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Standard Guide for Drying of Spent Nuclear Fuel¹

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1. Scope

1.1 This guide discusses three steps in preparing spent nuclear fuel (SNF) for dry storage: 1) evaluating the need for drying the SNF after removal from a water storage pool and prior to placement in extended dry storage, 2) drying the SNF, and 3) confirming that adequate dryness has been achieved.

1.1.1 The guide addresses drying methods and their limitations when applied to the drying of SNF that has been in storage at water pools. The guide discusses sources and forms of water that may remain in the SNF, in the SNF container, or in both after the drying process has been completed and also discusses the importance and potential effects the drying process and any residual water may have on fuel integrity and container materials during the dry storage period. The effects of residual water are discussed mechanistically as a function of the container thermal and radiological environment to provide guidance on situations that may require extraordinary drying methods, specialized handling, or other treatments.

1.1.2 The basic issues in drying are to: 1) determine how dry the SNF must be in order to prevent issues with fuel retrievability and/or container pressurization and corrosion during storage, handling and transfer and 2) to confirm that adequate dryness has been achieved. Achieving adequate dryness for undamaged commercial fuel may be straightforward but may become a complex issue for any SNF where cladding damage has occurred prior to or during placement and storage at the spent fuel pools. Dryness issues may also result from the presence of sludge, crud, and any other hydrated compounds that may be transferred, with the SNF, to the storage container and hold water and resist drying.

1.2 *This standard only discusses SNF drying and does not purport to address all of the SNF handling and safety concerns, if any, associated with the drying process(es). It is the responsibility of the user of this standard to establish appropriate safety and health practices and to meet regulatory requirements prior to and during use of the standard.*

2. Referenced Documents

2.1 ASTM Standards:²

C 1174 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
C 1562 Guide for Evaluation of Materials Used in Extended Service of Interim Spent Nuclear Fuel Dry Storage Systems

2.2 ANSI/ANS Standards:³

ANSI/ANS 8.1-1998 Nuclear Criticality Safety in Operations with Fissionable Materials Outside Reactors
ANSI/ANS-8.7-1998 Nuclear Criticality Safety in the Storage of Fissile Materials
ANSI/ANS-57.9 American National Standard Design Criteria for Independent Spent Fuel Storage Installation (Dry Type)

¹ This guide is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.13 on Spent Fuel and High Level Waste. Current edition was approved in _____ and published in _____.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

2.3 Government Documents:4

Title 10 on Energy, Code of Federal Regulations, Part 60, 10 CFR 60, U.S. Code of Federal Regulations, Disposal of High Level radioactive Wastes in Geologic Repositories

Title 10 on Energy, Code of Federal Regulations, Part 63, 10 CFR 63, U.S. Code of Federal Regulations, Disposal of High-Level Radioactive Wastes in Geologic Repository at Yucca Mountain, Nevada

Title 10 on Energy, Code of Federal Regulations, Part 71, 10 CFR 71, U.S. Code of Federal Regulations, Packaging and Transport of Radioactive Materials

Title 10 on Energy, Code of Federal Regulations, Part 72, 10 CFR 72, U.S. Code of Federal Regulations, Licensing Requirements for the Independent Storage of Spent Nuclear Fuel and High-Level Radioactive Waste

3. Terminology

3.1 *Definitions*—Terms used in this guide are as defined in Practice C 1174 or, if not defined therein as per their common usage, except where defined specifically for this guide in Section 3.2.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *CRUD*, *n*—*in nuclear waste management*, deposits on fuel surfaces from corrosion products that circulate in the reactor coolant. Compositions of the deposits reflect materials exposed to coolant and activation products formed during irradiation. Term was originally an acronym for “Chalk River Unidentified Deposits.”

3.2.2 *damaged fuel*, *n*—*in nuclear waste management*, nuclear fuel that has been geometrically altered in form/shape to a degree that may affect the integrity of the cladding or the retrievability from a (licensed) storage system or make the SNF unsuitable for transport in a licensed cask.

3.2.3 *disposal*, *n*—*in nuclear waste management*, the emplacement of radioactive materials and wastes in a geologic repository with the intent of leaving it there permanently. **10 CFR Part 63.2**

3.2.4 *failed fuel*, *n*—*in drying of spent nuclear fuel*, any breach, such as hairline cracks or holes in a cladding that may permit water into a fuel element.

3.2.5 *getter*, *n*—*in nuclear waste management*, a material (typically a solid) used to chemically react with certain gases (for example, H₂, O₂, H₂O vapor) to form a solid compound of low vapor pressure.

3.2.5.1 *Discussion*—A getter may also be used to absorb impurities in chemical and metallurgical processes.

3.2.6 *independent spent fuel storage installation (ISFSI)*, *n*—a system designed and constructed for the interim storage of spent nuclear fuel and other radioactive materials associated with spent fuel storage. **10 CFR Part 72**

3.2.7 *packaging*, *v*—*in nuclear waste management*, the production of an assembly of components used to ensure compliance with the requirements of **Title 10 of the Code of Federal Regulations, (CFR) Part 72** for independent storage of spent nuclear fuel and high-level radioactive waste or 10 CFR Part 71 for transportation of radioactive materials.

3.2.8 *repository*, *geologic repository*, *n*—*in nuclear waste management*, a disposal site, a permanent location for radioactive wastes.

3.2.9 *spent nuclear fuel (SNF)*, *n*—nuclear fuel that has been irradiated in a nuclear reactor and contains fission products, activation products, actinides, and un-reacted fissionable fuel. Normally spent fuel is contained in a metal cladding whose condition (undamaged, corroded, perforated, etc.) depends upon the original material properties as modified by the exposure/handling conditions during service and storage.

3.2.10 *sludge*, *n*—*in nuclear waste management*, a slurry or sediment containing nuclear waste materials, a residue, generally radioactive, that has been formed from processing operations, corrosion or other similar reactions.

3.2.11 *waste package*, *n*—*in nuclear waste management*, the waste form and any containers, shielding, packing and other materials immediately surrounding an individual waste container. **10 CFR Part 60**

3.2.11.1 *Discussion*—The waste package is expected to consist of an overpack (a container) into which commercial SNF, DOE SNF canisters and high level waste are to be placed for disposal at a repository.

3.2.12 *water*, *n*—*in drying of spent nuclear fuel*, it is the total amount of moisture (specified by weight, volume, or number of moles) present in a container as a combination of vapor, free or unbound liquid water, physisorbed water, chemisorbed water, and ice. The following specific terms for water are used in this document:

⁴ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

3.2.12.1 *bound water, n*—bound water includes adsorbed surface layers of water, and nearly all chemisorbed water.

3.2.12.2 *chemisorbed water, n*—water that is bound to other species by forces whose energy levels approximate those of a chemical bond.

3.2.12.3 *physisorbed water (adsorbed water), n*—water that is physically bound (as an adsorbate, by weak forces) to internal or external surfaces of solid material.

3.2.12.4 *trapped water, n*—unbound water that is physically trapped or contained by a surrounding matrix, blocked vent pores, cavities, or by the nearby formations of solids that prevent or slow the escape of water from the waste package. Note: Traps may have varying degrees of reversibility and a trap may be for practical purposes irreversible.

3.2.12.5 *unbound water, n*—water, in the solid, liquid, or vapor state, that is not physically or chemically bound to another species.

4. Significance and Use

4.1 This guide demonstrates the need for drying SNF during packaging for interim dry storage and provides technical information for use by SNF owners to determine the forms of water usually associated with spent nuclear fuel due to corrosion damage of the fuel, cladding and storage materials during irradiation and in storage pools. Drying may be needed to prepare the SNF for sealed dry storage, transportation, and/or permanent disposal at a repository. This guide provides information to aid in:

- 4.1.1 Selecting a drying system,
- 4.1.2 Selecting a drying method, and
- 4.1.3 Confirming that adequate dryness was achieved.

4.2 The guide can also aid in assessing:

4.2.1 Drying technologies. 4.2.1.1 Water remaining on and in commercial and research reactor spent nuclear fuels after removal from water basin storage may become an issue when the fuel is sealed in a dry storage system or transport cask. The movement to a dry storage environment typically results in an increase in fuel temperature due to the decay heat. This temperature change may be sufficient to cause the release of water remaining in a sealed dry package and result in container pressurization, fuel retrievability issues, and container corrosion.

4.2.1.2 Removal of the water associated with the SNF may be accomplished by a variety of technologies including: heating, imposing a vacuum over the system, flushing the system with dry gasses and/or combinations of these and other similar processes.

4.2.2 The achievement of adequate dryness.

4.2.2.1 Virtually all water removal processes are time dependent thus some residual water should be anticipated.

4.2.2.2 Drying processes may not readily remove the water that was retained in pores in fuel cladding, capillaries, sludge, crud, and as thin wetted surface films. Water that may be trapped within damaged SNF is especially difficult to remove.

4.2.2.3 Drying processes may be even less successful in removing bound water from the SNF and associated materials because removal of bound water will only occur when the threshold energy required to break the specific water-material bonds is available (applied) to the system. For spent nuclear fuel this threshold energy may come from the combination of thermal input and ionizing radiation.

4.2.2.4 The effectiveness of a drying procedure may be evaluated by measuring the response of the system after the drying operation is completed. For example, if a vacuum drying technology is used for water removal, a specific vacuum could be applied to the system, the vacuum pumps turned off and the time dependence of pressure rebound measured. The rebound response could then be associated with the residual water in the system.

4.2.3 The potential for residual water associated with the SNF, CRUD and sludge inside a sealed package to become available to react with the internal environment, the fuel, and the package materials as a result of extended time at equilibrium dry storage conditions.

