United States Department of Energy
Office of Environmental Management

***Interaction of DOE SNF
And Packaging Materials***

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*Sensitivity Analysis—Interaction of DOE SNF
And Packaging Materials*

September, 1998

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QUALITY ASSURANCE REQUIREMENTS

This document was prepared in accordance with the Quality Assurance requirements of the National Spent Nuclear Fuel Program as detailed in PMP 6.02, Preparation of Technical Documents, Rev. 0, December 19, 1997. Much of information in this document is based on the radiological content of SNFs calculated using the ORIGEN2 computer code and on chemical thermodynamic data subsequently calculated using HSC Chemistry[®] for Windows Chemical Reaction and Equilibrium Software. Neither of these software systems is "qualified" for use in technical documents of the National Spent Nuclear Fuel Program by meeting the requirements of DOE/RW-0333P, Supplement I as described in PMP 6.02 Attachment C. Therefore the data and conclusions presented in this document are "to be verified" (TBV) because they are based on "existing" (previously called "unqualified") data. Tables containing such data are annotated "TBV."

ABSTRACT

A sensitivity analysis was conducted to identify and evaluate potential destructive interactions between the materials in US Department of Energy (USDOE) spent nuclear fuels (SNFs) and their storage/disposal canisters. The technical assessment was based on the thermodynamic properties as well as the chemical and physical characteristics of the materials expected inside the canisters. No chemical reactions were disclosed that could feasibly corrode stainless steel canisters to the point of failure. However, the possibility of embrittlement (loss of ductility) of the stainless steel through contact with liquid metal fission products or hydrogen inside the canisters cannot be dismissed. Higher-than-currently-permitted internal gas pressures must also be considered. These results, based on the assessment of two representative 90-year-cooled fuels that are stored dry at 200°C in stainless steel canisters with internal blankets of helium, may be applied to most of the fuels in the USDOE's SNF inventory.

EXECUTIVE SUMMARY

A sensitivity analysis was conducted to evaluate the chemical and physical properties and the potential interactions of the materials that comprise typical spent nuclear fuels (SNFs) and the stainless steel canisters in which they will be stored, transported, and placed in a geologic repository for final disposition. The assessment, which was based on the known physical properties, the chemical behaviors, and thermodynamic properties of SNF and canister materials, was conducted to determine the feasibility of any interactions that could threaten the structural integrity of the canisters. Two major types of representative USDOE SNFs were considered: low enrichment zirconium clad metal alloy N Reactor fuels and high enrichment aluminum clad metal alloy ATR fuels. The canisters were assumed to consist of Type 316L stainless steels. The individual chemical reactivities and stabilities of all materials known to be present in greater than trace quantities were evaluated at 200 and 350°C, the nominal and maximum expected storage temperatures. The individual and combined physical and chemical behaviors of all identifiable (and thermodynamically credible) compounds in the gaseous, liquid and solid states were compared with respect to a) their relative chemical reactivities and b) the total amount of each that would be present and available to react over long periods of time in order to reach their ultimate states of stability, i.e. chemical equilibrium.

The assessment was based on the following assumptions: (1) dried SNFs containing negligible amounts of water are sealed in stainless steel canisters with a helium blanket, (2) fuel degradation occurs and releases all fuel components inside the canisters, and (3) nominal canister wall temperatures are 200°C. Based on these conditions, no credible mechanisms were identified for chemical reactions that could lead to structural failure. However, the possibility of liquid metal embrittlement (LME) of the canisters by fission products and other fuel materials cannot be ruled out under the conditions considered in this analysis. Although LME is not a result of chemical interaction or corrosion per se, it is an identifiable mechanism by which a ductile metal may become brittle and crack, thereby compromising the structural integrity of the canisters. It is also noted that the gases expected to be present in SNF canisters may reach pressures that exceed those for which the canisters are approved. Since this study assumed the presence of only a negligible amount of water in or on dry SNFs, any chemical or physical interactions that might occur when a significant amount of water is present were beyond the scope of the current assessment. Similarly, the potential effects hydrogen embrittlement from water or other sources of hydrogen other than ternary fission products were not addressed, as they are being assessed and reported elsewhere.

ACRONYMS, ABBREVIATIONS, AND DEFINITIONS

Accepted Data	Data considered as established fact (e.g., engineering handbooks, density tables, gravitational laws, or other physical constants) or data generally accepted by the scientific and engineering community and found to be technically defensible by those using it.
ATR	Advanced Test Reactor - Nuclear reactor located at the Idaho National Engineering and Environmental Laboratory
BOL	Beginning of Life - the time at which nuclear fuel begins its period of irradiation in a nuclear reactor. BOL is the point in time reference on which the chemical composition (especially radionuclides) and physical structure are based before nuclear fuel is irradiated.
DOE Standardized SNF Canister	A standardized Type 316L stainless steel canister to store packaged ATR and other government-owned spent nuclear fuels.
EOL	End of Life - the time at which nuclear fuel ends its period of irradiation in a nuclear reactor. EOL is the point in time reference on which the chemical composition (especially radionuclides) and physical structure are based after nuclear fuel is irradiated.
Existing Data	Formerly designated " <i>Unqualified Data</i> ." Data that were not acquired or developed in accordance with an approved Quality Assurance program that meets 10 CFR Part 60 Subpart G and do not meet the definition of "accepted data." The change in terminology is found in Revision 8 of DOE/RW-0333P.
Hydrogen Embrittlement	The loss or reduction of ductile properties of a metal as a result of hydrogen atoms having penetrated the interstitial spaces between metal atoms.
LME	Liquid Metal Embrittlement - the loss or reduction of ductile properties of a metal as a result of contact with a liquid metal.
MCO	Multi-Canister Overpack - A Type 316L stainless steel canister to store N Reactor and other government owned nuclear fuels.
MTU	Metric Ton (1,000 kg or 2,204.6 lbs.) of Uranium
N Reactor	A weapons materials production nuclear reactor located at the Hanford Reservation.
Sensitivity Analysis	An evaluation that systematically identifies and assesses technical issues, including those pertaining to the licensing of USDOE SNF canisters for storage, transport, or disposal.
SNF	Spent Nuclear Fuel
TBV	To be verified, especially pertaining to existing data or information processed by unqualified software.
Unqualified Data	See "Existing Data."

Unqualified Software

Computer codes and software that have not been qualified per the requirements of DOE/RW-0333P, Supplement I as described in PMP 6.02 Attachment C.

USDOE (or DOE)

U.S. Department of Energy

VLEU

Very Low Enriched Uranium

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1.0 INTRODUCTION

Maintaining the structural integrity of U.S. Department of Energy (USDOE) spent nuclear fuel (SNF) canisters during interim storage, transport, and repository disposal is required to prevent the spread of radionuclides to the environment. The canister materials of construction are selected for their expected resistance to degradation in the potential environments involved. However, the internal canister environments include the irradiated fuels with a complex inventory of fission products whose potential for interacting with canister materials has not been thoroughly analyzed nor understood, especially at elevated temperatures and with all of the chemical elements and compounds that will be present after decades of decay time for the radionuclides. Sensitivity analyses are conducted to make an initial assessment of technical issues potential affecting the licensing of USDOE SNF for storage, transport, or disposal. If no issues are identified, the analyses, performed to QA standards, are available to the licensee as qualified reference material to answer the "what if" questions of the U.S. Nuclear Regulatory Commission (USNRC) and others during the licensing process. If issues are identified, the analysis provides the technical basis for additional analysis, testing, or other efforts to resolve them in order to base the licensing of SNF canisters on solid technical grounds.

1.1 Objective

The objective of this sensitivity analysis is to determine if the fission products or any other materials available in USDOE SNF are capable of undergoing chemical or physical changes that would allow them to interact with SNF canister materials and significantly threaten their structural integrity during interim storage, transportation, or repository disposal. The assessment was planned and conducted in a manner that systematically evaluated the known credible mechanisms for such chemical and physical interactions. A primary objective was to use known chemical thermodynamic principles applied to the known chemical properties of the constituents to predict whether or not destructive interactions of the materials could occur and, if so, what they are. The atomic nature of such materials, their cladding protection, and changes that occur as a result of radioactive decay in typical USDOE SNF requiring disposal also are considered. It was the intention of the author and those who provided technical input to be as thorough as possible in evaluating all feasible (with respect to chemical thermodynamic properties) interactions of the chemical elements expected to be present. This document reports the results of such focused technical evaluations.

1.2 Scope

This sensitivity analysis evaluates the feasibility of the occurrence of chemical reactions or other interactions between all functional and structural components of two major types of DOE SNFs and the stainless steel canister packaging that will be used to store them in a geologic repository. The two types of fuel selected, one a high enrichment aluminum alloy clad fuel and the other a low enrichment zirconium-clad fuel, are representative of a major portion of the USDOE's current SNF inventory. The fuels were assumed to be dry, containing only negligible amounts of water when placed in the storage canisters. Consideration of significant amounts of water or other sources of hydrogen being present on or in the fuels was beyond the scope of this assessment. The chemical compositions of the fuels are based on realistic irradiation histories followed by 90 years of cooling time. Fuel materials that may be present in the gaseous, liquid, and solid states were assessed at nominal and maximum long-term storage temperatures of 200 and 350°C, respectively. The assessment considered only materials that will be inside the fuel canisters based on currently planned methods of drying, packaging and storing SNFs that are present in USDOE's SNF inventory.

This sensitivity analysis evaluates the chemical reactivities and possible physical interactions of all fuel materials (includes the fuel's structural materials, structural activation products, residual fuel meat, alloying metals, heavy metals and their decay products, and the fission products) with each other as well as with the canisters. Of greatest interest are components that may be in a physical form that will allow migration and

contact with the inner surfaces of the canister. Gaseous materials and liquids are the most mobile and, therefore, receive first attention. Solids cannot be ignored, however, because they can migrate by entrainment in the gaseous or liquid phases, or even by the subtle long-term effects of thermal gradients which will be present in any spent nuclear fuel canister. Detailed studies were conducted to predict both the direct and indirect (secondary, tertiary, etc.) potential chemical interactions of SNF materials with the inner surfaces of the stainless steel canisters in which they are expected to be packaged and stored in a geologic repository.¹ Each analysis consisted of a technical assessment of the chemical compositions, the potential chemical reactivities, and potential changes in the physical properties of both the SNF canisters and two types of SNF that comprise a substantial fraction of the USDOE's inventory.

