



Standard Guide for Drying Behavior of Spent Nuclear Fuel¹

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1. Scope

1.1 This guide is organized to discuss the three major components of significance in the drying behavior of spent nuclear fuel: evaluating the need for drying, drying spent nuclear fuel, and confirmation of adequate dryness.

1.1.1 The guide addresses drying methods and their limitations in drying spent nuclear fuels that have been in storage at water pools. The guide discusses sources and forms of water that remain in SNF, its container, or both, after the drying process and discusses the importance and potential effects they may have on fuel integrity, and container materials. 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 issue in drying is to determine how dry the SNF must be in order to prevent issues with fuel retrievability, container pressurization, or container corrosion. Adequate dryness may be readily achieved for undamaged commercial fuel but may become a complex issue for any SNF where cladding damage has occurred during fuel irradiation, storage, or both, at the spent fuel pools. Dryness issues may also result from the presence of sludge, crud, and other hydrated compounds connected to the SNF that hold water and resist drying efforts.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

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)

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 as described as follows.

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

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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>.

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>.

reactor coolant. Compositions 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 retrievability from a (licensed) storage system or make it unsuitable for transport in a licensed cask.

3.2.3 *disposal, n—in nuclear waste management*, the emplacement of radioactive 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 permits 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 complex 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, n—in nuclear waste management*, 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 its original material properties as modified by the conditions during its service life including storage conditions.

3.2.10 *sludge, n—in nuclear waste management*, a slurry or sediment containing nuclear waste materials, a residue that has usually been formed from processing operations, corrosion or water basin storage.

3.2.11 *waste package, n—in nuclear waste management*, the waste form and any containers, shielding, packing and other absorbent 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, chemi-

sorbed water, and ice. The following specific terms for water are used in this document:

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 surrounding matrix, blocked vent pores, cavities, or by the nearby formations of solids that prevent or slow escape. 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 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 for:

4.1.1 Evaluating what drying system should be used,

4.1.2 Drying methods, and

4.1.3 Methods to confirm that adequate dryness was achieved.

4.2 The guide can be used to determine:

4.2.1 Drying technologies that are designed to remove most of the unbound water but will not remove all forms of water. Water remaining on and in commercial and research reactor spent nuclear fuels coming 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 could be significant to cause the release of water remaining in a sealed dry package that may result in container pressurization, fuel retrievability issues, and container corrosion.

4.2.2 A methodology for evaluating drying processes that may not readily remove all forms of water that may be retained in pores in fuel cladding, capillaries, sludge, crud, and thin wetted surface films. Drying techniques are even less successful in removing bound water. Removal of bound water will only occur when the specific threshold energy is applied to break the bonds involved and release the water. For spent nuclear fuel this threshold energy may come from the combination of thermal input and ionizing radiation.

4.2.3 How the residual water retained with the SNF, CRUD and sludge inside a sealed package may become available to react with the internal environment, the fuel, and the package materials as a result of extended time at equilibrium dry storage temperatures, or as the direct result of radiolytic decomposition.

5. Evaluating the Drying Approach

5.1 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 hydride re-orientation process in the zircaloy cladding.

5.2 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:

5.2.1 Preclude geometric reconfiguration of the packaged fuel,

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

5.2.3 Minimize hydrogen generation or materials corrosion that could be a problem during transport or repository handling operations.

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

5.3.1 Nature and degree of fuel damage including its storage history,

5.3.2 Form of water in the packaged SNF container,

5.3.3 Thermal and radiological environments involved,

5.3.4 Degree of self heating contribution to the drying process,

5.3.5 Potential for corrosion and radiolytic degradation of the fuel and container material,

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

5.3.7 Interactions that need to be considered to set the bounds for residual water, and

5.3.8 Maximum allowable water based on items 5.3.5 through 5.3.7.

5.4 *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 failure. 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 than those used for non-failed 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. 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 for a 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 analysis of drying. In order to organize the information in this guide, the varieties of spent fuels in existence 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.

5.4.1 *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

5.4.2 *Fuel Conditions*—The following fuel conditions will be used in this document to categorize the needed level of drying required.

- 1 Fully intact cladding with no known penetrations
- 2 Cladding with known small pinholes or cracked cladding 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, CRUD 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)

5.5 *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 and sources are discussed below.

5.5.1 *Forms of Water*—The forms of water include unbound water, ice formed during drying, physisorbed water, and chemisorbed water.

5.5.1.1 *Unbound Water*—Unbound water has to be considered as 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 formation, capillaries, trapped water or thin wetted surface films.

5.5.1.2 *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 considerably higher than its specific heat (1 cal/g°C); consequently, liquid water may undergo a considerable temperature drop during drying. Since the melting heat of 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 He-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 also prevent ice formation. (See [Annex A2](#).)

