DISCLAIMER

This contractor document was prepared for the U.S. Department of Energy (DOE), but has not undergone programmatic, policy, or publication review, and is provided for information only. The document provides preliminary information that may change based on new information to be used specifically for Total System Performance Assessment analyses. The document is a preliminary lower-level contractor document and is not intended for publication or wide distribution.

Although this document has undergone technical reviews at the contractor organization, it has not undergone a DOE policy review. Therefore, the views and options of authors expressed may not state or reflect those of the DOE. However, in the interest of the rapid transfer of information, we are providing this document for your information per your request.

DMSS07
0/1 WM-11

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL COVER SHEET

1. QA: QA

Complete Only Applicable Items

2. ☐ Analysis — Check all that apply

Type of Analysis: ☐ Engineering ☐ Performance Assessment ☐ Scientific

Intended Use of Analysis: ☐ Input to Calculation ☐ Input to another Analysis or Model ☐ Input to Technical Document ☐ Input to other Technical Products

Describe use:

3. ☒ Model — Check all that apply

Type of Model: ☐ Conceptual Model ☒ Abstraction Model ☐ Mathematical Model ☐ System Model ☐ Process Model

Intended Use of Model: ☐ Input to Calculation ☒ Input to another Model or Analysis ☐ Input to Technical Document ☐ Input to other Technical Products

Describe use:
Provide Upper Limit, Conservative, and Best-Estimate models for the degradation of DSNF for use in TSPA.

4. Title:
DSNF and Other Waste Form Degradation Abstraction

5. Document Identifier (including Rev. No. and Change No., if applicable):
ANL-WIS-MD-000004 REV 01

6. Total Attachments:
N/A

7. Attachment Numbers - No. of Pages in Each:
N/A

	Printed Name	Signature	Date
8. Originator	Thomas A Thornton	TA Thornton	10/10/00
9. Checker	James C. Cunnane	Pampathi for JCC	10/10/00
10. Lead/Supervisor	Christine Stockman	Christine Stockman	10/10/00
11. Responsible Manager	V. Pasupathi	Pampathi	10/10/00

12. Remarks:

INFORMATION COPY

LAS VEGAS DOCUMENT CONTROL

ENCLOSURE

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT
ANALYSIS/MODEL REVISION RECORD

Complete Only Applicable Items

2. Analysis or Model Title:

DSNF and Other Waste Form Degradation Abstraction

3. Document Identifier (including Rev. No. and Change No., if applicable):

ANL-WIS-MD-000004 REV01

4. Revision/Change No.	5. Description of Revision/Change
REV 00	Initial Issue
REV 01	Extensive changes to model documentation. Clarify recommended model validation requirements, potential test work in support of model validation, and treatment of potential colloidal release forms. Reword assumptions concerning the dissolution kinetics of naval SNF to clarify that the CSNF dissolution model will bound the dissolution kinetics of the naval SNF. Revise immobilized Pu ceramic conservative degradation model. Revise HLW glass degradation model recommended for immobilized ceramic plutonium waste form to conform to that reported in ANL-EBS-MD-000016 REV00. Revise U-metal SNF degradation model to include results of National Spent Nuclear Fuel Program report on oxidation kinetics. Revise CSNF model recommended as representing naval SNF to conform to that finally given in ANL-EBS-MD-000015 REV00. Add (Section 6.4.3 and Table 3b) discussion of exposed surface areas for the various DSNF and immobilized Pu ceramic waste forms. Add discussion of the potential impact of unresolved TBVs in the Conclusions Section.

CONTENTS

Page

ACRONYMS 6

1. PURPOSE 7

2. QUALITY ASSURANCE 9

3. COMPUTER SOFTWARE AND MODEL USAGE 9

4. INPUTS 9
   - 4.1 DATA AND PARAMETERS 9
   - 4.2 CRITERIA 13
   - 4.3 CODES AND STANDARDS 13

5. ASSUMPTIONS 14

6. ANALYSIS/MODEL 16
   - 6.1 MODEL REQUIREMENTS 16
   - 6.2 TYPES OF DEGRADATION MODELS FOR TSPA 17
   - 6.3 MODEL SELECTION/ABSTRACTION 18
     - 6.3.1 DSNF Group 1 (Naval SNF) Models 19
     - 6.3.2 DSNF Group 2 (Pu/U Alloy) Models 19
     - 6.3.3 DSNF Group 3 (Pu/U Carbide SNF) Models 20
     - 6.3.4 DSNF Group 4 (MOX and Pu Oxide SNF) Models 20
     - 6.3.5 DSNF Group 5 (Th/U Carbide SNF) Models 21
     - 6.3.6 DSNF Group 6 (Th/U Oxide SNF) Models 21
     - 6.3.7 DSNF Group 7 (U-metal SNF) Models 22
     - 6.3.8 DSNF Group 8 (U Oxide SNF) Models 24
     - 6.3.9 DSNF Group 9 (Al-based SNF) Models 25
     - 6.3.10 DSNF Group 10 (Unknown SNF) Models 26
     - 6.3.11 DSNF Group 11 (U-Zr-Hx) Models 26
     - 6.3.12 Immobilized Ceramic Pu Disposition Waste Form Models 26
   - 6.4 ABSTRACTION SUMMARY–DSNF AND PU DISPOSITION FORM DEGRADATION MODELS 28
     - 6.4.1 Model Basis 28
     - 6.4.2 Model Uncertainties 30
     - 6.4.3 Surface Area of DSNF Groups and Immobilized Pu Ceramic Waste Form 30

7. CONCLUSIONS 31
   - 7.1 DSNF DEGRADATION MODELS VALIDITY 31
     - 7.1.1 Dissolution Models 31
     - 7.1.2 Colloid Formation 33
   - 7.2 RECOMMENDED MODEL USAGE FOR TSPA 34
     - 7.2.1 DSNF 34
     - 7.2.2 Immobilized Ceramic Pu Disposition Waste Form 36

CONTENTS (Continued)

Page

8. INPUTS AND REFERENCES 43
8.1 DOCUMENTS CITED 43
8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES 46

TABLES

Page

Table 1a. Comparison of Unirradiated/Uncorroded U-Metal and N-Reactor SNF Corrosion Rates 24
Table 1b. DSNF, Naval SNF, Pu Disposition Release/Degradation Models 37
Table 2. Summary and Comparison of N-Reactor SNF Stage 1 and Stage 2 Dissolution Rates (mg/m^2-d) 40
Table 3a. Dissolution Rates at pH 8.5, 0.002M CO_3^{--}, and 20% Oxygen Calculated from Proposed Models 41
Table 3b. Fractional DSNF Waste Form Dissolution Rates at 50°C, pH 8.5, 0.002M CO_3^{-}, and 20% Oxygen Calculated for Best-estimate Models 42

ACRONYMS

AMR	Analysis Model Report
ANL	Argonne National Laboratory
ASTM	American Society of Testing and Materials
ATR	advanced test reactor
DBE	design basis event
DOE	U.S. Department of Energy
DOE-OCRWM	U.S. Department of Energy - Office of Civilian Radioactive Waste Management
DSNF	DOE-owned spent nuclear fuel
EBR-II	experimental breeder reactor
ERR	experimental research reactor
FFTF	Fast Flux Test Facility
FFTF-DFA	Fast Flux Test Facility–Demonstration Fuel Assembly
FFTF-TFA	Fast Flux Test Facility–Test Fuel Assembly
FFTF-TDFA	Fast Flux Test Facility-Test Demonstration Fuel Assembly
FSV	Fort St. Vrain
HLW	high-level waste
LA	License Application
LLNL	Lawrence Livermore National Laboratory
LMITCO	Lockheed Martin Idaho Technologies Company
LWR	light water reactor
LWBR	light water breeder reactor
MGR	monitored geologic repository
MOX	mixed plutonium-uranium oxide fuel
MTHM	metric tons heavy metal
MWd	megawatt days
NNPP	Naval Nuclear Propulsion Program
NSNFP	National Spent Nuclear Fuel Program
PA	performance assessment
PB	Peach Bottom Reactor
PIP	Plutonium Immobilization Project
PNNL	Pacific Northwest National Laboratory
QARD	Quality Assurance Requirements Document
RIP	Repository Integration Program
SNF	spent nuclear fuel
SPR	single pass reactor
SRE	sodium reactor experiment
SRS	Savannah River Site
TBD	to be determined
TBV	to be verified
TMI	Three Mile Island
TRIGA	Training Research Isotopes – General Atomic
TSPA	Total System Performance Assessment
TSPA-SR	Total System Performance Assessment – Site Recommendation
WAC	waste acceptance criteria

1. PURPOSE

The purpose of this analysis/model report (AMR) is to select and/or abstract conservative degradation models for DOE- (U.S. Department of Energy) owned spent nuclear fuel (DSNF) and the immobilized ceramic plutonium (Pu) disposition waste forms for application in the proposed monitored geologic repository (MGR) postclosure Total System Performance Assessment (TSPA). Application of the degradation models abstracted herein for purposes other than TSPA should take into consideration the fact that they are, in general, very conservative. This activity is covered by item 6 of the *Development Plan for Waste Package Materials Department Analysis and Modeling Reports Supporting the Waste Form PMR* (CRWMS M&O 2000e). Using these models, the forward reaction rate for the mobilization of radionuclides, as solutes or colloids, away from the waste form/water interface by contact with repository groundwater can then be calculated. This forward reaction rate generally consists of the dissolution reaction at the surface of spent nuclear fuel (SNF) in contact with water, but the degradation models, in some cases, may also include and account for the physical disintegration of the SNF matrix. The models do not, however, account for retardation, precipitation, or inhibition of the migration of the mobilized radionuclides in the engineered barrier system (EBS). These models are based on the assumption that all components of the DSNF waste form are released congruently with the degradation of the matrix. The rate of release would be related to the rate of waste-form degradation as follows:

R_i = (degradation rate in mg/m^2-d) • (total surface area of SNF exposed to water in m^2) • (mass fraction of species i)

Several hundred distinct types of DSNF may potentially be stored in the MGR (DOE 1999, Appendix D). Therefore, each type cannot be examined viably for its effect on either repository preclosure design basis event (DBE) safety analyses or for postclosure TSPA. To enable analyses of a limited number of potential DSNF types to represent, or bound, the behavior of all DSNF disposed in the repository, the U.S. Department of Energy Office of Civilian Radioactive Waste Management (DOE OCRWM) and the National Spent Nuclear Fuel Program (NSNFP) collaborated to identify the DSNF groups. These groups are individual categories of spent fuel into one of which all DSNF types would fall for DBE and/or TSPA analysis purposes. The description of, and justification for, these spent fuel groupings for repository criticality, DBE, and TSPA analysis purposes are in the NSNFP report, *DOE Spent Nuclear Fuel Grouping in Support of Criticality, DBE, and TSPA-LA* (DOE 2000b). Also, the NSNFP has compiled a report that contains characteristics of the DSNF groups related to their postclosure performance and suggested models for waste-form dissolution: *DOE Spent Nuclear Fuel Information in Support of TSPA-SR* (DOE 1999).

The DOE SNF groups for total system performance analysis for the Site Recommendation (TSPA-SR) contained in the above documents and described in Sections 6.3.1 through 6.3.11 of this document (and a typical type of SNF in the group) follow:

- Group 1–Naval SNF
- Group 2–Pu/U alloy (Fermi SNF)
- Group 3–Pu/U carbide (FFTF-TFA SNF)
- Group 4–MOX and Pu oxide (FFTF-DFA/TDFA SNF)

- Group 5–Th/U carbide (Fort St. Vrain SNF)
- Group 6–Th/U oxide (Shippingport light water breeder reactor (LWBR) reflector SNF)
- Group 7–U-metal (N-Reactor SNF)
- Group 8–U oxide (Three Mile Island [TMI]-2 core debris)
- Group 9–Al-based SNF (Foreign Research Reactor [FRR] SNF)
- Group 10–unknown (miscellaneous SNF)
- Group 11–U-Zr-Hx (TRIGA SNF).

It should be noted that this grouping of DSNF types is different than the groupings recommended for DBE and criticality analyses in DOE (2000b). Thus, the degradation model for a single fuel type recommended herein for the TSPA analyses may not be applicable for that fuel type for DBE and/or criticality analyses.

Parameters and/or characteristics of these waste forms, used as input to the TSPA release rate models, may be reasonable and/or bounding assumptions concerning the materials; therefore, they need not necessarily be fully qualified to support repository licensing. Dissolution models for DSNF waste forms to be used in TSPA-LA (License Application) may also be assumptions or reasonable models and may not need to be fully validated. The TSPA analyses that use these assumptions as inputs will be appropriately validated and will document the consequences of using unqualified data as required by AP-3.10Q, *Analyses and Models*. The license granted to operate the repository would contain technical specifications based on these parameters/models. Also, the final recommended models apply to the direct degradation of the waste form only. The models do not explicitly cover radionuclide migration retardation or enhancement mechanisms such as colloid formation, other than to recommend that the formation/migration dynamics for colloid formation from the DSNF be taken as both qualitatively and quantitatively similar to that of CSNF and HLW glass.

If post-licensing analyses are required to demonstrate conformance of individual waste forms to waste acceptance criteria (WAC), they may require validated waste form dissolution models. If this approach is not taken, the post-licensing analysis will need to demonstrate through such activities as bounding analyses that using unqualified data and/or unvalidated models is acceptable (i.e., in compliance with AP-3.10Q).

Surplus plutonium (Pu) will be handled in the DOE complex in two ways: some of it will be converted into an immobilized ceramic waste form, and the rest will be converted to mixed oxide (MOX) fuel for use in commercial light water reactors. Therefore, a Group 12, representing the immobilized ceramic Pu disposition waste form, will be added to the other DSNF groups. This waste form will consist of disks of a Pu-containing titania-based ceramic enclosed in stainless steel cans that are, in turn, encased in a borosilicate high level waste (HLW) glass matrix (CRWMS M&O 1998a). This AMR will not select and/or abstract a degradation model for mixed oxide (MOX) SNF as a Pu disposition waste form because this form, if used, would be treated as commercial light water reactor (LWR) SNF. Therefore, throughout the remainder of this document, MOX will refer to the MOX SNF in Group 4.