1.3 Selection of Representative Spent Nuclear Fuels

The two types of SNF that were considered in this study are: (1) zirconium-alloy-clad fuels, represented by N Reactor fuels, and (2) aluminum-alloy-clad fuels, represented by Advanced Test Reactor (ATR) fuels.² As shown in Table 1, low enrichment N Reactor Fuels make up the largest number of fuel elements, the greatest total mass and the greatest mass of fissile and fertile heavy metals. High enrichment ATR fuels are important because they are among the highest burnup and, therefore, contain some of the greatest fission product inventories of the major fuels that exist in large quantities. Although these two types of fuels do not represent the compositions and structures of all other SNFs in the USDOE's inventory, they represent a large fraction. Much of the information about these fuels will be applicable to other types of fuels.

Table 1. Contribution of N Reactor and ATR Fuels to the USDOE's Total SNF Inventory Projected for CY 2035*

	Number of FHUs	Portion of total FHUs	Total Mass, kg	Portion of Total Mass	Mass of Heavy Metals, kg	Portion of Total Heavy Metals	Mass of U-235, kg	Portion of U-235
N Reactor Fuels	103,673	47.85%	3,524,882	40.22%	2,096,020	86.87%	25,165	23.27%
ATR Fuels	3,900**	1.80%	37,992	0.42%	3,399.8	0.14%	3,399.8	0.14%
Total of all USDOE SNF	216, 644	100%	8,763,307	100%	2,412,774	100%	108,136	100%

* Data source: National Spent Nuclear Fuel Program, "Spent Fuel Database," Version 3.0.0, Issued July, 1997. These are "existing data" designated "TBV."

** ATR fuels comprise approximately 11% of the approximately 35,600 aluminum clad fuel assemblies in this inventory.

1.4 Data

The thermodynamic, chemical, and physical property data that provided the bases for the prediction of the feasibility of chemical reactions and physical changes were taken from the HSC Chemistry® database (see Section 2.4). The database was compiled from publicly available chemistry, metallurgical, and engineering handbooks commonly used by universities and industry. For this document, such data are considered to be "accepted data" per DOE/RW-0333P. Radiological and compositional data for SNF were taken from ORIGEN2 computer code calculations. Those data have not been qualified per DOE/RW-0333P and are identified in this document as "TBV" meaning "to be verified." The definitions of the data quality levels used throughout this document are presented in ACRONYMS, ABBREVIATIONS, AND DEFINITIONS on pages xi and xii.

2.0 DESCRIPTION OF SENSITIVITY ANALYSES

The inventories of the component materials expected to be present in ATR and N Reactor fuels were obtained from ORIGEN2 calculations that were based on actual fuels.^{3,4,5,6,7,8,9,10,11} The selection of these specific fuels was based on their being representative of their lots with respect to structural materials and size, and upon their having relatively high burnups. The irradiation and decay histories of the selected fuels and their detailed radiological compositions, based on ORIGEN2 computer code calculations, are available from the primary author of this document. The details pertinent to this assessment are presented in Section 2.1. The actual ORIGEN2 calculations for ATR fuel were performed and/or provided by James W. Sterbentz and Allan R. Bringham of Lockheed Martin Idaho Technologies Company. The ORIGEN2 calculations for Mark IV N Reactor fuel were from Pacific Northwest National Laboratory.¹¹

2.1 Composition and Structure of Selected Fuels

The ORIGEN2 data were tabulated, sorted and combined [chemical] element by element using Microsoft® Excel 97 Sr-1 spreadsheets to obtain the total amount of every chemical element for which significant quantities are present. The levels above which elements were deemed to be *significant* were arbitrarily designated as 0.000001 grams per fuel assembly for ATR fuel and 0.002 grams per fuel assembly for N Reactor fuel. The much lower level of 0.000001 g was selected for ATR fuels because they are much smaller assemblies and contain less than 1/20th the amount of uranium (BOL) that is present in the more massive N Reactor Mark IV assemblies. In addition, ATR fuels have immensely greater irradiation histories (340 MW days/kg of U compared to 2.9 MW days/kg of U for N Reactor fuels) and, therefore, contain proportionally larger inventories of fission products. Consequently, the inclusion of all chemical elements present at levels above 0.000001 g per fuel assembly provides a paradigm for future work with extremely high burnup fuels. The actual inventories used in these studies for ATR and N Reactor fuels are presented in Tables 2 and 3, respectively, as are their irradiation histories. The amount of materials listed for ATR fuel in Table 2 and N Reactor fuel in Table 3 are presented as grams per fuel assembly. The masses provided by the ORIGEN2 calculations for the N Reactor fuel were in the units "grams per Metric Ton of Uranium (BOL)." They were converted to grams per fuel assembly based on an average of 22.7 kg of uranium (BOL) in Mark IV fuel elements.¹⁰ More specifically, the units "g/MTU" were converted to g/assembly by multiplying them by [(22.7 kg U/assembly)/(1000 kg/MTU)].

The quantities of fuel materials assumed to be present for these assessments were the total amount of the combined activation products (includes ALL structural material in fuels), actinides and daughters, and fission products. A breakdown of the materials from each of those three sources is presented for ATR fuel in Table 2. Only the total amount from all three sources is presented for N Reactor since the original data for that fuel were available only in hard copy (not electronically) at the time this analysis was made. The amount of time that would have been required and the potential for introducing errors were the reasons for not manually entering all of the data for all isotopes for N Reactor fuel. Since both fuels contain uranium as a metal or metal alloy (zero oxidation state), it is reasonable to assume that most of the fission products would be in the zero oxidation state or at least they would have been when first born. In the alloy matrix, some reactive fission products would react with each other (e.g. cesium and iodine) and have their respective oxidation states changed. But since minimal migration occurs inside the matrix, most of the less reactive fission and activation products as well as their decay products are assumed to be in their original oxidation state which is predominantly zero. This condition could continue throughout the normal irradiation process, defueling, and water storage periods until the fuel is dried and placed into a storage canister, assuming that the fuel cladding maintains its integrity.

Table 2. Chemical Composition of One ATR Fuel Assembly*

Irradiation history: 367.2 MW days - a "maximum burnup" ATR assembly, cooled 90 years, BOL Uranium - 93.5% enriched, 1075 grams of U-235

Activation Products &
Structural Materials, g/assembly

Al, total = 8682.00

Be, total = 0.000006

C, total = 1.9159

Ca, total = 0.000010

Co, total = 0.0003

Ce, total = 17.4223

Cu, total = 24.5050

Fe, total = 31.3904

Ga, total = 0.0038

H, total = 1.9189

He, total = 0.0028

In, total = 0.0000

Mg, total = 89.4000

Mn, total = 6.6040

Mo, total = 0.0002

Na, total = 0.0001

Ne, total = 0.0007

Ni, total = 1.9392

O, total = 1.9151

P, total = 0.0002

Pb, total = 1.9159

Sb, total = 0.0004

Si, total = 55.7370

Sn, total = 1.9146

Sr, total = 0.0000

Te, total = 0.0005

Ti, total = 6.7046

V, total = 0.0113

Zn, total = 11.2194

Zr, Total = 1.9153

Total = 8938.44 g

(for one FHU or Assembly)

Total overall mass of all components per element = 10105.0 g

Actinides

784.24 g

Lanthanides

115.283 g

Alkali Metals

21.9441 g

Inert Gases

65.6554 g

Totals from ORIGEN2 (grams)

AP+FP 9.32E+03

ACT+FP 1.17E+03

AP+ACT+FP 1.01E+04

AP - activation products (& structural materials)

FP - fission products

ACT - activation products and daughters

Cladding alone - per reference 6 with attached Paul Receipt Criteria

Total cladding is 4,420 g 99% is Al-6061 & 5% is Al-1100.

Al = 4,332.1 g

Si = 25.4 g

Mn = 11.8 g

Mg = 42.0 g

Cr = 8.7 g

The Fuel Matrix is originally UAlx.

The matrix contains UAlx + Al = 3,020 g

Before burnup it nominally contains 1156 g U

Therefore, the Al = 3020 - 1156 or 1,864 g Al in the matrix

Fission Products,
g/assembly

Ag, total = 0.0770

As, total = 0.0019

Ba, total = 28.0716

Bc, total = 0.000002

Br, total = 0.2791

C, total = 0.0000

Cd, total = 0.2050

Ce, total = 27.9500

Cs, total = 16.5420

Dy, total = 0.0010

Er, total = 0.000016

Bu, total = 0.8768

Gd, total = 0.4142

Ge, total = 0.0068

H, total = 0.000003

Ho, total = 0.000039

I, total = 1.8924

In, total = 0.0193

Kr, total = 4.9562

La, total = 14.5401

Mo, total = 39.0698

Nb, total = 0.0004

Nd, total = 48.7982

Pd, total = 3.6640

Pr, total = 13.4400

Rb, total = 5.4020

Rh, total = 4.7970

Ru, total = 19.2605

Sb, total = 0.0827

Se, total = 0.7154

Sm, total = 9.2590

Sr, total = 0.4026

Sr, total = 6.3239

Th, total = 0.0039

Tc, total = 9.1420

Tc, total = 4.1340

Xe, total = 60.6964

Y, total = 6.9272

Zr, total = 54.3920

Total = 382.346 g

Total Mass of All Elements (continued)

Sn, FP = 0.4026

Sr, total = 6.3239

Th, total = 0.0039

Tc, total = 9.1420

Te, AP = 0.0005

Te, FP = 4.1340

Th, total = 0.0030

Ti, total = 6.7046

U, total = 775.7802

V, total = 0.0113

Xe, total = 60.6964

Y, total = 6.9272

Zn, total = 11.2194

Zr, FP = 54.3920

Zr, AP = 1.9153

Mass of all Chemical Elements in
One Fuel Assembly, grams

Al, total = 8682.00

Ag, total = 0.0770

Am, total = 0.2790

As, total = 0.0019

Ba, total = 28.0716

Be, total = 0.000008

Br, total = 0.2791

C, total = 1.9159

Ca, total = 0.000010

Cd, total = 0.2050

Ce, total = 27.9500

Cm, total = 0.000015

Co, total = 0.0003

Cz, total = 17.4223

Cs, total = 16.5420

Cu, total = 24.5050

Dy, total = 0.0010

Er, total = 0.000016

Bu, total = 0.8768

Fe, total = 31.3904

Ga, total = 0.0038

Gd, total = 0.4142

Ge, total = 0.0068

H, total = 1.9189

He, AP = 0.0028

He, Actin = 0.0047

Ho, total = 0.000039

I, total = 1.8924

In, total = 0.0193

Kr, total = 4.9562

La, total = 14.5401

Mg, total = 89.4000

Mn, total = 6.6040

Mo, AP = 0.0002

Mo, FP = 39.0698

Na, total = 0.0001

Nb, total = 0.0004

Nd, total = 48.7982

Ne, total = 0.0007

Ni, total = 1.9392

Np, total = 5.0030

O, total = 1.9151

P, total = 0.0002

Pa, total = 0.0001

Pb, total = 1.9159

Pd, total = 3.6640

Pr, total = 13.4400

Pu, total = 3.1780

Ra, total = 0.0000

Rb, total = 5.4020

Rh, total = 4.7970

Ru, total = 19.2605

Sb, AP = 0.0004

Sb, FP = 0.0827

Se, total = 0.7154

Si, total = 55.7370

Sm, total = 9.2590

Sn, AP = 1.9146

Total = 10105.0 g per Assembly

This column continues to the left.