5.5.1.3 *Physisorbed Water*—Physisorbed water is found on all surfaces of the SNF and the container. Typical water concentrations are about 0.03 to 0.05 g/m²/monolayer. The binding force is weak and the water layer can be removed at relatively low temperatures with an adequate vacuum drying technique. Cracks and open pores in the surface may act as capillaries that may hinder the evaporation of the water. SNF cladding with cracks, surface corrosion, porosity, or oxide spallation may hold significant physisorbed water. Corrosion products on exposed fuel meat may also retain physisorbed water, especially corrosion products from metallic U fuels.

5.5.1.4 *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 at temperatures and/or ionizing radiation corresponding to the specific bonding energy of the 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 discussed 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 of the form Al(OH)₃ (or Al₂O₃·3H₂O) which begin dehydrating near 100°C to the form AlO(OH) (or Al₂O₃·H₂O) which is stable to >340°C. Zirconium cladding may form the hydrated oxides ZrO(OH)₂ or Zr(OH)₄ during irradiation. The potential water

content 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.)

5.5.2 *Sources of Water:*

5.5.2.1 *CRUD and Sludge:*

(1) *CRUD on Commercial SNF*—Surface CRUD deposits on commercial SNF are corrosion products from reactor coolant system materials or other chemicals from within the system inventory. The amount and type of the deposits are dependent on the reactor type and its water chemistry. Characteristic CRUD areal density for PWR fuel is <5 mg/cm² 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 μm (<0.001 in.) but potentially reaching 100-μm (0.004-in.) thick (2). CRUD deposits on BWR fuel average 25 to 76 μm (0.001 to 0.003 in.) and may reach 250 μm (0.010 in.) maximum thickness (2). The contribution to the source of water from CRUD on the surface of commercial SNF appears to be small.

(2) *Sludge in SNF Operations*—Sludge may accumulate in SNF wet storage systems from two primary sources: (1) water 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. For groups A–D fuels in defect conditions 1 and 2 from well-controlled wet storage systems, sludge is probably not a concern. For fuel group A–D with defect conditions 3–6 and groups E–I fuels, especially with defect conditions 3–6, the quantity and characteristics of the sludge carryover and its impact on drying needs to be evaluated. 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.

5.5.3 *Water in SNF Packages:*

5.5.3.1 *Commercial SNF, Group A, Defect Conditions 1 – 4*—LWR fuel without any through-cladding defects will not allow water inside fuel rods. Even very small pinholes or cracks, however, may result in water held in the fuel to cladding gap and the rod plenum after drying. PWR fuel may also trap water in guide tubes if the dashpot drain hole is blocked with sludge or CRUD. A typical LWR rod defect is characterized by a combination of primary and secondary defects. Whereas the primary defect is regarded to be the location of the original penetration, secondary defects may be located some distance from the primary defect and 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.

5.5.3.2 *Clad Metallic U fuels (Groups F and G), Defect Conditions 1 – 4*—Clad metallic U and most U alloy fuels will

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

not allow water inside intact cladding. Even the smallest pinholes with water egress, however, 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 internal environment becomes sufficiently anoxic, the U metal will 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).

5.5.3.3 *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.

5.5.3.4 *Miscellaneous Research Fuels, Groups C, D, and E*—A wide variety of research reactor fuels have been irradiated. These fuels will respond to water according to their fuel meat, cladding composition, and integrity. Research reactor fuels generally have relatively low burnup and low decay heat. The low decay heat may dictate the use of a specialized heated drying process. Dry storage temperatures and radiation levels may be so low that water radiolysis and secondary oxidation reactions may not occur or may be insignificant.

5.6 *SNF 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 lifetime in storage.

5.6.1 *Commercial Reactor Fuels:*

5.6.1.1 Commercial nuclear fuel is irradiated in a water environment at elevated temperature and pressure. If a breach of the cladding occurs in-core, the internal gas will be released and the pressurized water may enter into the fuel rod. Upon removal from the core, the fuel is stored in a water basin with the water temperature typically less than 40°C and water pressure equivalent only to that resulting from its depth in the basin water. Both the reactor core water and basin water typically have tightly controlled chemistry and purity that may prevent fuel damage.

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

5.6.1.3 The expected thermal performance of an SNF cask or package can be modeled to determine the expected dry storage temperature profile of 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.

5.6.2 *Research/DOE Reactor Fuels:*

5.6.2.1 Research reactor fuel and most other DOE fuels are also irradiated in water. The temperatures and pressures tend to vary widely, but they are typically lower than those of a commercial power plant. Fuel lifetimes are also quite variable in DOE 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, with a total fuel irradiation lifetime less than a year.