The objective of this document is to use the two DOE SNF group-related studies, published analyses, and results of experimental degradation tests to abstract models for the degradation rate

of the SNF groups. Further, this AMR will recommend using a subset of these models to provide bounding TSPA analyses of the DOE SNF and immobilized Pu ceramic disposal waste forms.

The intended usage of the abstracted DSNF and immobilized Pu ceramic waste form models is to provide forward-reaction-rates (unmitigated by back-reaction) as input into TSPA analyses. Although directly used in analyses that estimate the rate of mobilization of radionuclides, the expected insensitivity of the TSPA to the specific degradation rates calculated by the model limits the model's importance to the TSPA (CRWMS M&O 2000f, Section 7, bullets 11-16). The models provide a source term for other radionuclide transport/inhibition processes. The models derived in this report do this by combining the material degradation models, which predict degradation in units of mass of DSNF dissolved per unit of exposed surface area per unit time, with conservative estimates of the exposed surface area of the SNF available for water contact. By using models for degradation that bound the actual rates for the DSNF and conservative estimates of the exposed surface area, assurance is provided that the repository performance is bounded by the rates. Should the TSPA indicate in future analyses (due to design changes or other unforeseen conditions) that the performance of the MGR is, in fact, sensitive to the degradation, the model may require reanalysis to remove excessive conservatism.

2. QUALITY ASSURANCE

The Quality Assurance (QA) program (DOE 2000c) applies to this analysis. All types of waste packages were classified as Quality Level-1 in *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System* (CRWMS M&O 1999e, p. 7). This analysis applies to all of the waste package designs included in the Monitored Geologic Repository (MGR) Classification Analyses. Reference CRWMS M&O (1999e) is cited as an example. The development of this analysis is conducted under activity evaluation *1101213FM3 Waste Form Analyses & Models - PMR* (CRWMS M&O 1999g). The models abstracted in this document involved no direct use of experimental data, and, therefore, no electronic data management was required.

3. COMPUTER SOFTWARE AND MODEL USAGE

No computer software was used in the analysis or abstraction of the degradation models discussed in this report. No experimental data or data obtained from calculational models were used to produce the models abstracted in this report. The degradation models analyzed herein are intended to support radionuclide release source terms in the TSPA analyses performed by the Performance Assessment Office (PA) of the CRWMS M&O.

4. INPUTS

4.1 DATA AND PARAMETERS

Data, information, and models for the degradation of DSNF and Pu disposition waste forms were obtained from laboratory experiments, DOE reports, NSNFP reports, and OCRWM AMRs.

- Documents by Thornton (1998a, 1998b) and CRWMS M&O (2000f) provide analyses demonstrating that even under extremely conservative assumptions for the degradation and/or pyrophoric behavior of the DSNF, the contribution of the DSNF to the postclosure site dose is negligible. Input values for the degradation rate used in the sensitivity analyses did not require qualification because it is a parametric study that used the maximum conceivable degradation rates of the waste form to perform the analysis. This analysis does not require qualification because it does not provide direct input to the abstraction of any of the degradation models.

- CRWMS M&O (2000f, Section 6.7.1 and 7, bullets 11-16) provides analyses that show that the dose rates at the site boundary resulting from the failure of DSNF-containing waste packages are insensitive to the degradation rates of the DSNF waste forms. The Repository Integration Program (RIP) code used by the PA for this analysis is qualified software. However, the code input values for the degradation rate used in this AMR do not require qualification because this is a parametric study using the maximum conceivable degradation rates of the waste form to perform the analysis.

- DOE (2000b) establishes and justifies the DSNF groups to be used for TSPA-SR analysis purposes. This report proposes that the degradation behavior of each DSNF group can be adequately represented by the behavior of a surrogate SNF type within the group. The conclusions of this report are supported by TSPA analyses performed using the RIP TSPA code (Thornton 1998a, 1998b; and CRWMS M&O 2000f, Section 6.7.1 and Section 7, bullets 11-16) which show that the postcontainment site-boundary dose is insensitive to the degradation rate of the DSNF or individual components of the DSNF. This information does not require qualification because no parameter from this report is directly used in selecting or abstracting degradation models. Appendix D of DOE (2000b) contains the equivalent metric tons heavy metal (MTHM) inventory for each of the TSPA-SR DSNF groups. The data used in this AMR compares the relative importance of each group in formulating a composite degradation model for all DSNF. While the data are required to be qualified for other documents supporting the TSPA, they are used here to indicate the relative quantities of the DSNF groups only. Therefore, they do not require qualification for use in abstracting group dissolution models in this AMR.

- DOE (1999) contains proposed dissolution models and MTHM inventory for each of the DSNF TSPA groups identified in DOE (2000b). The suggested models were evaluated and/or abstracted in, or selected for, this AMR. The information in the document related to the models may need to be validated to demonstrate conformance to waste acceptance criteria (WAC) of specific waste forms for emplacement. Appendix A of the referenced DOE report contains information on the surface area for each of the TSPA-SR DSNF groups, and Appendix D contains the equivalent MTHM inventory. The data from this report is used for comparative purposes to indicate the conservatism inherent in the dissolution models analyzed in this AMR and is not directly used in the generation of the N-reactor SNF-based dissolution model that is recommended for use for all DSNF (except the naval SNF). The data, therefore, does not need to be qualified for its usage herein.

- Pasupathi (2000) is information included in a report generated by the NSNFP, which contains an analysis of the oxidation rates of metallic uranium in dry air, humid air, saturated water vapor, and liquid water. The report also provides correlation for the oxidation rates of metallic uranium based on literature data for unirradiated/uncorroded uranium metal. The correlation provided in the reference forms a partial basis for the dissolution rate expression for N-reactor SNF recommended/derived in Section 6.3.7 of this AMR. The data analyzed in the NSNFP report is a comprehensive representation of the available literature on uranium metal oxidation. The NSNFP report shows that the reference data have been compiled in numerous publications and used extensively in the past for the analysis of the behavior of metallic uranium. The data and analyses in the report, thereby, provide a comprehensive database adequate for the usage both in the NSNFP report and for the purpose of providing a basis for the models abstracted in this AMR. For these reasons the correlation derived in the report for the oxidation rate of uranium metal in liquid water as a function of temperature may be regarded as validated and may be used in Section 6.3.7 as a partial basis for the N-reactor SNF dissolution model.

- Gray and Einziger's (1998) report contains the results of flow-through dissolution tests on samples of N-reactor SNF. The model described in their report is used here to abstract a model for the degradation of U-metal DSNF. This model, in turn, will be used to abstract degradation models for other DSNF groups; therefore, validation to support the demonstration of conformance to waste acceptance criteria of the specific waste forms for repository emplacement may be necessary. The data/information is currently unqualified pending AP-3.15Q, *Managing Technical Product Inputs*. and/or AP-SIII.2Q, *Qualification of Unqualified Data and the Documentation of Rationale for Accepted Data,* evaluation analysis.

- Wiersma and Mickalonis' (1998) report contains the results of dissolution testing conducted on samples of aluminum-based SNF from the Savannah River Site (SRS). This AMR used their data to select a model for the degradation of aluminum-based SNF. The new model, in turn, will be used to show only the low-dissolution kinetics comparison to uranium metal-based SNF. Because of this restricted use, qualification is not necessary for the purposes of this AMR. It should be noted, however, that the data could require qualification to support the demonstration of conformance to WAC of the aluminum-based DSNF waste forms for emplacement.

- CRWMS M&O (2000b) is an AMR generated under AP-3.10Q that abstracts models for the formation and transport of radionuclides in colloidal form from CSNF and HLW glass waste packages. Although no direct information is provided in this AMR concerning the formation or transport of colloids from DSNF, the case is made that they may be treated similarly as the colloids from the CSNF. This information is used in Section 5 to support the assumption that colloid formation from DSNF are not significantly different than for CSNF and HLW glass, and, thus, do not need to be specifically addressed in this AMR and in Section 7.2.1 to justify using the CSNF and HLW glass colloid models in CRWMS M&O (2000b) as surrogates for DSNF colloid behavior.

- Batt (1999) and Hurt (2000) are National Spent Nuclear Fuel Program letter reports that provide information concerning the formation of colloids from the degradation of metallic uranium-based (N-reactor) and MOX DSNF waste forms. This information is used in Section 5 to support the assumption that colloid formation from DSNF is not significantly different than for CSNF and HLW glass and, thus, does not need to be specifically addressed in this AMR and in Section 7.2.1 to justify using the CSNF and HLW glass colloid models as surrogates for the DSNF colloid behavior. As DSNF colloid testing continues at ANL (Mertz 2000), the results will be used as confirmatory data for the assumptions and usage in this AMR, or, if appropriate, revisions to these assumptions and conclusions will be made.

- CRWMS M&O (2000c) is an AMR generated under AP-3.10Q that abstracts models for the dissolution rate of HLW glass under repository groundwater exposure conditions. The models in CRWMS M&O (2000c) are not yet validated pending completion of the AP-3.10Q process. However, the abstracted model is used here to represent the degradation of the immobilized ceramic Pu disposition waste form.

- CRWMS M&O (1998b) contains abstracted models for waste-form materials. In some cases, these models were a source of the models used for comparison with the models abstracted here. The individual models do not require validation because it is not expected that they will be used for licensing.

- CRWMS M&O (2000a) is an AMR generated under AP-3.10Q that abstracts models for the dissolution of uranium dioxide-based commercial LWR SNF (CSNF) under repository groundwater exposure conditions. The model described in CRWMS M&O (2000a) is used to abstract a degradation model for uranium-oxide based DSNF. The model has completed the AP-3.10Q process and is considered validated.

- CRWMS M&O (1998a) contains a description of the immobilized ceramic Pu disposal waste form and describes how it is incorporated into a waste canister. The information is used in this AMR to justify the types of dissolution models, a model for glass dissolution and a model for ceramic dissolution, used respectively for the conservative and best-estimate models for the Pu waste form addressed in Section 6.3.12. The information is not used in this AMR to directly formulate the degradation model for the immobilized ceramic Pu disposition waste form; therefore, the model does not need to be qualified for this purpose.

- CRWMS M&O (2000g, Section 2.2.2) indicates that the Pu-ceramic corrosion rate will be considerably less than that of the HLW glass. This is further supported by analyses in CRWMS M&O (2000c), which demonstrate that the HLW glass rates invoked in CRWMS M&O (2000g) are consistent with the HLW glass model. This is also supported by the indication in the TSPA-VA models and the initial corrosion data for immobilized Pu ceramic in Shaw (1999) that the dissolution rate of borosilicate glass is significantly greater than that of titanate-based crystalline material. In the immobilized ceramic waste form, the Pu is to be encapsulated in disks of ceramic matrix similar to the chemical composition of synroc, a titanate-based pyrochlore. The ceramic disks would then be enclosed in stainless steel cans that would then be encased in a borosilicate glass monolith inside the HLW waste canister (CRWMS M&O 1998a, Section 2.2). Water, therefore, would have to first penetrate the

stainless steel HLW canister, the glass matrix, and the stainless steel can before it could contact the Pu-containing crystalline material. Accounting for the dissolution of the HLW glass in the overall TSPA for the immobilized Pu ceramic, therefore, may not be necessary considering the relative durability of the ceramic in which the Pu is actually encased. However, the similarity of the glass composition of the Pu-ceramic disposition waste form to the HLW glass compositions may need to be verified if the degradation of the glass in the canister is part of the TSPA analysis.

- Shaw (1999, Section 6.1) is a preliminary report from the plutonium immobilization project at Lawrence Livermore National Laboratory (LLNL). Shaw's report contains a recommended correlation for the rate of dissolution of the currently envisioned Pu ceramic waste form that is recommended as the best estimate model for this type of waste form. Data/models for the immobilized Pu ceramic waste form may need to be qualified to support the demonstration of conformance to WAC of this waste form for emplacement.

- CRWMS M&O (2000g, Section 2.2, Table 2-10) contains a comparison of HLW glass and Pu-ceramic corrosion rates, which shows that the HLW corrosion rates bound the Pu-ceramic rates.

- LMITCO (Lockheed Martin Idaho Technologies Company) (1997, Section 2.1.8) contains information on the dissolution behavior of unirradiated U-Zr-Hx fuel at high-temperature conditions. The data are not required to be qualified because they are not used as direct inputs into the abstraction model. Information from LMITCO (1997) is used here to qualitatively indicate the very low dissolution rate of U-Zr-Hx compared to the other DSNF groups. Neither is data qualification required for use in this AMR as the data are used for comparison and corroboration purposes only. However, data/models for the degradation of the U-Zr-Hx waste form may need to be qualified to support the demonstration of conformance to WAC of this waste form for emplacement.

4.2 CRITERIA

The models selected and/or abstracted in this AMR are not based on project-level criteria. The criteria for the recommended models are that they provide appropriate bounding values for the DSNF for use in the TSPA.

4.3 CODES AND STANDARDS

ASTM Standard C 1174-97, *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geologic Disposal of High-Level Radioactive Waste,* is used to support the degradation model development methodology, categorize the models developed with respect to their usage for long-term TSPA, and relate the information/data used to develop the model to the requirements of the standard.

5. ASSUMPTIONS

The NSNFP is continuing to support testing related to the dissolution/degradation behavior of DSNF in the MGR per the *NSNFP Release-Rate Test Program Plan* (DOE 1998). The testing performed under this program supports the assumptions used in this analysis. The naval SNF disposition program will provide appropriate confirmation of Assumptions 5.3 and 5.4. Testing in progress and to be performed will be evaluated with respect to continuing verification of the assumptions listed below. Assumptions used for the analyses contained herein and those that may require verification through the continuing dissolution testing supported by the NSNFP and PIP follow:

5.1 Degradation of the DSNF waste form is congruent; all components of the waste form matrix are released at the same rate as the matrix material. This assumption is based on the observations of the condition of the uranium dioxide-based commercial light water reactor (LWR) SNF and the N-reactor metallic uranium-based SNF degradation test samples in the Pacific Northwest National Laboratory (PNNL) tests (Gray and Einziger 1998).

This assumption is used to justify the use of the degradation models examined in Section 6 for the congruent release of radionuclides from the SNF. The uranium dioxide-based LWR SNF showed congruent dissolution in flow-through testing (CRWMS M&O 2000a) (Gray and Einziger 1998, Section 3.2). Some limited testing of MOX and aluminum-based SNF supports the congruent dissolution assumption but is not extensive enough to be conclusive. The N-reactor SNF testing has not yet involved enough of the somewhat heterogeneous N-reactor samples to firmly establish congruent radionuclide release for the U-metal SNF. Additionally, the immobilized ceramic Pu waste form has shown indications of some incongruent release behavior in as yet incomplete testing (Bourcier 1999). Therefore, this assumption needs to be verified as conservative to support licensing of the DSNF waste forms for emplacement, unless such verification can be demonstrated to be unnecessary.