* Data source: ORIGEN2 calculations, James W. Sterbentz, LMITCO. (See references 3 and 5.) TBV. This table contains "existing data" to be verified per the QA program requirements of DOE/RW-0333P.

Table 3. Chemical Composition of Mark IV Outer Assembly N Reactor Fuel*

High burnup 2921 MW days/MTU or 66.3 MW days/assembly g/fuel assembly (amounts less than 0.002 g are ignored)		
U (BOL)	22,700	←ref. 1 (BOL)
U (EOL)	22,541	←from ORIGEN2
Zr (clad)	1,568.0	←calc from ref 1
Zr (FP)	11.297	←from ORIGEN2
Zr, total =	1,579.3	
Pu =	63.946	
Sn =	23.417	
Al =	18.278	
Xe =	14.269	
Nd =	11.073	
Fe =	10.106	
Mo =	9.332	
Ba =	6.590	
Ce =	6.458	
Ru =	5.550	
Cs =	4.783	
La =	3.373	
Ni =	3.151	
Cr =	3.071	
Pr =	3.062	
Si =	2.976	
Pd =	2.831	
Am =	2.542	
Eu =	2.524	
Sm =	2.454	
Tc =	2.293	
N =	1.827	
Cu =	1.780	
Rh =	1.603	
Y =	1.335	
Te =	1.319	
Np =	1.462	
Sr =	1.201	
		Continued from other column
		g/fuel element
		Rb = 1.056
		Kr = 0.994
		I = 0.665
		Mn = 0.645
		Mg = 0.599
		Be = 0.227
		Cd = 0.225
		Ag = 0.197
		Gd = 0.166
		Sc = 0.161
		Pb = 0.159
		C = 0.129
		H ₂ = 0.086
		V = 0.082
		Ti = 0.079
		Hf = 0.077
		W = 0.077
		Br = 0.064
		Na = 0.032
		In = 0.018
		Co = 0.016
		B = 0.005
		Tb = 0.005
		Dy = 0.002
		Total = 24,338.7 grams
Continued in next column		

* Data source: R. A. Schwarz (See reference 11.) TBV. This table contains "existing data" to be verified per the QA program requirements of DOE/RW-0333P.

2.2 Design and Structure of Storage Canisters

The canisters in which the fuels will be stored will be fabricated from stainless steel, most likely Type 316L with ASTM Standard Specification SA-312.^{12,13,14,15} The chemical composition of Type 316L stainless steel, a face centered austenitic stainless steel, is presented in Table 4.¹⁶ Stainless steels are resistant to chemical attack by virtue of a protective film of chromic oxide (Cr₂O₃) that forms when the elemental chromium in the alloy is exposed to oxygen in the air. That layer is continuously replenished in an air environment; however, it is not replenished when oxygen is absent, as is the case with the blanket of inert gas inside a fuel canister. Hence, the present assessment considers the chromium in stainless steel to be present as elemental chromium and not (in significant quantities) as the oxide.

Table 4. Chemical Composition of Type 316L Stainless Steel*

Chemical Element	Weight Percent
Fe as Fe metal	65.4%
Cr as Cr metal except for Cr_2O_3 surface film	17.0%
Ni as Ni metal	12.0%
Mo	2.5%
Mn	2.0%
Si	1.0%
P	0.045%
S	0.03%
C	0.03% max

* Data Source: ASM Handbook. (See reference 15.) These data are classified as "accepted data" by the QA program requirements of DOE/RW-0333P.

2.2.1 USDOE Standardized Canisters for ATR Fuel

The currently proposed canister for ATR fuel is the DOE Standardized Canister that is expected to be fabricated from 18-inch-outside-diameter tube with $\frac{3}{8}$ -inch-thick walls, either 10 or 15 feet long.¹² DOE Standardized Canisters are proposed to have dished end caps that are $\frac{1}{2}$ inch thick and are welded in place using weld rod that in this study is assumed also to be Type 316L stainless steel. The shorter 10-foot-long canister is considered to be the more likely model. It would have an inner surface area of approximately 45,000 square centimeters or 6,970 square inches. The total mass of stainless steel in the canister itself would be approximately 358 kg or 788 lbs.

2.2.2 Multi-canister Overpacks for N Reactor Fuel

The Multi-Canister Overpack (MCO) for N Reactor fuels is expected to be a 165-inch-long 24-inch outside diameter cylinder with $\frac{1}{2}$ -inch-thick walls and somewhat thicker flat disk end plates. It would have an inner surface area of approximately 81,000 square centimeters or 12,600 square inches. The total mass would be approximately 875 kg or 1,920 lbs. This MCO design will accommodate up to A) four fuel baskets (each containing 54 Mark IV assemblies) and one scrap basket, or B) four fuel baskets (each containing 48 Mark IA assemblies) and two scrap baskets.^{14, 15, 17} Case A was selected for this assessment because it is the more conservative case with approximately 6,000 kg of fuel material compared to approximately 4,500 kg of fuel material in case B. The larger amount of fuel material is considered to be more conservative in that it provides more material for any potential chemical reactions with the canister. The total mass of fuel material present in case A, including scrap, is equivalent to 243 Mark IV outer fuel assemblies. This "243 Mark IV outer assemblies equivalent" mass was used for N Reactor fuel in the assessment that follows. That number of assemblies would contain a maximum of 68.9 kg of U-235, based on a maximum pre-irradiation enrichment of 1.25% for Mark IA fuels (Mark IV are 0.947% U-235), which is well below the recommended repository limit of 200 kg of U-235 per canister for very low enriched uranium (VLEU).¹⁸

2.3 Assumed Conditions for Stored Spent Nuclear Fuels

In addition to the characteristics described above for ATR and N Reactor fuels and for the ATR and MCO canisters, the conditions listed below are assumed for the current sensitivity analysis:

- 1) The fuels are aged 90 years out of the reactor, nominally representing the storage of 1995 fuels until year 2035 plus an additional 50 years in a geologic repository.
- 2) The fuels are dry with only a negligible amount of water associated with oxide and hydroxide hydrates.

- 3) The canisters maintain their integrity and hold all gaseous and liquid fuel components in addition to a blanket of helium gas that is placed in the canister at one atmosphere pressure at ambient temperature (25°C) when it is sealed.
- 4) The fuel cladding fails, making all fuel components inside the canister available to react with all other fuel components and with the canister. (Assumption that all materials in the structure of the fuel cladding are available to react is *extremely conservative*. Even if the cladding cracks and releases the fuel meat, the majority of the materials in the structure of the cladding would remain in place because it is not credible for all of the cladding to release all of its individual elemental chemical constituents at the maximum temperatures expected for SNF.)
- 5) The temperatures after 50 years in the geologic repository are nominally 200°C but could be as high as 350°C if placed near commercial nuclear fuel in the same repository. For conservatism, temperatures as high as 400°C are considered for some cases where a temperature profile of reactivity is used.
- 6) The cylindrical canisters are situated horizontally in the repository, meaning that any liquid or fluid-entrained solids from the fuel could accumulate along the length of the bottom inner surface of the canisters. However, it is unlikely that most canisters will be *exactly* horizontal, so the collection of fluids over a small surface area at one end of the canister can be assumed.

2.4 Thermodynamic Feasibility Calculations

The potential reactivities of the fuel and canister materials were evaluated using the HSC Chemistry[®] for Windows Chemical Reaction and Equilibrium Software on a 166 MHZ Dell OptiPlex GXi personal computer with a Microsoft Windows 95 operating system.¹⁹ The results and subsequent conclusions obtained from this software and reported in the document are "unqualified" because at the time this document was written, the HSC Chemistry[®] for Windows Chemical Reaction and Equilibrium Software was not "qualified" per PMP 6.02 and DOE/RW-0333P. The software was used to determine the thermodynamic feasibility of chemical reactions occurring between any and all of the individual fuel components and the inner surfaces of the canisters. The results of such calculations cannot predict that the indicated chemical reactions will definitely occur, but that such reactions are thermodynamically feasible and are limited only by chemical kinetics over extended periods of time. The evaluations were comprehensive in that they considered both direct and indirect reactivities between fuel and canister materials. Indirect reactivities are based on the properties of secondary species which may occur after the original subject materials have inter-reacted to form intermediate materials.

