of UO_2 particle (m)	Normal 7.0×10^{-4}, 3.0×10^{-3}	Guenther, et al. (1991); Belle (1961). Sensitivity Analysis indicates high sensitivity. Continue evaluating.
Radius of UO_2 grain (m)	Constant 1.25×10^{-5}	Einziger, et al. (1992); Belle (1961). Sensitivity Analysis indicates low sensitivity.
Cladding correction factor	Constant 1.0	A factor that describes the fraction of cladding protection lost. Assumes no cladding protection when the factor is 1.0.
Subgrain fragment radius of UO_2 particle after transgranular fracture (m);	Normal 5.0×10^{-7} 2.0×10^{-6}	Used only if fuel conversion takes place from UO_2 to $UO_{2.4}$ and U_3O_8; used only by the CSNF dissolution models that are dependent on exposed surface area. Mohanty, et al. (2002). Distribution based on distribution of grains or particles. Sensitivity Analysis indicates high sensitivity. Continue evaluating.
Pre-exponential factor for spent fuel dissolution rate from (mg $^{-2}$ d^{-1})	Log-uniform 1.2×10^{3}, 1.2×10^{6}	See the text and Table 1.

English conversion in the text

4. System-Level Sensitivity Analysis

The sensitivity of the CSNF dissolution rates in PA was exercised to illustrate the influence of the dissolution rate on the peak expected dose, which is the system-level performance metric. Sensitivity was studied by observing changes to the peak expected dose with respect to a base case. The details and results of an example exercise are given in Mohanty, et al [2004]. For example, dissolution models 1 and 2 were exercised to see the effects of various factors involved on the dose. Similarly, the two models of surface area were exercised to see the effects of particles and grains on the dose. Finally, various potentially possible distributions of the parameter values were also exercised to see the sensitivity of the choice on the dose.

5. Summary

The literature survey and independent analysis of CSNF dissolution kinetics relevant to the potential YM repository provide several key understandings. Presence of calcium and silica cations could decrease the CSNF dissolution rates more than an order of magnitude. Low pH, near 3, increase the CSNF dissolution rates by as much as a factor of 20. Iron components could form reducing environments, which reduce the CSNF dissolution rates by more than an order of magnitude. Dry oxidation and hydration in the early period for initially failed WPs may occur with limited likelihood. These processes could increase the effective surface area by a factor of 10-1000. The radionuclide release from the grain boundary and gap inventory appears to be substantial and the true matrix dissolution rates could be lower than the apparent dissolution rates by as much as an order of magnitude. Both immersion and drips are possible groundwater contact modes with CSNF. Drip tests were conducted at drip rates much higher than the repository conditions. The CSNF dissolution rates at lower drip rates could be lower by more than an order of magnitude. Partial protection by failed cladding could decrease the CSNF dissolution rates more than 50 times. Based on these key observations, models and parameters for the CSNF dissolution rates are presented for use in PA. Two models for representing the CSNF surface area are also presented. Finally, some independent PA exercises for system-level sensitivity are introduced to illustrate the influence of the dissolution rate on the dose.

6. References

T. Ahn, Dry Oxidation and Fracture of LWR Spent-Fuels, NUREG-1566, U. S. Nuclear Regulatory Commission, Washington, D. C., 1996

J. Belle. ed., Uranium Dioxide: Properties and Nuclear Applications, Washington, D.C., U.S. Atomic Energy Commission, 1961

Bechtel SAIC Company, LLC, CSNF Waste Form Degradation: Summary Abstraction, ANL-EBS-MD-000015 REV 02, 2004

C. S. Brossia, G. A. Cragnolino and D. S. Dunn, Effect of Oxide Thickness on the Localized Corrosion of Zircaloy, CORROSION 2002, Paper No. 02549, NACE, 2002

I. Casas, E. Cera and J. Bruno, Kinetic Studies of Natural Uranium Minerals for the Long-Term Evolution of Spent Nuclear Fuel under Oxidizing Conditions, Mat. Res. Soc. Symp. Proc., Vol. 294, p. 521 - 526, 1993

J. Cunnane, Commercial Spent Fuel Tests at ANL, Yucca Mountain Project, Argonne National Laboratory, CLST Appendix 7 Meeting, OCRWM, 1999

R. E. Einziger, L. E. Thomas, H. C. Buchanan, and R. B. Stout, Oxidation of Spent Fuel in Air at 175 to 195 °C, J. of Nuclear Materials, Vol. 190, p. 53 - 60, 1992