5.6.2.2 SNF storage for DOE fuels varies somewhat on the basis of total irradiation, fuel type, and decay heat. The elimination of reprocessing in the U.S., however, resulted in a basic trend toward placing all types of DOE SNF into extended basin storage and dry storage systems. The primary considerations involved with movement of largely metallic SNF and research/DOE SNF into dry storage are the lack of significant latent decay heat, the wide range of fuel cladding materials, and the cladding integrity involved.

5.6.2.3 A wide variety of environments are possible in dry storage of DOE SNF due to the types of dry storage employed. Three primary types of dry storage systems are currently in use: 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 typically 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 typically insufficient to heat the cask above exterior ambient conditions.

5.6.2.4 Vented well-type and facility storage systems have the advantage that residual water in and around the SNF can evaporate or radiolyze over long times and escape from the system. However, this situation may also work in reverse because canisters containing cool fuels may aspirate water from the external atmosphere as a function of external temperature and dew point. Such water ingress during “dry” storage may significantly increase the overall chemisorbed water content of the SNF over the storage period, especially if the SNF is badly damaged.

5.7 *Potential Effects of Residual Water on SNF and Containers as a Function of Environment*—The presence of water in storage containers for dry storage of SNF can be released by direct decomposition of the chemically bonded species, vaporization of the physisorbed and the free water, and radiolytic decomposition. These forms of water and decomposition products could cause corrosion, pressurization and possibly embrittlement issues for the storage of spent fuel.

5.7.1 *Radiolysis:*

5.7.1.1 The radiolysis of residual water within a sealed spent fuel package releases free oxygen and hydrogen for internal corrosion reactions. Radiolysis occurs as a result of gamma, beta, neutron or alpha particle interaction with the water molecule. Neutron radiolysis is a major factor during

reactor operation but diminishes rapidly after fuel removal from the active core, and is insignificant by the end of the pool storage term.

5.7.1.2 Gamma radiolysis that may act on water and hydroxyl groups that are external and internal to the fuel is 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 also decreases relatively rapidly as a function of time; therefore, the potential for gamma radiolysis will decrease during the fuel storage term, and should become inconsequential after about 15 years.⁶

5.7.1.3 Beta particles radiolysis of water occurs only close proximity to the fuel surfaces and hydrated species. In the case where corrosion products are fairly distributed in sludges, the contribution by the beta emitting isotopes to radiolysis could be significant.

5.7.1.4 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 more work is needed on the issue (13).

5.7.2 Hydrogen—Fuel, Cladding, and Packaging Reactions:

5.7.2.1 Radiolytic decomposition of water and most metal corrosion reactions with water generate hydrogen. 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 by performing a material and energy balance using the temperature, radiation levels, materials, and water contained in the package (15).

5.7.2.2 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. Hydrogen may also be absorbed into Zircaloy cladding making it more susceptible to fracture. The effects of hydrogen are well understood and numerous ASTM test methods are available for evaluating these effects in materials (16). In general, these effects increase with increases in the hydrogen content of a metal or alloy. Hydrogen content increases with increasing hydrogen fugacity which is generally greater in aqueous environments than in gaseous atmospheres (17). Hydrogen entry into fuel or container materials may also be driven by galvanically coupled dissimilar metals if an electrolyte is present. Low-pressure gaseous hydrogen acting on materials for very long times may involve different mechanisms than those observed for high hydrogen fugacity. Therefore, high-

pressure hydrogen effects data should not be extrapolated to the low-pressure case of SNF storage.⁷

5.7.2.3 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 corrosion rate for water released within the container which will release more hydrogen gas,
- (4) The hydrogen diffusion, venting, corrosion, gettering, and recombination rates for the gas interacting with the system,
- (5) Net void volume with respect to and hydrogen reaction with metal and ignition, and
- (6) Mass of metal with respect to hydrogen embrittlement.

5.7.2.4 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 back out of the getter material. The performance of the getter material usually requires higher temperature to increase hydrogen dissolution kinetics.

5.7.3 Water Corrosion Reactions:

5.7.3.1 Because of the expected quantities of water typically involved and the substantial mass of typical dry storage containers, water corrosion damage to the structural materials will typically not be a significant factor in adequate dryness, however, the corrosion production of hydrogen could increase the effect of pressurization and other hydrogen effects. Potential exceptions to the corrosion damage generalization 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.

5.7.4 Fission Product Reactions:

5.7.4.1 Some fission products, if released from fuel during storage, could react with residual water to form a more corrosive environment for the storage cask. Cs, Rb, and I are the fission products of primary concern. Krypton and Xenon may also be released and add to internal pressures. Also, 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 may result in caustic cracking of stainless steel weldments at elevated dry storage temperatures (>110°C). Iodine would be expected to

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

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.

behave similar to chlorine in attacking stainless steel packaging components if sufficient residual tensile stress and ion concentrations are present.