In these types of chemical calculations the amount of each chemical element must be expressed in moles. The total number of moles of each chemical element that would be present in fully loaded fuel canisters are presented in Table 5. These data, based on 20 ATR assemblies and N Reactor fuel equivalent to 243 Mark IV outer assemblies in their respective canisters, comprise the initial raw input data for the thermodynamic calculations that are described below.^{12, 17}

Table 5. Spent Fuel Components Expressed in Moles of Each Chemical Element*

ATR Fuel 20 Assemblies in One Canister (Number of Moles per Canister)				N Reactor Fuel Equivalence of 243 Mark IV Outer Assemblies in One MCO Canister (Number of Moles per Canister)			
Alphabetically, by chemical element		By number of moles, descending		Alphabetically, by chemical element		By number of moles, descending	
Al	6435.878	Al	6435.878	Ag	0.4452	U (BOL)	23176.891
Ag	0.0143	Mg	73.5802	Al	164.6243	U (EOL)	23014.550
Am	0.0230	U	66.0238	Am	2.5424	Zr, total	4207.073
As	0.0005	Si	39.6705	B	0.1003	Zr (clad)	4176.979
Ba	4.0861	H ₂	19.1894	Ba	11.6545	Al	164.6243
Be	0.000004	Zr	12.1091	Be	6.1290	Pu	65.0161
Br ₂	0.0349	Fe	11.2410	Br ₂	0.0967	Sn	47.9394
C	3.1931	Xe	8.9921	C	2.6201	Fe	43.9708
Ca	0.000005	Mo	8.0143	Cd	0.4858	Zr (FP)	30.09396
Cd	0.0365	Cu	7.7181	Ce	11.2015	Xe	26.4084
Ce	3.9900	Nd	6.7634	Co	0.0656	Si	25.7353
Cm	0.000001	Cr	6.7009	Cr	14.3525	Mo	23.6339
Co	0.0001	Ba	4.0861	Ca	8.7452	Nd	18.6599
Cr	6.7009	Ce	3.9900	Cu	6.8061	N ₂	15.8588
Cs	2.4875	Ru	3.8102	Dy	0.0034	Cr	14.3525
Cu	7.7181	Zn	3.4310	Eu	4.0355	Ru	13.3401
Dy	0.00013	C	3.1931	Fe	43.9708	Ni	13.0432
Er	0.000002	Ti	2.7994	Gd	0.2565	Ba	11.6545
Eu	0.1154	Ca	2.4875	H ₂	10.4806	Ce	11.2015
Fe	11.2410	Mn	2.4058	HF	0.1054	H ₂	10.4806
Ga	0.0011	La	2.0936	I ₂	0.6264	Ca	8.7452
Gd	0.0527	Pr	1.9077	In	0.0384	Cu	6.8061
Ge	0.0019	Tc	1.8469	Kr	2.8763	Pd	6.4648
H ₂	19.1894	Y	1.5567	La	5.9013	Be	6.1290
He	0.0377	Sr	1.4058	Mg	5.9928	Mg	5.9928
Ho	0.000005	Rb	1.2636	Mn	2.8483	La	5.9013
I ₂	0.1473	Sm	1.2312	Mo	23.6339	Tc	5.6275
In	0.0034	O ₂	1.1970	N ₂	15.8588	Pr	5.2812
Kr	1.1829	Kr	1.1829	Na	0.3358	Eu	4.0355
La	2.0936	Rh	0.9324	Nd	18.6599	Sm	3.9647
Li	0.000001	Pd	0.6887	Ni	13.0432	Rh	3.7846
Mg	73.5802	Ni	0.6607	Np	1.4989	Y	3.6484
Mn	2.4058	Te	0.6400	Pb	0.1865	Sr	3.3159
Mo	8.0143	Np	0.4222	Pd	6.4648	Rb	3.0000
Na	0.0001	Sn	0.3904	Pr	5.2812	Kr	2.8763
Nb	0.0001	Pu	0.2659	Pu	65.0161	Mn	2.8483
Nd	6.7634	Pb	0.1851	Rb	3.0000	C	2.6201
Ne	0.0007	Se	0.1811	Rh	3.7846	Am	2.5424
Ni	0.6607	I ₂	0.1473	Ru	13.3401	Te	2.5116
Np	0.4222	Eu	0.1154	Se	0.4958	Np	1.4989
O ₂	1.1970	Gd	0.0527	Si	25.7353	I ₂	0.6264
P	0.00014	He	0.0377	Sm	3.9647	Se	0.4958
Pa	0.000005	Cd	0.0365	Sn	47.9394	Cd	0.4858
Pb	0.1851	Br ₂	0.0349	Sr	3.3159	Ag	0.4452
Pd	0.6887	Am	0.0230	Tb	0.0069	Ti	0.4031
Pr	1.9077	Ag	0.0143	Tc	5.6275	V	0.3901
Pu	0.2659	Sb	0.0136	Te	2.5116	Na	0.3358
Rb	1.2636	V	0.0044	Ti	0.4031	Gd	0.2565
Rh	0.9324	In	0.0034	U (BOL)	23176.89	Pb	0.1865
Ru	3.8102	Ge	0.0019	U (EOL)	23014.55	HF	0.1054
Sb	0.0136	Ga	0.0011	V	0.3901	W	0.1020
Se	0.1811	Ne	0.0007	W	0.1020	B	0.1003
Si	39.6705	As	0.0005	Xe	26.4084	Br ₂	0.0967
Sm	1.2312	Tb	0.0005	Y	3.6484	Co	0.0656
Sn	0.3904	Th	0.0003	Zr (clad)	4176.979	In	0.0384
Sr	1.4058	P	0.0001	Zr (FP)	30.0940	Tb	0.0069
Tb	0.00049	Dy	0.0001	Zr, total	4207.073	Dy	0.0034
Tc	1.8469	Co	0.0001				
Te	0.6400	Nb	0.0001				
Th	0.0003	Na	0.0001				
Ti	2.7994	Ca	0.000005				
U	66.0238	Pa	0.000005				
V	0.0044	Ho	0.000005				
Xe	8.9921	Be	0.000004				
Y	1.5567	Er	0.000002				
Zn	3.4310	Cm	0.000001				
Zr	12.1091	Li	0.000001				

* Data sources the same as for Tables II and III of this document. TBV. They are "existing data" to be verified per the QA program requirements of DOE/RW-0333P.

The HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software is quite versatile. However, it cannot handle equilibrium analyses for all 69 chemical elements shown in Table 5 at the same time. It was, therefore, necessary to approach such calculations systematically. First, a series of screening calculations was performed for each type of fuel to confirm the relative chemical reactivities of the elements that would be expected (by a scientist or engineer) to be most reactive. Then, after the most reactive elements had been identified and confirmed, some elements with similar properties were combined (or substituted) and entered as input data as if they were single elements. For example, the number of moles of the rare gases xenon and krypton were combined and then calculated only as moles of krypton. Another example is combining the moles of noble metals ruthenium, palladium and rhodium, and then entering them all as ruthenium. The groups of chemical elements that were combined for the initial input of raw data into the HSC software calculations are presented in Table 6 for both ATR and N Reactor fuels. Such combinations (or substitutions) were used only when there was a sound technical basis for doing so. The calculations for each group of chemical elements were based on the properties of the most reactive element in the group (e.g., Ru in the group of Ru, Pd, and Rh) or the element with overwhelmingly the greatest mass (e.g., Cs in the group of Cs, Na and Rb). In a few cases, the substitution was driven by the availability of reaction product data in the software data base. Whenever a group of combined (or substituted) elements was shown to be reactive with the canister or other fuel materials, additional calculations were performed in order to delineate the behaviors of the individual elements in the combined group. Some elements that occur only in very small amounts were simply combined with the most chemically similar elements present, like americium (an actinide) in ATR fuel being combined with neodymium (not an actinide) and other chemically similar lanthanides. The chemical and physical properties on which these combinations were based, as well as the bases for interpretation of the results of the calculations are available in open scientific literature. The primary sources of such information for the current study are listed in the references at the end of this document.^{20, 21, 22, 23, 24, 25, 26, 26}

Equilibrium calculations were performed using HSC Chemistry® for Windows Software for each fuel at 100, 200 and 350°C. The analysis at 100°C was included for comparison and to obtain a spectrum of data to make it easier to identify trends. Sometimes 400°C was used for the same reason. Only the two middle (200 and 350°C) temperatures are pertinent to actual long-term conditions in a geologic repository.

Table 6. Groups of Chemical Elements Combined for Initial Equilibrium Calculations with HSC Chemistry® for Windows Software

ATR Fuel Components	N Reactor Fuel Components
Al, Ga, In	Al, In, B
Ba	Ba, Mg, Sr, Cd, Be
Br ₂	C
Ce, Pr	Ce, Pr
Cs, Rb, Na	Cs, Rb, Na
Cu, Ag	Cu, Ag
Fe, Co, Ni	Fe, Co, Ni
H ₂	H ₂
He, Kr, Xe	He, Xe, Kr
I ₂	I ₂ , Br ₂
Mg, Zn, Cd	Mo, Cr, W, V
Mn, Tc	N
Mo, Cr	Nd, Am, Eu, Gd, Dy, Sm, Y, Tb, La
Nd, Am, Eu, Gd, Dy, Sm, Y, Tb, La	O ₂
O ₂	Pu, Np
Pu, Np	Ru, Pd, Rh
Ru, Pd, Rh	Si
Si, C, Ti, Zr, Sn, Ge	Tc, Mn
Sr	Te, Se
Te, Se	U
U	Zr, Sn, Ti, Hf, Pb

3.0 RESULTS OF SENSITIVITY ANALYSES

The elemental compositions of both fuels are complex, as illustrated by the large number of chemical elements listed in Table 2 for ATR fuel and Table 3 for N Reactor fuel. The original fuel matrices of both types of fuel selected for this assessment are uranium metal (zero oxidation state) or uranium that is alloyed with other metals, primarily aluminum. These metallic compositions contribute to the predominantly "chemical reducing environments" inside both types of fuels and later inside the canisters. Since the fission products formed during irradiation in the reactor also are predominantly metals, the chemical nature of the fuel matrices of irradiated fuels is at least as strongly reducing as were the unirradiated fuels. Any strongly oxidizing species that form in the fuel matrices of ATR or N Reactor fuels (e.g., fission product iodine as I_2) would readily react with any of a number of metals to reach their "reduced" equilibrium oxidation states. Indeed, most such species would be completely reacted and no longer in elemental form well before the time of the fuel cladding failure assumed for the current sensitivity analysis. Such chemical reactions between fuel components would occur only to the degree that there are reactants present. Hence, the extent of such reactions and the composition of the reaction products are controlled by the amounts of the reacting species present in the least molar (or "equivalent") quantities. When the reaction products are ultimately released into the canister environment, they would be in the form of chemical compounds or ionic species, and not as the pure chemical elements themselves. Chemical thermodynamic software HSC Chemistry[®] for Windows Chemical Reaction and Equilibrium Software was used to predict what those compounds or chemical species could be.

It should be noted that both types of fuels selected for this assessment contain metal uranium fuel matrices in contrast to many other fuels that contain uranium as U(IV), commonly as the ceramic form UO_2 . The chemical environments inside such oxide fuels would not be as strongly reducing as are those in ATR and N Reactor fuels.

3.1 Gaseous SNF Materials

The first significant change that occurs when cladding fails inside SNF canisters is the release of any materials in the gaseous or liquid states. Gases are the most mobile, so they are addressed first.

3.1.1 Fission Product Gases

Significant amounts of fission product gases will accumulate inside SNF canisters when they are released from the fuel. An unknown portion of the fission product gases may have already escaped the cladding while in the reactor and during the subsequent storage period before entering the canister. Nevertheless, this assessment assumes that the entire inventory is still present when the fuels are sealed inside the SNF canisters. The entire inventory of the fission product gases krypton and xenon, combined with the original blanket of helium, would fill the canisters for each type of fuel to the calculated maximum pressures presented in Table 7. The ORIGEN2 code also indicates that a very small amount of the rare gas neon would be present in ATR fuel at a level that is negligible compared to krypton and xenon. It is noted that these pressures from inert gases alone could exceed the specified pressure loadings in the Disposability Interface Specification for DOE SNF canisters.²⁷ The possibility of metal hydrides releasing gaseous hydrogen at storage temperatures (discussed later) and the vapor pressures of any liquid metals (discussed later) could also contribute to the total pressure inside stored SNF canister, thereby exceeding the specified pressure loadings even further.