5.2 N-reactor SNF is an adequate conservative surrogate for the degradation rate of the DSNF. N-reactor SNF comprises ~84% by MTHM of the total quantity of DSNF other than the naval SNF. This assumption is based on the observation in preliminary studies (Gray and Einziger 1998) that the rate of dissolution of the metallic uranium-based N-reactor SNF has significantly exceeded that of the uranium oxide-based commercial SNF that will comprise most of the total SNF to be emplaced in the MGR. Also, examination of the literature available for other waste forms (DOE 1999) indicates that the degradation rate of N-reactor fuel generally exceeds that of the other forms. This assumption is used in Section 6.4 to support the judgement that even if an individual type of DSNF for which the inventory is low has a dissolution rate greater than N-reactor SNF, the contribution to the total DSNF release is negligible.

5.3 Commercial LWR SNF will be used as the surrogate for naval SNF in repository performance analyses. The basis for this assumption is the robust design of the naval SNF. Expected releases from naval SNF waste packages were provided in Mowbray (2000). Because of its robust design, the radionuclide releases from naval SNF waste packages are considerably less than releases from commercial LWR SNF waste packages; accordingly, this assumption is conservative. Naval SNF represents approximately one-tenth of one

percent of the spent fuel MTHM inventory. The information contained in Mowbray (2000) is qualified data. This assumption is used in Section 6 to support the use of LWR SNF as a conservative surrogate for the naval SNF.

5.4 The formation and transport of colloids (resulting from the degradation of the DSNF and immobilized ceramic Pu waste forms) is similar, both qualitatively and quantitatively, to colloids formed from the degradation of CSNF and HLW glass forms. Thus, the colloid models developed in CRWMS M&O (2000b, Section 6.2) may be applied to the DSNF and immobilized ceramic Pu waste forms for the purposes of the TSPA-SR. The bases for this assumption are (1) the DSNF represents a small fraction of the total inventory of CSNF and HLW glass in the repository, and so the colloid contribution to the boundary dose will be dominated by these two waste forms (CRWMS M&O 2000b); (2) the DSNF will be codisposed in waste packages with HLW glass containers (CRWMS M&O 2000d, Attachment 1, Section 3); and (3) the borosilicate glass matrix for the Pu waste form is compositionally very similar to the HLW glass. It is recognized in making this assumption that some limited preliminary information currently available concerning colloid formation from the degradation of N-reactor SNF (the largest component by weight of the DSNF inventory) indicates there may be significantly more colloids formed from this waste form than the CSNF and/or HLW glass (Mertz 2000, Section 1.0). Testing is being conducted at Argonne National Laboratory (Mertz 2000) to characterize colloid formation from the degradation of N-reactor and MOX SNF, and this information will be used as it becomes available to support either the validation or the modification of this assumption. This assumption is used in Sections 6.4 and 7.2.1 to justify recommendations for addressing the immobilized ceramic Pu and DSNF colloids by methods similar to those given in CRWMS M&O (2000b, Section 6.2).

6. ANALYSIS/MODEL

6.1 MODEL REQUIREMENTS

The purpose of the analyses contained in this document is to provide upper-limit, conservative, and best-estimate models for the degradation of DSNF and the immobilized ceramic Pu disposition waste form under environmental conditions appropriate to the MGR. Since degradation of the DSNF is not identified as a principal factor but is related to the other factors Defense Spent Nuclear Fuel, Navy Fuel, and Pu Disposition Waste Form Performance, and Colloid Associated Radionuclide Performance in the TSPA analyses, the relative importance of the model is medium. It also has been indicated in current TSPA analyses (CRWMS M&O 2000f) that repository performance is insensitive to the DSNF degradation rates. To develop these models, a surrogate SNF is selected to represent the degradation behavior of each group for each of these three kinds of models. As discussed below and shown in Table 1b, the degradation model surrogate selected for any given group/model combination will not necessarily be a SNF type within the group. Neither will the same surrogate SNF necessarily be chosen for each kind of degradation model within a given group.

An examination of the available experimental or analytical degradation rate behavior data for the DSNF groups in this report shows that, in general, insufficient data exists to formulate or abstract separate derived models for each group. Because of this, the limited degradation behavior data for each group are generally compared with the degradation behavior of ceramic, uranium dioxide SNF, or uranium metal SNF for which more extensive data are available.

The reason for providing the three types of models (upper-limit, conservative, and best-estimate) is to provide the user of the models in the M&O PA office appropriate flexibility in the application of the degradation model(s) to any particular postclosure performance scenario. In some cases, a bounding, or very conservative, model would be appropriate, and such models would require less rigorous experimental data to support them. To the extent DOE can use margin and conservatism to support licensing of a given DSNF waste form, the data applicable to that waste form may not need to be qualified. In cases where best-estimate models are appropriate, more rigorous data support and qualification would be required.

The model selection/abstraction in this analysis incorporates the model logic shown in Figure 3 of ASTM Standard C 1174-97, *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geologic Disposal of High-Level Radioactive Waste*. Validation of the degradation models used or abstracted in this AMR may not be necessary if the TSPA or other performance analyses are shown to be very insensitive to the degradation rate of the waste form or if the use of a highly conservative model, such as instantaneous release model, still results in acceptable performance of the MGR. If validation of the release model selected were required, it would be performed using confirmatory testing per the requirements of ASTM C 1174-97. In this standard the types of materials degradation models are defined as follows:

Mechanistic Model–A model derived from fundamental laws governing the behavior of matter and energy. It corresponds to one end of a spectrum of models with varying degrees of empiricism.

Semi-empirical Model–A model based partially on one or more mechanisms and partially on data from experiments.

Empirical Model–A model based only on observations or data from experiments, without regard to mechanism or theory.

Bounding Model–A model that yields values for dependent variables or effects that are expected to be either always greater than or always less than those expected for the variables or effects to be bounded.

The types of models described in the ASTM standard (mechanistic, semi-empirical, empirical, bounding) are classified as such by their degree of mechanistic representation of the mode of degradation; whereas, the models described in this AMR analysis (best-estimate, conservative, upper-limit) are classified by their degree of conservatism in predicting degradation rates. There is, however, a general correlation between the ASTM model logic and that of this analysis. In this analysis the upper-limit degradation models would generally correspond to bounding-to-empirical models per the ASTM concept; the conservative degradation models would generally correspond to empirical-to-semi-empirical models per the ASTM concept; and the best-estimate degradation models would correspond to semi-empirical-to-mechanistic models per the ASTM concept. The degradation models examined in this analysis will also be identified by their correspondence to the ASTM concept (see Table 1B).

6.2 TYPES OF DEGRADATION MODELS FOR TSPA

These analyses will provide three types of models for TSPA application purposes: best-estimate, conservative, and upper-limit.

Upper-limit Degradation Models–The upper-limit degradation model provides the most conservative estimate of dissolution rate to be used in any postclosure waste package or EBS performance case. The upper-limit model generally gives unrealistically high estimates of the degradation rate of the waste forms. An upper-limit model may be appropriate in cases where the results of the TSPA or other performance analyses are either very insensitive to the degradation rate of the waste form or where the use of such a model still results in acceptable performance of the MGR. An upper-limit model uses dissolution data, or models abstracted from experimental data, only in that such data clearly shows that the bounding model predicts release rates always well in excess of actual dissolution rates.

An example of a situation in which an upper-limit degradation model would be appropriate is that of the postclosure TSPA analysis of the N-reactor SNF disposal. Preliminary TSPA analysis of the DSNF in the MGR (Thornton 1998a, 1998b) had indicated that for large incremental time steps (> 1,000 years) in the TSPA analyses, the boundary dose resulting from the failure of waste packages containing DSNF is very insensitive to the release rates from the DSNF waste form. Subsequent more detailed analyses (CRWMS M&O 2000f) have supported the conclusion that even complete dissolution of the waste form still results in calculated site boundary doses below the required limits. The upper-limit release rate for the DSNF in this case would be the assumption of complete release within a TSPA (i.e., RIP code) analysis time step or instantaneous release.

Conservative Degradation Models—The conservative degradation models provide an estimate of dissolution rate that reflects the higher rate end of dissolution data available. A conservative model for waste-form degradation would be appropriate in cases where the dissolution database, from which the model was developed, showed wide data spreads or sensitive dependency on waste-form characteristics that could not be definitively controlled, described, or determined for the emplacement condition. A conservative model would be expected to encompass the dissolution kinetics of all SNF types within a DSNF TSPA group.

An example of a situation in which a conservative degradation model would be appropriate might be that of the postclosure TSPA of HLW glass-containing waste packages. Preliminary TSPA analyses showed that the release expected from the HLW glass-containing waste packages were not as significant a contributor to boundary dose as the release from waste packages containing commercial LWR spent fuel. By using a release model that represents the release rate from HLW glass compositions that dissolve at the highest rates and applying these rates to the entire HLW glass inventory, the highest plausible release rates could be used while boundary doses could still be shown to be within regulatory limits.

Best-estimate Degradation Models—Best-estimate models would be appropriate when the use of overly conservative formulations in the TSPA produce results that indicate marginal MGR performance. Best-estimate models might also be used in analyses not directly related to TSPA, such as parametric studies, waste package design support, or other such analyses where full validation of the model might not be required. Best-estimate models would generally require the most extensive experimental data to support validation. Moreover, in many cases the best estimate model itself is the result of a conservative analysis of the experimental data (e.g., the Pu ceramic model derived in Shaw (1999, Section 6.1). A best-estimate model would be used when sufficient dissolution data exists to abstract one, and the characteristics of the waste form can be shown to correspond to the characteristics of the materials that provided the dissolution database.

The modes of degradation of interest are oxidation, corrosion, and/or dissolution of the waste forms in air, water vapor, liquid water, and associated radionuclide release rates. These modes are to be encompassed under the general heading of degradation model. The basis for the analysis will be data/analyses for those parameters pertaining to the degradation of N-reactor spent fuel, LWR SNF, and the immobilized ceramic Pu disposal waste form. Section 6.3 will describe the models suggested for each DSNF group.

6.3 MODEL SELECTION/ABSTRACTION

This section describes the upper-limit, conservative, and best-estimate dissolution models suggested for use in licensing each DSNF group, and a summary of these models is in Table 1. This table shows the three types of models recommended for each DSNF group: (1) the immobilized ceramic Pu disposition form, the surrogate material for which the model was developed, (2) the literature/document source reference for the model, and (3) the ASTM C 1174-97 (1997) classification of the model. A discussion of the development of the individual models for each fuel group follows.

The Program will determine for each model whether that model needs to be validated to support the demonstration of conformance to WAC of individual waste forms or whether sufficient margin/conservatism exists to make model validation unnecessary.

In some cases, adjustments of one or more orders of magnitude to degradation rates are recommended. These adjustments, which were extracted from DOE (1999), are based on only a limited amount of data available for the behavior of the waste forms or similar materials but are considered conservative. Moreover, in some cases (such as the uranium metal and immobilized Pu ceramic waste form) even the best-estimate models abstracted are the result of conservative analyses of the experimental dissolution data.

Models for degradation of all the surrogate waste forms discussed in this section, Section 6.4, and Table 1B do not need to be validated to support license application submittal because the degradation response of the surrogate is a characteristic to be used to develop technical specifications for acceptance and emplacement of the DSNF. As documented in this section, DOE will use scientific judgement supported with available data and models to make the assumed performance of DSNF a reasonable estimate of the actual performance. Degradation models that will show specific waste forms perform as well as or better than the assumed performance of the surrogate may need to be qualified to support the demonstration of conformance to WAC of those waste forms for emplacement.

6.3.1 DSNF Group 1 (Naval SNF) Models

Commercial LWR SNF will be used as the surrogate for naval SNF in repository performance analyses. Expected releases from naval SNF waste packages was provided in Mowbray (2000). Because of its robust design, the radionuclide releases from naval SNF waste packages are considerably less than releases from commercial LWR SNF waste packages; accordingly, this assumption is conservative. Naval SNF represents approximately one-tenth of one percent of the spent fuel MTHM inventory. The information contained in Mowbray (2000) is qualified data.

6.3.2 DSNF Group 2 (Pu/U Alloy) Models

There are several individual types of Pu/U alloy-based DSNF primarily comprised of U-Mo and U-Zr alloys although smaller quantities of U-Th and U-Fe alloy are part of this group (DOE 1999, Section 6.2). These alloy fuels are generally clad in zirconium alloy, but some small quantities have aluminum, stainless steel, or tantalum alloy cladding. The largest single fuel types in this group, comprising slightly over 90% by weight of uranium of the total Group 2 inventory, are the zirconium-clad U-Mo Fermi reactor SNF and stainless steel-clad U-Zr alloy Annular Core Research Reactor SNF. Studies of the dissolution behavior of U-Mo and U-Zr alloys, reported in DOE (1999), give dissolution rates for the alloy, which depend sensitively on the amount of alloying molybdenum and zirconium. They generally show U-Mo dissolution rates to be slightly higher than U-metal and U-Zr alloy slightly lower than U-metal. Also, the total inventory of this SNF waste form is very small compared to the other DSNF types (see Table 3b). From this behavior it is recommended that the best-estimate degradation rate for the Group 2 fuels under wet oxic and humid oxic conditions be taken as the model for U-metal from DOE (1999, Section 6.7), as follows:

$$R\ [kg/m^2\text{-}s] = 1.88 \times 10^3 \exp(-7970/T_K)\ \text{(wet oxic conditions)} \qquad \text{(Eq. 1a)}$$

which converts to mg/m^2-d units as follows:

$$R\ [mg/m^2\text{-}d] = 1.88 \times 10^3 \exp(-7970/T_K)\ [kg/m^2\text{-}s][10^6\ mg/kg][3600\ s/h][24\ h/d]$$

$$= 1.62 \times 10^{14} \exp(-7970/T_K)$$

and

$$R\ [kg/m^2\text{-}s] = 0.27 \times 10^2 \exp(-7240/T_K)\ \text{(humid oxic conditions)} \qquad \text{(Eq. 1b)}$$

which converts to mg/m^2-d units as follows:

$$R\ [mg/m^2\text{-}d] = 0.27 \times 10^2 \exp(-7240/T_K)\ [kg/m^2\text{-}s][10^6\ mg/kg][3600\ s/h][24\ h/d]$$

$$= 2.33 \times 10^{12} \exp(-7970/T_K)$$

and the conservative model should be taken as 10X this value.