4.2.3.1 Thermal gradients within the package evolve with time and water will tend to migrate to the cooler portions of the package.

4.2.3.2 Radiolytic decomposition of hydrated and other water containing compounds may release moisture to the package.

4.2.3.3 Extended time at temperature, coupled with the presence of ionizing radiation, may provide the energy necessary to release bound or trapped water to the package.

5. Evaluating the Drying Approach

5.1 The proper approach to drying SNF will depend on fuel type, condition and associated materials. Additionally, the approach may depend on the expertise and experience of the firm(s) conducting the drying operation. There is no single, correct or even preferred approach. For example, non-failed commercial fuel may be dried by one approach, failed fuel by another approach and DOE research reactor fuels by yet another approach. Furthermore, the variables that must be considered in selecting a drying approach for one fuel type will differ significantly those that are important for another fuel type. For example, hydrogen/hydride behavior should be considered in fuel systems clad with zirconium based alloys but are not important to aluminum or stainless steel clad SNF. However, in any event, the proper drying approach will minimize the potential for damage of the fuel during the drying operation and during subsequent dry storage.

5.2 Some forms of fuel degradation—such as cladding pinholes or cracks—may form before or during the dry storage period without violating design or licensing requirements. However, damage such as small cladding cracks or pinholes formed during the dry storage period could cause the fuel to be re-classified as failed fuel for repository disposal considerations. The objective in drying commercial LWR SNF containers is to eliminate enough water to preclude “gross” damage to commercial fuel or its cladding during dry storage and transport. The drying process itself must not damage the fuel. For example, the thermal cycling during the drying process for commercial LWR SNF may affect the hydrogen/hydride behavior in the cladding. Heating the SNF during a drying operation may dissolve precipitated hydrides and allowing the SNF to cool may cause hydride reprecipitation. The hydride orientation and therefore the properties of the fuel cladding may be affected by the dissolution-precipitation process.

5.3 DOE research and production reactor SNF that is not treated or reprocessed, will eventually be stored in sealed canisters within dry storage systems that may or may not be regulated by the NRC. DOE dry storage canisters are expected to contain the SNF through interim storage, transport, and repository packaging. The objectives of drying processes used on this fuel are to:

5.3.1 Preclude geometric reconfiguration of the packaged fuel,

5.3.2 Prevent internal damage to the canister from over-pressurization or corrosion, and

5.3.3 Minimize hydrogen generation or materials corrosion that present problems during storage, transport or repository handling operations.

5.4 The decision to select the drying methodology for treating fuel for interim dry storage or disposition in a geologic repository could be based on the following factors:

5.4.1 Irradiation and storage history,

5.4.2 Nature and degree of fuel damage,

5.4.3 Forms of water in the packaged SNF container,

5.4.4 Thermal and radiological environments involved,

5.4.5 Degree to which self-heating may contribute to the drying process,

5.4.6 Potential for corrosion and radiolytic degradation of the fuel and container material during drying and storage,

5.4.7 Mechanisms of water interaction with the fuel and container components, and

5.4.8 Maximum allowable water after drying is completed.

5.5 *Categorization of SNF and Defects for Drying*

Evaluation—Water in SNF storage and transport containers can be a potential cause, result, or both, of fuel cladding damage or “failed fuel.” However, there is not a single, universal definition of a “failed fuel”. The NRC ISG-1 Rev 2 defines damaged fuel as “spent nuclear fuel with known or suspected cladding defects greater than a hairline crack or a pinhole leak that have potential for release of significant amount of fuel particles.” For the purposes of SNF transport per 10 CFR 71.55, fuel is essentially regarded as “failed” only when the geometric form of the fuel has been “substantially altered.” For the purposes of dry cask storage per 10 CFR 72.22, the SNF cladding is required to: “be protected against degradation and gross rupture.” Gross rupture is defined as that which could result in the release of significant quantities of fuel materials and fission products to the storage environment. For the purposes of receipt of SNF containers at a geologic repository, 10 CFR 961 defines three categories of commercial LWR “failed fuel:”

Class F-1 failed fuel has visually observable failure or damage

Class F-2 failed fuel has “radioactive leakage”

Class F-3 failed fuel is badly damaged and requires “encapsulation”

Each of these damaged or failed fuels could potentially require different handling/treatment operations than those used for nonfailed fuel. It is, therefore, important when addressing the potential for fuel damage or failure due to moisture in the SNF containers to be clear about the kind and extent of cladding damage that is present and could result from the drying/dry storage operations. It is particularly important to note that SNF could be regarded as intact or non-failed for the purposes of storage or transport performance but “failed” for the purposes of geologic repository disposal. This potential exists because of the relatively predictable performance of damaged fuel during dry storage term versus the very difficult prediction of performance in geologic time. Commercial SNF may be characterized as intact or failed through the use of one or more of the following processes: operating records (core history and handling), visual examinations, ultrasonic testing, wet or dry sipping, and eddy current testing. Fuel type and the presence/type of defects involved are essential starting points for evaluation of drying operations. In order to organize the information in this guide, selected varieties of spent fuels have been placed into categories with a letter designation for consideration. Similarly, the types of defects to be considered are identified with a number designation. The identities of these categories are provided below.

5.5.1 SNF Grouping—The following groupings for SNF are used in this guide to distinguish between the specific SNF types:

- A Commercial PWR/BWR, U oxide or mixed oxide fuel in Zr-alloy cladding
- B Mixed carbide fuel with SiC cladding (in graphite)
- C U oxide or mixed oxide fuel in stainless steel cladding
- D U-ZrH fuel in Zr-alloy or stainless steel cladding
- E U oxide or mixed oxide fuel in Al-alloy cladding
- F UAl_x fuel or U-ZrH fuel in Al-alloy cladding
- G U metal and U alloy fuel in Zr-alloy, Al-alloy or stainless steel cladding
- H U carbide fuel with pyrolytic carbon cladding
- I Unclad U metal or oxide fuel

5.5.2 Fuel Conditions—The following are used in this document to categorize fuel conditions.

- 1 Fully intact cladding with no known penetrations
- 2 Cladding with known small pinholes or hairline cracks that may allow entry/exit of moisture (Not considered “failed” fuel per 10 CFR 71/72) (Class F-1 equivalent)
- 3 Fuel with visible or suspected sludge or coatings that may hold significant water
- 4 Cladding with known large cracks or holes that will allow free entry/exit of moisture (Considered “failed” fuel) (Class F-2 or F-3 equivalent)
- 5 Fuel with major cladding damage from previous fuel oxidation, exposure to water, or both (Damaged from previous entry/exit of moisture)
- 6 Rubblized fuel that has little or no intact cladding, high surface area, and previous exposure to water (Includes fuel pins or elements that have been sectioned for analysis or study) (Class F-3 equivalent)

5.6 Forms of Residual Water in SNF Containers—After drying, residual water in a variety of forms may remain on the fuel, fuel cladding, or internal components of the container. These forms include unbound water, ice formed during drying, physisorbed water, and chemisorbed water.

5.6.1 Unbound Water—Unbound water is potentially present in SNF containers. In the case of SNF transferred from a water storage pool to a dry container system, unacceptable amounts of unbound water may remain in the container if the drying procedure does not remove the water properly. Sources of unbound water after vacuum drying may include pooling, ice, trapped water, thin wetted surface films and water in capillaries.

5.6.2 Ice Formation—Ice formation can be a root cause for residual water in SNF containers that have undergone vacuum drying. In vacuum drying the gas pressure is reduced below the vapor pressure of the water to evaporate the liquid phase. The heat of vaporization of water (539.6 cal/g) is considerable higher than its specific heat (1 cal/g/°C); consequently, liquid water may undergo a considerable temperature drop during drying. Since the heat of melting ice (79.7 cal/g) is relatively small, the energy removed from the liquid by evaporation can cause the water to freeze. Drying operation design steps may be necessary to prevent the water from freezing in the container or in the vacuum lines. Drying procedures with thermal homogenization steps such as a helium backfill or use of other hot inert gases usually prevent ice formation. It is also important to route vacuum lines to avoid low spots. Throttling of vacuum pumps to slow the rate of vacuum drying may also prevent ice formation. (See [Annex A2](#).)

5.6.3 Physisorbed Water—Physisorbed water is found on all external surfaces of the SNF and the container. Typical water concentrations are about 0.03 to 0.05 g/m²/monolayer. The binding force holding the water to the surface is weak and the water layer can be removed at relatively low temperatures by vacuum drying. Cracks, open pores and corrosion products on/in the surface may hinder evaporation and hold significant quantities of physisorbed

water. Corrosion products on exposed fuel meat may also retain physisorbed water, especially corrosion products from metallic U fuels.

5.6.4 Chemisorbed Water—Chemisorbed water may exist as a hydroxide or hydrate in the native oxides or corrosion products on the fuel, cladding, or container materials. The dehydration of hydroxides occurs via the reformation of water molecules, which are released from the lattice when the thermal energy or energy from ionizing radiation equals or exceeds the specific bonding energy of the hydrated compound. A number of uranium oxide hydrates may be formed as a result of uranium or uranium oxide contact with water. These chemical species are outlined in **Annex A1**. Chemisorbed water may also be found in cladding materials and the materials of container construction. Aluminum metal in water forms a number of surface hydroxides such as $\text{Al}(\text{OH})_3$ (or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) which begin dehydrating near 100°C to the form $\text{AlO}(\text{OH})$ (or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) which is stable to $>340^\circ\text{C}$. Zirconium cladding may also form the hydrated oxides $\text{ZrO}(\text{OH})_2$ or $\text{Zr}(\text{OH})_4$ during irradiation. The potential water content in hydrated zirconium oxides is small and will not be released below 500°C **(1)**.⁵ (See **Annex A1** for other hydroxides and hydrates formed from water contact with typical fuel and container materials.)