Since these noble gases are all chemically inert with respect to all other materials present under the physical and chemical conditions of these SNF canisters, one hundred percent of such gases that escape the fuel matrix would simply collect inside the sealed canisters. They would not corrosively attack the stainless steel fuel canisters nor significantly affect them other than to contribute to the pressure and facilitate the transfer of

Table 7. Internal Pressure of Fuel Canisters From Rare Gases After Ninety Years of Decay*

Temperature, °C	ATR Fuel, 20 assemblies inside a 10-ft-long 18-in-diameter Standardized DOE SNF Canister	N Reactor Fuel, 243 Mark IV outer assemblies equivalent inside a Multi-Canister Overpack (MCO)
	(Pressure in atmospheres)	(Pressure in atmospheres)
20	1.65	2.04
100	2.06	2.56
200	2.62	3.24
350	3.45	4.27

* Source of data: Hand calculated using the universal gas law equation and the amounts of gasses presented in Table 5. They are based on 1.0 atmosphere of helium blanket when packaged at 25°C plus fission product krypton and xenon. TBV. These are "existing" data to be verified per PMP 6.02 and DOE/RW-0333P.

heat from the fuel to the canister walls. Although no material, including Type 316L stainless steel, is completely impermeable to gases - especially gases with small diameter molecules like monatomic helium - the rate of such permeation has been shown to be extremely low.²⁸ Based on the reported rates of permeation of helium through stainless steel, it would take around 10×10^{40} years for the helium to escape through the 3/8-inch-thick stainless steel wall of a DOE standardized SNF canister. Krypton and xenon, with atomic radii of 1.03 and 1.24 Ångströms, respectively, would escape even more slowly than helium atoms with an atomic radius of 0.49 Ångströms. Hence, inert gases will not escape by permeating the canister walls. That also means that the quality of the welds and seals will become the factors that govern the integrity of SNF canisters with respect to gases.

3.1.2 Atmospheric Gases

The major gases in the atmosphere (diatomic nitrogen and oxygen and triatomic water vapor) will not permeate stainless steel canister from the outside for the same reasons presented in Section 3.1.1 for fission product gases not escaping so long as the canister is sealed and maintains its integrity.²⁸ In addition, according to Fick's law the ingress of gases from the outside would be inhibited by the presence of a positive internal concentration gradient which in the case of gases, is the same as a pressure gradient.²⁹ Possible long term effects of atmospheric gases or any other external materials on the stainless steel canister itself are beyond the scope of this assessment.

3.1.3 Hydrogen and the Formation of Hydrides

The behavior of hydrogen in this assessment is based solely on the amount of hydrogen indicated by the ORIGEN2 calculations presented in Tables II and III. This hydrogen is solely from nuclear sources such as ternary fission products and do not include any unknown amount of residual water that might be present after the fuels are dried and packaged.³⁰ This is consistent with the assumption (assumption 2 in Section 2.3) "*fuels are dry with only a negligible amount of water associated with oxide and hydroxide hydrates.*" The potential effects of larger amounts of hydrogen on SNFs and stainless steel canisters have been evaluated and reported elsewhere.³¹

Although the amount of hydrogen present from nuclear sources may be small compared to the amount that could be present in hydroxides, hydrated oxides, and occluded water, there are still more moles of hydrogen (considered as molecular H_2) than krypton in both ATR and N Reactor fuels. If the total amount of hydrogen associated with both types of fuel were present inside the canisters as elemental diatomic hydrogen gas, it would essentially double the internal gas pressures listed in Table 7.

According to calculations with the HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software, it is thermodynamically favorable for hydrogen to react with cerium, barium, praseodymium, neodymium, zirconium, plutonium, and uranium (in the order listed) to form metal hydrides at both 200 and 350°C. It is important to remember that the formation of such metal hydrides in the current scenarios depends upon the availability of the component materials; that is, upon the availability of both the metals and the hydrogen as discussed below.

When hydrogen atoms interstitially penetrate a metal, the resulting hydride is essentially an "intermetallic" compound or alloy in which both the metal and hydrogen remain in the zero oxidation state. The reported empirical composition of hydrides of the metals listed above are primarily MH_2 , although MH , MH_3 , and MH_4 may be possible in some cases. The metals most likely to form metal hydrides, along with the maximum number of moles of each that could be present in an SNF canister, are presented in Table 8. Since the assumed maximum amount of hydrogen available in the current scenario is 19.2 moles for ATR fuel and 10.5 moles for N Reactor fuel, the greatest amounts of metal hydrides that would be expected to form with these metals are 9.6 and 5.3 moles, respectively, based on the stoichiometry associated with MH_2 . Conversely, the capability of forming hydrides of each of those metals under the current scenarios with only hydrogen from nuclear sources present depends upon the availability of the metals which may be governed by two factors: (a) not having already reacted with something else to form more stable compounds (likely limiting factor in the fuel meat) and (b) their physical accessibility (likely limiting factor in fuel cladding where a more tenuous mechanism such as permeating through the alloy is required for the hydrogen to reach the reactive metal).

Table 8. Maximum Amounts of Reactive Metals Available to Form Hydrides in the SNF Canister Environment*

ATR Fuel in One DOE Standardized SNF Canister (19.2 moles of hydrogen based on assumption that only hydrogen from nuclear sources is present)		N Reactor Fuel in One MCO (10.5 moles of hydrogen based on assumption that only hydrogen from nuclear sources is present)	
(Metal)	(Moles)	(Metal)	(Moles)
Cerium	4.0	Cerium	11.2
Barium	4.1	Barium	11.7
Praseodymium	1.9	Praseodymium	5.3
Neodymium	6.8	Neodymium	18.7
Zirconium	12.1	Zirconium (fission product only)	30.1
(all fission product)		Zirconium (cladding)	4,180
Plutonium	0.3	Plutonium	65
Uranium	66	Uranium	23,000

* Source of Data: Hand calculated from data in Table 5. TBV. They are "existing data" to be verified per the QA program requirements of DOE/RW-0333P.

The likelihood of forming metal hydrides under the current scenarios was evaluated for both types of fuel using the HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software, based on the assumption that the total amounts of hydrogen indicated by the ORIGEN2 calculations and listed in Table 5 were indeed present. It is also assumed that only those amounts of hydrogen were present. For ATR fuel the predominant species of hydrides at both 200 and 350°C will be NdH_2 followed by much smaller amounts of BaH_2 and CeH_2 . More reactive cerium is not the leading former of hydrides because according to HSC software calculations, it is less available, having already formed more stable intermetallic compounds with aluminum, magnesium and the cesium-rubidium solution discussed later. Less ZrH_2 is expected to form in ATR fuel than in the N Reactor fuel because there is much less zirconium available in ATR fuel. Also, according to HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations, a portion of the zirconium in ATR fuel would preferentially form silicides and not be available to react with hydrogen. Again, it is noted that the theoretical conditions of this assessment may not be entirely consistent with the hydride formation actually experienced with SNF fuels in water cooled reactors and subsequent

water storage as reported elsewhere in considerable detail.³¹ In any case, it is almost certain that some metal hydrides will be present in SNFs.

For N Reactor fuel, the equilibrium inventory of metal hydrides at 200°C is predicted by HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations to consist of nearly 50% BaH₂, a slightly lesser amount of ZrH₂, and a much smaller amount of NdH₂. At 350°C the predominant species is ZrH₂, followed by much lesser amounts of BaH₂ and NdH₂, according to HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations. Literature indicates that ZrH₂ may not form at a "substantial rate" below temperatures of at least 250°C.³² However, the long periods of time associated with repository storage—90 years in the current scenario—may justify the assumption that it is at least not unreasonable to assume that the HSC Chemistry® software's equilibrium states are achieved. Although zirconium is thermodynamically less likely to form hydrides than are barium and neodymium, ZrH₂ is predicted to be the predominant hydride at 350°C at least partially because there is so much more of it than there is of the other major hydride forming metals. Notably, much (perhaps most) of the zirconium hydride is believed to be formed with fission product zirconium and not with structural zirconium from the cladding for two reasons. First, fission product zirconium is formed in the fuel matrix where it is immediately available to react with any ternary fission product hydrogen generated there or even by the "n,p" reaction in which neutrons replace protons in the nuclei of atoms exposed to the high neutron flux from the fissioning uranium (and plutonium) in the fuel matrix. Second, structural zirconium in Zircaloy-2 is physically protected by the zirconium oxide film that forms when it is manufactured and is reinforced by exposure to water at high temperatures in the reactor. The presence of a thick layer of ZrO₂ is reported to inhibit but not prevent the penetration of hydrogen into zirconium alloys where it can form hydrides, mostly ZrH₂.³²

The formation of significant amounts of metal hydrides, especially zirconium hydrides, is widely recognized as undesirable for two reasons. First, the intrusion of air could cause rapid combustion of metal hydrides, in the case of ZrH₂ yielding Zr(OH)₂ and water which in turn could then react with alkali metals. Second, hydrides can release gaseous hydrogen when heated and generate extremely high pressures inside the fuel canisters. The presence of hydrogen gas at high pressures and temperatures also increases the potential for hydrogen damage of the SNF canisters. At 350°C, the highest temperature studied in this assessment, only a small portion (less than 10%) of the hydrogen from BaH₂, NdH₂ and ZrH₂ would be released into the canister environment. It would require much higher temperatures to release the majority of it as hydrogen gas, for example 50% of the hydrogen associated with NdH₂ and ZrH₂ is not released until it is heated to 950°C according to HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations. BaH₂ must be heated to nearly 1150°C to release 50% of its hydrogen.

Based on the limited amounts of materials available in the scenarios considered in this assessment, it appears unlikely that a large amount of the hydrogen would ever be released inside the canister as gaseous hydrogen. Conversely, it must be assumed that at least some of the hydrogen would be released, especially at 350°C. Any released hydrogen gas would contribute to the internal gas pressure of the fuel canister. Its contact with the canister, of course, would be equally distributed over the entire 45,000 sq. cm. or 81,000 sq. cm., respectively, of the inner surfaces of the DOE standardized SNF canisters for ATR fuel or MCOs for N Reactor fuel.