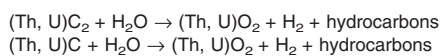
5.7.5 Galvanic Coupling with Aluminum Clad Fuel:

5.7.5.1 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 sufficient electrolyte is present, resulting 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 cyclic water ingress is possible.

5.7.6 Carbide Fuel—Water Reactions:

5.7.6.1 Carbide fuels 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, often using SiC as a cladding material. The finished fuel particles are then dispersed in porous compacts of pyrocarbon and typically encapsulated in a graphite sheath or block.

5.7.6.2 The intrinsic rate of hydrolysis of ThC₂ and UC₂ in moisture is quite rapid, proceeding 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:



5.7.6.3 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, particularly in the older literature reports.

5.7.6.4 The reaction of graphite or pyrocarbon with water produces hydrogen, CO, and CO₂. However, the reaction rate is extremely slow at temperatures below 200°C, so that the reaction is of no consequence at storage temperatures (25-27).

5.7.6.5 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).

5.7.7 Water-Fuel Oxide and Cladding Reactions and Consequences:

5.7.7.1 If water internal to commercial fuel rods is not fully removed, further water oxidation of the fuel pins toward a UO₃ hydrate may rupture or “unzip” the fuel cladding (see Annex A1 for fuel oxide reaction data) as 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. Recent work indicates that UO₂ begins to form hydrated phases within six weeks at fuel storage temperatures (30). Sintered UO₂ forms metaschoepite when reacted with deionized water. These low-density hydrated compounds may continue the cladding rupture sequence in damaged rods.

5.7.8 Gas Pressurization:

5.7.8.1 Pressure inside the storage container is increased both by reactions that form gas as a reaction product or by failure of a clad that release gas from the spent fuel. Any 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 estimate 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, and
- (10) Container and basket materials corrosion rates.

5.7.8.2 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 considered. 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.

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

5.7.9 Nuclear Criticality:

5.7.9.1 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 moderating 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 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 need to reflect the condition and radiation level of the SNF and the expected types of water that need to be removed. The kinetics of drying is a function of the physical (geometric) configuration and chemical composition or 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.) of the system, the applied temperature, the purity of the materials in the system, the ambient pressure, and the specific convection/diffusion restrictions imposed by the 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 water pumping speed of the vacuum system and the conductance path between the vacuum source and the water source are major factors in water removal efficiency. Tests have demonstrated that fuel with pinholes can be dried in a well-controlled system even after water has penetrated into the rod (31). However, in these particular tests, two drying steps with a thermal homogenization by He-backfilling were needed to fully remove the unbound water in the rod.

6.1.2 Ice Formation and Removal:

6.1.2.1 The decay heat of commercial SNF is generally inadequate to prevent ice formation during drying. Vacuum step 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 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 will 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 involved. 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 and purity of chemical species involved. The water removal temperatures for some expected compounds (the actual temperatures may be lower due to the

ionizing radiation energy input involved with spent fuel) (35) are discussed in Annex A1.

6.1.4.2 Because of practical limits on the drying temperature, some chemisorbed water will always be present inside the SNF container. If a drying temperature higher than the storage temperature can be used, the release of such water through thermal decomposition would be avoided. Release of water from the chemical compounds may still occur, but the rate would depend on temperature and dehydration kinetics 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, and vacuum level. In commercial vacuum drying processes (see Annex A2), temperature is generally not a controlled variable and fuel decay heat determines the drying temperature. 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 The commercial spent fuel can also be dried using the Forced Helium Dehydration (FHD) system such the HOLTEC process (36). This process requires a pressure relief valve to limit the canister pressure. Also, the temperature is controlled 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 dry 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:

7.1.2.1 Preclude geometric reconfiguration of the packaged fuel,

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

7.1.2.3 Minimize hydrogen generation or materials corrosion that could be a problem 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 requirements for transportation, storage systems, or both, involved. 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 such 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.