These equations were derived from data in the open literature for the corrosion of unirradiated metallic uranium and uranium alloy, and the suggested degradation model for Group 2 SNF was obtained from DOE (1999, Section 6.7) for unirradiated uranium metal. Because the data/information upon which the suggested model in this reference is based is from open literature sources, it is from uncontrolled sources and, thus, may need to be validated to support the demonstration of conformance to WAC of specific waste forms.

6.3.3 DSNF Group 3 (Pu/U Carbide SNF) Models

Group 3 SNF consists primarily of fuel from the Fast Flux Test Facility (FFTF) with most of the balance from the Sodium Reactor Experiment (SRE). Both consist of mixed-carbide-fissile fuel particles in a nongraphite matrix. Only a very limited amount of information concerning the chemical reactivity is available. Because of the lack of specific information concerning degradation behavior and the indication that the fissile particles could be very reactive, the abstracted best-estimate and conservative-degradation rate models abstracted should be taken as 100X the dissolution rate of the uranium metal SNF (DOE 1999, Section 6.3). That is, no credit are taken for lower degradation rates in the best-estimate model formulation for this waste form.

The suggested degradation model for Group 3 SNF was obtained from DOE (1999, Section 6.3). The data/information upon which the suggested model in this reference is based is scarce and from old open literature sources.

6.3.4 DSNF Group 4 (MOX and Pu Oxide SNF) Models

Group 4 SNF is composed of a mixture of uranium and Pu oxides with various cladding materials. Although several dozen SNF types are in this category, the largest single type is the

FFTF DFA (demonstration fuel assembly) and TFA (test fuel assembly) fuel, contributing over 50% of the uranium by weight. Since the fuel material is either uranium oxide or Pu oxide, the dissolution kinetics of the fuel form is not expected to be materially different from that for commercial LWR SNF. The best-estimate and conservative models abstracted are those for the LWR SNF, i.e., no credit will be taken for lower degradation rates in the best-estimate model formulation for this waste form.

The suggested degradation model for Group 4 SNF is that abstracted in an AMR titled *CSNF Waste Form Degradation: Summary Abstraction* (CRWMS M&O 2000a) for commercial UO_2 fuel. The data/information upon which the suggested model in this reference is based is qualified data generated in support of the CRWMS M&O by PNNL and the Lawrence Livermore National Laboratory (LLNL) for uranium-dioxide based commercial LWR SNF, a material similar, but not identical, to the SNF in this group.

6.3.5 DSNF Group 5 (Th/U Carbide SNF) Models

This SNF group consists primarily of thorium or uranium-carbide particles coated with pyrolytic carbon or silicon carbide embedded in a carbonaceous matrix. Over 90% by weight of MTHM of this group is Fort St. Vrain (FSV) fuel, with the remainder being Peach Bottom (PB) fuel. The PB fuel may be more damaged than the FSV fuel although there is little qualified information concerning the condition of either. Fuel in this group, whose protective coatings and matrix are intact, would be expected to have dissolution kinetics similar to those of pure silicon carbide. SNF with a damaged coating or matrix would be expected to have dissolution kinetics similar to uranium carbide (DOE 1999, Section 6.5; CRWMS M&O 1998a, Section 6.3.2.1). DOE (1999, Sections 6.5 and 6.7) contains comparative values for the corrosion rates of silicon carbide, uranium carbide, and uranium metal. The suggested uranium carbide corrosion rate was about 10X that of uranium metal. For these reasons, the recommended best-estimate degradation model is that for silicon carbide given in DOE (1999) and the conservative rate model is taken as 10X that for uranium metal.

The suggested degradation model for Group 5 SNF was obtained from DOE (1999, Section 6.5). The data/information upon which the suggested model in this reference is based is from open literature sources.

6.3.6 DSNF Group 6 (Th/U Oxide SNF) Models

Thorium uranium oxide spent fuels primarily consist of the Shippingport light-water breeder reactor reflector SNF with the remainder from the Dresden and experimental research reactor (ERR) thorium-uranium-oxide SNF. The Shippingport fuel was clad in zirconium alloy, and the Dresden and ERR fuels were clad in stainless steel. The thorium-uranium-oxide fuel consisted of sintered pellets similar to commercial LWR fuel pellets.

Several reports discussed in DOE (1999, Section 6.6) attest that the mixed thorium uranium was more corrosion resistant than pure uranium dioxide, as much as five orders of magnitude more corrosion resistant. Since the dissolution of the thorium-uranium oxide was not specifically measured, the approach taken is to use a ceramic release model that conservatively bounded data for unirradiated LWBR fuel (DOE 1999, Section 6.6). Thus, the use of the ceramic synroc

model was abstracted as the best-estimate model and 1000X the ceramic model as the conservative model.

6.3.7 DSNF Group 7 (U-metal SNF) Models

The zirconium-clad N-reactor SNF constitutes over 95% of this group with small quantities of aluminum-clad-single-pass reactor (SPR) and EBR-II-metallic uranium SNF. A significant fraction of the N-reactor fuel is visibly damaged, and much of the rest could have small pinholes/cracks in the cladding. The exposed uranium metal surfaces of the N-reactor fuel elements show extensive corrosion resulting from the many years of direct exposure to the K-basin water (Abrefah et al. 1995; Abrefah et al. 1999, Figure 3.1; Welsh et al. 1997, Section 1.0, Figures 3.3-3.7).

Experimental studies have been conducted in the past on unirradiated and uncorroded uranium metal and uranium-metal alloy, and some of this work is summarized in DOE (1999, Section 6.7). Additionally, the NSNFP has conducted an analysis of the kinetics of uranium metal oxidation (Pasupathi 2000) in which a correlation for the dissolution kinetics of unirradiated/uncorroded uranium metal in water was derived from several literature sources as follows:

$$k\,(\mathrm{mg/cm^2\text{-}hr}) = 5.03 \times 10^9 \exp(-A/RT_K), \text{ or}$$

Eq. 2A

$$k\,(\mathrm{mg/m^2\text{-}day}) = 1.21 \times 10^{15} \exp(-A/RT_K)$$

where k is the corrosion rate, A is the activation energy for dissolution (66.4 ± 2.0 kJ/mol), R is the gas constant (8.314 J/mol-K), and T_K is the temperature in kelvins.

PNNL has conducted dissolution tests on samples of the N-reactor SNF which generally indicate that the rates of dissolution somewhat exceed those of the unirradiated/uncorroded uranium metal or alloy. The PNNL experimental work was performed on N-reactor SNF samples taken from an undamaged/uncorroded area of an N-reactor fuel element (Gray and Einziger 1998, Section 2.2 and Figure 1A). The results indicated that there were two stages in the dissolution behavior of the N-reactor SNF samples tested: an initial Stage 1 rate and, after an incubation period, a faster Stage 2 dissolution rate. The Stage 1 dissolution resembled the congruent dissolution noted in the similar PNNL dissolution experiments on uranium-dioxide based LWR SNF samples; that is, the uranium went directly into solution as the soluble uranyl species (UO_2^{++}) via the following reactions:

$$U + O_2 \rightarrow UO_2$$

$$UO_2 + H_2O + \tfrac{1}{2} O_2 \rightarrow UO_2^{++} + 2OH^-$$

This Stage 1 congruent dissolution of the matrix was correlated with the following expression:

$$\log R\,(\mathrm{mg/m^2\text{-}d}) = 8.52 + 0.347 \log[CO_3^-] + 0.088\,\mathrm{pH} - 1929/T_{K1} \qquad \text{(Eq. 2B)}$$

where $[CO_3^{--}]$ is the molar concentration of carbonate in the contacting solution. The flow-through test data that was used to generate this expression qualified as service condition test results under the testing/modeling logic of ASTM C 1174-97 (1997). Unsaturated drip testing of metallic uranium, which serves as characterization testing under the logic of ASTM (1997), showed that alteration phases could form, which would potentially retard the release of solutes from the N-reactor SNF, and this could be responsible for the lower Stage 1 rates (Hurt 2000).

During Stage 2, the dissolution ceased to be congruent and disintegration of some of the fuel matrix, which formed a sludge-like material primarily consisting of U_4O_9 and/or the mineral form Schoepite ($UO_3 \cdot 2H_2O$), was observed. It was also postulated that the Stage 2 dissolution may have been faster because it coincided with the depletion of dissolved oxygen and consequent formation of an anoxic condition in the contacting water, represented by the following equation:

$$U + 2H_2O \rightarrow UO_2 + 2H_2$$

The rates of dissolution that were observed for Stage 2 ranged from 10,000 mg/m^2-d at 25°C to 290,000 mg/m^2-d at 75°C for some samples. The temperature dependence of the dissolution was similar to that for unirradiated/uncorroded uranium metal in the Pasupathi (2000) study, although the absolute rates were higher for the N-reactor SNF (see Table 1a below). Stage 2 dissolution generally began around sixty days into the testing. Table 2 gives values for the Stage 1 dissolution rate as calculated from the above rate expression and for the experimental Stage 2 dissolution rates of the PNNL study. It should be noted that the N-reactor SNF dissolution testing is still underway; and, therefore, the results upon which this model was derived are preliminary.

In most of the cases where Stage 2 dissolution was initiated, it began around 60 days into the test, a very short period in terms of TSPA analyses. A significant fraction of the N-reactor fuel had been stored in a damaged condition under water at the K-basins at Hanford, and the metallic uranium has been exposed to the water environment. Therefore, the degradation model for unirradiated and unexposed U-metal derived in DOE (1999) and recommended for the Group 2 (U/Pu alloy), Group 3 (Pu/U carbide), and Group 10 (unknown) SNF is not recommended for the N-reactor SNF, which forms the basis for Group 7. Although the PNNL experimental data is limited, it indicates that Stage 2 dissolution kinetics should be followed for the N-reactor SNF. Based on these analyses, the abstracted best-estimate degradation rate model for the U-metal SNF is selected so as to encompass the highest directly observed congruent dissolution rates in the PNNL studies or 1.8 x 10^5 mg/m^2-d (0.75 mg/cm^2-hr) at 75°C and 13,000 mg/m^2-d (0.05 mg/cm^2-hr) at 25°C (Gray and Einziger 1998, Section 4.3).

It was noted above that the samples of N-reactor SNF tested in the flow-through testing at PNNL were from an undamaged and uncorroded portion of an N-reactor fuel element. No dissolution testing has been conducted on samples of damaged/corroded N-reactor SNF, although this damaged/corroded condition would be expected to be the case in repository environment exposure after breach of the waste package in the repository. In other studies at PNNL concerning the ignition properties (Abrefah et al. 1999, Table S.1) and oxidation kinetics of N-reactor SNF (Abrefah et al. 1998), samples of N-reactor SNF taken from the damaged/corroded

areas of the N-reactor fuel elements showed higher oxidation rates than undamaged/uncorroded samples.

Table 1a compares values for Stage 2 dissolution rates of N-reactor SNF obtained experimentally by Gray and Einziger (1998) with rates calculated from the correlation recommended for water dissolution of uranium metal in Pasupathi (2000, Table 2-5), and 5 times and 25 times this value. Note that the reaction rates given for the N-reactor SNF are approximately a factor of two to five higher than those given using Equation 2A. Note also that use of the lower (64.4 kJ/mol) one standard deviation (1σ) uncertainty given in the equation 2A expression for the activation energy (66.4 ± 2.0 kJ/mol) would result in another factor of 2 to 3 in the reaction rate in this temperature range. Thus, the combination of these two factors would result in roughly a factor of 5 increase on the nominal equation 2A reaction rate, which would represent the most defensible best-estimate model kinetics.

In the PNNL N-reactor SNF experimental work (Gray and Einziger 1998, Section 4.3), the highest dissolution rate inferred by cesium release results (but not directly observed as congruent uranium dissolution) was 290,000 mg/m^2-day (1.21 mg/cm^2-hr). This is approximately a factor of 1.6 higher than the maximum value of 180,000 mg/m^2-day observed for congruent dissolution of the uranium. Combining this inferred rate for the N-reactor SNF and a 2σ uncertainty (95%) lower activation energy of 62.2 kJ/mol would result in another approximate factor of 5 over the best-estimate rate for use as the conservative model.

Table 1a. Comparison of Unirradiated/Uncorroded U Metal and N-Reactor SNF Corrosion Rates

Temp (°C)	N-Reactor SNF[1]	U-metal[2]	U-metal[3]	5X U-metal[2]	25X U-metal[2]
25	0.05 mg/cm^2-hr (1.30×10^4 mg/m^2-day)	0.01mg/cm^2-hr (2.77×10^3 mg/m^2-day)	0.03 mg/cm^2-hr (6.21×10^3 mg/m^2-day)	0.06 mg/cm^2-hr (1.39×10^4 mg/m^2-day)	0.29 mg/cm^2-hr (6.93×10^4 mg/m^2-day)
75	0.75 mg/cm^2-hr (1.80×10^5 mg/m^2-day)	0.54 mg/cm^2-hr (1.31×10^5 mg/m^2-day)	1.08 mg/cm^2-hr (2.60×10^5 mg/m^2-day)	2.71 mg/cm^2-hr (6.51×10^5 mg/m^2-day)	13.57 mg/cm^2-hr (3.26×10^6 mg/m^2-day)

(1) from Gray and Einziger 1998, Section 4.3
(2) from Equation 2A using the nominal activation energy of 66.4 kJ/mol
(3) from Equation 2A using the 1σ minimum activation energy of 64.4 kJ/mol

For these reasons it is recommended that the best-estimate model for the dissolution of the N-reactor SNF be taken as 5 times, and the conservative model be taken as 25 times, the Pasupathi (2000) model represented by Equation 2A.