Theoretically, the following two phenomena are possible when gaseous hydrogen is present under the conditions of the current scenarios: (1) it may penetrate the stainless steel canister via the mechanism of disassociated monatomic hydrogen atoms diffusing between the interstitial spaces inside the crystalline structure of the stainless alloy to form hydrides, the potential significance of which is addressed elsewhere^{29, 31, 33}, and (2) there could be an extremely slow but continual penetration of the stainless steel canister at a rate governed by the crystalline structure of the alloy and expressed by diffusivity constant of hydrogen in stainless steel.^{28, 29} In either case, once hydrogen atoms are inside stainless steel, including the welds and their heat affected zones, hydrogen embrittlement can occur. In the present scenarios with dry fuels in which only ternary fission product hydrogen is considered, the potential for a significant amount of damaging hydrogen embrittlement to occur is obviously less than when hydrogen from other sources is present. The potential for hydrogen damage that would compromise the structural integrity of SNF canisters was not assessed further in

this study. That assessment was deferred to other more conservative and possibly more realistic assessments in which larger amounts of hydrogen are considered.³¹

3.1.4 Vapor Pressure of Liquid Materials

The inert gases and hydrogen are not the only species in 90-year-cooled ATR and N Reactor fuels that would contribute to the pressure inside sealed SNF canisters. All materials in the gaseous state at any given temperature would contribute to the total pressure inside the canister, as would any liquids through their vapor pressures (more specifically, through the partial pressures of their miscible or dissolved components). For example cesium metal, which is a liquid between 29 and 685°C, would contribute 5.9 mm of mercury (or 0.0078 atmospheres) of vapor pressure if present in the SNF canister at 350°C, the highest temperature evaluated in these studies. Rubidium, the only other alkali metal fission product likely to be present in a significant amount, is a liquid between 30 and 701°C, and has a vapor pressure of 4.1 mm of Hg (or 0.0053 atmospheres) at 350°C. These metals are very reactive and at least a portion of them would react with other SNF materials (halogens, selenium, and tellurium, as discussed later). However, cesium and rubidium are present in molar quantities that exceed the molar quantities of identified potential reactants that also are in the fuel. Therefore it must be assumed that some elemental liquid cesium and/or rubidium will indeed be present in elemental form inside SNF canisters, as discussed in more detail later in this report.

The physical states of the lowest-melting-temperature elemental components of 90-year-aged ATR and N Reactor fuels are presented in Table 9 for the temperatures considered in this assessment. It is important to note that the physical states listed are for pure unreacted form of the chemical elements. Such pure chemical elements would exist in these forms inside a SNF canister *only if they did not react with each other or other fuel materials*. In reality, at least a portion of most of them would react with other materials to form chemical compounds, as discussed later. The reaction products, whether they are themselves liquids or are dissolved in liquids, would almost certainly exert less total vapor pressure than if they were present in pure unreacted form. And, the liquid metals could also be miscible with other material as discussed later. Hence, it is conservative but still realistic with respect to gas pressure inside SNF canisters to assume that they are present in elemental chemical form.

Table 9. Physical State of Fuel Components IF They Were Present in Elemental Form*

Chemical Element	Temperature			
	(25°C)	(100°C)	(200°C)	(350°C)
Br ₂	Liquid	Gas	Gas	Gas
Cd	Solid	Solid	Solid	Liquid
Cs	Solid	Liquid	Liquid	Liquid
Ga	Solid	Liquid	Liquid	Liquid
H ₂	Gas	Gas	Gas	Gas
He	Gas	Gas	Gas	Gas
I ₂	Solid	Solid	Gas	Gas
In	Solid	Solid	Liquid	Liquid
Kr	Gas	Gas	Gas	Gas
Li	Solid	Solid	Liquid	Liquid
N ₂	Gas	Gas	Gas	Gas
Na	Solid	Liquid	Liquid	Liquid
Ne	Gas	Gas	Gas	Gas
O ₂	Gas	Gas	Gas	Gas
P	Solid	Solid	Solid	Liquid
Pb	Solid	Solid	Solid	Liquid
Rb	Solid	Liquid	Liquid	Liquid
Se	Solid	Liquid	Liquid	Liquid
Sn	Solid	Solid	Liquid	Liquid
Xe	Gas	Gas	Gas	Gas

*See reference 25. This table contains "accepted data" per PMP 6.02 and DOE/RW-0333P.

3.1.5 The Halogens

Although elemental bromine (Br_2) and iodine (I_2) would both be gases at the canister temperatures of 200 and 350°C, neither would be present as such in either of the SNF canister environments addressed in this assessment. According to HSC Chemical software equilibrium calculations, these and all other elemental halogens would be chemically reduced by any of the alkali or alkaline earth metals present, including cesium, rubidium, barium and strontium in that order. ATR and N Reactor fuels contain 40-fold and 30-fold excesses, respectively, of the molar amount of each of these metals required to reduce the total inventories of halides present to alkali halide and alkaline earth halide salts like CsBr , RbI , SrBr_2 and BaI_2 . All bromide and iodide salts of cesium, rubidium, barium, and strontium have melting points greater than 600°C (except SrI_2 at 402°C); therefore, these halide salts would remain in solid form and would not corrosively attack the inner surfaces of the stainless steel canisters. This is true when water is absent, which is an assumed condition in this assessment. The limited amount of hydrogen (described above), precludes the formation of water from inside the canisters. Any water in quantities great enough to significantly contribute to halide corrosion of the stainless steel canister would have to come from external sources which is beyond the scope of the current assessment. Such water would react with the excess alkali metals (that is, alkali metals not already oxidized by a halogen) to form hydroxides before it could accumulate in an amount large enough to form an aqueous halide system that would be corrosive to the stainless steel canister. If such a large amount of water were to intrude, excess water (after the alkali metals have all reacted) could accumulate and provide a medium in which metal salts could dissolve and form solutions that would be potentially corrosive to the stainless steel canisters. The entrainment of such salts in liquid cesium or other non-polar (non-aqueous) liquids would not be very likely to set up the conditions required for a chemical attack on the stainless steel canister.

3.1.6 Oxygen

The small but significant amount of oxygen listed by the ORIGEN2 code for ATR fuels is associated with the aluminum 6061 alloy cladding as a surface layer of alumina (Al_2O_3). This oxygen is already in the reacted (reduced) form of a metal oxide and would not be available to react with and degrade the iron, nickel, chromium or manganese in the stainless steel canisters. HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations indicate that there are numerous fuel components that would preferentially react with or hold oxygen more strongly than the iron, nickel or chromium in stainless steel at 350°C and 3.4 atmospheres pressure. Specifically, calcium, plutonium, neodymium, magnesium (a significant component of aluminum alloy 6061), cerium, strontium, zirconium and aluminum (in that order) are all thermodynamically more stable and are more likely to hold the oxygen as oxides than is the chromium in stainless steel. Oxygen is thermodynamically more likely to associate with these fuel materials than with the stainless steel components (iron, nickel and chromium) of the canister. Hence, it would be thermodynamically favorable for oxygen to be driven from the stainless steel to the fuel and not vice versa, although it is impossible to predict if this would actually occur. It is impossible to predict if this would or would not actually occur in an SNF canister. In either case, there is no credible likelihood that the oxygen associated with ATR fuel would ever corrosively attack the stainless steel canisters. This assessment uses the conservative assumption that the oxygen in the protective layer of Cr_2O_3 on the stainless steel does associate with the thermodynamically more stable fuel materials, thereby leaving the iron-chromium-nickel-manganese alloy and not the chromic oxide layer to protect the integrity of the stainless steel canister structure from the inside. The outside surface of the canister is, of course, continuously exposed to air and maintains its protective layer of Cr_2O_3 intact.

The ORIGEN2 data for N Reactor fuel in these studies do not include oxygen. However, it is believed that the Zircaloy-2 cladding of Mark IV fuel would have an oxide coating similar to that encountered on the surfaces of zirconium fuels processed at the Idaho Chemical Processing Plant and confirmed by autoclave tests.³⁴ In addition, oxygen levels of 1,000 to 1,600 parts per million are typical in Zircaloy. The presence of such levels of oxygen contributes to the hardness desired for nuclear fuel cladding. Oxygen, along with alloyed tin, iron, chromium and nickel, is an integral part of the structure of the alloy that is stable at

temperatures up to at least 790°C.³⁵ Similar to the oxygen associated with the structural materials in ATR fuels, such oxygen in N Reactor fuels would not be released from the structural Zircaloy-2 and, therefore, would not be available to react with other materials.

The ORIGEN2 code calculations also indicate that a substantial amount of nitrogen is present in the structural materials of N Reactor fuel. Any nitrogen that is present in the Zircaloy-2, whether added for phase stability or if present simply as a contaminant from exposure to air, would contribute to phase stability and almost certainly be present as a nitride. Like oxygen and the other elements previously listed for Zircaloy, nitrogen will remain an integral part of the structure of the alloy at temperatures up to at least 790°C.³⁵ If, however, any nitrogen gas were to be present inside the SNF canister, it would function essentially as an inert gas and would not participate in likely oxidation/reduction reactions between the materials known to be present. It would, at most, form nitrides that would not contribute to the degradation of the stainless steel canisters.

With the possible exception of hydrogen, none of the gaseous materials identified in this assessment would be expected to contribute significantly to the degradation of stainless steel fuel canisters or cause them to lose their integrity under the defined conditions. Potential degradation of stainless steels from exposure to hydrogen must be addressed as determined by the results of other studies.³¹

3.2 Liquid SNF Materials

After gases, liquids are naturally the most mobile state of matter. The only chemical elements that *could* be present as liquids in elemental form at the temperatures studied for ATR and N Reactor fuel canisters were listed previously in Table 9. This does not mean that they *would* be present either partially or entirely in the unreacted zero oxidation state elemental form, but that they are the only elements that would be in liquid state *if they were present*. These same elements are presented in Table 10 in descending order of the total amount present in each type of fuel canister. It must be emphasized that these elements are presented in the amounts of pure element that would be present if they did not react with any other materials in the SNF system. Another way to look at them is from the perspective of the total amount of each chemical element that could be present *before* they react with any other materials.

