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Standard Guide for
Drying Behavior of Spent Nuclear Fuel[1]

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1. Scope

1.1 This guide discusses three steps in preparing spent nuclear fuel (SNF) for placement in a sealed dry storage system: (*1*) evaluating the needs for drying the SNF after removal from a water storage pool and prior to placement in dry storage, (*2*) drying the SNF, and (*3*) demonstrating 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 stored in water pools. The guide discusses sources and forms of water that may remain in the SNF, the container, or both after the drying process has been completed. It also discusses the important and potential effects of the drying process and any residual water 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: (*1*) to determine how dry the SNF must be in order to prevent problems with fuel retrievability, container pressurization, or container corrosion during storage, handling, and transfer, and (*2*) to demonstrate that adequate dryness has been achieved. Achieving adequate dryness may be straightforward for undamaged commercial fuel but complex for any SNF where cladding damage has occurred prior to or during placement and storage at the spent fuel pools. Challenges in achieving adequate dryness may also result from the presence of sludge, CRUD, and any other hydrated compounds. These may be transferred with the SNF to the storage container and may hold water and resist drying.

1.1.3 Units are given in both SI and non-SI units as is industry standard. In some cases, mathematical equivalents are given in parentheses.

1.2 *This standard only discusses SNF drying and does not purport to address all of the 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]
C859 Terminology Relating to Nuclear Materials
C1174 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
C1562 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]The U.S. government documents listed in 2.3 or referenced in this standard guide are included as examples of local regulations and regulatory guidance that, depending on the location of the dry storage site, may be applicable. Users of this standard should adhere to the applicable regulatory documents and regulations and should consider applicable regulatory guidance.

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

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3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide but not defined herein, refer to Terminology C859 or Practice C1174.

3.2 *Definitions of Terms Specific to This Standard:* Refer to SFST-ISG-1 for additional definition details.

3.2.1 *breached spent fuel rod, or failed fuel, n*—spent fuel rod with cladding defects that permit the release of gas from the interior of the fuel rod. A breached spent fuel rod may also have cladding defects sufficiently large to permit the release of fuel particulate. A breach may be limited to a pinhole leak or hairline crack, or may be a gross breach.

3.2.2 *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."

3.2.3 *damaged SNF, n—in nuclear waste management*, any fuel rod of fuel assembly that cannot fulfill its fuel-specific or system-related functions.

3.2.4 *disposal, n—in nuclear waste management*, the emplacement of radioactive materials and wastes in a geologic repository with the intent of leaving them there permanently.

3.2.5 *getter, n—in nuclear waste management*, a material (typically a solid) used to chemically react with certain gases (for example, H_2, O_2, H_2O vapor) to form a solid compound of low vapor pressure.

3.2.5.1 *Discussion*—Some fuel rod designs include an internal getter to remove residual hydrogen/moisture from the internal rod atmosphere.

3.2.6 *grossly breached spent fuel rod, n*—a subset of breached rods. A breach in spent fuel cladding that is larger than a pinhole leak or a hairline crack and that may permit fuel particulate release.

3.2.7 *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.

3.2.8 *intact SNF, n*—any fuel that can fulfill all fuel-specific and system-related functions, and that is not breached. Note that all intact SNF is undamaged, but not all undamaged SNF is intact, since in most situations, breached spent fuel rods that are not grossly breached will be considered undamaged.

3.2.9 *packaging, or SNF storage container, n—in nuclear waste management*, an assembly of components used to ensure compliance with the applicable requirements for independent storage of spent nuclear fuel and high-level radioactive waste or for transportation of radioactive materials.

3.2.10 *pinhole leaks or hairline cracks, n*—minor cladding defects that will not permit significant release of particulate matter from the spent fuel rod, and therefore present a minimal concern during fuel handling and retrieval operations. (See discussion of gross defects for size concerns.)

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

3.2.12 *spent nuclear fuel (SNF), n*—nuclear fuel that has been irradiated in a nuclear reactor and contains fission products, activation products, actinides, and unreacted fissionable fuel.

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

3.2.14 *undamaged SNF, n*—SNF that can meet all fuel-specific and system-related functions. Undamaged fuel may be breached. Fuel assemblies classified as undamaged SNF may have assembly defects.

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

3.2.16 *water, n—in drying of spent nuclear fuel*, refers to the various forms of H_2O present in the fuel storage container. 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 H_2O, physisorbed H_2O, chemisorbed H_2O, and ice. The following specific terms for water are used in this document:

3.2.16.1 *bound water, n*—adsorbed surface layers of water and chemisorbed water.

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

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

3.2.16.4 *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 the escape of water from the waste package.