C. Ferry, P. Lovera, C. Poinssot and P. Garcia, Enhanced Diffusion under Alpha Self-irradiation in Spent Nuclear Fuel: Theoretical Approaches, J. Of Nuclear Materials, Vol. 346, p. 48 - 55, 2005a

C. Ferry, C. Poinssot, V. Broudic, C. Cappelaere, L. Desgranges, P. Garcia, C. Jegou, P. Lovera, P. Marimbeau, J.-P. Piron, A. Poulesquen, D. Roudil, J.-M. Gras and P. Bouffioux, Synthesis on the Spent Fuel Long Term Evolution, CEA-R-6084, CEA Saclay, France, 2005b

P. A. Finn, Y. Tsai and J. C. Cunnane, Corrosion Tests of LWR Fuels - Nuclide Release, Mat. Res. Soc. Symp. Proc., Vol. 713, p. 607 - 614, 2002

P. A. Finn, R. Finch, E. Buck and J. Bates, Corrosion Mechanisms of Spent Fuel under Oxidizing Conditions, Mat. Res. Soc. Symp. Proc. Vol. 506, p. 123 - 131, 1998

P. A. Finn, J. C. Hoh, S. F. Wolf, S. A. Slater and J. K. Bates, The Release of Cesium and the Actinides from Spent Fuel under Unsaturated Conditions, Mat. Res. Soc. Symp. Proc. Vol. 412, p. 75 - 81, 1996

R. J. Finch, E. C. Buck, P. A. Finn and J. K. Bates, Oxidative Corrosion of Spent UO_2 Fuel in Vapor and Dripping Groundwater at 90 °C, Mat. Res. Soc. Symp. Proc. Vol. 556, p.431, 1999

R. Forsyth, An Evaluation of Results from the Experimental Programme Performed in the Studsvik Hot Cell Laboratory, SKB TR 97-25, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden, 1997

R. S. Forsyth and L. O. Werme, The Corrosion of Spent UO_2 Fuel in Synthetic Groundwater, Mat. Res. Soc. Symp., Vol. 50, p. 327 - 336, 1985

B. Grambow, A. Loida, A. Martinez-Esparza, P. Díaz-Arocas, J. de Pablo, J.-L. Paul, G. Marx, J.-P. Glatz, K. Lemmens, K. Ollila and H. Christensen, Source Term for Performance Assessment of Spent Fuel as a Waste Form, EUR 19140EN, European Commission, Nuclear Science Technology, 2000

W. J. Gray, Flowthrough Dissolution Testing of LWR Spent Fuel, Workshop on Significant Issues and Available Data, Waste Form Degradation and Radionuclide Mobilization, Expert Elicitation Project, San Francisco, California, November 18 - 19, 1997

W. J. Gray, Dissolution Testings of Spent Fuel, Presentation to Nuclear Waste Technical Review Board Meetings, Pacific Northwest Laboratory, October 14 - 16, Las Vegas, NV, 1992

W. J. Gray and C. N. Wilson, Spent Fuel Dissolution Studies FY 1991 to 1994, PNL-10540, Pacific Northwest National Laboratory, Richland, Washington, 1995

R. J. Guenther, D. E. Blahnik, U. P. Jenquin, J. E. Mendel, L. E. Thomas, and C. K. Thornhill, Characterization of Spent Fuel Approved Testing Material-ATM-104, PNL-5109-104, Richland, WA, Pacific Northwest National Laboratory, 1991

C. Jégou, B. Muzeau, V. Broudic, S. Peuget, A. Poulesquen, D. Roudil and C. Corbel, Effect of External Gamma Irradiation on Dissolution of the Spent UO_2 Fuel Matrix, J. of Nuclear Materials, Vol. 341, p. 62 -82, 2005

C. Jégou, S. Peuget, V. Broudic, D. Roudil, X. Deschanels, and J. M. Bart, Identification of the Mechanism Limiting the Alteration of Clad Spent Fuel Segments in Aerated Carbonate Groundwater, J. of Nuclear Materials, Vol. 326, p. 144 - 155, 2004

C. Jégou, S. Peuget, J. F. Lucchini, C. Corbel, V. Broudic, and J. M. Bart, Effect of Spent Fuel Burnup and Compositions and Alteration of the $U(Pu)O_2$ Matrix, Mat. Res. Soc. Symp., Vol. 663, p. 399 - 408, 2001