Table 10. Relative Amounts of Chemical Elements in SNFs That Are Liquid at 350°C*

ATR Fuel in One Canister			N Reactor Fuel in One MCO		
Chemical Element	Number of moles	Mass	Chemical Element	Number of moles	Mass
Cs	2.49	330 g	Sn	47.94	5,690 g
Rb	1.26	106 g	Cs	8.75	1,160 g
Sn	0.39	46 g	Rb	3.00	256 g
Pb	0.186	38 g	Se	0.496	39 g
Se	0.181	14.3 g	Cd	0.486	55 g
Cd	0.036	4.1 g	Na	0.336	7.7 g
In	0.0034	0.39 g	Pb	0.187	39 g
Ga	0.0011**	0.08 g**	In	0.0384	4.4 g
P	0.00014**	0.004 g**			
Na	0.0001**	0.002 g**			
Li	0.000001**	0.000007 g**			

* TBV. "Existing data" to be verified per PMP 6.02 and DOE/RW-0333P.

** Not enough material to be significant with respect to formation of potentially reactive materials in a SNF canister.

3.2.1 Alkali Liquid Metals

The alkali metals are extremely reactive in elemental form. In the closed environment of a SNF canister, a portion of the alkali metals cesium and rubidium would be oxidized by the halogen fission products bromine and iodine as previously discussed. They would also react with any oxygen or water that might contact them.

The HSC Chemical software equilibrium calculations indicate that some unreacted excess cesium and rubidium (beyond what will be oxidized by halogens or other species) will be present in both ATR and N Reactor SNF canisters. Sodium, if present in the same state, would accompany the cesium and rubidium. Sodium and lithium are listed by the ORIGEN2 code as being present in much lesser amounts than cesium and rubidium and, therefore, need not be considered separately from chemically cesium and rubidium. If a greater amount of lithium were present, it might need to be considered separately, because (surprisingly) its miscibility with a cesium-rubidium mixture is very slight.³⁶

The elemental alkali metals cesium and rubidium in the canister environment would be entirely miscible with each other, as illustrated by the phase diagram for the binary alloy system for cesium and rubidium in Figure 1.³⁶ The greater molar quantity of cesium (compared to rubidium) for both ATR and N Reactor fuels, dictates that the solutions of these metals in SNF canisters would likely consist of 60 to 90 wt % cesium with a melting point of approximately 15 to 20°C. The behavior of such a liquid metal system in the SNF canister environment would be similar for both the 200 and 350°C scenarios considered in this assessment, although the Cs-Rb vapor pressure would be substantially greater at the higher temperature. At both temperatures the bimetallic vapor would penetrate the entire closed system and be adsorbed onto virtually all exposed surfaces.

Two scenarios are possible with the condensed cesium-rubidium metal at this point: (1) it is likely that some of the liquid cesium/rubidium would remain in place on the exposed surfaces as it forms a thin film of intermetallic alloys with metals on or near the surface of the various fuel materials; and (2) It is less likely but possible that the metal combinations or alloys that form during contact with the condensed cesium-rubidium alloy would have even lower melting temperatures and, thereby, increase the amount of liquid phase material inside the canister. Eventually, at least a portion of the liquid metal could condense and collect on the bottom inner surface of the canister. The most significant difference between the 200 and 350°C scenarios is that the lower temperature model takes longer, due to the lower vapor pressure of the cesium/rubidium combination at the lower temperature. Although no specific information was found for stainless steel resistance to a liquid cesium-rubidium system, austenitic stainless steels (including Types 304L, 316 and Nitronic 50) offer

Cs-Rb Phase Diagram

Figure 1. Binary Alloy Phase Diagram of Cesium-Rubidium. ("Accepted data" per PMP 6.02 and DOE/RW-0333P.)

excellent resistance to liquid sodium and potassium at 350°C.²⁶ Chemically similar cesium-rubidium would behave the same with respect to stainless steel corrosion^{26, 29, 35} Lithium, however, is different and would attack stainless steel if it were present in a large enough quantity—but it is not.

3.2.2 Non-alkali Liquid Metals

Other metals that melt at temperatures below 350°C, including tin, lead, cadmium, and indium, are likely to dissolve in or alloy with cesium-rubidium due to their predicted miscibilities and/or solubilities. This is based on their reported individual immiscibilities in binary systems with cesium and with rubidium.³⁶ In addition, it is possible, that these metals could be even more soluble or miscible in systems with more than just the two metals in the binary systems reported in reference 36. Any such dissolved tin or lead would likely be of fission product or actinide decay product origin in the fuel matrix and not from the aluminum alloy 6061 cladding of ATR fuel or Zircaloy cladding of N Reactor fuel. The majority of the tin (83% in ATR fuel and 98% in N Reactor fuel) and virtually all of the lead (>99.9%) in both types of fuels are in the cladding and would not be released into the canister environment, contrary to the conservative assumption of this assessment that they will be released. In both types of fuel, most of the fission product tin would be melted at 350°C.²⁵ At 200°C the tin would not melt, but it could dissolve in or form intermetallic compounds with rubidium and cesium.³⁵ Cadmium, which is present in greater quantities in N Reactor fuel than in ATR fuel, can dissolve in the cesium/rubidium system and may form CsCd_{13} or other intermetallic species. Only a few grams of indium would be present in an MCO filled with N Reactor fuel and even less would be present in a DOE standardized canister filled with ATR fuel, but the presence of liquid indium dissolved in cesium/rubidium is a distinct possibility.

The small amount selenium in both types of fuel would most likely never be released from the fuel matrix in elemental form. Thermodynamically, selenium along with the larger amount of chemically similar tellurium, would be expected to form selenides and tellurides in compounds that would be analogous to metal sulfides. HSC Chemistry[®] for Windows Chemical Reaction and Equilibrium Software equilibrium calculations indicate that selenium is more reactive than tellurium. Also, since it melts at a lower temperature (221°C), it would almost certainly react and be “consumed” before tellurium which is still a solid at 350°C. Selenium would preferentially react with magnesium to form MgSe if magnesium were to become available from the structural aluminum alloy 6061 in ATR fuel. If the magnesium in the structural material of ATR fuel is unavailable (physically inaccessible to the potential reactant), or if it is absent as is the case with N Reactor fuel, selenium would react with fission product cerium, strontium and cesium, in that order. It would form the selenides CeSe , SrSe and Cs_2Se , respectively. Another reason that reaction with magnesium is unlikely is the fact that fission product selenium and tellurium are both generated by fissioning uranium inside the fuel matrix where they are physically closer—indeed in intimate contact—with cerium, strontium, and cesium, which also are present only as fission products. The more abundant and less mobile solid phase tellurium also would react with magnesium, if it were available, and then with the remaining strontium and cesium to form SrTe and Cs_2Te . It is less likely to form CeTe . Interestingly, neither selenium nor tellurium is thermodynamically likely to react with barium which was combined with strontium as a surrogate in the earlier chemical equilibrium calculations for N Reactor fuel. So for this particular calculation, the molar quantities of fission product barium present in both ATR and N Reactor fuels could not be combined with strontium. They were entered separately.

3.2.3 Metals Contacting Liquid Cesium and Rubidium

It is virtually impossible to predict all of the elements and intermetallic compounds that could dissolve in or form additional alloys with condensed cesium and rubidium. Indeed, most of the metals present in both ATR and N Reactor fuels have the ability to form various alloys that melt at higher temperatures than do the individual component metals. In addition, many can also form solid solutions with eutectic phases that may liquefy at lower temperatures than do the individual component metals. However, it appears that only a very small amount of the myriad of elements present in the complex assortment of fission products in these 90-

year-cooled fuels would actually dissolve in a CsRb solution.³⁶ Based on the limited solubilities or immiscibilities of these materials in cesium, as presented in Table 11, very little additional material will dissolve in the liquid cesium-rubidium. Indeed, there is a strong case for predicting that there will be an accumulation of some liquid cesium-rubidium on the bottom inside surface of the canisters with N Reactor fuel, up to a maximum of several hundred grams. While the liquid would be composed predominantly of cesium and rubidium (probably 60 to 90% cesium), it could contain a small amount of most of the other chemical elements listed in Table 11, either dissolved in the cesium-rubidium solution or in adjacent droplets of immiscible liquids.³⁶

Table 11. Solubility and/or Miscibility of Spent Nuclear Fuel Components in Liquid Cesium Based on Published* Phase Diagrams of Binary Alloys with Cesium

Chemical Element	Behavior in Liquid Cesium	Chemical Element	Behavior in Liquid Cesium
Aluminum	A miscible CsAl phase exists above 200°C, so some Al would dissolve.	Lead	Forms numerous intermetallic forms; however, all but a trace of Pb in SNF is in stable structural materials. Any lead present should dissolve.
Antimony	Forms alloys and intermetallic forms. The amount of Sb in SNF is extremely small and should readily dissolve.	Lithium	Immiscible
Barium	Immiscible	Magnesium	Immiscible
Beryllium	Miscibility is immeasurably low below 400°C.	Niobium	Immiscible
Bismuth	Forms Cs alloys and intermetallic forms. The amount of Bi in SNF is extremely small and should readily dissolve.	Rubidium	Entirely miscible at ambient temperatures and above.
Calcium	Immiscible	Sodium	Entirely miscible at ambient temperatures and above.
Cadmium	The compound CsCd ₁₃ and others are possible. All Cd would readily dissolve.	Strontium	Immiscible
Copper	Extremely low miscibility.	Tellurium	Te (also Se for which no phase diagram was available) will interact with Cs as described in the text.
Gallium	Some alloys are possible. The amount of Ga in SNF is extremely small and should readily dissolve.	Tin	Alloys and intermetallic forms are likely to form in gram quantities from fission product Sn. Structural Sn (from Zircaloy cladding) is less likely to be available.
Germanium	Numerous alloys and intermetallic compounds form. The very small amount of Ge in SNF should readily dissolve.	Titanium	Immiscible
Hafnium	Not known, but likely to be immiscible similar to Zr.	Vanadium	Immiscible
Indium	Numerous alloys and intermetallic compounds exist. The small amount of In in SNF should readily dissolve.	Zinc	Immiscible
Lanthanides	It appears that all lanthanides are immiscible in Cs.	Zirconium	Immiscible

* Massalski, Thaddeus B., Binary Alloy Phase Diagrams, American Society for Metals, Metals Park, OH, 1986 ("Accepted data" per PMP 6.02 and DOE/RW-0333P).

Based on HSC Chemistry® for Windows Chemical Reaction and Equilibrium Software calculations, it is not thermodynamically favorable for liquid or condensed cesium and rubidium or their vapors to react with or corrode Type 304L stainless steel. The addition of molybdenum metal to the equilibrium calculation does not change the results, indicating that Type 316L stainless steel (which contains molybdenum) also is an acceptable material of construction with respect to compatibility with the ATR and N Reactor fuel materials assessed here. The addition of nitrogen, vanadium and niobium to the assessment yields similar results for Nitronic 50 stainless steel. The chemical reactions that would comprise corrosion of the stainless steel are not feasible. However, "corrosion" per se is not the only way that the physical properties of stainless steel can be degraded as discussed below.