6.3.8 DSNF Group 8 (U Oxide SNF) Models

TSPA Group 8 consists of uranium dioxide-based SNF removed from commercial LWRs or similar SNF from test reactors. About half of the total inventory of approximately 178 MTHM

comes from the TMI-2 core and, therefore, is not intact fuel. The other half is substantially undamaged SNF from other commercial reactors. The dissolution kinetics per unit area of the damaged fuel, such as the TMI rubble, would be expected to be similar to the kinetics of the uranium-dioxide based LWR spent fuel reported in CRWMS M&O (2000a, Eq. 11, Table 14) but with a substantially enhanced effective surface area for release.

$$\log_{10} R\ (\mathrm{mg/m^2\text{-}d}) = 5.479057 + [-2457.050662\ (1/T_K)] + [1.510878\ (-\log_{10}(CO_3^{--}))] + [-1.729906\ (-\log_{10}(O_2))] + [0.234718\ \mathrm{pH}] + [-0.799526\ \log_{10} \mathrm{BU}] + [400.755947\ (-\log_{10} O_2)\ (1/T_K)] + [780.806133\ (\log_{10} \mathrm{BU})\ (1/T_K)] + [0.172305\ (\log_{10} \mathrm{BU})\ (-\log_{10}(CO_3^{--}))] + [0.174428\ (\log_{10}\mathrm{BU})\ (-\log_{10} O_2)] + [-0.271203\ (\log_{10}\mathrm{BU})\ (\mathrm{pH})] + [-0.339535\ (-\log_{10}(CO_3^{-}))^2] \qquad \text{(Eq. 3)}$$

where T_K is the temperature in kelvins, CO_3^- is the molar concentration of carbonate ion in the liquid phase, BU is the spent fuel burnup in MWd/kgU, and O_2 is the oxygen partial pressure in atmospheres in the gas phase.

This model for the degradation rate of uranium-dioxide spent fuel was derived from dissolution tests that qualified as service condition and/or characterization tests under the testing/modeling logic of ASTM C 1174-97 (1997). These tests represented the maximum forward-dissolution-reaction rate for the material with no back reactions that would inhibit dissolution. The fact that the dissolution reaction represented the maximum rate was verified by the observations of congruent dissolution and the lack of precipitated alteration phases on the test specimens during the tests. Vapor-phase tests were also performed on samples of the commercial LWR SNF that served as characterization tests per the logic of ASTM C 1174-97. These tests indicated that alteration phases could form on the SNF, and these phases would inhibit the overall dissolution rate (CRWMS M&O 2000a, Sections 6.3.1 and 6.3.2). Therefore, the testing overall demonstrated the conservatism inherent in using Equation 3 for the dissolution rate for uranium-dioxide based SNF.

DOE (1999, Section 6.8) suggests a surface-area enhancement factor of 100 for a release model representing the Group 8 SNF. Thus, the abstracted best-estimate-degradation model for intact uranium dioxide based Group 8 SNF should be the same as the degradation model for commercial LWR SNF (Equation 3), and the conservative degradation model for intact Group 8 fuel should be 100X the best-estimate model. The abstracted best-estimate and conservative-degradation models for the non-intact Group 8 SNF is 100X the intact fuel best-estimate model, i.e., no credit is taken for lower degradation rates in the best-estimate model formulation for this waste form.

6.3.9 DSNF Group 9 (Al-based SNF) Models

This group consists of fuels based on a uranium aluminide, uranium silicide, or uranium oxide particle phase dispersed in a continuous aluminum alloy matrix. The fission product radionuclides remain in the dispersed phase; therefore, the dissolution of the dispersed phase material is the parameter most germane to the release of the radionuclides upon contact with groundwater. The dissolution rate of interest is expressed in terms of $\mathrm{mgU/m^2\text{-}day}$.

Much of this spent fuel (~36%) is from foreign research reactor sources, with the balance from domestic research reactors such as the high flux irradiation reactor (HFIR), the advanced test reactor (ATR), and university research reactors (DOE 1999, Appendix D). SRS has conducted dissolution studies on SRS reactor spent fuel samples at 25°C in both J-13 well water and bicarbonate solutions (Wiersma and Mickalonis 1998, Table 3) and on unirradiated samples at 25°C and 90°C (Wiersma and Mickalonis 1998, Table 4). Flow-through dissolution tests at 25°C subsequently performed at PNNL on similar samples gave results similar to the SRS study (Gray 2000, Table 7). The SRS data showed dissolution rates for the irradiated SNF of 0.19-0.22 mgU/m^2-day in J-13 well water and 22-36 mgU/m^2-day in bicarbonate solution. The corrosion data for the unirradiated fuel samples showed that the dissolution rate at 90°C was approximately 10X the rate at 25°C. The J-13 well-water data is selected for the best-estimate degradation model because the groundwater chemistry at the time of waste-package failure is expected to be approximately that of the J-13 well water. Since bicarbonate is a potentially more aggressive water condition (CRWMS M&O 2000a, Table 23), the bicarbonate data is used as the basis for the conservative model.

6.3.10 DSNF Group 10 (Unknown SNF) Models

Group 10 SNF consists of a small amount of uranium nitride SNF and fuel with unknown matrices. This group consists of only about 0.2% of the total inventory of DSNF in MTHM. Because of the unknown fuel matrix material and the small volume, the degradation models for this group are based on the dissolution kinetics of unirradiated uranium metal, similar to the Group 2 SNF. Therefore, the abstracted best-estimate and conservative models are the same as for the Group 2 SNF.

6.3.11 DSNF Group 11 (U-Zr-Hx) Models

TRIGA test reactor fuel comprises ~97% of the total Group 11 SNF inventory of ~1.6 MTHM (DOE 1999, Appendix D). The TRIGA fuel consists of a dispersion of fine particles of metallic uranium dispersed in a zirconium hydride matrix (U-Zr-Hx). Uranium loadings varied from approximately 8 to 45 wt% (LMITCO 1997, Section 1).

Unirradiated U-Zr-Hz fuel has been shown to have good elevated temperature corrosion resistance (LMITCO 1997, page 2-5). However, there is no known qualified data for the dissolution rate of this material in repository-relevant water and temperature conditions. For this reason the NSNFP DSNF information report (DOE 1999, Section 6.11) proposes that the dissolution rate for this DSNF form be taken as 0.1X the uranium oxide SNF dissolution rate. The low total inventory in MTHM of the U-Zr-Hx SNF makes the repository TSPA performance of this material insensitive to the degradation model for this waste form.

6.3.12 Immobilized Ceramic Pu Disposition Waste Form Models

The waste form for the immobilized Pu will be cold-pressed, titania-based pyrochlore ceramic disks containing approximately 10.5 wt% embedded Pu as PuO_2. These disks will be stacked in stainless steel cans, which are, in turn, embedded inside a canister filled with a vitrified borosilicate filler glass similar to the HLW glass waste form (CRWMS M&O 1998a, pp. 2-3,

Tables 2.2.3-1 and 2.2.4-1). Although the ceramic waste form is similar to synroc (CRWMS M&O 1998a, Section 6.3.2.2) in that it is titania-based, there is limited dissolution rate data (Shaw 1999, Section 6.1) specifically for this ceramic. Shaw (1999, Section 6.1) and Bourcier (2000, Section IV) give the best-estimate model proposed in this report for the dissolution rate, K, at 25°C of a combination zirconolite brannerite pyrochlore ceramic:

For pH < 7

$$\log_{10} K = -0.167\ (pH) - 4.66$$

For pH ≥ 7

$$\log_{10} K = 0.25\ (pH) - 8 \qquad \text{(Eq. 4)}$$

With a temperature dependence given by,

$$\ln(K_2/K_1) = (E_a/R)\ (T_2-T_1)/(T_2T_1)$$

and K is the dissolution rate in g/m^2-day, T is the temperature in kelvins, E_a is 16 kcal/mol, and R is 8.314 J/mol-K (1.987 cal/mol-K).

The dissolution rates represented by these expressions are inherently somewhat conservative since they are based on the results of Single Pass Flow-Through Tests (Shaw 1999, Section 6.1), which are designed to measure a forward reaction rate under conditions far from thermodynamic equilibrium and do not take into account the buildup of dissolved components in the contacting water or the development of protective layers.

Bourcier (2000, Figure 14) shows that these expressions for the best-estimate model provide dissolution rates, which generally fit the spread of experimental data in the low pH region, while slightly overpredicting the experimentally determined rates in the high pH region. A factor of 10X the best-estimate model would bound all the dissolution rates and is, therefore, recommended for use of the conservative model for the immobilized Pu ceramic.

This model represents the dissoluton of the titanate ceramic matrix of the waste form. The studies, which supported the development of this model, showed that the release of plutonium was generally congruent with the dissolution of the ceramic matrix, but that this needed to be verified by further testing (Bourcier 1999). A rate model similar to this best-estimate model has been used in external criticality analyses for degraded waste packages (CRWMS M&O 1998a), and dissolution rate experiments at ANL/LLNL sponsored by the PIP continue to provide data in support of model development and validation. It is anticipated that validation of this model would enable its usage in the TSPA safety or reasonable representation cases for the immobilized ceramic Pu waste form.

Since the stainless steel cans into which the immobilized Pu ceramic is emplaced are in turn to be embedded in a HLW glass matrix, a degradation model for the glass may be required if dissolution of the glass is a necessary precondition for exposure of the ceramic to water. The HLW glass dissolution models that should be used in this case should be that developed in (CRWMS M&O 2000c, Section 7) as follows:

$$R/S_{im}\,(g/m^2\text{-}d) = k_{eff} \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT_K) \qquad \text{(Eq. 5)}$$

where

S_{im} = the effective reacting surface area of the glass in which the ceramic disks are embedded when immersed in the groundwater and is taken as 20X the geometric surface area,

$$R = 0.00831 \text{ kJ/mol-K}$$

for $pH < pH_m$; $\log_{10} k_{eff} = 9 \pm 1$, $\eta = -0.6 \pm 0.2$, and $E_a = 58 \pm 15$ kJ/mol
for $pH \geq pH_m$; $\log_{10} k_{eff} = 6.9 \pm 0.5$, $\eta = 0.4 \pm 0.1$, and $E_a = 80 \pm 10$ kJ/mol
and $pH_m = 2.1 + 1149/T_K$

6.4 ABSTRACTION SUMMARY–DSNF AND PU DISPOSITION FORM DEGRADATION MODELS

6.4.1 Model Basis

A summary of the selected/abstracted group-specific-upper-limit, conservative, and best-estimate degradation models to be used to license the DSNF and immobilized ceramic Pu waste forms is given in Table 1b.

For all groups, other than the naval DSNF group, the recommended upper-limit model to be used in safety case TSPA analyses is complete dissolution of the waste form during a single TSPA code (e.g., RIP) time step upon exposure of the waste form to groundwater. This is chosen as the upper-limit model in part because TSPA analyses performed for the DSNF (Thornton 1998a, 1998b) have shown that the overall effect of the failure of DSNF-containing waste packages does not significantly contribute to the repository site boundary dose. This document also recommends that the U-metal (Group 7) conservative and best-estimate models be used, along with the U-metal fuel surface area (7×10^{-5} cm^2/g) given in DOE (1999, Appendix B), as surrogate for all but the naval DSNF in cases where less conservative models are required or deemed appropriate by PA personnel.

The group-specific conservative and best-estimate degradation models described in Section 6.3 may be used in the demonstration of conformance to WAC analyses for specific waste forms. It is recognized, however, that they are currently based on limited and generally unqualified corrosion, dissolution, or oxidation data for most of the DSNF groups.

Qualified data/information are used in other AMRs to abstract the uranium dioxide-based SNF degradation model (CRWMS M&O 2000a) and borosilicate glass (as a surrogate for the immobilized ceramic Pu disposition waste form) degradation model (CRWMS M&O 2000c). The data used to generate the metallic uranium-based SNF degradation models were taken under a PNNL QA program.

Commercial LWR SNF will be used as the surrogate for naval SNF in repository performance analyses. Expected releases from naval SNF waste packages was provided in Mowbray (2000). Because of its robust design, the radionuclide releases from naval SNF waste packages are considerably less than releases from commercial LWR SNF waste packages; accordingly, this

assumption is conservative. Naval SNF represents approximately one-tenth of one percent of the spent fuel MTHM inventory. The information contained in Mowbray (2000) is qualified data. The other data and/or information on which the DSNF group models were based are unqualified; therefore, in this analysis they are used for comparison purposes only because it is recommended herein that the N-reactor SNF (Group 7) best-estimate and conservative models be applied to the total DSNF radionuclide inventory for TSPA. The reasons for proposing that these models be used to represent the degradation behavior of the entire DSNF inventory follow:

- The N-reactor SNF model predicts dissolution rates greater than most other groups.
- The total inventory of the Group 3 SNF (the only group showing reaction rates greater than the uranium metal SNF) is only 0.10 MTHM compared to the total inventory of ~2,400 MTHM (DOE 1999, Appendix D).
- There is insufficient qualified information/data to support detailed degradation models for each DSNF type or group.
- TSPA calculations for DSNF (CRWMS M&O 2000f, Section 6.7.1 and Section 7, bullets 11-16) showed that the postclosure site boundary doses are insensitive to the DSNF release model.

Table 3a gives a comparison of the dissolution rates for each fuel group at 50°C (328 K) and 100°C (373 K) for pH 8, 0.002 molar CO_3^- in the contacting water and 20% oxygen in the gas phase. Also included in this table is the approximate inventory in MTHM of each of the DSNF groups. Table 3b further gives an example of the mass fractional degradation rate at 50°C using Equation 2 above, which demonstrates the rapid corrosion rates of these waste forms compared to the long time frames of the TSPA RIP code representation. When the dissolution rates calculated from the models and the relative MTHM are compared for the DSNF groups, it can be seen that use of the Group 7 degradation model to conservatively bound the entire DSNF inventory is justified. Aside from the Group 7 U-metal SNF, the groups that have the highest release rates also have the lowest MTHM. The only DSNF type that the available data indicates dissolves faster than metallic uranium SNF is the Group 2 Pu/U carbide, and the inventory of this fuel is four orders of magnitude lower than that of the N-reactor SNF.

The abstracted best estimate and conservative models for the degradation of the immobilized Pu ceramic disposition waste form are based on the titanate ceramic dissolution model described in Shaw (1999, Section 6.1) and Bourcier (2000, Section IV). The best-estimate model uses the parameters given in Boucier (2000, Table 5) and the conservative model is taken as 10 times the rate given by the best-estimate model. Instantaneous release in a single RIP time step is recommended as the bounding model for postclosure TSPA purposes (CRWMS M&O 2000f, Section 7). If required for the TSPA, the HLW glass model to be used in conjunction with the immobilized Pu ceramic model is that given in CRWMS M&O (2000c).