L. H. Johnson, N. C. Garisto and S. Stroess-Gascoyne, Used-Fuel Dissolution Studies in Canada, Waste Management '85, edited by R. G. Post and M. E. Wacks, p. 479 - 482, Tucson, Arizona, 1985

C. Lin, B. Leslie, R. Codell, H. Arlt and T. Ahn, Potential Importance of Fluoride to Performance of the Drip Shield, Proceedings of 10th International High-Level Radioactive Waste Management Conference, Las Vegas, Nevada, March 30 - April 3, Published on CD-ROM, American Nuclear Society, 2003

C. Manepally, R. Fedors, G. Adams, and S. Green, Effects of Drift Degradation on Environmental Conditions in Drifts, Eos Transactions, Vol. 84 (46) Fall Meeting Supplement, Abstract H21D-0836, American Geophysical Union 2003 Fall Meeting, San Francisco, CA, December 8 - 12, 2003

S. Mohanty, R. Codell, J. M. Menchaca, R. Janetzke, M. Smith, P. LaPlante, M. Rahimi, and A. Lozano, System-Level Performance Assessment of the Proposed Repository at Yucca Mountain Using the TPA Version 4.1 Code, CNWRA 2002-05, Revision 2, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, 2004

S. Mohanty, T. J. McCartin, and D. W. Esh, Total-system Performance Assessment (TPA) Version 4.0 Code: Module Description and User's Guide, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, 2002

S. Mohanty, G. A. Cragnolino, T. Ahn, D. S. Dunn, P. C. Lichtner, R. D. Manteufel, and N. Sridhar, Engineered Barrier System Performance Assessment Code: EBSPAC Version 1.0 ß, Technical Description and User's manual, CNWRA 96-001, San Antonio, TX, Center for Nuclear Waste Regulatory Analyses, 1996

OCRWM, DOE/NRC Technical Exchange on Total System Performance Assessment (TSPA) for Yucca Mountain, Abstraction of Waste Package and Drip Shield Degradation, D. Stahl, Las Vegas, NV, 2006

OCRWM, CSNF Waste Form Degradation: Summary Abstraction, ANL-EBS-MD-000015, Revision 01, 2003

V. M. Oversby and VMO Konsult, Uranium Dioxide, SIMFUEL, and Spent Fuel Dissolution Rates - A Review of Published Data, TR-99-22, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden, 1999

C. Poinssot, C. Ferry, P. Lovera, C. Jegou and L.-M. Gras, Spent Fuel Radionuclide Source Term Model for Assessing Spent Fuel Performance in Geological Disposal. Part II: Matrix Alteration Model and Global Performance, J. of Nuclear Materials, Vol. 346, p. 66 -77, 2005

C. Poinssot, Ed., Synthesis on the Long Term Behavior of the Spent Nuclear Fuel, Vol. 1, CEA-R-5958 (E), CEA Saclay, France, 2001

J. Quiñones, J. A. Serrano, P. P. Díaz Arocas, J. L. Rodríguez Almazà, J. Cobos, J. A. Esteban and A. Martínez-Esparza, Influence of Container Base Material (Fe), Mat. Res. Soc. Symp. Proc. Vol. 663, p. 435 - 439, 2001

S. Röllin, K. Spahiu and U.-B. Eklund, Determination of Dissolution Rates of Spent Fuel in Carbonate Solutions under Different Redox Conditions with a Flow-through Experiment, J. of Nuclear Materials, Vol. 297, p. 231 - 243, 2001

D. W. Shoesmith, Fuel Corrosion Processes under Waste Disposal Conditions, J. of Nuclear Materials, Vol. 282, p. 1 - 31, 2000

C. Stockman, Discussion in the Presentation of the Near-field Environment in the Total System Performance Assessment: Waste Form Degradation Expert Elicitation, Workshop of Significance Issues and Available Data: Waste Form Degradation and Radionuclide Mobilization Expert Elicitation (WFEE) Project San Francisco, California, Alburquerque, NM, Sandia National Laboratories, 1997

S. Stroes-Gascoyne, L. H. Johnson, P. A. Beeley and D. M. Sellinger, Dissolution of Used CANDU Fuel at Various Temperatures and Redox Conditions, Mat. Res. Soc. Symp. Proc., Vol. 50, p. 317 - 326, 1985

J. C. Tait and J. L. Luht, Dissolution Rates of Uranium from Unirradiated UO_2 and Uranium and Radionuclides from Used CANDU Fuel Using the Single-Pass Flow-Through Apparatus, 06819-REP-01200-0006 R00, Atomic Energy of Canada Ltd., Whiteshell Laboratories, 1997