The diffusion of extraneous materials into stainless steel can potentially change its physical properties and structural integrity if it occurs on a large enough scale. Two primary types (mechanisms) of diffusion of material into or through a metal occur by the formation of substitutional solid solutions or interstitial solid

solutions.^{29, 33} Substitutional solid solutions occur when atoms of the intruding or solute material actually replace (or substitute) atoms of the solvent or major constituents, i.e., it actually occupies the place of the original atom in the crystalline structure of the alloy. This mechanism occurs only between solute and solvent atoms of similar size. Interstitial solid solutions are formed when the solute atoms are physically small enough to fit between the interstices of the crystalline solvent atoms. Interstitial diffusion occurs only when the solute atoms have an apparent diameter smaller than 59% the diameter of the solvent atoms.²⁹ The atomic radii of cesium and rubidium, the most likely invading materials, and those of the major components of stainless steel are presented in Table 12. Cesium and rubidium atoms are clearly much larger than the primary atoms in stainless steels; hence, neither substitutional nor interstitial diffusion pose a potential threat to the integrity of the SNF canisters.^{23, 24, 25} The relatively high melting range of stainless steel, approximately 1,000°C higher than the 350°C maximum temperature considered in this assessment, also contributes to the physical integrity of its micro crystals. This, in turn, promotes resistance to substitutional diffusion by similar sized atoms.²⁶

Table 12. Atomic Radii of the Major Components of Stainless Steel and Heavy Alkali Metals*

Fe	Ni	Cr	Mn	Mo	Rb	Cs
1.72Å	1.62Å	1.85Å	1.79Å	2.01Å	2.98Å	3.34Å

*Table of Periodic Properties of the Elements, Sargent-Welch Scientific Company, Skokie, IL 60077 (1980)
("Accepted data" per PMP 6.02 and DOE/RW-0333P)

3.2.4 Liquid Metals in Contact With Stainless Steel

Intergranular corrosion, i.e., the penetration and corrosion of materials between the grains of the stainless steel in the canister is not a credible failure mechanism because the selected materials of construction do not sensitize (and become susceptible to intergranular corrosion) at temperatures below 500°C. Type 316L stainless steel (ASTM Standard Specification SA-312) planned for DOE Standardized SNF canisters and possibly for MCOs would not be susceptible to such attack at 350°C, the highest temperature considered in this assessment.^{29, 33, 37}

Liquid metal embrittlement (LME) is described in the ASM Handbook as "catastrophic brittle failure . . . when a ductile metal is coated with liquid metal and is subsequently stressed in tension."^{16, 37} A mandatory requirement in order for LME to occur is a prolonged *intimate* contact of the solid alloy with a liquid metal. Such contact can be prevented by even a thin film layer of oxide several Ångströms thick, which is the reason that stainless steels are generally less susceptible to LME than are carbon steels and other alloys that are not protected by an oxide surface film. However, austenitic stainless steels like the Type 316L stainless steel planned for SNF canisters can and do experience LME when exposed to certain liquid metals.^{38, 39} In addition, the replacement of an air atmosphere with a helium blanket when the fuel is sealed inside the canister would mean that air would not be available to replenish the Cr₂O₃ protective film on the inner surfaces of the canisters.

Technically, LME is not corrosion (degradation that results from the chemical interaction of fuel and canister materials), but a "degradation of mechanical properties of the solid alloy."^{37, 38, 39} Alloys that experience LME become brittle and less ductile and, therefore, are more likely to crack in stressed locations. Stresses produced by welding alone have been reported to produce cracking of austenitic stainless steel exposed to liquefied zinc. The requirement of a "robust design" for the DOE standardized canister, including the ability to withstand a 30-foot drop (10CFR Part 71.73), makes it clear that LME of the stainless steel cannot be tolerated.²⁶

The ASM Handbook lists (alphabetically by chemical symbol) aluminum, silver, cadmium, copper, indium, lead, antimony, selenium, tin, tellurium and zinc (of the metals present in SNF) as being capable of causing liquid metal embrittlement of ferritic and/or austenitic stainless steels.^{37, 40} The high melting temperatures of

elemental aluminum, silver, copper, antimony, tellurium and zinc preclude those materials from being present as pure liquids. However, the alkali metals rubidium and cesium (discussed previous) which may be present as liquids inside the canister, can indirectly contribute to LME of stainless steel by transporting dissolved or entrained metals to the stainless steel surface. Based on the liquid metal solubilities and miscibilities presented in Table 11, some aluminum, some cadmium, some indium, some lanthanides, any available lead, and some tin *could* dissolve in liquid rubidium/cesium and reach the stainless steel surface in that manner. The possibility of LME degradation of the stainless steel fuel canisters from exposure to these metals in liquid form cannot be ruled out.

The melting temperatures of the remaining metals known to cause LME in stainless steel, cadmium, indium, lead, selenium and tin, are low enough that they could exist as elemental liquids at the 350°C maximum temperature considered in this assessment independent from their relative miscibilities in liquid cesium/rubidium. However, selenium is unlikely to be present as a liquid metal because it, along with chemically similar tellurium, will likely have reacted with the alkali and alkaline earth metals to form selenide and telluride analogs of the sulfides as reported earlier. The possibility of LME of the stainless steel from exposure to liquid cadmium, indium, lead, selenium, tellurium and tin cannot be ruled out, but the likelihood is small in comparison to those metals listed in the previous paragraph.

3.2.5 Molten Salts

Molten salt corrosion is unlikely for two reasons: (1) in the strongly reducing chemical environment of the canister, few salts form; and (2) the salts that are known to be present in significant quantities have high melting temperatures that keep them in the solid state at 350°C.²⁵ The solubility of the salts most likely to be present (alkali halides) in liquid cesium-rubidium is not known; however, based on the general insolubility of polar compounds in non-polar liquids (like molten cesium-rubidium), such dissolved salts can be eliminated as a credible source of chemical attack on the stainless steel canisters.

Perhaps the best-known corrosion mechanism associated with liquid state materials is one that is commonly encountered in aqueous media; the galvanic cell.⁴¹ The components that are required to form a galvanic cell are a cathode, an anode, and an electrolyte. Theoretically, any two metals can form the anode and cathode since no two elements have exactly the same electric potentials. The conditions assumed for this sensitivity analysis provide the presence of approximately fifty elements that exist as metals in the zero oxidation state providing numerous cathodes and anodes. This system, however, lacks an electrolyte. While the liquid cesium-rubidium will conduct a flow of electrons, it does not provide a medium in which iron, nickel, chromium or manganese ions can dissolve and flow to a cathode. Therefore, any corrosion that occurs with such a liquid metal system would not be an electrochemical reaction of the type traditionally known as galvanic corrosion.^{38, 41}

None of the liquid materials identified in this assessment would be expected to contribute significantly to the *chemical* degradation of stainless steel fuel canisters or cause them to lose their integrity under the defined conditions. However, the possibility of *physical* degradation of the stainless steel canister by liquid metal embrittlement (LME) cannot be ruled out.

3.3 Solid SNF Materials

Liquid and gaseous state materials (fission products, specifically) are the assigned materials of focus for the current sensitivity analysis. By definition, solid state materials are less mobile than are liquid or gaseous state materials. However, over long periods of time, and especially at elevated temperatures, components of materials in the solid state can and do migrate. Both physical and chemical changes can occur when different metals contact each other. Such contact is assumed between uranium metal and the inner wall of the stainless steel SNF canister following failure of fuel cladding.

Uranium forms low-melting eutectics with elements from the group chromium, cobalt, iron, manganese, and nickel. "Low-melting" in this case means eutectics with liquid phases in the low 800 or high 700°C range, compared to approximately 300°C higher for uranium metal and another 200 to 300°C higher for uranium-aluminum alloys. The use of alloys containing these elements (Cr, Fe, Mn and Ni) for cladding metallic uranium is, therefore, limited to temperatures below approximately 700°C. The experimental data presented in Table 13 indicate the relative rates of uranium penetration through an unspecified [18:10:1] stainless steel crucible wall at temperatures of 740°C and above. The stainless steel crucible wall thickness is not specified for the referenced test, but the crucibles used in other tests reported in the same document were 0.0625 inches thick. Below that temperature, uranium diffusion is much slower. This is nearly 400°C hotter than the highest temperature of 350°C considered for this assessment, thereby providing a wide margin of safety against the diffusion penetration of uranium metal through stainless steel.⁴²

Table 13. Uranium Metal Penetration of Stainless Steel at Elevated Temperatures*

Temperature, °C	Duration of test, hours	Penetration
950	16	Complete (0.0625 in.)
760	24	Complete (0.0625 in.)
742	72	0.005 in.
735	168	Nil

* Data source: Tipton, C. R., REACTOR HANDBOOK, VOLUME I, MATERIALS, Interscience Publishers, Inc., New York (1960) These have been determined to be "existing data." TBV.

None of the solid materials identified in this assessment would be expected to contribute significantly to the degradation of stainless steel fuel canisters or cause them to lose their integrity under the assumed packaging conditions and storage temperatures.

4.0 SUMMARY/CONCLUSIONS

The chemical properties and potential reactivities of the materials expected to be present in dry, 90-year-cooled, ATR and N Reactor SNF stored in a helium atmosphere inside stainless steel canisters were assessed to determine the likelihood of the canisters degrading enough to lose their structural integrity. With the possible exceptions of: (a) exceeding the specified pressure loadings for the canisters; (b) hydrogen embrittlement of the canisters (addressed elsewhere - see reference 31); and (c) liquid metal embrittlement, no significant mechanisms of degradation were determined by which DOE Standardized Canisters or Multi-Canister Overpacks would be likely to fail at nominal repository storage temperatures of 200°C or even as high as 350°C. This assessment, based on the known physical and chemical properties, published thermodynamical properties, and calculated radiological compositions of spent nuclear fuels, indicates that the foregoing potential mechanisms of structural failure of Type 316L stainless steel canisters could not be ruled out, even though they are deemed to be very unlikely under the conditions studied. Resolution of these potential problems will be required before this mode of disposition can be approved for spent nuclear fuels. This assessment did not address the potential effects of the ultimate intrusion of air or water into SNF canisters. These results, based on the assessment of two typical and representative fuels, may be applied to most of the fuels in the USDOE's SNF inventory.

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