7.2.1.3 Most of the chemisorbed water will still be present after standard drying process. The effects of having this residual water in the system must be determined with enough accuracy to show that it will not exceed the system requirements. Such determinations involve the following:

- (1) Estimation of the location of the chemisorbed water (relates directly to SNF, fuel damage, corrosion products and sludge carried into the package),
- (2) Generation of average temperature history starting when the container was sealed and covering normal and allowable off-normal operating conditions,
- (3) Estimation of the quantity of chemisorbed water in the system subject to corrosion reaction and radiolysis, and estimation of the rates for such corrosion and radiolytic decomposition,
- (4) Estimation of the rates for reaction/recombination of radiolyzed species by other materials within the container (if allowed by the regulator),

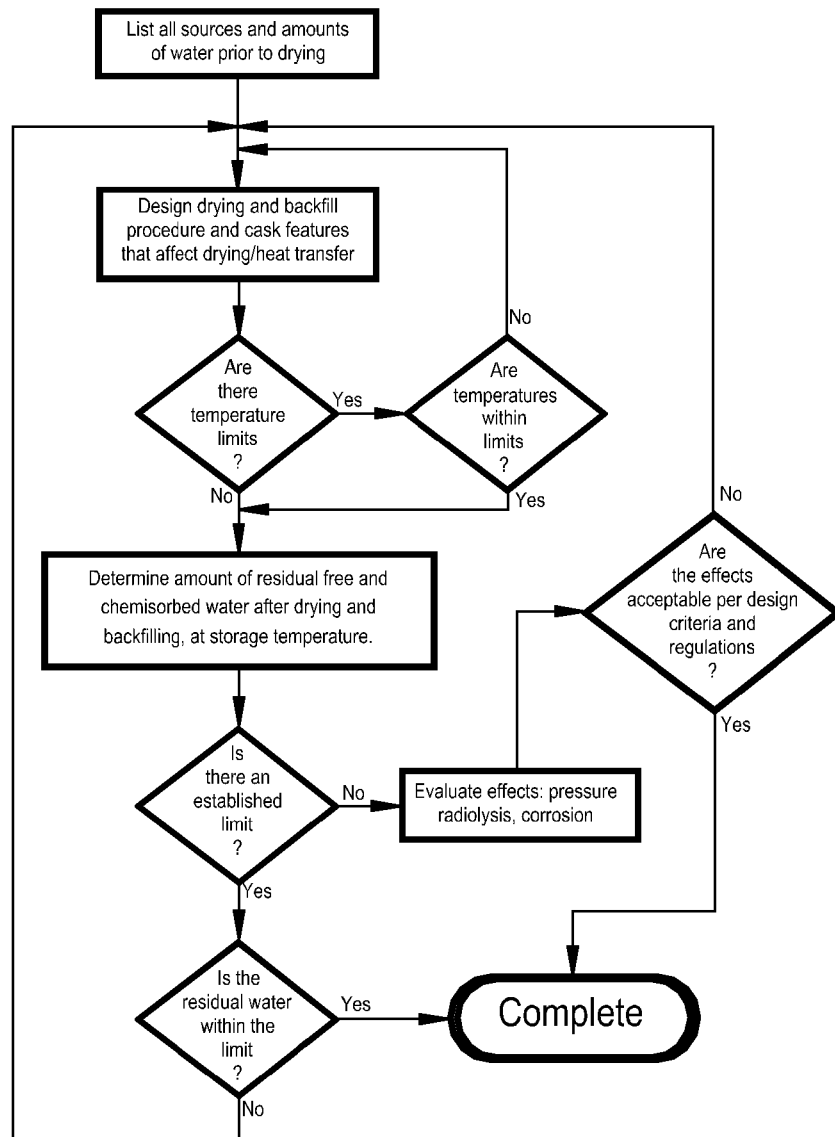


FIG. 1 Flowchart for Evaluation of Spent Fuel Drying Procedures

(5) Estimation of equilibrium water vapor pressure over the fuel as function of temperature, and

(6) Estimation of the reaction of the water with the fuel, cask components, and therefore rate of generation of hydrogen.

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

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 minimum requirement of maintaining a 4.10^{-4} MPa (3 Torr) pressure for 30 minutes indicates that less than one mole of residual gas (released from trapped or physisorbed water, or ice) is inside the cask (38). Container size, decay heat, potential for ice formation, substantial quantities of chemisorbed water, and damage to fuel elements 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 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 significant corrosion or SNF cladding damage.

(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 a sample of 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 or chemical corrosion within the container.

7.2.3 Process Knowledge:

7.2.3.1 The process knowledge approach is documentation that shows the SNF, the drying, and the storage history was 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 dry storage. Process knowledge arguments may be relatively simple for pristine commercial SNF with complete records but may be impractical for many DOE fuels. A process knowledge approach for DOE fuels would require estimates or bounding values for the potential quantity of residual water, the extent of SNF corrosion, and the prior and expected temperature profile of the fuel.

ANNEXES

(Mandatory Information)

A1. CHEMICAL FORMS OF BOUND WATER AND THEIR CHARACTERISTICS

INTRODUCTION

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

The specific chemistries of hydrated compounds are typically complex and may vary as a function of the environment and time involved with 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 not revert to their natural mineralogical form for many years.