5.7 Potential Sources of Water:

5.7.1 General Service Environment. Water surrounds most SNF until they are placed in a dry storage environment. Commercial and research reactor fuels are irradiated in water, stored in water pools and transferred to dry storage containers while the fuel and the container are both under water. The water may cling to the surfaces it contacts, seep into cracks and crevices and pool in low places in the storage container. In most cases, the primary source of water in the dry storage package is readily apparent. However, several other potential sources of water should be considered.

5.7.2 CRUD and Sludge:

(1) CRUD on Commercial SNF—CRUD deposits on commercial SNF are corrosion products from reactor coolant system materials and/or other materials/chemicals from within the system inventory. The amount and type of the deposits are dependent on the reactor type and water chemistry. Characteristic CRUD areal density for PWR fuel is $<5 \text{ mg/cm}^2$ with an inhomogeneous distribution over the fuel surface, typically deposited on the bottom half of the fuel rods as a layer averaging less than $25 \mu\text{m}$ ($<0.001 \text{ in.}$) but potentially reaching $100\text{-}\mu\text{m}$ (0.004-in.) in thickness **(2)**. CRUD deposits on BWR fuel average 25 to $76 \mu\text{m}$ (0.001 to 0.003 in.) in thickness and may reach a thickness of $250 \mu\text{m}$ (0.010 in.) **(2)**. The contribution of CRUD to the water content on the surface of commercial SNF is typically small.

(2) Sludge in SNF Operations—Sludge may accumulate in SNF water storage systems from two primary sources: **(1)** corrosion of the SNF and other materials in the storage pool, **(2)** dirt and dust entering from loading doors, HVAC systems, etc. Both sources of sludge are similar in that they may hold significant quantities of water and could get transferred with the fuel into dry storage containers unless appropriate cleaning operations are employed. Sludge is probably not a concern for fuels in groups A–D that have defect conditions 1 or 2 and are from well-controlled wet storage systems. However, the quantity and characteristics of the sludge carryover and its impact on drying should be evaluated for fuels in group A–D that have defect conditions 3–6 and for fuel groups E–I, especially those with defect conditions 3–6. Analyses of sludge accumulated from wet storage of damaged DOE metallic uranium fuels **(3)** showed that a variety of aluminum, iron, and uranium hydrous oxides made up over 90 % of the dry weight of the sludge.

5.7.3 Water in SNF Packages:

5.7.3.1 Commercial SNF, Group A, Defect Conditions 1 – 4—LWR fuel without any through-cladding defects (Condition 1) will not allow water inside fuel rods. However, even very small pinholes or cracks (Condition 2) may result in water penetrating the cladding during storage and being held in the fuel-to-cladding gap and the rod plenum after drying. Similar water retention may also occur in fuels in Condition 4. PWR fuel in Condition 3 may also trap water in guide tubes if the dashpot drain hole is blocked with sludge or CRUD; however even if the dashpot drains are not blocked, they can be approximately 15 cm (6 in.) above the bottom of the guide tube and will not drain unless the assembly is tipped over. A typical LWR rod in Condition 4 is characterized by a combination of primary and secondary defects. The primary defect is regarded to be the location of the original penetration and secondary defects may be located at some distance from the primary defect. The secondary defects are normally attributed to local hydride blistering **(4)**. The defects are holes of different sizes that allow water to penetrate and fill the free volume of the rod and may retard water removal during drying operations.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

5.7.3.2 *Clad Metallic U fuels (Groups F and G), Defect Conditions 1 – 4*—Clad metallic U and most U alloy fuels will not allow water inside intact (Condition 1) cladding. However, water ingress through even the smallest pinholes (Condition 2 or 4) may have a noticeable effect in metallic U. Water, even at basin temperatures, will oxidize U metal sufficiently to rupture or “unzip” fuel cladding (5). If the oxidation processes cause the internal environment to become sufficiently anoxic, the U metal will react with the hydrogen that has been produced and start forming UH_3 . Free reactive surfaces of UH_3 may impact safety considerations for drying operations in the presence of residual moisture or air (6).

5.7.3.3 *Mixed Carbide Fuels, Groups B and H*—Mixed carbide fuels encapsulated in pyrolytic carbon, graphite, or both, are designed for gas-cooled reactors and are not designed to be exposed to water. If such fuels become soaked with water for any reason (dry storage mishaps, incursion of water into dry wells, etc.), drying may be quite difficult due to potential adsorption of water in the pores of the graphite or carbon.

5.7.3.4 *Miscellaneous Research Fuels, Groups C, D, and E*—A wide variety of research reactor fuels have been irradiated. The response of these fuels to water will depend on the fuel meat, cladding composition, and cladding integrity. Research reactor fuels generally have relatively low burnup and low decay heat. The low decay heat may dictate the use of specialized heating processes to achieve adequate dryness. Dry storage temperatures and radiation levels may be so low that water radiolysis and secondary oxidation reactions may not occur or may be insignificant. However, many of the research reactor fuels have been damaged during storage and, because of the damage, may be difficult to dry. Each group of research reactor fuels should be evaluated separately because of the wide variations in type and condition.

5.8 *SNF Exposure Environments*—The dryness required for a given nuclear fuel will often relate directly to the radiation, time, temperature, and water chemistry environment to which it was exposed during reactor operation and pool storage. Specific fuels typically have an environmental exposure history that provides input into probable drying requirements. The drying process must reliably establish water vapor pressures levels such that detrimental chemical reactions are limited for the proposed dry storage lifetimes.

5.8.1 *Commercial Reactor Fuels:*

5.8.1.1 Commercial nuclear fuel is irradiated in a water environment at elevated temperature and pressure. If a breach of the cladding develops while the fuel is in-core, the internal gas will be released and the pressurized water may enter into the fuel rod. Upon removal from the reactor core, the fuel is stored in a water basin with the water temperature typically less than 40°C. The water pressure acting on the fuel depends on the depth of the fuel in the basin water. Both the reactor core water and basin water typically have tightly controlled chemistry that may prevent or at least minimize fuel damage.

5.8.1.2 The heat generated by the SNF during storage in water basin drops off predictably as the fission products decay. After a suitable cooling time (aged for at least 1 year) (7), the SNF may be moved out of basin storage and placed into a dry storage cask system.

5.8.1.3 The thermal performance of an SNF cask or package can be modeled to determine the expected dry storage temperature profile in the system as a function of time (8). Design or regulatory requirements may establish short term temperature limits for SNF cladding. The limits to ensure cladding integrity are, in part, a function of burnup, cladding design and fuel pressurization. Limits from 400°C (9) to 570°C (10) have been suggested and the evaluation of the desired limit should involve consideration of hydride dissolution and re-precipitation processes, thus the hydrogen content of the fuel cladding should be reasonably well estimated.

5.8.2 *Research/DOE Reactor Fuels:*

5.8.2.1 Research reactor fuel irradiation temperatures and pressures vary widely, but are typically lower than those of a commercial power plant. Fuel lifetimes are also quite variable in DOE production and test reactors. Research reactors may operate with little or no change in fuels for many years and the fuel may be exposed to stagnant water or a humid air environment between operating cycles. DOE production reactors may provide the opposite extreme as the fuel is changed out on a schedule to provide the optimum isotope production desired and the total fuel irradiation lifetime may be less than a year.

5.8.2.2 Conditions necessary for successful dry storage of DOE SNF will vary somewhat on the basis of total irradiation, fuel type, and decay heat. The elimination of reprocessing in the U.S. essentially resulted in placing the vast majority of DOE SNF into extended basin storage and a few dry storage systems. The primary considerations involved with movement of these, largely metallic, DOE SNF into interim dry storage include the lack of significant latent decay heat, the wide range of fuel cladding materials, and the lack of cladding integrity in many fuels. One possible approach to determining the necessary dry storage conditions may include demonstrating that, because of the pre-storage damage to the fuel, any anticipated in-storage degradation would not compromise subsequent disposition options.

5.8.2.3 Three primary types of dry storage systems are currently in use for DOE SNF: Underground well storage, active vented storage, and passive vented storage. Underground well storage and interior facility storage typically operate at temperatures between ambient and 60°C, and the SNF is not sealed in a small confined space because containment is provided by the well or the facility itself. Exterior cask storage systems may be very similar to those used for commercial SNF except that the latent decay heat is insufficient to heat the cask above exterior ambient conditions. The experience and expertise gained in operating the current dry storage systems for DOE SNF should be carefully considered if the DOE SNF is subsequently transferred to alternative dry storage systems for future storage or disposition.

5.8.2.4 Vented dry storage systems can evaporate or radiolyze residual water over long times and allow water to escape from the system. However, this situation may also work in reverse because canisters containing cool fuels may aspirate water from the external atmosphere depending on the external temperature and dew point. Water evaporation and/or aspiration during “dry” storage may significantly change the overall chemisorbed water content of the SNF over the storage period, especially if the SNF is badly damaged. Characterization of SNF behavior in such vented systems may provide insight into the probable behavior of DOE SNF in alternative dry storage systems.

5.9 *Potential Effects of Residual Water on SNF and Containers*—Water present in containers for dry storage of SNF can be released to the container environment by direct, thermally induced decomposition of the chemically bonded species, vaporization of physisorbed and free water, and radiolytic decomposition. The released water and decomposition products may cause corrosion, pressurization and possibly embrittlement issues for the dry storage of SNF.