The fraction of the released radionuclides that may be in colloids versus solutes has not been determined experimentally for the DSNF and immobilized ceramic Pu waste forms, although there is NSNFP-sponsored work in progress concerning colloid formation from the degradation of N-reactor (U-metal) and MOX SNF. Until the results from these experiment are available, it

is proposed herein that the colloid formation and radionuclide attachment/detachment kinetics for the DSNF be taken as that for the CSNF given in CRWMS M&O (2000b, Section 6.2.1.2). Due to the compositional similarity of the borosilicate glass matrix to the HLW glass, the formation and radionuclide attachment/detachment characteristics of colloids released as a result of the degradation of the immobilized ceramic Pu waste form should be taken as that of the HLW glass in CRWMS M&O (2000b, Section 6.3).

6.4.2 Model Uncertainties

The application of the degradation models abstracted in this document involves the extrapolation of data over periods of time that are orders of magnitude greater than the experimental test periods used to generate the data. ASTM C1174-97 (1997, Section 24) recommends that uncertainties in the extrapolation of such models be minimized through the use of models whose mathematical forms are as mechanistic as possible. However, it can be seen from the abstractions above that the lack of any directly relevant experimental dissolution/degradation data for many of the DSNF waste forms, and the relatively small amount of data for those that have been tested, makes the generation of mechanistic models problematic. Additionally, uncertainties in the data used to generate the models–such as in the surface area measurements used to calculate normalized dissolution rates (Gray and Einziger 1998, Section 2.5)–produce significant uncertainties even in the short term application of the models. For this reason, and because preliminary TSPA analyses (Thornton 1998a, 1998b) have shown that the overall performance of the MGR is very insensitive to the degradation rate of the DSNF, the emphasis in this document, whenever possible, is on the application of upper-limit or bounding degradation models.

6.4.3 Surface Area of DSNF Groups and Immobilized Pu Ceramic Waste Form

The abstracted models for the degradation rates of the DSNF groups are generally expressed in terms of the weight of material released per unit surface area of SNF exposed to water per unit time, typically in units of mg/m^2-day. In order to use the conservative and best-estimate models abstracted in this report to calculate the actual release rate from a waste form exposed to water after failure of a waste package, it is, therefore, necessary to use a conservative estimate for the exposed surface area of the fuel. It is not necessary to use a value for the surface area for the upper-limit model since this model, which is total release of the inventory, is not dependant on exposed surface area.

The N-reactor SNF, represented in group 7, constitutes approximately 85% by weight of the total DSNF inventory, and is known to have extensively damaged cladding, in terms of both gross damage and cracking. Although some of the other fuel groups contain fuel types described as intact, such as MOX and the aluminum-based fuels, there is no known documentation of analyses that demonstrate the cladding will maintain fully intact until the time of delivery to the repository, and likewise no known studies showing the cladding will remain intact after waste package failure. DOE (1999, Appendix B) calculated the geometric surface area of potentially exposed fuel based on the geometric characteristics of representative fuels within the groups. Where the fuel group contained damaged fuel, or fuel suspected to be damaged, a roughness factor for the surface area of 5 was applied. The result is the estimate of exposed surface area per gram of fuel group given in the third column of Table 3b. If the best-estimate and/or

conservative degradation models for each DSNF group are required for licensing of specific waste forms for repository emplacement, then those models should use the estimated surface area for the individual groups in calculating overall release rates for waste packages containing those groups. If a repository TSPA analysis, such as, for example, the reasonable representation case, requires a calculation of the overall release from DSNF waste forms, then the weighted average specific surface of 0.03 m^2/g calculated using column 4 and footnote (c) of Table 3b could be used.

For the immobilized Pu ceramic waste form, the multiplication factor (to account for the combined effects of enhanced surface area and radiation damage effects) to be used in conjunction with the best estimate and conservative models should be 30 (Shaw 1999, Section 6.2). The effective surface area to be used in conjunction with the these models is the geometric surface area of the Pu-containing ceramic disks embedded in the HLW glass, 0.0123 m^2 per ceramic disk (CRWMS M&O 1998a, footnote (b) of Table 3b), multiplied by this factor of 30. This translates to an effective surface area of 0.369 m^2 per ceramic disk for the disk design described in CRWMS M&O (1998a, Section 2.2.1).

7. CONCLUSIONS

This document and its conclusions may be affected by technical product input information and assumptions that require confirmation. Any changes to the document or its conclusions that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database.

In particular, the conclusions may be affected by the confirmation of currently unvalidated inputs concerning the dissolution of U-metal SNF (Gray and Einziger 1998), the dissolution of unirradiated/uncorroded U-metal (Pasupathi 2000), the dissolution rates of the immobilized PU ceramic (Shaw 1999), and unvalidated assumptions concerning the use of LWR SNF as a surrogate for naval SNF (Sections 5.3 and 5.4) and the similarity of DSNF colloid behavior to that of CSNF and HLW glass (Section 5.5). There are analytical activities and tests sponsored by OCRWM, NNPP, and NSNFP currently underway that should enable confirmation of these inputs and assumptions. Should these inputs and assumptions not be confirmed/validated, then the only DSNF degradation model, which could be used for the TSPA-SR or TSPA-LA, would be the Upper Limit model (i.e., complete dissolution of the waste form during one TSPA time step). This model does not require confirmation/validation because it represents the fastest possible release kinetics.

7.1 DSNF DEGRADATION MODELS VALIDITY

7.1.1 Dissolution Models

The only DSNF waste forms for which there are directly applicable dissolution data suitable for generating a degradation model are the Group 7 (uranium metal), and Group 9 (Al-based) DSNF. It is anticipated that new dissolution data for Group 4 (MOX) DSNF (DOE 1998) will become available in the near future. This DSNF data is currently unqualified. In contrast to this, sufficient qualified experimental data for the dissolution of commercial uranium dioxide LWR

spent fuel similar to the Group 8 DSNF (CRWMS M&O 2000a) and HLW glass (CRWMS M&O 2000c) have been generated under the OCRWM QARD program to generate adequate semi-empirical models for the dissolution rate of these waste forms.

The NSNFP has sponsored dissolution testing at PNNL of N-reactor SNF, but this testing is not yet complete. Likewise, the dissolution testing for the Al-based DSNF sponsored by NSNFP at SRS is not yet complete; therefore, the results should be regarded as preliminary. NSNFP has also initiated dissolution testing of MOX DSNF, but the results are, at this time, not yet sufficient to formulate a degradation model. There is also testing of candidate Pu immobilized ceramic compositions underway at ANL, PNNL, and LLNL that may enable improved release models in future revisions of this AMR.

There are no known current plans at NSNFP or elsewhere to perform dissolution tests on surrogates of the other DSNF groups. Thus, the models referred to in Table 1 for those groups are not expected to be validated. However, these models do not require validation if the models recommended for TSPA-SR (i.e., the U-metal SNF models) conservatively bound the degradation rates calculated from these models, and the analyses in this report demonstrate that they do.

The results of TSPA sensitivity analyses for DSNF (CRWMS M&O 2000f) indicate that the performance of the repository is very insensitive to the DSNF degradation kinetics. If, because of this insensitivity, the upper-limit model is the only one used for TSPA analyses, then validation of the other models would be unnecessary since they would not be used. Since the upper-limit release model is that of instantaneous release of all radionuclides, it does not require validation since it represents the maximum possible rate for TSPA analyses. If validation of the best-estimate and/or conservative degradation models for the individual DSNF groups is required for licensing of specific waste forms for repository emplacement, then those models would need to be validated using confirmatory test data per the requirements in ASTM C 1174-97. The criteria for validation would be the similarity or closeness of the confirmatory test data to the release rates predicted by the models. There is currently some limited information concerning the degradation of N-reactor and aluminum-based DSNF from the NSNFP-sponsored testing programs. Further NSNFP-sponsored confirmatory testing is either underway or planned for N-reactor, MOX, and aluminum-based DSNF. Testing for the degradation rates of samples from the other fuel groups is not currently anticipated.

Therefore, the conservative and best-estimate models selected/abstracted in this document for the various DSNF waste-form groups have various degrees of technical data support in their generation. Only the Group 8 (U oxide) dissolution model will become a validated model (CRWMS M&O 2000a), but usage of this model for the rest of the DSNF in TSPA would be non-conservative. The other DSNF models would require qualification and/or confirmatory testing per the ASTM C 1174-97 logic if they were to be directly invoked to license specific waste forms for emplacement. Additionally, the available information shows that the only DSNF group that has dissolution rates greater than those of the Group 7 uranium metal SNF is the Group 3 (U/Pu carbide) SNF, and the inventory of this material is extremely small. For these reasons it is concluded that the Group 7 conservative and best-estimate dissolution models would likely bound the degradation rate of the total DSNF inventory. The supportive data based on the

dissolution testing sponsored by the NSNFP at PNNL would need to be qualified per AP-SIII.2Q, Section 5.5 of AP-3.10Q, or the model derived accepted under AP-3.15Q.

The upper-limit model for the DSNF inventory would be that of complete release during one time step of the TSPA analysis. This model does not require qualification, validation, or confirmatory testing since it represents essentially the instantaneous mobilization of all the contents of a waste package containing DSNF. Only the total inventory of radionuclides in the inventory of DSNF would need to be qualified. Thus, the upper-limit model proposed for the DSNF and Pu disposal waste forms are impacted primarily by the total inventory of radionuclides that are present in the SNF.

The conservative and best-estimate models abstracted herein for use in TSPA for the DSNF waste forms are primarily impacted by the validity of the uranium metal-based SNF dissolution models. The conservative and best-estimate models recommended herein for the degradation of the immobilized ceramic Pu waste form are primarily impacted by the validity of the titanate-ceramic degradation models (CRWMS M&O 2000c).

If used as direct input to the TSPA, both the conservative and best estimate models (based on the degradation kinetics of the N-reactor SNF) need to be further validated. Validation would be done primarily by comparison of the degradation analysis results (i.e., the degradation rates predicted by the models) with accepted or qualified data from performance confirmation studies. These studies would probably primarily consist of NSNFP-sponsored flow-through testing at PNNL and unsaturated test data generated at ANL on N-reactor SNF specimens. The criterion for validation would be the closeness of the new test data to the best-estimate model predictions and the consequent verification that the conservative model(s) overpredict the experimental degradation rates.

The other models, which may require validation, are the conservative and best-estimate models for the degradation of the immobilized Pu ceramic waste form and the naval fuel models. Tests underway concerning the dissolution of the immobilized Pu ceramic waste form are expected to produce data in support of the validation of the titanate ceramic model (see Section 7.2.2 below). Information in support of the demonstration that the degradation of the naval SNF is bounded by the CSNF model is to be provided by NNPP.

Other performance confirmation studies that may produce information useful for helping validate these models could include the NSNFP-sponsored testing of MOX and aluminum-based DSNF and testing of N-reactor SNF at Hanford in support of the Hanford K-basin N-reactor SNF dry storage program. The testing of the MOX and Al-based DSNF could support validation by demonstrating that the degradation rate of these fuel forms is always less than that predicted from the N-reactor SNF-based models.

7.1.2 Colloid Formation

Compared to colloids formed from the corrosion of HLW glass, very little radionuclide-bearing colloidal material was detected in tests on the corrosion product of the uranium dioxide-based commercial LWR SNF (CRWMS M&O 2000b, Section 6.1.1.1). In particular, no colloids with embedded radionuclide phases similar to those observed in HLW glass tests were observed in the

much fewer number of CSNF tests. Even less information is currently available concerning the quantity or types of colloids formed from DSNF corrosion, but preliminary tests at ANL (Batt 1999; Hurt 2000) indicate that colloid formation from metallic uranium-based DSNF may be significant. DSNF colloid formation and characterization testing has been initiated by NSNFP at ANL for N-reactor and MOX DSNF samples, but the results are still preliminary. For modeling purposes it will be assumed that only colloids with reversibly attached radionuclides are formed in the corrosion of the DSNF (CRWMS M&O 2000b, Section 6.3). This essentially means that DSNF colloids speciation and attachment/detachment kinetics will be similar to that of the CSNF colloids. This assumption is potentially non-conservative and will require validation as pertinent results of ongoing confirmatory tests become available.

7.2 RECOMMENDED MODEL USAGE FOR TSPA

7.2.1 DSNF

The upper-limit model for each DSNF group and the Pu disposal waste form should be taken as complete release of radionuclides upon exposure to groundwater within one time step of the TSPA analysis. The upper-limit model should be used in the TSPA safety case since the conservative and best-estimate models are currently unqualified and require further test data for qualification. Use of a model other that the upper-limit model for TSPA could result in difficulties during subsequent efforts to demonstrate conformance to WAC requirements for waste form emplacement. Upper-limit models should also be used in cases where their usage in TSPA analyses results in acceptable boundary doses, and when other less conservative models are not needed. It should be noted that, as shown by the fractional release values in Table 3b, the release rates of the various waste forms on current TSPA time scales are very rapid for all the models, essentially releasing all material within a single time step. Future applications of the RIP TSPA codes may or may not require more refined models for the various DSNF waste forms.

The conservative release models represent practical bounding cases for the degradation of a specific DSNF group or waste form. It is recommended that the N-reactor SNF conservative degradation model, with the weighted average DSNF effective exposed specific surface area of 0.10 m^2/g given in Section 6.4.3 and Table 3b and as adjusted for the relative density of the particular SNF matrix with respect to that of metallic uranium, be used to represent the entire DSNF inventory (with the exception of the naval SNF, which uses the CSNF model) for TSPA analyses in cases where PA personnel determine that a less conservative model than the upper-limit model is justified as follows:

$$\text{Rate in mg/cm}^2\text{-hr} = 1.26 \times 10^{11} \exp(-66{,}400/RT_K)(\rho_{matrix}/\rho_{U\text{-}metal})$$

where R is the gas constant (8.314 J/mol-K). (Eq. 5)

where ρ_{matrix} is the density of the spent fuel matrix, and $\rho_{U\text{-}metal}$ is the density of uranium metal.

This model could be used in the TSPA analyses for the reasonable representation case. This model has not as yet been validated and may require confirmation through confirmatory testing per the requirements of ASTM C 1174-97 (1997).