This annex attempts to provide a broad review of the hydrated compounds specifically identified as corrosion products in nuclear systems, based on the limited sampling and testing documented in the literature. Where a related mineralogical form of the compound may contain significantly different water content, that fact is noted because the specific environmental history involved with some fuels could have resulted in formation of the mineralogical form of the compound.

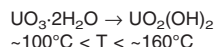
A1.1 Hydrates of Uranium Oxides

A1.1.1 Uranium Trioxide Hydrates:

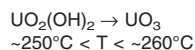
A1.1.1.1 The structural formula for the mineral, schoepite is $(\text{UO}_2)_6\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$ (39). The formation of UO_3 -based hydrates has been documented by a number of authors (40-45). Review of these reports identified three forms of UO_3 -based hydrates: $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O}$, 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 N-Reactor elements (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 hydrates exist that might have different dehydrating kinetics. Wheeler et. al. (40) acknowledged the possibility that modified forms of the schoepite could exist. Hoekstra and Siegel (41) suggest two forms of the dihydrate and four forms of the monohydrate (α -, β -, γ - $\text{UO}_3 \cdot \text{H}_2\text{O}$, and α - $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$).

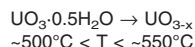
A1.1.1.3 The thermal decomposition of these hydrates have been studied in detail by others (48, 49) and reviewed by Hoekstra and Siegel (50). The experiments were performed using Thermogravimetric and Differential Thermal Analysis (DTA). Results of the tests showed the following reactions:



(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:



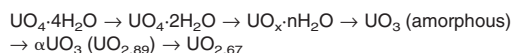
A1.1.2 Uranium Peroxide Hydrates:

A1.1.2.1 The UO_4 -based hydrates (uranium peroxide hydrates) have historically been prepared in the laboratory from solutions of uranyl nitrate and hydrogen peroxide in two different crystalline forms:



A1.1.2.2 Its natural analogue is the studtite. It can also be prepared by the reaction of uranium dioxide with hydrogen peroxide. Thermal decomposition reaction data on these hy-

drates dates back to 1951 (51). The dehydration process for $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ has 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 surface coatings 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, which confirmed the observations of the earlier investigators. However, the decomposition of the dihydrate product starts at a temperature of 100°C and a complete removal of waters of hydration for the K-Basin UO_4 -hydrate sample occurred at about 400°C. The weight loss that was observed at temperatures above 420°C was attributed to reduction of the UO_3 product to a lower oxidation state, U_3O_8 . More recent thermal decomposition data (56) indicates the following thermal decomposition sequence for studtite:



$$\text{where } 3.0 \leq x \leq 3.5 \text{ and } 0 \leq n \leq 0.5$$

A1.1.2.3 For this thermal decomposition sequence, initial decomposition also occurred at 100°C and the final 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 sludge that contains hydrated compounds and contribute to bound water inventory in storage containers. Such hydrated forms may include: (a) hydroxides of zirconium, (b) iron hydroxides, and (c) aluminum hydroxides.

A1.2.2 Aluminum Hydroxides:

A1.2.2.1 Aluminum hydroxide exists in a number of compounds that 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 scheme of decomposition sequence is illustrated in Fig. A1.1. The sequence shows a decomposition temperature range between 100°C and 600°C.

A1.2.2.3 The amount of chemisorbed water in the form of boehmite could be significant, approximately 1.7 L, based on surveys of the average ATR spent fuel plates (55). Assuming a

TABLE A1.1 Hydrates of U-oxides

Compound	Volume Relative to UO_2	Structure	Formation Conditions
$\text{UO}_3 \cdot 2\text{H}_2\text{O}$ Dihydrate	2.62	Orthorhombic; consists of pseudo hexagonal sheets of $[\text{UO}_2(\text{OH})_2]_n$ held together by hydrogen bonded H_2O	Exposure of anhydrous UO_3 to water at 25 to 75°C
$\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ Hypoichiometric Monohydrate	1.85	Hypoichiometric form of α - $\text{UO}_3 \cdot \text{H}_2\text{O}$	Heating $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ in air at 100°C or UO_3 in water at 80 to 300°C
$\text{UO}_2(\text{OH})_2$ or $\text{UO}_3 \cdot \text{H}_2\text{O}$ Monohydrate	1.84	Orthorhombic, consists of pseudo hexagonal sheets of $\text{UO}_2(\text{OH})_2$	
$\text{UO}_3 \cdot 0.5\text{H}_2\text{O}$ Hemi-hydrate	1.73	Triclinic	Hydrothermally at 300 to 400°C

TABLE A1.2 Aluminum Hydroxides

Mineral Name	Chemical Composition	Crsytallographic 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	Crsytallographic Designation	Crystal Structure
Goethite	Iron(III) Hydroxide	α -FeOOH	Orthorhombic
Lepidocrocite	Iron Hydroxide	γ -FeOOH	Orthorhombic
Ferrihydrite	Amorphous Ferric Hydroxide	Fe ₅ HO ₈ ·4H ₂ O	Hexagonal
	Iron(II) Hydroxide	Fe(OH) ₂	
Hydro-haematite	Iron(III) Hydroxide	Fe(OH) ₃	

conservative 0.0034 cm oxide thickness based on a 9 % thinning of aluminum cladding (0.038 cm).