5.9.1 *Radiolysis:*

Radiolysis of residual water within a sealed spent fuel package releases free oxygen and hydrogen which may be involved in internal corrosion reactions. Radiolysis occurs as a result of gamma, beta, neutron or alpha particle interaction with residual water molecules.

5.9.1.1 Neutron radiolysis is a major contributor to ionizing radiation during reactor operation but diminishes rapidly after fuel removal from the active core, and is insignificant by the end of the pool storage term. 5.9.1.2 Gamma interactions with water and hydroxyl groups that are external and internal to the fuel may be an issue for both the fuel itself and other hydrated compounds within the radiation field (inside the cask). Gamma radiolysis of hydrated uranium oxides will occur in fields of 100 000 R/h or greater. Such radiolysis has resulted in H₂ pressure increases of up to 10 psi in an enclosed system (11, 12). Gamma activity in SNF decreases relatively rapidly as a function of time; thus, the potential for gamma effects on storage will decrease during the fuel storage term, and should become inconsequential after about 15 years.⁶

5.9.1.3 Beta radiolysis of water occurs only in close proximity to the fuel surfaces and when the beta decay takes place very near hydrated species. Therefore, in the case where corrosion products are uniformly distributed in sludges or sludges are in contact with fuel surfaces, the contribution by the beta emitting isotopes to water radiolysis could be significant.

5.9.1.4 Alpha particles have a low linear-energy-transfer rate but alpha emitters are long lived and represent the longest term issue for water radiolysis. Alpha radiolysis occurs only when the alpha emitter is in direct contact with the hydrated species. Therefore, alpha radiolysis is generally limited to hydrated fuel compounds or fuel-bearing sludges within the container. The actual rates for alpha radiolysis are not well defined and additional work is needed to clarify the potential for an alpha related issue (13).

5.9.2 *Hydrogen—Fuel, Cladding, and Packaging Reactions:*

5.9.2.1 Hydrogen is generated by the radiolytic decomposition of water and by most metal corrosion reactions. In order to ensure that a flammable environment cannot be present in the event of a container rupture accident, the hydrogen content in SNF containers is usually limited to below 4 %, the lower flammability limit (14). The hydrogen generation can be predicted with reasonable accuracy by performing a material and energy balance based on the temperature, radiation levels, materials, and water contained in the package (15).

5.9.2.2 Hydrogen may be a problem for SNF container materials over long storage times. Hydrogen tends to collect in steels at locations of high stress and surface discontinuity and may embrittle certain steels, especially high strength ferritic and martensitic steels. Hydrogen may also be absorbed into Zircaloy cladding making it more susceptible to fracture. The effects of hydrogen are fairly well predictable and numerous ASTM test methods are available for evaluating hydrogen effects in materials (16). In general, these effects increase with increases in the hydrogen content and/or strength of a metal or alloy. Hydrogen content increases with increasing hydrogen fugacity

⁶ Considerable work is currently in progress to quantify the effects of radiolysis in both the Pu and U oxyhydroxide systems.

which is generally greater at a surface during corrosion by aqueous environments than during exposure in gaseous atmospheres (17). Hydrogen entry into fuel or container materials may also be driven by galvanically induced corrosion of the anode in coupled dissimilar metals if an electrolyte is present. High pressure hydrogen effects data, in general, should not be used to predict the impact of hydrogen on SNF storage containers.⁷ Austenitic stainless steels and low strength ferritic and ferritic-pearlitic steels are relatively insensitive to low pressure hydrogen exposures.

5.9.2.3 The hydrogen lower flammability threshold may be reached within a sealed container before pressure and corrosion could become significant. Assuming that free and physisorbed water is removed with vacuum drying, the issue of adequate dryness relates directly to the hydrogen mass balance:

- (1) The potential mass of hydrogen in the chemisorbed water within the system,
- (2) The potential for thermal or radiolytic decomposition of the compounds holding the water, hydrogen, or both,
- (3) The rate of hydrogen generation by corrosion from the water released within the container, (4) The hydrogen diffusion, venting, corrosion, gettering, and recombination rates for the gas interacting with the system,
- (5) Net void volume within the container,
- (6) The rate of hydrogen reaction with metals such as zirconium based alloys, and
- (7) Mass of metal that may absorb hydrogen.

5.9.2.4 Hydrogen getters have been used in some SNF storage systems. Hydrogen gettering may be effective if the radiation levels are low enough that the hydrogen is not radiolyzed from the getter material. Successful performance of getter materials may require high temperature to increase the tendency for hydrogen-getter interactions.

5.9.3 *Water Corrosion Reactions:*

5.9.3.1 The expected quantities of residual water after drying are typically small relative to the substantial mass of typical dry storage containers, water corrosion damage to the structural materials should not be a significant factor in establishing adequate dryness. However, the corrosion induced production of hydrogen could increase the effect of pressurization and initiate other hydrogen effects. Potential exceptions to the anticipated lack of corrosion damage include:

- (1) Small containers of badly damaged fuel materials previously exposed to water,
- (2) Fuels that may contain large quantities of water that cannot be removed with drying processes,
- (3) Reactive cladding fuels with high surface area, especially those with fuel damage,
- (4) Fuels that would be expected to release reactive fission products at a temperature sufficient to allow corrosion cracking of container welds, and
- (5) Fuels contaminated with significant chlorides.

5.9.4 *Fission Product Reactions:*

5.9.4.1 Release of some fission products from fuel during storage could, by reacting with residual water, increase the corrosive nature of the storage environment. Cs, Rb, and I are the fission products of primary concern with regard to corrosion. Krypton and Xenon release may add to internal container pressures and transmutation of Kr to Rb isotopes may help spread Rb throughout the container. Cesium and rubidium may react with residual water to form caustic hydroxides that could lead to caustic cracking of stainless steel weldments at elevated dry storage temperatures (>110°C). Iodine would be expected to behave similar to chlorine in attacking stainless steel packaging components if sufficient residual tensile stress and ion concentrations are developed. None of these fission product interactions are anticipated to present major problems but should not be dismissed as the conditions for adequate dryness are established

5.9.5 *Galvanic Coupling with Aluminum Clad Fuel:*

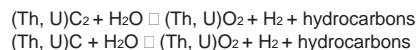
5.9.5.1 Internal water corrosion is a primary concern for the storage of aluminum-clad SNF under environmental conditions where residual water may be present. This concern comes from the large quantities of stainless steel that are typically present in approved storage containers. Galvanic coupling between the stainless steel and aluminum will occur if the steel and aluminum alloys are in electrical contact and sufficient electrolyte is present. Galvanic coupling will result in accelerated corrosion of the aluminum cladding components, potentially jeopardizing SNF retrievability. This concern is primarily important with relatively cold fuel in vented storage systems where water ingress is possible.

5.9.6 *Carbide Fuel—Water Reactions:*

⁷ Unpublished SRS data on testing of austenitic stainless steel tritium shipping containers used intermittently for 15 years to hold tritium at 1 psig indicated that tritium did diffuse into the steel structure, but to a depth less than required to cause fracture unless the material was highly stressed.

5.9.6.1 Carbide fuels, which represent only a small fraction to the SNF inventory, are irradiated in a gas atmosphere and are normally not stored in water. However, many carbide fuels have come into contact with water due to reactor or storage incidents. The majority of the DOE graphite fuels are dispersion fuels, in which coated uranium carbide, thorium carbide spheres, or both, are held in a carbonaceous matrix. The coating or cladding material is often SiC. The fuel particles are dispersed in porous compacts of pyrocarbon and typically encapsulated in a graphite sheath or block. If the SiC cladding is penetrated, the reaction of the fuel with moisture may be quite rapid.

5.9.6.2 The intrinsic rate of hydrolysis of ThC₂ and UC₂ in moisture proceeds at a penetration rate as fast as 24 μm/day. Bulk samples of ThC₂ powder hydrolyzed completely in ambient laboratory air within 12 hours (18). Uranium and thorium carbides react with water or water vapor to form hydrogen and low molecular weight hydrocarbons:



5.9.6.3 The low molecular weight hydrocarbons consist primarily of methane (CH₄), ethylene (C₂H₄), and ethane (C₂H₆), with minor amounts of acetylene (C₂H₂) and the C₃H_x to C₆H_x alkanes, alkenes, and alkynes (1, 19-24). The reported product distributions vary substantially, and reflect the effects of impurities in the carbides and variations in analysis techniques. In any event, careful consideration should be given to the flammability of the hydrocarbons if damage to the SiC cladding on the carbide spheres is established or anticipated.

5.9.6.4 The reaction of graphite or pyrocarbon with water to produce hydrogen, CO, and CO₂ is extremely slow at temperatures below 200°C, so that the reaction is considered to be of no consequence at temperatures anticipated for dry storage (25-27).

5.9.6.5 Silicon carbide reacts with water vapor to form silica (SiO₂), carbon dioxide, carbon monoxide, and hydrogen at temperatures above 600°C, and silica, methane, hydrogen, carbon dioxide, and carbon monoxide below 600°C (28, 29). However, the rate of reaction is extremely slow at temperatures below 500°C (15) and is therefore not considered to be important in evaluating dry storage of carbide fuels.