3.2.16.5 *unbound/free 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 Drying of the SNF and fuel cavity of the SNF container and its internals is needed to prepare for sealed dry storage, transportation, or permanent disposal at a repository. This guide provides technical information for use in determining the forms of water that need to be considered when choosing a drying process. This guide provides information to aid in (*a*) selecting a drying system, (*b*) selecting a drying method, and (*c*) demonstrating that adequate dryness was achieved.

4.2 The considerations affecting drying processes include:

4.2.1 Water remaining on and in commercial, research, and production reactor spent nuclear fuels after removal from wet 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, which may be sufficient to cause the release of water from the fuel. The water release coupled with the temperature increase in a sealed container may result in container pressurization, corrosion of fuel or assembly structures, or both, that could affect retrieval of the fuel, and container corrosion.

4.2.2 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 gases, and combinations of these and other similar processes.

4.2.3 Water removal processes are time, temperature, and pressure-dependent. Residual water in some form(s) should be anticipated.

4.2.4 Drying processes may not readily remove the water that was retained in porous materials, capillaries, sludge, CRUD, and as thin wetted surface films. Water trapped within damaged SNF may be especially difficult to remove.

4.2.5 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 applied to the system. For spent nuclear fuel this threshold energy may come from the combination of thermal input from decay heat and forced gas flow and from the ionizing radiation itself.

4.2.6 The adequacy 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, especially unbound water, in the system.

4.2.7 Residual water associated 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 under dry storage conditions.

4.2.8 Thermal gradients within the container evolve with time, and as a result water vapor will tend to migrate to the cooler portions of the package. Water may condense in these areas. Condensed water will tend to migrate to the physically lower positions under gravity such as the container bottom.

4.2.9 Radiolytic decomposition of hydrated and other water-containing compounds may release moisture, oxygen and hydrogen to the container.

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

5. Evaluating the Drying Approach

5.1 The proper approach to drying SNF is fuel and system-specific, and thus will depend on fuel type, fuel condition, fuel basket design, and associated materials (such as the neutron absorber in the basket). There is no single correct or even preferred approach. Intact commercial fuel may be dried by one approach, SNF with breached fuel rods by another approach, and research and production reactor fuels by yet another approach. Furthermore, the variables that must be considered in selecting a drying approach for one fuel type may differ significantly from 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 is not important to aluminum or stainless steel clad SNF. The proper drying approach will minimize the potential for damage of the fuel during the drying operation and subsequent dry storage. Reference (**1**) provides additional information regarding vacuum drying.

5.1.1 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 reclassified as failed fuel for disposal. Fuel is classified at the time of loading, so the drying process should be chosen to balance the risks caused by the presence of water in the container and the risks incurred by removing the water.

5.2 Thermal cycling during drying of commercial light water reactor SNF may affect the hydride morphology in the cladding. Heating the SNF during a drying operation may dissolve precipitated hydrides, and subsequent cooling may result in hydride reprecipitation. The hydride orientation and therefore the properties of the fuel cladding may be affected by the dissolution-reprecipitation process.

5.3 Research reactor and other non-commercial SNF that is not treated or reprocessed may be stored in sealed canisters within regulated dry storage systems. Such dry storage canisters may be expected to contain the SNF through interim storage, transport, and repository packaging. The objectives of drying processes used on this fuel are virtually identical to the drying objectives for commercial fuels and are to:

5.3.1 Preclude geometric reconfiguration of the packaged fuel,

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

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

5.4 The selection of the drying methodology for treating fuel for interim dry storage or disposition in a geologic repository will involve many factors including the following:

5.4.1 Irradiation and storage history (for example, the decay heat output and the amount of hydrogen in the cladding),

5.4.2 Nature and degree of fuel damage (for example, quantity of breached rods or rods containing water),

5.4.3 Forms of water in the container (for example, absorbed water)

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

5.4.5 Impact of residual water on corrosion and degradation of the fuel and container material during drying, storage, and disposal,

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

5.4.7 Maximum allowable amount of water remaining in the container after drying is completed.

5.5 *Categorization of SNF and Defects for Drying Evaluation*—This standard guide pertains to fuels that contain any cladding breach, such as hairline cracks or holes that may permit water ingress into a fuel element or the release of fuel materials from the fuel element. Such breaches may cause the fuel to be categorized as failed or damaged. Failed fuel may also be categorized as in 10 CFR 961, which separates failed commercial light water reactor fuel into three classes:

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"

Drying treatments may depend on the fuel condition. Each category of damaged or breached fuel rods could require handling/treatment operations that differ from those used for intact fuel. It is important when considering a drying process to be clear about the class of breached fuel rods in the fuels being dried. A given fuel element could be regraded as intact for the purposes of storage or transport performance but as having breached fuel rods for the purposes of geologic repository disposal. The classifications differ because the performance of damaged fuel is typically more predictable over dry storage periods than over geologic time. SNF may be characterized as damaged or undamaged or failed through the use of one or more of the following processes: review of operating records (core history and handling), visual examinations, ultrasonic testing, wet or dry sipping, and eddy current testing.