ATR plate dimensions: 124.45 cm long, 7.58 cm average arch width
 Exposed aluminum: 2 sides, 19 plates per assembly, 30 assemblies per canister
 Surface area: 124.45 cm · 7.58 cm · (2) · (19) · (30) = 1075397.34 cm²
 Boehmite properties: density 3.01 g/cc, thickness = 0.0034 cm, M.W. = 119.98 g/mol
 Boehmite moles: 1075397.34 · 0.0034 · 3.01/119.98 = 91.73 moles
 Boehmite water content: 91.73 moles of water, 18 g/mol (water) = 1651 g or mL

A1.2.3 Hydrates of Zirconium Oxides:

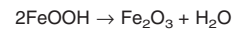
A1.2.3.1 Hydrolysis of zirconium oxides will generate hydroxide of Zr that includes: (a) ZrO₂·xH₂O, (b) Zr(OH)₄, and (c) ZrO(OH)₂. The ZrO(OH)₂ is known to decompose at about 120°C for ZrO₂.

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 known iron corrosion products are listed in **Table A1.3**.

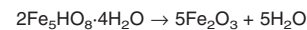
A1.2.4.2 Goethite, the most common form of iron oxyhydroxide decomposes differently for the two types known. The Type A, synthetic form, decomposes over two different tem-

perature ranges; while Type B, mineral form, decomposes at a single temperature. The decomposes reaction is:

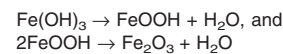


A1.2.4.3 Bakker et al. (56) have concluded from spectroscopic and magnetic studies that a molecular level prereactional dehydroxylation of the lepidocrocite begins at a temperature between 150 and 170°C with the formation of superparamagnetic ζ -Fe₂O₃ nuclei, although the overall conversion of ζ -FeOOH to ζ -Fe₂O₃ starts at about 200°C.

A1.2.4.4 The decomposition of the ferrihydrite as reported by Mitov et al. (57) to start 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 hydroheamatite usually contain 5.4 to 8 % H₂O (58) and shows characteristic dehydration with a rising temperature 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 the decomposition which is dependent on the heating rate, the maximum temperature and the drying atmosphere for the fuel will determine the quantity of the hydrated water form that may remain due to the presence of uranium oxides hydrates. The following are the thermal decomposition temperatures:

Compound/Reaction	Drying Temperature
Waters of Hydration:	
UO ₂ (OH) ₂ ·H ₂ O → UO ₂ (OH) ₂ + H ₂ O	≤150°C
UO ₄ ·4H ₂ O → UO ₄ ·2H ₂ O + 2H ₂ O	25–100°C
Metal Hydroxyls:	
UO ₂ (OH) ₂ → UO ₃ + H ₂ O	>250°C
2UO ₄ ·2H ₂ O → 2UO ₃ + O ₂ + 4H ₂ O	~150°C (pure >425°C)
Al(OH) ₃ → AlOOH + H ₂ O	120–300°C ^A
2AlOOH → Al ₂ O ₃ + H ₂ O	>350°C
Fe(OH) ₃ → FeOOH + H ₂ O	>120°C
2FeOOH → Fe ₂ O ₃ + H ₂ O	250°C
2Fe ₅ HO ₈ ·4H ₂ O → 5Fe ₂ O ₃ + 5H ₂ O	400°C

^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, kinetics indicates that about 85 % of the decomposition will occur in about one hour at temperature.