5.9.7 *Water-Oxide (Fuel) Reactions and Consequences:*

5.9.7.1 Cladding damage may lead to water ingress into the fuel rods and to subsequent water retention if drying operations do not fully remove the moisture. Residual water may oxidize the fuel pins toward a low density UO₃ hydrate and may subsequently rupture or “unzip” the fuel cladding (see Annex A1 for fuel oxide reaction data). The cladding rupture is a direct result of the volume expansion from hydrated compound formation. The hydrated compound, UO₃·2H₂O, for example has a volume 2.6 times that of the starting UO₂. Evaluations of the reaction process indicate that UO₂ begins to form hydrated phases within six weeks if exposed to moisture at fuel storage temperatures (30). Additionally, sintered UO₂ forms metaschoepite when reacted with deionized water. The formation of low-density hydrated compounds and cladding rupture sequence may continue in damaged rods containing residual moisture. Such reactions may impact the handling and transport of SNF that becomes severely damaged during extended dry storage.

5.9.8 *Gas Pressurization:*

5.9.8.1 Pressure inside the storage container is increased both by reactions that form gas as a reaction product or by failure of a clad to release gas from the spent fuel. However, reaction of these gases with constituents found inside the storage container will decrease the build-up of the pressure. At an equilibrium state, the internal pressure of the storage container will be determined by the gas generation and reaction processes. Quantitative estimates of the pressure will need to consider the following variables:

- (1) Dead volume of the enclosed container,
- (2) Quantity of free, physisorbed and chemisorbed water,
- (3) Location of the water relative to high radiation fields,
- (4) Inventory of gaseous radioactive decay products,
- (5) Radiogenic gas formation rates,
- (6) Inventory and available surface area of solid decay products,
- (7) Inventory of dust, CRUD, and sludge,
- (8) Temperature profile as a function of time,
- (9) Initial backpressure and composition of the inert gas backfill,
- (10) Container and basket materials corrosion rates, and
- (11) The number of damaged fuel rods and the fission product content of the rods .

5.9.8.2 The inability to accurately determine pressure and an exact hydrogen concentration within a sealed system affects the specific design criteria for the container. To circumvent this issue, regulators and designers typically use “worst case” scenarios for container pressurization which assume that only reactions that may increase pressure are occurring. Such calculations yield values of up to 0.35 MPa (50.8 psi) internal pressurization of a commercial fuel container from hydrated uranium oxides heated to 250°C by decay heat after sealing. See example calculation in [Appendix X1](#).

5.9.8.3 The significance of pressure increases on the storage system due to water will depend on the design of the system, the presence of pressure relief devices, and the regulatory limits imposed on the system.

5.9.9 *Nuclear Criticality:*

5.9.9.1 The criticality effects of trapped water and potential fuel displacement/geometric rearrangement of fuel assemblies loaded into large casks for drying and storage need to be considered. The removal of water from casks also results in removal of soluble neutron absorbers (boron) with the water. The potential for unusual fuel configurations and the moderating potential of water trapped in the fuel must be taken into consideration for fuel movement safety analyses. The effective multiplication factor (k_{eff}) of the storage system depends on the mass distribution of neutron absorbers, moderators and fissionable materials. The operation and handling of the fissile materials should be governed by the [ANSI/ANS standards 8.1](#) and 8.7-1998.

6. Drying Spent Nuclear Fuel

6.1 *Drying Process Parameter Determination*—Drying temperatures, vacuum level, time, and the number of backfill/re-evacuation cycles will depend on the condition and radiation level of the SNF and the expected amount and type (unbound, chemisorbed, trapped, etc.) of water that needs to be removed. The kinetics of drying will depend on the physical (geometric) configuration of the storage and drying system, the chemical composition of the phases (such as $\text{UO}_2(\text{OH})_2$, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, etc.) present in the system, the temperature of the system, the ambient conditions, the capacity of the drying system and the specific convection/ diffusion restrictions imposed by the system and materials.

6.1.1 *Removal of Unbound Water:*

6.1.1.1 Unbound water removal is primarily limited by the geometry of the system and the physical location of the water in the system. The operating speed of the water removal system is a major factor in drying an SNF container. For example, if vacuum drying technologies are used, the conductance path between the vacuum source and the water source will control water removal efficiency. Tests have demonstrated that fuel with pinholes in the cladding can be dried in a well-controlled system even after water has penetrated into the fuel rod (31). However, in these particular tests, two drying steps with a thermal homogenization by He-backfilling were needed just to fully remove the unbound water in the rod.

6.1.2 *Prevention of Ice Formation:*

6.1.2.1 The decay heat of commercial SNF is generally inadequate to prevent ice formation during vacuum drying.

Staged increases in the vacuum level and hold cycles with or without helium backfill are typically used in commercial drying processes to prevent ice formation. Research reactor fuels and commercial fuels that are damaged or have been in extended wet storage may require external application of heat during the drying process or specialized vacuum-backfill-vacuum cycles or operation at pressures well above the triple point to prevent ice formation while effectively removing water.

6.1.3 *Removing Physisorbed Water:*

6.1.3.1 Removal of physisorbed water depends on the relative humidity in the system which relates directly to the number of superficial water layers that can be desorbed. For small mass, thin layered materials, and “wet” materials of a small particle size, first order desorption kinetics generally apply. Dry air at 50°C should desorb the superficial physisorbed water layers in 10 to 30 hours. Less time is required with a vacuum at 20°C. Surface water physisorbed onto wetted UO_2 powder has been shown to desorb starting about 150°C with the reaction essentially complete at 230°C (32).

6.1.3.2 For large mass, thick beds, and convoluted vacuum paths, complex “falling rate” kinetics (33) are required to calculate appropriate drying conditions. In falling rate kinetics, the liquid is assumed to be uniformly distributed in the solid material being dried. The convection and diffusion restrictions resulting from pores in the solid and isolated cavities within the package cause the drying rate to fall exponentially once the unbound water has been removed. INEEL studies (34) have shown that the falling rate kinetics approach accurately represents the drying behavior of badly damaged spent fuel and may even allow a method to accurately predict dryness.

6.1.4 *Removal of Chemisorbed Water:*

6.1.4.1 Removal of chemisorbed water depends on the specific chemical species present in the dry storage container and purity of species involved. The water removal temperatures for some compounds expected to be present in SNF packages (35) are discussed in Annex A1. However, the actual temperatures required for water removal may be lower than those listed in ANNEX A1 due to the energy input from ionizing radiation.

6.1.4.2 Because of practical limits to the drying temperature, some chemisorbed water may be present inside a dried SNF container. This chemisorbed water may be released to the container environment when the combination of thermal energy and ionizing radiation cause decomposition of the moisture containing compound. If a drying temperature higher than the storage temperature can be used, the release of such water through thermal decomposition may be avoided. Release of water from the chemical compounds may occur regardless of the drying temperature, but the rate would depend on SNF storage temperature and dehydration kinetics and/or on the rate of radiolytic decomposition reactions involved. The latter can generate other radiolytic products that include hydrogen.

6.2 Drying Processes Parameters:

6.2.1 The basic parameters in vacuum drying are time, temperature, vacuum level and the conductance of the water removal pathway. In commercial vacuum drying processes (see Annex A2), temperature is generally not a controlled variable and fuel decay heat determines the drying temperature. The temperature of the SNF will generally rise during vacuum drying because of the lack of cooling and care must be taken to keep temperatures below some maximum level. Commercial processes typically have minimal flexibility, but the following operational adjustments may be made to improve drying results:

- (1) Removal of unbound water by slightly tilting the cask toward the drain tube.
- (2) Use of a vacuum lance to suck unbound water from the bottom of the cask.
- (3) Repetition of the vacuum drying cycle with inert gas backfill cycles between vacuum drying for effective thermal equilibration.

- (4) Hot air or nitrogen purge of the cask (used especially on fuels with low decay heat).

6.2.2 Research and material production reactor fuel drying processes (see Annex A2) generally require external heat input. However, the fuel or cladding material, fuel damage during irradiation and prior storage, and chemical reactivity may make these drying processes much more restrictive than those used for commercial fuels.

6.2.3 Commercial spent fuel has also been effectively dried using the Forced Helium Dehydration (FHD) system such the HOLTEC process (36). This proprietary process which removes water from the fuel and container by circulating dry helium through the container and over the SNF, requires a pressure relief valve to limit the canister pressure and temperature control to prohibit water boiling inside the canister.

7. Confirmation of Adequate Dryness

7.1 Establishing the Requirements for Drying:

7.1.1 Interim dry storage of commercial SNF per 10 CFR 72 requires that the drying criteria should eliminate enough water to preclude “gross” damage to commercial fuel cladding during storage.

7.1.2 DOE dry storage canisters are expected to contain the SNF through interim storage, transport, and repository packaging. The objectives of drying processes used on this fuel are remove sufficient water to preclude:

- 7.1.2.1 Geometric reconfiguration of the packaged fuel,

- 7.1.2.2 Damage to the canister from overpressurization or corrosion, and

- 7.1.2.3 Hydrogen induced damage and/or materials corrosion that could present problems during transport or repository handling operations.

7.2 Confirming Dryness:

7.2.1 Evaluating Adequate Dryness:

7.2.1.1 A container can be considered adequately dried when the overall dried condition of the package (including fuel, sludge, CRUD, baskets, containment, etc.) meets all the transportation and/or storage requirements. An evaluation of dryness must first summarize the starting system water inventory, and then determine if sufficient water was removed by the drying process to ensure that the requirements will be met or exceeded (see Fig. 1).