The best-estimate degradation model represents a best estimate of the actual dissolution rate for the DSNF group. The best-estimate N-reactor SNF release-rate model (as adjusted for the relative density of the particular SNF with respect to that of metallic uranium) could be used to represent the release rate of the entire DSNF inventory (with the exception of the naval SNF) in TSPA cases that PA personnel determine require a more realistic representation of the actual degradation kinetics:

$$\text{Rate in mg/cm}^2\text{-hr} = 2.52 \times 10^{10} \exp(-66{,}400/RT_K)(\rho_{matrix}/\rho_{U\text{-metal}})$$

where R is the gas constant (8.314 J/mol-K). (Eq. 6)

where ρ_{matrix} is the density of the spent fuel matrix, and $\rho_{U\text{-metal}}$ is the density of uranium metal.

The conservative and best estimate release models should not be used in safety case applications of the performance assessment codes since they are currently largely based on unvalidated data/analyses. Validation of the conservative and best-estimate U-metal dissolution models would require analysis per AP-SIII.2Q and may require further service condition and confirmatory testing per ASTM C 1174-97. Saturated flow-through testing at PNNL and unsaturated drip testing at ANL continues on N-reactor SNF that could be used to support the validation this model.

It is expected that the application of the DSNF degradation models to the safety case for the TSPA-SR will involve usage of the upper-limit models or perhaps conservative models. Decisions as to exactly which models will be used will depend upon the sensitivity of the TSPA results to the models and the generation of dissolution test data sufficient to abstract and support the model. It is anticipated that the overall postclosure TSPA will be insensitive to the dissolution rate of the DSNF or Pu disposition waste forms (CRWMS M&O 2000f, Section 7.).

The upper-limit group 7 (U metal) degradation model should also be used in the case of TSPA analyses wherein the metallic uranium-based SNF (primarily the N-reactor SNF) is assumed or analyzed to be pyrophoric in the emplacement condition. For bounding calculations, it should be assumed that the entire radionuclide inventory in the DOE SNF is released during the TSPA time step analyzed after waste package failure and contact with water/moisture.

There are currently little data or information available concerning the speciation of the material released from the DSNF waste forms between solute and colloid forms. Some as yet incomplete information indicates that more colloids may form from the degradation of N-Reactor fuel (which will constitute approximately 80% of the DSNF inventory by weight) than for the CSNF and HLW glass waste forms under repository conditions (Gray and Einziger 1998, Section 4.2; Hurt 2000). It is currently planned to co-dispose all the N-reactor SNF canisters, called Multicanister Overpacks or MCOs, with HLW glass canisters in approximately 160 waste packages (two MCOs and two HLW glass canisters per waste package). Also, it is also currently planned that all DSNF (with the exception of the naval SNF and the immobilized Pu waste forms) canisters will be co-disposed with HLW glass in their waste packages (five HLW canisters with one DSNF canister in the center) (CRWMS M&O 2000d, Attachment I, Table I-1). Because of this co-disposal plan for DSNF and because the quantity of DSNF in the repository will only be a few percent by weight of the total SNF and HLW glass inventory, it is

recommended that for TSPA-SR, the colloid formation/migration dynamics recommended in CRWMS M&O (2000b), based on CSNF colloid behavior, be applied to the DSNF waste forms. In the event that the TSPA-SR becomes sensitive to this assumption, it must be validated or modified through further analysis or testing. Testing that can be used to support the validation of the use of the colloid model of CRWMS M&O (2000b) for DSNF is currently being performed at ANL (Mertz 2000).

7.2.2 Immobilized Ceramic Pu Disposition Waste Form

For the immobilized ceramic Pu disposal waste form, the upper-limit degradation model should be taken as the instantaneous release of all the Pu from the waste package upon postclosure contact with groundwater. Since this model represents a bounding upper case, it does not require validation for its usage.

The conservative model for the degradation of the immobilized ceramic Pu disposition waste form should be taken as the dissolution rate of the borosilicate glass matrix with the assumption that the plutonium is homogeneously dispersed in the glass phase when contacted by groundwater.

For the best-estimate case, the release of the immobilized ceramic Pu should be taken as the dissolution rate of the ceramic, taken as the high pH dissolution rate given in Shaw (1999) with an exposed surface area of the ceramic corresponding to the total geometric surface area of the Pu-containing ceramic disks in a waste canister. This estimate will still be somewhat conservative because it doesn't take credit for the glass-matrix coverage of surface areas on the Pu ceramic disks.

These conservative and best-estimate models for the immobilized ceramic Pu have not been validated. If used in the TSPA, they would require validation per AP-SIII.2Q and/or confirmatory testing per the requirements of ASTM C1174. There are tests currently being performed at ANL that could provide support for validation of these models if they are used in the TSPA.

Table 1b. DSNF, Naval SNF, Pu Disposition Release/Degradation Models

Waste Type	DSNF Group (1-1)	Upper-limit Model			Conservative Model			Best-estimate Model		
		Surrogate	Model	Ref.	Surrogate	Model	Ref.	Surrogate	Model	Ref.
DSNF	1. Naval	See Section 6.3.1	See Section 6.3.1	(1-7)	See Section 6.3.1	See Section 6.3.1	(1-7)	See Section 6.3.1	See Section 6.3.1	(1-7)
DSNF	2. Pu /U Alloy	Fermi	Full release over TSPA time step	N/A	U – 6% Mo	(bounding) 10 X Unirradiated U-metal best-estimate Wet oxic conditions: R (kg/m^2-s) = 1.88 x 10^4 exp (-7970/T_K) Humid oxic conditions: R (kg/m^2-s) = 0.27 x 10^3 exp (-7240/T_K)	(1-9)	U - 8% Mo	(semi-empirical) Unirradiated U-metal best-estimate Wet oxic conditions: R (kg/m^2-s) = 1.88 x 10^3 exp (-7970/T_K) Humid oxic conditions: R (kg/m^2-s) = 0.27 x 10^2 exp (-7240/T_K)	(1-9)
DSNF	3. Pu/U Carbide	FFTF	Full release over TSPA time step	N/A	UC_2	(bounding) 100 X Unirradiated U-metal best-estimate R (kg/m^2-s) = 100 x [1.88 x 10^3 exp (-7970/T_K)]	(1-8)	UC_2	(bounding) 100 X Unirradiated U-metal best-estimate: R (kg/m^2-s) = 100 x [1.88 x 10^3 exp (-7970/T_K)]	(1-8)
DSNF	4. MOX and Pu Oxide	LWR SNF	Full release over TSPA time step	N/A	LWR SNF	(bounding) 100 X Intact U Oxide best-estimate	(1-6)	UO_2	(semi-empirical) U Oxide best-estimate model	(1-5)
DSNF	5. Th/U Carbide	UC_2	Full release over TSPA time step	(1-4)	UC_2	(bounding) 10 X Unirradiated U-metal best-estimate	(1-4)	SiC	(semi-empirical) R (kg/m^2-s) = 0.6 x 10^{-12}	(1-4)
DSNF	6. Th/U Oxide	FSV	Full release over TSPA time step	N/A	ThO_2 - 2 wt% UO_2	(bounding) 1000 X Best-estimate	(1-3)	Synroc	(semi-empirical) k (mg/m^2-d) = 82.0 x 10$^{(-1000/T_K)}$	(1-3)
DSNF	7. U-Metal-Based	N-Reactor	Full release over TSPA time step	N/A	N-reactor	(semi-empirical) 1.26 x 10^{11}exp(-66400/RT_K) mg/cm^2-hr R = 8.314 J/mol-K	(3)	N-reactor	(semi-empirical) 2.52 x 10^{10}exp(-66400/RT_K) mg/cm^2-hr R = 8.314 J/mol-K	(2)

Waste Type	DSNF Group [1-1]	Upper-limit Model			Conservative Model			Best-estimate Model		
		Surrogate	Model	Ref.	Surrogate	Model	Ref.	Surrogate	Model	Ref.
DSNF	8a. Intact U Oxide	LWR SNF	Full release over TSPA time step	N/A	LWR SNF	(bounding) 100 X Intact U Oxide best-estimate	(1-6)	LWR SNF	(semi-empirical) Commercial LWR SNF dissolution model[a]	(1-6)
DSNF	8b. Damaged U Oxide	TMI	Full release over TSPA time step		TMI	(bounding) 100 X Intact U Oxide best-estimate		TMI	(bounding) 100 X Intact U Oxide best-estimate	
DSNF	9. Al-based	FRR, ATR	Full release over TSPA time step	N/A	U-Al alloy in bicarbonate solution	(bounding) 36 mgU/m^2-d @ 25°C 360 mgU/m^2-d @ 90°C	(5)	SRS U-Al SNF in J-13 well water	(empirical) 0.22 mgU/m^2-d @ 25°C 2.20 mgU/m^2-d @ 90°C	(5)
DSNF	10. Unknown	N/A	Full release over TSPA time step	N/A	N/A	(bounding) 10 X Unirradiated U-metal best-estimate	(1-11)	N/A	(empirical) Unirradiated U-metal best-estimate	(1-11)
DSNF	11. U-Zr-Hx	TRIGA	Full release over TSPA time step	N/A	U-Zr-Hx	(bounding) 0.1 X U-oxide best-estimate	(1-12) and (7)	U-Zr-Hx	(empirical) 0.1 x U-oxide best-estimate	(1-12) and (7)
Pu	N/A	N/A	Full release over TSPA time step	N/A	Multi-phase titanate ceramic	10 times the best-estimate ceramic model (b)	(4) and (6)	Multi-phase titanate ceramic	(semi-empirical) (b) pH < 7 Log_{10} R = -0.167 (pH) – 4.66 pH ≥ 7 Log_{10} R = 0.25 (pH) – 8 R in g/m^2-d	(4) and (6)

Notes: (bounding)–indicates a bounding model per the materials behavior modeling logic of ASTM C 1174-97
(empirical)–indicates an empirical model per the materials behavior modeling logic of ASTM C 1174-97
(semi-empirical)–indicates a semi-empirical model per the materials behavior modeling logic of ASTM C 1174-97
(mechanistic)–indicates a mechanistic model per the materials behavior logic of ASTM C 1174-97

[a] Commercial LWR SNF Dissolution Model

Source: CRWMS M&O (2000a, Section 6.2.2.2, Equation 11 and Table 14)

$$Log_{10} R\ (mg/m^2\text{-}d) = 5.479057 + [-2457.050662\ (1/T_K)] + [1.5110878\ (-\log_{10}(CO_3))] + [-1.729906\ (-\log_{10}O_2)] + [0.234718\ pH] + [-0.799526\ \log_{10} BU] + [400.755947\ (-\log_{10} O_2)\ (1/T_K)] + [780.806133\ (\log_{10} BU)\ (1/T_K)] + [0.172305\ (\log_{10} BU)\ (-\log_{10}(CO_3))] + [0.174428\ (\log_{10}BU)\ (-\log_{10} O_2)] + [-0.271203\ (\log_{10}BU)\ (pH)] + [-0.339535\ (-\log_{10}(CO_3))^2]$$

[b] The effect of enhanced surface area (over the geometric surface area of the ceramic disks) and radiation effects in the ceramic matrix is to increase the effective surface area for dissolution by a factor of 30 (Shaw 1999, Section 6,2)

Sources/references:

(1) DOE (1999)
- (1-1) Table 5-2
- (1-2) Not used
- (1-3) Section 6.6 and Figure 6-4
- (1-4) Section 6.5 and Figure 6-3
- (1-5) Section 6.4
- (1-6) Sections 6.4 and 6.8
- (1-7) Section 6.1
- (1-8) Section 6.3
- (1-9) Section 6.2 and Figure 6.1
- (1-10) Not used
- (1-11) Section 6.10
- (1-12) Section 6.11

(2) Gray and Einziger (1998, Section 4.1, Equation 3)

(3) Gray and Einziger (1998, Figures 3-13)

(4) Shaw (1999)

(5) Wiersma and Mickalonis (1998, Tables 3 and 4)

(6) CRWMS M&O (2000c)

(7) LMITCO (1997, Section 2.1.8)

Table 2. Summary and Comparison of N-Reactor SNF Stage 1 and Stage 2 Dissolution Rates (mg/m^2-d)

T(°C)	CO_3^- (molar)	pH	HNO3 (molar)	J-13 well water	Unirradiated U-Metal Rate[6]	Measured[1] Stage 1 Rate (mg/m^2-d)	Calculated[2] Stage 1 Rate (mg/m^2-d)	Measured[3] Maximum Stage 2 Rate (mg/m^2-d)
25	2×10^{-2}	5	--	--	394	63	79	[5]
25	2×10^{-2}	8	--	--	394	160	145	220
25	2×10^{-4}	10	--	--	394	50	44	100
75	2×10^{-2}	10	--	--	18379	2100	1851	4000
75	2×10^{-4}	5	--	--	18379	200	142	1000
75	2×10^{-4}	8	--	--	18379	150	250	180,000
25	N/A	5	1×10^{-5}	--	394	38	--	[5]
25	N/A	3	1×10^{-3}	--	394	130	--	[5]
25	2×10^{-3}	8.5	--	X	394	[4]	72	13000
75	2×10^{-3}	8.5	--	X	18379	[4]	614	55000

(1) As given in Table 1 of Gray and Einziger (1998)
(2) Calculated using Equation 1: $\log R\ (mg/m^2\text{-}d) = 8.52 + 0.347 \log[CO_3^-] + 0.088\ pH - 1929/T_K$
(3) As estimated from the Cs release plots from Figures 7 through 15 of Gray and Einziger (1998)
(4) These samples showed only Stage 2 dissolution behavior
(5) These samples showed only Stage 1 dissolution behavior
(6) Calculated from the expression for wet oxic condition corrosion: $R = 1.88 \times 10^3 \exp(-7970/T_K)\ kg/m^2\text{-}s = 1.62 \times 10^{14} \exp(-7970/T_K)\ mg/m^2\text{-}d$ from DOE (1999)

Table 3a. Dissolution Rates at pH 8.5, 0.002M CO_3^{--}, and 20% Oxygen Calculated from Proposed Models