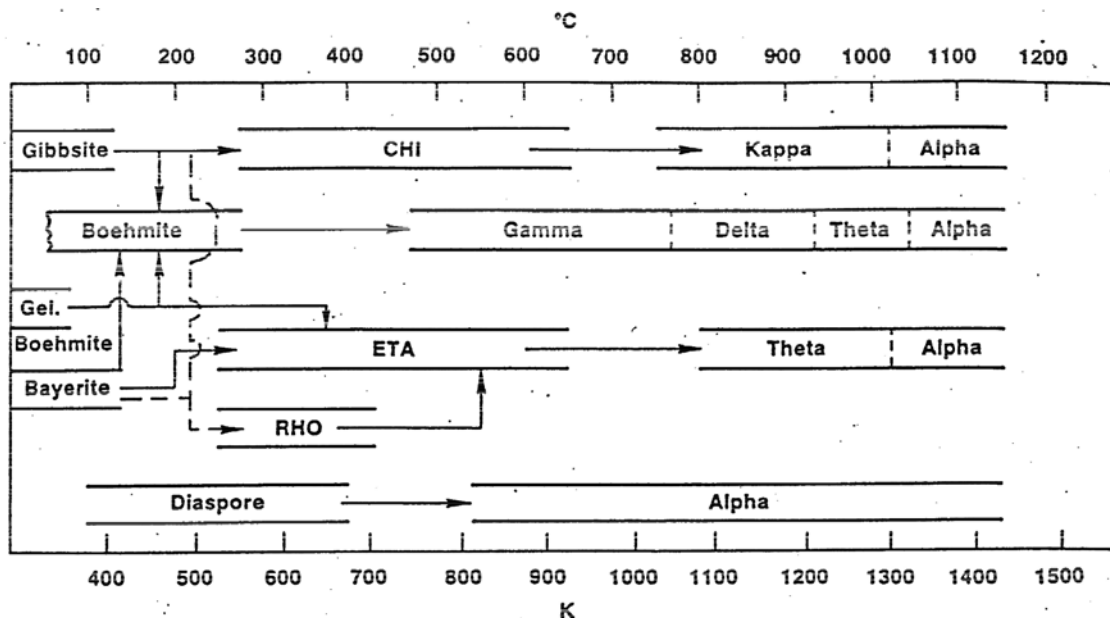


FIG. A1.1 Transformation Sequence $\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3$

A2. DRYING PROCESSES

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 sucked out.

(6) External heating or 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, though the quick disconnects are sometimes removed for greater conductance.

(8) Reduce container internal pressure to less than 3 Torr.

(a) To minimize freezing, some processes call for pressure reduction in stages holding pressure some time at each stage before continuing down 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 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 for heat conduction in thermal analysis. While increased temperatures improve drying, the 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 so they are not used routinely.

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

A2.2.1 The following method is being used at the DOE Hanford Site 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. The efficiency of this method has not

been confirmed but data is being collected to evaluate the long-term effectiveness of the method.

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

(1) The cask headspace is vented through a venting system 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 back-filled with helium above atmospheric pressure. The cask/MCO is allowed to cool down using the tempered water at ~15°C. A final helium back-fill to a set pressure of 11.25 psig is performed; the MCO is then sealed and moved to the interim storage location.

(8) Failure to meet this requirement results in repeating the drying cycle at steps 5 through 7.

A2.3 DOE Drying Approach for Fuel Rubble

A2.3.1 The following is a summary of a falling rate approach used at the Idaho National Engineering and Environmental Laboratory to dry fuel rubble in containers that also contained a grout material. The falling rate approach assumes that water must be extracted from a solid material. The fuel was placed into vented dry storage after drying.

(1) Dewater the fuel containers.

(2) Load the fuel rubble containers in the drying furnace.

(3) Preheat the containers in the furnace system to 310 to 524°C (590 to 975°F).

(4) Pump down while maintaining a maximum of 10 Torr variance between the furnace and vacuum lines.

(5) Isolate the vacuum system and measure the drying rate every 60 min for the first 10 hours, and every thirty minutes after the 10-hour point is reached.

(6) Continue to pump down the system until a falling rate drying range is reached. (The falling rate drying range is one in which the drying rate continues to decrease with each successive measurement on 30 minute intervals.)

(7) Compute a 10 % falling rate value for the drying cycle based on the initial falling rate values obtained.

(8) Continue falling rate drying until the total vacuum is less than 35 Torr, the rate of change of the vacuum system is less than 0.07 Torr/min for at least 25 minutes, and the vacuum measures no more than the 10 % falling rate value calculated for the vacuum cycle.

(9) Minimum drying time is 16 hours at 310°C (590°F).

APPENDIX

(Nonmandatory Information)

X1. SAMPLE CALCULATION

X1.1 The following sample calculation provides an example of uranium oxyhydrate (UO₃·H₂O) corrosion product pressurization of a container assuming worst case conditions (no back reactions):

X1.1.1 One kg of UO₃·2H₂O (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:

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

where:

P_1 = 1 atm (helium),

V_1 = 500 L,

R = 0.0821 atm · liter/mol K, and

T_1 = 298.15 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 (H₂O → H₂ + ½ O₂) we have one mole of steam going to 1.5 moles of gas (Note: It is also possible to have H₂O → ½ H₂ + ½ H₂O₂) 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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