G. F. Thomas and G. Till, The Dissolution of Unirradiated UO_2 Fuel Pellets under Simulated Disposal Conditions, Nuclear and Chemical Waste Management, Vol. 5, p. 141 - 147, 1984

M. E. Torrero, E. Baraj, J. De Pablo, J. Giménez and I. Casas, Kinetics of Corrosion and Dissolution of Uranium Dioxide as a Function of pH, Int. J. Chemical Kinetics, Vol. 29, p. 261 - 267, 1997

TRW Environmental Safety Systems Inc., Waste Form Characterization Report, edited by R. B. Stout and H. R. Leider, University of California, Lawrence Livermore National Laboratory, Livermore, CA, 1997

U. S. Nuclear Regulatory Commission, NRC, Integrated Issue Resolution Status Report, NUREG-1762, Washington, D. C., 2002

K. M. Wasywich and C. R. Frost, Behavior of Used CANDU Fuel Stored in 150 °C Moisture-Saturated Air, 3rd International High Level Radioactive Waste Management (IHLRWM) Conference, Las Vegas, NV, April 12 - 16, Proceedings of High Level Radioactive Waste Management, Vol. 1, La Grange Park, IL, American Nuclear Society, p. 1166 - 1173, 1992

R. G. Wescott, M. P. Lee, N. A. Eisenberg, T. J. McCartin, NRC Iterative Performance Assessment Phase 2, NUREG-1464, U. S. Nuclear Regulatory Commission, Washington, D. C., 1995

C. N. Wilson, Results from NNWSI Series 3 Spent Fuel Dissolution Tests, PNL-7170, Pacific Northwest Laboratory, Richland, Washington, 1990

C. N. Wilson and W. J. Gray, Measurement of Soluble Nuclide Dissolution Rates from Spent Fuel, Mat. Res. Soc. Symp. Proc., Vol. 176, p. 489 - 498, 1990

NRC FORM 335 U.S. NUCLEAR REGULATORY COMMISSION
(9-2004)
NRCMD 3.7

BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER
(Assigned by NRC, Add Vol., Supp., Rev., and Addendum Numbers, if any.)
NUREG-1914

2. TITLE AND SUBTITLE
Dissolution Kinetics of Commercial Spent Nuclear Fuels in the Potential Yucca Mountain Repository Environment

3. DATE REPORT PUBLISHED

MONTH	YEAR
October	2008

4. FIN OR GRANT NUMBER

5. AUTHOR(S)
T. M. Ahn and S. Mohanty

6. TYPE OF REPORT
Technical

7. PERIOD COVERED *(Inclusive Dates)*

8. PERFORMING ORGANIZATION - NAME AND ADDRESS *(If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)*

Division of High-Level Waste Repository Safety
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

9. SPONSORING ORGANIZATION - NAME AND ADDRESS *(If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)*

Same as above

10. SUPPLEMENTARY NOTES
T. M. Ahn, NRC Project Officer

11. ABSTRACT *(200 words or less)*

This report provides a summary of a literature survey and an independent analysis of relevant experimental data on the dissolution rate of commercial spent nuclear fuel (CSNF) for disposal at the potential high-level waste repository at Yucca Mountain, Nevada. This analysis was carried out to identify models and parameters for the CSNF dissolution rate, for use in performance assessment (PA) models. The survey and analysis focused on three key areas that potentially control the CSNF dissolution rate: (i) in-package water chemistry; (ii) CSNF conditions before aqueous dissolution; and (iii) the modes of groundwater contact with CSNF from the failure of the drip shield and the waste package components. Based on the key findings, two models and their parameters for the CSNF dissolution rates are presented to be used in PA. Two models and their parameters for determining the exposed CSNF surface area for water contact are also presented. These models and parameters are used for determining the rate of radionuclide transfer from CSNF into the contacting water in the WP. PA was conducted to assess the sensitivities of the identified models and parameter values, and the associated uncertainties in radionuclide release.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

commercial spent nuclear fuel
dissolution kinetics
radionuclide release
high level waste
literature survey and analysis
performance assessment
model

13. AVAILABILITY STATEMENT
unlimited

14. SECURITY CLASSIFICATION
(This Page)
unclassified
(This Report)
unclassified

15. NUMBER OF PAGES

16. PRICE

Printed
on recycled
paper

Federal Recycling Program