Fuel type and the presence and type of defects are essential inputs for evaluating 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 Group*—The following groups are used to distinguish between SNF types:

A Commercial oxide fuel in Zr-alloy cladding
B Carbide or oxide particle fuel with SiC coating (in graphite)
C Oxide fuel in stainless steel cladding
D U-ZrH fuel in Zr-alloy or stainless steel cladding
E Oxide fuel in Al-alloy cladding
F UAl_x or U-ZrH fuel in Al-alloy cladding
G Metal fuel in Zr-alloy, Al-alloy or stainless steel cladding
H Carbide or oxide particle fuel with only pyrolytic carbon coating
I Unclad metal or oxide fuel

5.5.2 *Fuel Conditions*—The following Fuel Conditions are designated:

1 Fully intact cladding with no known penetrations
2 Cladding with small pinholes or hairline cracks that may allow entry/exit of moisture
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
5 Fuel with major cladding damage from previous fuel oxidation, exposure to water, or both
6 Rubblized fuel that has little or no intact cladding, high surface area, and previous exposure to water (Includes fuel rods or elements that have been sectioned for analysis or study)

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 liquid water, ice formed during drying, physisorbed water, and chemisorbed water.

5.6.1 *Unbound Water*—Unbound water may be present in containers of SNF transferred from a water storage pool. Water retention depends on the condition of the fuel, the container design, and the drying process. Sources of unbound water after vacuum drying may include trapped water and water in capillaries.

5.6.2 *Ice*—Ice formation can be a cause for water retention 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 ratio of the heat of vaporization of water (539.6 cal/g) to the specific heat (1 cal/g K) corresponds to a large temperature change; consequently, liquid water may undergo a considerable temperature drop during drying. Since the heat of fusion of water (79.7 cal/g) is relatively small, the energy removed from the liquid by evaporation can cause the remaining water to freeze. Measures 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 (for example, cladding and assembly hardware) and the container internals (for example container walls, baskets, etc.). Typical water concentrations are about 0.03 to 0.05 g/m^2 per monolayer. The binding force holding the water to the surface is weak and the water layer can be removed at relatively low temperatures (<50°C) by vacuum drying or forced gas dehydration. Cracks, open pores, and corrosion products may hinder evaporation and hold physisorbed water by virtue of additional surfaces. Corrosion products on exposed U plate fuel are notable for retaining physisorbed water.

5.6.4 *Chemisorbed Water*—Chemisorbed water may exist in a hydroxide or hydrate in the native oxides or corrosion products on the fuel, cladding, or container materials. The dehydration of hydroxides or hydrates occurs by the reformation of water molecules, which are released when the thermal energy or energy from ionizing radiation equals or exceeds the 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. Chemisorbed water may also be found in cladding and container materials. Aluminum metal in water forms a number of surface hydroxides such as $Al(OH)_3$ (or $Al_2O_3 \cdot 3H_2O$) which begin dehydrating near 100°C to the form $AlO(OH)$ (or $Al_2O_3 \cdot H_2O$) which is stable to >340°C. Zirconium cladding may also form the hydrated oxides $ZrO(OH)_2$ or $Zr(OH)_4$ during irradiation. The water content of hydrated zirconium oxides is small, and the water will not be released below 500°C (2). See Annex A1 for other hydroxides and hydrates formed from water contact with typical fuel and container materials.

5.7 *Sources of Water:*

5.7.1 *General Service Environment for Water Reactor Fuel*—Water surrounds most SNF assemblies until they are placed in a dry storage environment. The fuel is 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. Locations for water that should be considered include:

(1) Regions beneath the assemblies,
(2) Dash pots in pressurized water reactor guide tubes,
(3) Water rods in boiling water reactor fuel, and
(4) Crevices in grid spacers, baskets, and assemblies.
(5) Neutron absorber.

Additionally, potential impacts of the drying operation itself should be considered. For example, drying operations could cause blistering and delamination in the neutron absorber if water is trapped in the structures.