7.2.1.2 The free and most physisorbed water should be removed using a standard drying process (see Annex A2 for examples). For vacuum drying processes, adequate water removal is normally evaluated using vacuum pressure rebound measurements that can be correlated to the total unbound water inventory within a sealed container with some qualifying assumptions about ice formation, sludge, and fuel damage. The quantity of residual water indicated by the pressure rebound would need to be accepted as being less than that which would cause unacceptable pressurization, container corrosion, or fuel degradation. An example of a pressure rebound assessment is to reduce the container pressure to < 3.0mm Hg and demonstrate that this vacuum is maintained throughout a 30 minute

isolation period. Moisture removal using a forced gas drying process is confirmed by monitoring the moisture content in the outlet gas.

7.2.1.3 Chemisorbed water may still be present after a standard drying process, especially for SNF in Conditions 3 through 6. The effects of having this residual water in the system must be determined with enough accuracy to show that the residual chemisorbed moisture content will not exceed the system requirements. Such determinations involve estimation of:

- (1) Amount and location of the potentially hydrated compounds that may contain chemisorbed water. This estimation relates directly to SNF, fuel damage, corrosion products and sludge carried into the package,
- (2) Temperature history of the container during drying, starting when the container was sealed and continuing through normal and allowable off-normal operating conditions,
- (3) Quantity of chemisorbed water that remains in the hydrated compounds after the thermal excursions during drying,
- (4) Rates for thermal and radiolytic decomposition of the hydrated compounds,
- (5) Rates for reaction/recombination of radiolyzed species by other materials within the container (if allowed by the regulator),
- (6) Equilibrium water vapor pressure over the fuel as function of temperature, and
- (7) Reaction of the water with the fuel, cask components to generate hydrogen and/or pressurize the container.

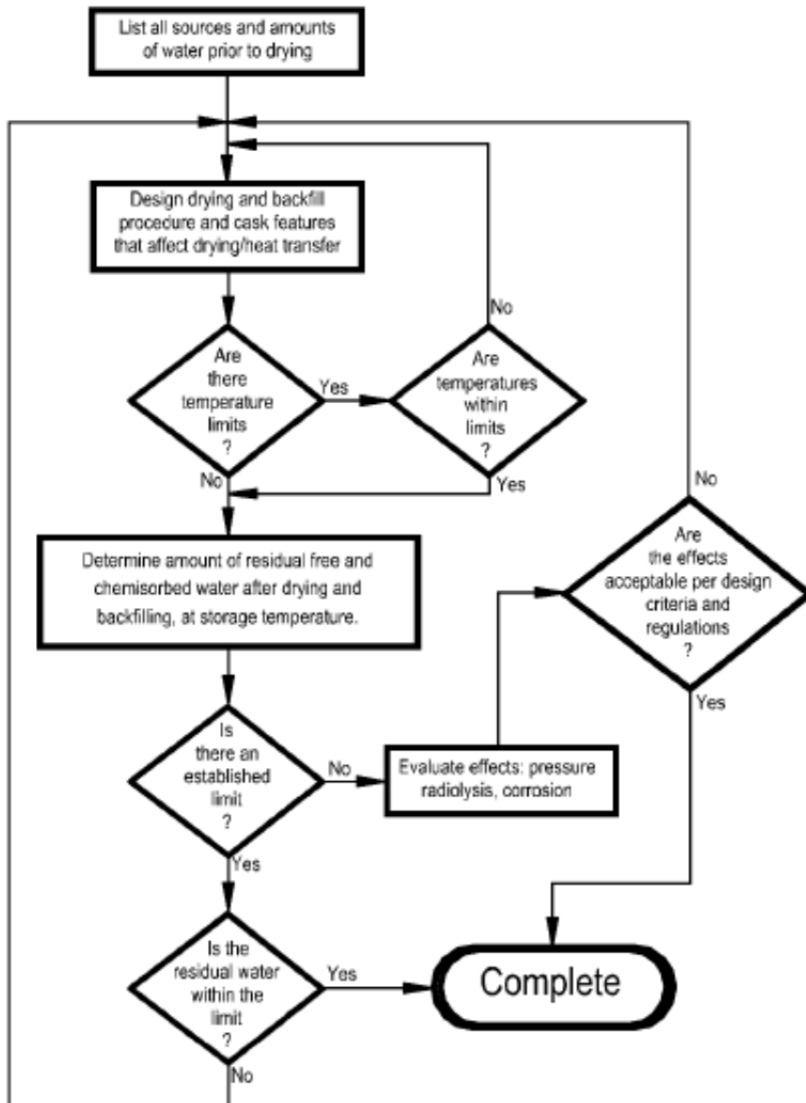


FIG. 1 Flowchart for Evaluation of Spent Fuel Drying Procedures

7.2.1.4 For heated vacuum drying processes where water removal rate can be measured as a function of time, the use of a falling rate kinetics analysis (37) may allow an analytical determination of how much physisorbed and loosely bound water remains in an enclosed container. This approach uses the rate of change of water vapor removal during drying to calculate the total remaining water that can be removed at the drying temperature.

7.2.2 Measurement:

7.2.2.1 Pressure Measurement:

(1) *Pressure Rebound Test*—A pressure rebound check performed in connection with the drying process is one method currently being used to show compliance to dryness requirements. Such pressure rebound measurements consist of showing that an evacuated cask loaded with SNF will retain vacuum for a specified period without a pressure rise greater than a specified limit. For a commercial SNF the requirement of maintaining a 4.10⁻⁴ MPa (3 Torr) pressure for 30 minutes has been used to suggest that less than one mole of residual gas is inside the cask (38). However, container size, decay heat, potential for ice formation, the potential substantial quantities of chemisorbed water associated with damaged SNF should be considered in specifying test pressure, hold time, pressure rise, and repetition (see A2.1 and A2.2).

(2) *Pressure Testing/Monitoring During Storage*—SNF container/cask pressurization data, if determined over the storage term, may be useful in verifying that the initial drying process was adequate and that any residual water within the system was insufficient to cause "gross" damage of commercial SNF, reconfiguration of DOE SNF or corrosion and/or pressurization of the container.

(3) *Water Vapor Pressure Measurement*—Solid state devices, absolute humidity gauges/sensors mounted in-line at the cask exhaust during drying can provide data on how much water remains after the drying process.

7.2.2.2 *Internal H₂ Concentration*—If the internal gas composition of the canister/cask can be obtained, analysis for hydrogen concentration may be used as an indicator of the water that was present and released as a result of radiolysis and/or corrosion within the container.

7.2.3 Process Knowledge:

7.2.3.1 The process knowledge may be used to demonstrate that the SNF, the drying, and the storage history were such that a problematic quantity of water could not have been present within the canister or cask. Generally this is an unacceptable method for confirming dryness, but may be useful as supporting evidence. The process knowledge approach requires very good records of the history of the fuel irradiation, drying, and storage. Process knowledge arguments may be relatively simple for pristine commercial SNF with complete records but may be impractical for many DOE fuels and commercial fuels in conditions 3 through 6. A process knowledge approach for damaged commercial fuels and most DOE fuels may require estimates or bounding values for the potential quantity of residual water which may require knowledge of the extent of SNF corrosion and the prior and expected temperature profiles of the fuel.

ANNEXES
A1. COMPOUNDS CONTAINING CHEMISORBED WATER
INTRODUCTION

Chemisorbed water includes the water of hydration, metal hydroxyls, and metal oxyhydroxides distributed either on the surface or throughout the SNF or materials associated with the SNF. These water containing compounds may form from water corrosion of fuel components (cladding or fuel matrix), fuel support structures, or fuel containment systems, or from hydrolysis or hydration of metal oxides associated with the fuel components, containment, or storage basin environment (that is, sludge).

The specific characteristics of hydrated compounds are typically complex and may vary as a function of the chemistry and temperature of environment at the time of their formation. Both amorphous and crystalline forms of the compounds may be present, and the crystalline forms may exist as more than one polymorph depending on formation history. The short term hydrated reaction products formed in a reactor or in a water basin may also differ chemically and crystallographically from the same general compound formed as a mineral over geologic time. In this regard, some compounds found routinely in nuclear fuel systems are typically not present in nature and are thought to be metastable forms that will require decades or centuries to revert to their natural mineralogical form. This annex provides a broad review of the hydrated compounds specifically identified as corrosion products in nuclear systems. However, the data presented are based on the limited sampling and testing documented in the literature. Whenever a mineralogical form of a compound identified by reactor sampling may have a significantly different water contents than the identified form, that fact is noted, because the environmental history of some fuels could have resulted in formation of the mineralogical form of the compound.

A1.1 Hydrates of Uranium Oxides
A1.1.1 Uranium Trioxide Hydrates:

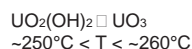
A1.1.1.1 The structural formula for the mineral, schoepite is $(\text{UO}_2)_6\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$ (39). The formation of UO_3 -based hydrates in systems related to SNF has been documented by a number of authors (40-45). Review of these reports identified three forms of UO_3 -based hydrates: $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O}$, and $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$. Table A1.1 lists some of the characteristics of these hydrates.

A1.1.1.2 The mineral phase, paraschoepite, with a corresponding composition of $\text{UO}_2.86 \cdot 1.5\text{H}_2\text{O}$ was identified on the surface of metallic uranium fuel elements from N-Reactor (46). The paraschoepite is a modified form of schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) although it may be an inadequately described mineral that is not a valid mineralogical species (47). Other modified forms of the uranium containing hydrates that have different dehydrating kinetics may also exist. Wheeler et. al. (40) acknowledged the possibility of modified forms of the schoepite while Hoekstra and Siegel (41) suggest two forms of the dihydrate and four forms of the monohydrate (a-, b-, g- $\text{UO}_3 \cdot \text{H}_2\text{O}$, and a- $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$).