DSNF GROUP	Approximate Fuel Matrix Density, ρ [b] in g/cm^3 ($\rho/\rho_{Group\ 7}$)	Inventory (MTHM)[a]	Best-estimate Corrosion Rate[c] @ 50°C (mg/m^2-d)	Best-estimate Corrosion Rate[c] @100°C (mg/m^2-d)	Conservative Corrosion Rate[c] @ 50°C (mg/m^2-d)	Conservative Corrosion Rate[c] @ 100°C (mg/m^2-d)
Group 1–Naval SNF	(see 6.3.1)	65	(see 6.3.1)	(see 6.3.1)	(see 6.3.1)	(see 6.3.1)
Group 2–Pu/U Alloy	19.05 (1)	8.5	3.1×10^3	8.5×10^4	3.1×10^4	8.5×10^5
Group 3–Pu/U Carbide	11.28 (0.59)	0.1	1.84×10^5	5.04×10^6	1.84×10^5	5.04×10^6
Group 4–MOX and PU Oxide	11.03 (0.58)	11.59	6.21	35.51	621	3551
Group 5–Th/U Carbide	9.35 (0.49)	24.52	0.025	0.025	1.52×10^4	4.17×10^5
Group 6–Th/U Oxide	9.87 (0.52)	46.98	0.034	0.088	34	88
Group 7–U Metal-Based	19.05 (1)	1984.81	1.1×10^5	3.0×10^6	5.5×10^5	1.5×10^7
Group 8a–Intact U Oxide[e]	9.86 (0.52)	166.2 (8a + 8b)	9.32	22.8	932	2280
Group 8b–Damaged U Oxide	9.86 (0.52)	--	932	2280	932	2280
Group 9–Al-Based	2.70 (0.14)	19.54	~0.03	~0.3	~5	~50
Group 10–Unknown SNF	19.05[d] (1)	4.24	3.1×10^3	8.5×10^4	3.1×10^5	8.5×10^6
Group 11–U-Zr-Hx	6.89 (0.36)	1.51	0.40	2.2	39	220
Pu Immobilized Ceramic	5.5 (0.29) (g)	N/A	0.011 (f)	0.31 (f)	0.11 (h)	3.1(h)

Source: [a] DOE (1999, Appendix D, Radionuclide Inventory Summary of DOE SNF and HLW)

[b] DOE (1999, Appendix C, Attachment A)

[c] $R = R_{group7} \times (\rho/\rho_{group\ 7})$

[d] Conservatively taken to be that of metallic uranium

[e] Equation 3, nominal burnup of 40 MWd/kgU

[f] Shaw (1999, Section 6.1, Table 6)

[g] CRWMS M&O (1998a, Section 2.2.1); note also that the estimated Pu content of the ceramic is 10.5% per Section 2.2.3

[h] 10 times best estimate; Section 6.3.12

Table 3b. Fractional DSNF Waste Form Dissolution Rates at 50°C, pH 8.5, 0.002M CO_3^{--}, and 20% Oxygen Calculated for Best-estimate Models

DSNF GROUP	Best-estimate Release Rate (mg/m^2-d)	Exposed Specific Surface Area (m^2/g) [a]	Exposed Total Surface Area (m^2) [c]	Fractional Corrosion Rate (d^{-1})
Group 1–Naval SNF	(see 6.3.1)	See Section 6.3.1	(see 6.3.1)	(see 6.3.1)
Group 2–Pu/U Alloy I	3.1×10^{3}	1.2×10^{-3}	2.04×10^{4}	3.7×10^{-3}
Group 3–Pu/U Carbide	1.84×10^{5}	2.7×10^{-3}	5.40×10^{2}	0.84
Group 4–MOX and PU Oxide	6.21	4.0×10^{-3}	9.27×10^{4}	4.3×10^{-5}
Group 5–Th/U Carbide	0.025	2.2×10^{-2}	1.08×10^{6}	1.1×10^{-6}
Group 6–Th/U Oxide	0.034	3.6×10^{-4}	3.38×10^{4}	2.4×10^{-8}
Group 7–U Metal-Based	1.1×10^{5}	7.0×10^{-5}	2.86×10^{5}	0.7×10^{-2}
Group 8a–Intact U Oxide[e]	9.37	4.0×10^{-1}	1.33×10^{8}	4.3×10^{-3}
Group 8b–Damaged U Oxide	937	4.0×10^{-1}	--	4.3×10^{-1}
Group 9–Al-Based	~0.03	6.5×10^{-3}	2.54×10^{5}	1.4×10^{-4}
Group 10–Unknown SNF	3.1×10^{3}	4.0×10^{-1}	3.39×10^{6}	1.24
Group 11–U-Zr-Hx	0.40	1.0×10^{-4}	3.02×10^{2}	1.1×10^{-7}
Pu Immobilized Ceramic	1.33×10^{-3}	2.5×10^{-5} [b]	N/A	3.3×10^{-11}
Total I	N/A	N/A	1.38×10^{8}	N/A

Source: [a] DOE (1999, Appendix B, Attachment A)

[b] CRWMS M&O (1998a, Sections 2.2.1 and 2.2.2):
surface area per disk =
1 inch thick and 2.625 inches in diameter = $[2\pi\ (2.625/2)^2 + \pi(2.625)(1)]\ in^2/disk\ [0.0254\ m/in]^2 = 0.0123\ m^2/disk$
weight per disk = (9755 g/can)/ (20 disks/can) = 487.75 g/disk
so, specific surface area = $(0.0123\ m^2/disk)/(487.75\ g/disk) = 2.5 \times 10^{-5}\ m^2/g$

[c] Obtained by multiplying the specific surface area given in column 3 in m^2 per gram by the inventory of the DSNF group given in Table 3a; using 1 MTHM = 2000 kg = 2,000,000 g. The total MTHM from column 3 of Table 3a is approximately 2333 MTHM or 4.67×10^9 g. Thus the weighted average specific surface area is $1.38 \times 10^8\ m^2 / 4.67 \times 10^9\ g \cong 0.03\ m^2/g$

8. INPUTS AND REFERENCES

8.1 DOCUMENTS CITED

Abrefah, J.; Buchanan, H.C.; Gerry, W.M.; Gray, W.J.; and Marschman, S.C. 1998. Dry Air *Oxidation Kinetics of K-Basin Spent Nuclear Fuel.* PNNL-11786. [Richland, Washington]: Pacific Northwest National Laboratory. TIC: 243094.

Abrefah, J.; Gray, W.J.; Ketner, G.L.; Marschman, S.C.; Pyecha, T.D.; and Thornton, T.A. 1995. *K-Basin Spent Nuclear Fuel Characterization Data Report.* PNL-10778. Richland, Washington: Pacific Northwest National Laboratory. TIC: 243197.

Abrefah, J.; Huang, F.H.; Gerry, W.M.; Gray, W.J.; Marschman, S.C.; and Thornton, T.A. 1999. *Analysis of Ignition Testing on K-West Basin Fuel.* PNNL-11816. Richland, Washington: Pacific Northwest National Laboratory. TIC: 248558.

Batt, D.L. 1999. Minutes, Release Rate Test Team Meeting Minutes from November 4, 1999. CCN00-001277. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. TIC: 248427.

Bourcier, W.L. 1999. *Interim Report on Development of a Model to Predict Dissolution Behavior of the Titanate Waste Form in a Repository and Compilation of Data from SPFT Ceramic Dissolution Tests.* PIP-00-003. Livermore, California: Lawrence Livermore National Laboratory. TIC: 248554.

CRWMS M&O (Civilian Radioactive Waste Management System Management and Operating Contractor) 1998a. *Immobilized in Ceramic.* Volume II of *Report on Intact and Degraded Criticality for Selected Plutonium Waste Forms in a Geologic Repository.* BBA000000-01717-5705-00020 REV 01. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19981217.0112.

CRWMS M&O 1998b. "Waste Form Degradation, Radionuclide Mobilization, and Transport Through the Engineered Barrier System." Chapter 6 of *Total System Performance Assessment-Viability Assessment (TSPA-VA) Analyses Technical Basis Document.* B00000000-01717-4301-00006 REV 01. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19981008.0006.

CRWMS M&O 1999a. Not Used.

CRWMS M&O 1999b. Not Used.

CRWMS M&O 1999c. Not Used.

CRWMS M&O 1999d. Not Used.

CRWMS M&O 1999e. *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System.* ANL-UDC-SE-000001 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990928.0216.

CRWMS M&O 1999f. Not Used.

CRWMS M&O 1999g. *1101213FM3 Waste Form Analyses & Models - PMR.* Activity Evaluation, December 14, 1999. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19991217.0048.

CRWMS M&O 2000a. *CSNF Waste Form Degradation: Summary Abstraction.* ANL-EBS-MD-000015 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000121.0161.

CRWMS M&O 2000b. *Waste Form Colloid-Associated Concentrations Limits: Abstraction and Summary.* ANL-WIS-MD-000012 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000525.0397.

CRWMS M&O 2000c. *Defense High Level Waste Glass Degradation.* ANL-EBS-MD-000016 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000329.1183.

CRWMS M&O 2000d. *Inventory Abstraction.* ANL-WIS-MD-000006 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000414.0643.

CRWMS M&O 2000e. *Waste Package Materials Department Analysis and Modeling Reports Supporting the Waste Form PMR.* Development Plan TDP-EBS-MD-000005 REV 01. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000202.0173.

CRWMS M&O 2000f. *Performance Assessment Sensitivity Analyses of Selected U.S. Department of Energy Spent Fuels.* ANL-WIS-MD-000001 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000710.0530.

CRWMS M&O 2000g. *Waste Package Related Impacts of Plutonium Disposition Waste Forms in a Geologic Repository.* TDR-EBS-MD-000003 REV 01 ICN 01. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000510.0163.

DOE (U.S. Department of Energy) 1998. *NSNFP Release-Rate Test Program Plan.* DOE/SNF/REP-022 Rev. 0. Washington, D.C.: Department of Energy. TIC: 245353.

DOE (U.S. Department of Energy) 1999. *DOE Spent Nuclear Fuel Information in Support of TSPA-SR.* DOE/SNF/REP-0047, Rev. 0. Washington, D.C.: Department of Energy. TIC: 245482.

DOE (U.S. Department of Energy) 2000a. Not Used.

DOE (U.S. Department of Energy) 2000b. *DOE Spent Nuclear Fuel Grouping in Support of Criticality, DBE, TSPA-LA.* DOE/SNF/REP-046 Rev.0, Idaho Falls, Idaho: U.S. Department of Energy, Idaho Operations Office. TIC: 248046

DOE (U.S. Department of Energy) 2000c. *Quality Assurance Requirements and Description.* DOE/RW-0333P, Rev. 10. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000427.0422

Gray, W.J. 2000. *Dissolution Rates of Aluminum-Based Spent Fuels Relevant to Geologic Disposal.* PNNL-11979. Richland, Washington: Pacific Northwest National Laboratory. TIC: 248761.

Gray, W.J. and Einziger, R.E. 1998. *Initial Results from Dissolution Rate Testing of N-Reactor Spent Fuel Over a Range of Potential Geologic Repository Aqueous Conditions.* DOE/SNF/REP-022, Rev. 0. Washington, D.C.: U.S. Department of Energy. TIC: 245380.

Hurt, W.L. 2000. May 11, 2000, Release Rate Test Review Meeting Minutes. CCN 00-012071. Idaho Falls, Idaho: INEEL, Bechtel Bwxt. TIC: 248756.

LMITCO (Lockheed Martin Idaho Technologies Company) 1997. *Uranium-Zirconium Hydride Fuels for TRIGA Reactors.* UZR-28. Idaho Falls, Idaho: Idaho National Engineering and Environmental Laboratory. TIC: 245412.

Mertz, C.J. 2000. *Test Plan for the Characterization of Spent Nuclear Fuel Colloids.* SNF-3A-121, Revision 0. [Argonne, Illinois]: Argonne National Laboratory. TIC: 247671.

Mowbray, G.E. 2000. Revised Source Term for Naval Spent Nuclear Fuel and Special Case Waste Packages. Letter from G.E. Mowbray (DOD) to Dr. J.R. Dyer (DOE/YMSCO), September 6, 2000, with attachments. ACC: MOL.20000911.0354.

Pasupathi, P. 2000. *Metallic Uranium Dissolution Correlation from National Spent Nuclear Fuel Program Draft Report on the Oxidation Of Metallic Spent Fuel.* Input Transmittal 00334.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000831.0029.

Shaw, H., ed. 1999. *Plutonium Immobilization Project Input for Yucca Mountain Total Systems Performance Assessment.* PIP-99-107. Livermore, California: Lawrence Livermore National Laboratory. TIC: 245437.

Thornton, T.A. 1998. HPPP Issue 1; Preliminary TSPA for a Pyrophoric Event Involving N-Reactor SNF Waste Packages Interoffice correspondence from Thornton, T.A. (CRWMS M&O) to Clouet, J.S., Sareen S.S., and David Stahl, September 21, 1998 ACC: MOL.19981019.0001.

Thornton, T.A. 1998. HPPP Issue 1; Preliminary TSPA for N-Reactor SNF Waste Packages. Interoffice correspondence from T.A. Thornton (CRWMS M&O) to J.S. Clouet, S.S. Sareen, and D. Stahl, June 1, 1998, LV.WP.TAT.05/98-111, with attachment. ACC: MOL.19980730.0142.

Welsh, T.L.; Baker, R.B.; Hoppe, E.W.; Schmidt, A.J.; Abrefan, J.; Tingey, J.M.; Bredt, P.R.; Golcar, G.R.; and Makenas, B.J. 1997. *Analysis of Sludge from Hanford K East Basin Canisters.* HNF-SP-1201. [Richland, Washington]: Duke Engineering & Services Hanford. TIC: 248549.

Wiersma, B.J. and Mickalonis, J.I. 1998. *Preliminary Report on the Dissolution Rate and Degradation of Aluminum Spent Nuclear Fuels in Repository Environments.* WSRC-TR-98-00290. Aiken, South Carolina: Westinghouse Savannah River. TIC: 245382.

8.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

AP-3.10Q, Rev. 2, ICN 3. *Analyses and Models.* Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000918.0282.

AP-3.15Q, Rev.1, ICN 2. *Managing Technical Product Inputs.* Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000713.0363.

AP-SIII.2Q, Rev. 0, ICN 2. *Qualification of Unqualified Data and the Documentation of Rationale for Accepted Data.* Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19991214.0625.

ASTM C 1174-97. 1997. Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste. West Conshohocken, Pennsylvania: American Society for Testing and Materials. TIC: 246015.