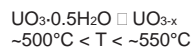
A1.1.1.3 The thermal decomposition of these uranium containing hydrates have been studied in detail (48, 49) and reviewed by Hoekstra and Siegel (50). Thermogravimetric and Differential Thermal Analysis (DTA) experiments showed the following reactions:



(1) The decomposition of $\text{UO}_2(\text{OH})_2$ then follows at higher temperatures:



(2) $\text{UO}_2(\text{OH})_2$ can also decompose to $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$. The decomposition reaction of $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$ is represented as:


A1.1.2 Uranium Peroxide Hydrates:

A1.1.2.1 The UO_4 -based hydrates (uranium peroxide hydrates)

have been prepared in the laboratory from solutions of uranyl nitrate and hydrogen peroxide. Two different crystalline forms of the hydrates were developed:

UO₃·4H₂O at temperatures below 50°C, and
UO₃·2H₂O above 70°C

A1.1.2.2 The natural analogue of the UO₄-based hydrates is the studtite which can be prepared by the reaction of uranium dioxide with hydrogen peroxide. Thermal decomposition reactions for these hydrates have been studied by many researchers (51-54). The early decomposition data indicated initial dehydration between 60 to 100°C and final decomposition at 420 to 550°C. Experimental work conducted to determine the thermal decomposition behavior of the tetrahydrate taken from surfaces of spent nuclear fuel stored at the Hanford site K-Basins water pool (55) shows the tetrahydrate decomposition occurs between 50 and 100°C with a loss of two molecules of water and confirms the observations of the earlier investigators. However, the decomposition of the dihydrate products from K-Basin starts at a temperature of 100°C and a complete removal of waters of hydration occurred at about 400°C. The weight loss that was observed at temperatures above 420°C was attributed to reduction of the UO₃ product to a lower oxidation state, U₃O₈. More recent thermal decomposition data (56) indicates the following thermal decomposition sequence for studtite:

UO₃·4H₂O □ UO₃·2H₂O □ UO₃·nH₂O □ UO₃ (amorphous)
□ αUO₃ (UO_{2.89}) □ UO_{2.67}

where 3.0 # x # 3.5 and 0 # n # 0.5

A1.1.2.3 For this thermal decomposition sequence, initial decomposition occurred at 100°C and was completed between 100 and 300°C.

A1.2 Hydrated Corrosion Products

A1.2.1 Corrosion of the fuel cladding, structural support materials and storage racks can generate surface films and sludge that contains hydrated compounds and contributes to the bound water inventory in storage containers. Such hydrated forms may include hydroxides of: (a) zirconium, (b) iron, and (c) aluminum.

A1.2.2 Aluminum Hydroxides:

A1.2.2.1 A number of aluminum hydroxide compounds are listed in Table A1.2.

A1.2.2.2 Several studies have been performed for the thermal decomposition of the aluminum trihydroxides and the oxide hydroxide. The general decomposition sequence is illustrated in Fig. A1.1 and shows a decomposition temperature range between 100°C and 600°C.

A1.2.2.3 The amount of chemisorbed water in boehmite on the average ATR spent fuel plates (55) is approximately 1.7 L, based on a conservative 0.0034 cm film thickness

TABLE A1.1 Hydrates of U-oxides

Compound	Volume Relative to UO ₃	Structure	Formation Conditions
UO ₃ ·2H ₂ O Dihydrate	2.62	Orthorhombic; consists of pseudo hexagonal sheets of [UO ₂ (OH) ₂] _n held together by hydrogen bonded H ₂ O	Exposure of anhydrous UO ₃ to water at 25 to 75°C
UO ₃ ·0.8H ₂ O Hypostoichiometric Monohydrate	1.85	Hypostoichiometric form of α-UO ₃ ·H ₂ O	Heating UO ₃ ·2H ₂ O in air at 100°C or UO ₃ in water at 80 to 300°C
UO ₃ (OH) ₂ or UO ₃ ·H ₂ O Monohydrate	1.84	Orthorhombic, consists of pseudo hexagonal sheets of UO ₂ (OH) ₂	
UO ₃ ·0.5H ₂ O Hemi-hydrate	1.73	Triclinic	Hydrothermally at 300 to 400°C

TABLE A1.2 Aluminum Hydroxides

Mineral Name	Chemical Composition	Crystallographic Designation	Crystal Structure
Gibbsite	Aluminum Trihydroxide	α -Al(OH) ₃	Monoclinic
Bayerite	Aluminum Trihydroxide	γ -Al(OH) ₃	Monoclinic
Nordstrandite	Aluminum Trihydroxide	Al(OH) ₃	Triclinic
Doyleite	Aluminum Trihydroxide	Al(OH) ₃	Triclinic
Boehmite	Aluminum Oxide Hydroxide	γ -AlO(OH)	Orthorhombic
Diaspore	Aluminum Oxide Hydroxide	α -AlO(OH)	Orthorhombic
Tohdite	Aluminum Oxide Hydroxide	5Al ₂ O ₃ ·H ₂ O	Hexagonal

TABLE A1.3 Iron Hydroxides

Mineral Name	Chemical Compound	Crystallographic Designation	Crystal Structure
Goethite	Iron(III) Hydroxide	α -FeOOH	Orthorhombic
Lepidocrocite	Iron Hydroxide	γ -FeOOH	Orthorhombic
Ferrihydrite	Amorphous Ferric Hydroxide	Fe ₂ HO ₈ ·4H ₂ O	Hexagonal
Hydro-haematite	Iron(II) Hydroxide	Fe(OH) ₂	
	Iron(III) Hydroxide	Fe(OH) ₃	

A1.2.3 Zirconium Hydroxides:

A1.2.3.1 Hydrolysis of zirconium oxides may generate hydroxides of Zr, including: (a) ZrO₂·xH₂O, (b) Zr(OH)₄, and (c) ZrO(OH)₂. The ZrO(OH)₂ is known to decompose at about 120°C to form ZrO₂.

A1.2.4 Iron Hydroxides:

A1.2.4.1 The hydroxides of iron that will contribute to bound water are Fe(OH)₃, Fe₅HO₈·4H₂O and FeOOH. These iron based corrosion products are listed in **Table A1.3**.

A1.2.4.2 Goethite, the most common form of iron oxyhydroxide, may exist in a synthetic or mineral form. These two forms of Goethite decompose differently with Type A, the synthetic form, decomposing over two different temperature ranges while Type B, the mineral form, decomposes at a single temperature. The decomposition reaction is:

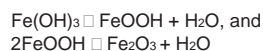


A1.2.4.3 Bakker et al. (56) have studied decomposition of the iron hydroxide Lepidocrocite and concluded from spectroscopic and magnetic studies that a molecular level pre-reactional dehydroxylation begins at a temperature between 150 and 170°C and that the overall conversion of ζ -FeOOH to ζ -Fe₂O₃ starts at about 200°C.

A1.2.4.4 The decomposition of the ferrihydrite (57) starts at 400°C and is not completed until the temperature reaches of about 475°C. The decomposition reaction is:



A1.2.4.5 Naturally occurring hydrohaematite usually contain 5.4 to 8 % H₂O (58) and shows characteristic dehydration with a rising temperature over the range of about 129 to 150°C. The weight loss is observed until a temperature of 877°C with a inflection at 447°C. The decomposition reactions are:



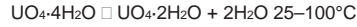
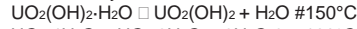
A1.3 Summary

A1.3.1 The literature data shows that thermal treatments may be possible for the removal of water from most hydrated species associated with oxides and hydroxides. The kinetics of decomposition are 1) dependent on the heating rate, maximum temperature and the drying atmosphere for the fuel and 2) determiners of the quantity of the

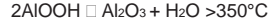
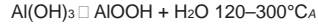
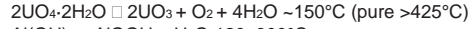
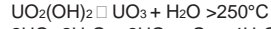
hydrated water that may remain in the container. The following are the thermal decomposition temperatures for various hydrated species:

Compound/Reaction Drying Temperature

Waters of Hydration:



Metal Hydroxyls:



A Metastable forms of this reaction product may begin to form at temperatures as low as 80°C .

A1.3.2 For hydrated compounds with a decomposition temperature of 250°C or below, kinetics indicates that about 85 % of the decomposition will occur in about one hour at temperature.

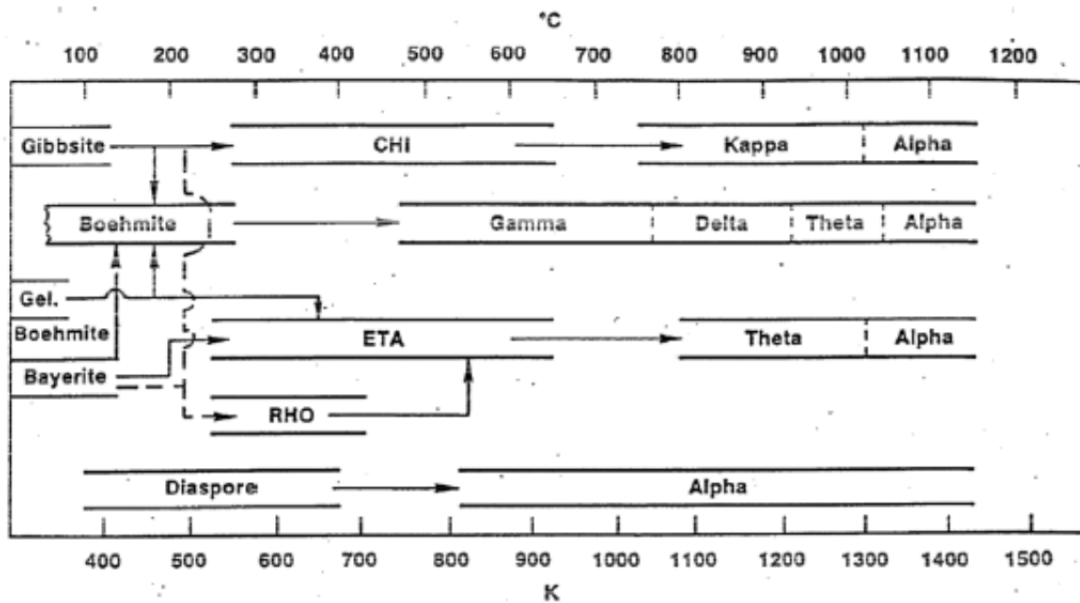


TABLE A1.2 Aluminum Hydroxides

Mineral	Chemical	Crystallographic	Crystal
Name	Composition	Designation	Structure
Gibbsite	Aluminum Trihydroxide	$\alpha\text{-Al}(\text{OH})_3$	Monoclinic
Bayerite	Aluminum Trihydroxide	$\gamma\text{-Al}(\text{OH})_3$	Monoclinic
Nordstrandite	Aluminum Trihydroxide	$\text{Al}(\text{OH})_3$	Triclinic
Doyleite	Aluminum Trihydroxide	$\text{Al}(\text{OH})_3$	Triclinic

Mineral	Chemical	Crystallographic	Crystal
Name	Composition	Designation	Structure
Boehmite	Aluminum Oxide Hydroxide	γ -AlO(OH)	Orthorhombic
Diaspore	Aluminum Oxide Hydroxide	α -AlO(OH)	Orthorhombic
Tohdite	Aluminum Oxide Hydroxide	$5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Hexagonal

TABLE A1.3 Iron Hydroxides

Mineral	Chemical	Crystallographic	Crystal
Name	Compound	Designation	Structure
Goethite	Iron(III) Hydroxide	α -FeOOH	Orthorhombic
Lepidocrocite	Iron Hydroxide	γ -FeOOH	Orthorhombic
Ferrihydrite	Amorphous Ferric Hydroxide	$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$	Hexagonal
	Iron(II) Hydroxide	$\text{Fe}(\text{OH})_2$	
Hydro-haematite	Iron(III) Hydroxide	$\text{Fe}(\text{OH})_3$	

FIG. A1.1 Transformation Sequence $\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3$

A2. DRYING PROCESSES

Drying technologies have been developed to preserve the integrity of SNF and fuel storage systems while the nuclear industry and the US DOE await government decisions concerning used fuel disposition. Documentation of the drying technologies is extensive and includes an annotated bibliography for drying nuclear fuel (59). Numerous helpful resources are listed in that bibliography and reference to those resources is recommended as technologies and practices for drying SNF are being developed and refined.

A2.1 Typical Commercial Fuel Vacuum Drying Process

A2.1.1 The following sequence summarizes the processes in use for drying commercial SNF for cask storage:

- (1) Load container with commercial SNF in the water basin.
- (2) Install the lid.
- (3) Remove container from basin. Water may or may not be drained before lifting the container out of the pool.
- (4) Complete draining of water; most commercial containers do not have bottom drains, so they are drained by pumping or pressurizing with a gas.
- (5) Some systems are designed such that a long tube may be inserted to the bottom of the container after pumping or blowdown, and the residual free water at the container bottom may be sucked out.
- (6) External heating or the flow of heated gas through the container may be used for some systems, especially if the loaded fuel has low decay heat.
- (7) Attach vacuum system to the container port. This may be through a quick disconnect fitting, although the quick disconnects are sometimes removed to improve the conductance of the vacuum system.
- (8) Reduce container internal pressure to less than 3 Torr.

(a) To minimize freezing, some processes call for pressure reduction in stages and holding pressure for some time during each stage before reducing the pressure to less than 3 Torr.

(9) Close vacuum system valves and verify that vacuum remains stable.

(a) The minimum requirement (NUREG-1536, Chapter 9) is 30-minute hold time “maintaining a constant pressure” (<3 Torr) to verify adequate water removal.

(b) Stricter requirements may be specified for some systems or some fuel conditions.

(10) If an unacceptable pressure rise occurs, open vacuum valves and continue pumping.

(11) Once a stable vacuum is achieved, close the vacuum system valves and backfill the container with helium to the positive pressure specified for the system.

(12) Some systems require a second evacuation before backfilling with helium to the final system pressure. This second evacuation may be to a different vacuum level than that prescribed for the first evacuation and verification.

(13) Close the vent and drain ports, remove all lines, and seal the ports.

NOTE A2.1—The duration of vacuum cycles may be limited because helium backfill gas is required to conduct heat from the SNF to the container walls and minimize the temperature rise in the SNF. Increased temperatures during the vacuum dry will certainly improve drying; however, there may be cladding and component temperature limits cannot be exceeded.

NOTE A2.2—Helium backfill between cycles may be allowed to hold for additional time before a second evacuation to allow more water to evolve. However, there are practical time limits for such operations. In unusual cases where there is reason to believe that water removal will be especially difficult, the evacuated helium may be analyzed for water content. However, such approaches increase operations time and worker radiation exposure and are not used routinely.

A2.2 DOE (N-Reactor) Fuel Drying Process

A2.2.1 The DOE Hanford Site has developed and used the following method for drying of Zircaloy and Al alloy clad, metallic uranium fuel elements for interim dry storage. The metallic uranium SNF is received at the drying facility in a sealed transportation cask. The SNF container (Multi-Canister Overpack (MCO)) within the cask is vented to the cask headspace, which was purged and filled with ~3 psig helium at the SNF storage basin after loading of the MCO was completed. The corroded fuel is pre-washed to remove most of the sludge prior to loading into the MCO.

A2.2.2 The major process steps at the drying facility are:

(1) The cask headspace is vented and purged with helium, after which the cask lid is removed.

(2) The vacuum drying system is connected to the process ports in the MCO shield plug and the tempered water system is connected to the cask.

(3) The tempered water system heats the cask and the MCO to ~45°C by circulating warm water through the annulus region between the MCO and the cask surrounding it.

(4) When the MCO temperature reaches 45°C the bulk water in the MCO is removed and transferred to a receiving and treatment system.

(5) Following removal of the bulk water, the MCO is purged with helium and the vacuum pump is started. A helium purge of ~1.5 scfm is maintained until pressure in the MCO drops to below 7.5 Torr, after which it is secured while the vacuum pump continues to run.

(6) Upon reaching a pressure below 0.5 Torr, the MCO is isolated and a pressure rebound test is performed. The MCO pressure must remain below 2.3 Torr for 1 hour or the drying cycle (step 5) is repeated.

(7) If the rebound test is satisfactory, the MCO is backfilled with helium to above atmospheric pressure.

(7) If the rebound test is unsatisfactory steps 5-7 are repeated.

(8) The cask/MCO is cooled using the tempered water at ~15°C.

(9) A final helium back-fill to a pressure of 11.25 psig is performed.

APPENDIX

X1. SAMPLE CALCULATION

X1.1 The following sample calculation provides an example of uranium oxyhydrate ($\text{UO}_3 \cdot \text{H}_2\text{O}$) corrosion product pressurization of a container assuming worst case conditions (no back reactions):

X1.1.1 One kg of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (322 g/mole) contains 3.106 moles U and 6.212 moles of water (weighing 111.82 g). For a 24-in. diameter fuel container with 500 L of “free” volume backfilled with 1 atm of helium, sealed and subsequently heated with decay heat to 250°C during storage. The pressure increase for release of the bound water can be calculated as:

$$P_1 V_1 = n_1 R T_1 \quad (\text{X1.1})$$

where:

$$P_1 = 1 \text{ atm (helium),}$$

$$V_1 = 500 \text{ L,}$$

$$R = 0.0821 \text{ atm} \cdot \text{liter/mol K, and}$$

$$T_1 = 298.15 \text{ K.}$$

X1.1.2 Solving for the He:

$$n_1 = (1 \text{ atm}) (500 \text{ L}) / (0.08206 \text{ atm L/mol K}) (298.15 \text{ K}) = 20.436 \text{ moles of He}$$

X1.1.3 Solving for final pressure (P_2 at 250°C) assuming the water is released as steam:

$$P_2/P_1 = n_2 T_2 / n_1 T_1 \text{ or } P_2 = (P_1) (n_2) (T_2) / (n_1) (T_1)$$

$$P_2 = (1 \text{ atm}) (20.436 \text{ moles He} + 6.212 \text{ moles H}_2\text{O}) (523.15 \text{ K}) / (20.436 \text{ moles He}) (298.15 \text{ K}) = 2.289 \text{ atm (33.639 psia or 231.4 kPa)}$$

X1.1.4 However, if the water is radiolytically decomposed to hydrogen and oxygen ($\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$) we have one mole of steam going to 1.5 moles of gas (Note: It is also possible to have $\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{H}_2\text{O}_2$) and the pressure is therefore increased proportionately to 3.434 atm (50.408 psia or 347.5 kPa).

X1.2 This calculation assumes full decomposition of the hydroxide and radiolysis of water molecules which is unrealistic but provides an upper bounding calculation. Similar calculations may be made for any specific container system using expected sources and quantities of bound water, and the free volumes associated with loading the specific SNF being packaged. More mechanistic calculations for pressurization will require new data on radiolysis rates on uranium compounds and recombination reactions.

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