5.7.2 *CRUD and Sludge:*

5.7.2.1 *CRUD on Commercial SNF*—CRUD deposits on commercial SNF may include corrosion products from reactor coolant system materials or other materials/chemicals from the system inventory. The amount and type of the deposits are dependent on the reactor type, operating fuel duty, and water chemistry. Characteristic CRUD area density for pressurized water reactor fuel is <5 mg/cm^2 with an inhomogeneous distribution over the fuel surface, typically deposited on the upper/hotter portions of the fuel rod as a layer averaging less than 25 µm (0.001 in.) but potentially reaching 100 µm (0.004 in.) in thickness (3). CRUD deposits on boiling water reactor fuel average 25 to 76 µm (0.001 to 0.003 in.) in thickness and may reach a thickness of 250 µm (0.010 in.) (3). Depending on CRUD type and fuel pool chemistry, CRUD levels may be reduced during pool storage. The contribution of CRUD to the water content on the surface of commercial SNF is typically small.

5.7.2.2 *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, ventilating 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 the fuel is appropriately cleaned. Sludge is probably not a concern for fuels in SNF Groups A–D that have Fuel 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 SNF Groups A–D that have Fuel Conditions 3–6 and for SNF Groups E–I, especially those with Fuel Conditions 3–6. Analyses of sludge accumulated from wet storage of damaged metallic uranium fuels (4) 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 Associated with Specific Fuel Types:*

5.7.3.1 *Commercial SNF, SNF Group A, Fuel Conditions 1–4*—Light water reactor fuel without any through-cladding defects (Fuel Condition 1) will not allow water inside fuel rods. However, even very small pinholes or cracks (Fuel Condition 2) may result in water penetrating the cladding during reactor operations and pool storage, and being held in the fuel-to-cladding gap and the rod plenum after drying. Similar water retention may also occur for Fuel Condition 4. Pressurized water reactor fuel in Fuel Condition 3 may also retain water in guide tubes if (*a*) the dashpot drain hole is blocked or partially blocked with sludge or CRUD, (*b*) if the discharge point is elevated above the tube bottom or (*c*) in some designs if there are spaces such as in the tube-in-tube design. Adequate removal of the residual water will depend primarily on the temperature–pressure conditions at the specific location within the fuel assembly. For example, the water associated with the thimble tube dashpots is at the bottom of the assembly which in most drying scenarios is the cooler region during the drying process. A typical light water reactor rod in Fuel Condition 4 is characterized by a combination of primary and secondary defects. The primary defect is the original penetration, and secondary defects may be located at some distance from it. The secondary defects are normally attributed to local hydride blistering (5). The defects are holes of different sizes that allow water to penetrate and fill the free volume of the rod. The size and location of the defects may retard water removal.

5.7.3.2 *Clad Metallic U Fuels (SNF Groups F and G), Fuel Conditions 1–4*—Clad metallic U and most U allow fuels will not allow water inside intact (Fuel Condition 1) cladding. Vacuum drying of such fuels has been performed for intact Zircaloy-clad fuels from Hanford K-basin (6). Drying tests on unirradiated mock-ups have been performed to demonstrate drying capability for Magnox elements from Sellafield water basins as a contingency for dry storage (7). However, water ingress through even the smallest pinholes (Fuel Condition 2 or 4) may have a noticeable effect on metallic U fuel. Even at basin temperatures, water may oxidize U metal sufficiently to rupture or "unzip" fuel cladding (8). If the oxidation processes cause the internal environment to become sufficiently anoxic, hydrogen will be produced, and the U metal will react to form UH_3. Exposed surfaces of UH_3 may react vigorously with residual moisture or air (9).

5.7.3.3 *Mixed Carbide Fuels, SNF Groups B and H*—Mixed carbide fuels encapsulated in pyrolytic carbon, graphite, or both, are designed for gas-cooled reactors and should not 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 to absorption of water

in the pores of the graphite or carbon. An aqueous solution can penetrate the graphite matrix of an HTGR fuel element through its open pore system, and under normal conditions a spherical element takes up about 8 mL of solution (**10**).

5.7.3.4 *Miscellaneous Research and Production Reactor Fuels, SNF 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 composition, cladding alloy, and cladding integrity. Research reactor fuels generally have low decay heat output, which 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 are insignificant. However, many of the research and production reactor fuels have been damaged during storage and, therefore, may be difficult to dry. Each group of these should be evaluated separately because of the wide variations in type and condition.

5.8 *SNF Exposure Environments*—The dryness required for a given fuel is often related to the duration of exposure and the radiation, temperature, and water chemistry to which it was exposed during reactor operation and storage. Specific fuels typically have an environmental exposure history that provides input into probable drying requirements. The drying process should reliably establish water vapor pressures levels such that the remaining water is insufficient to cause detrimental chemical reactions during dry storage.

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 fuel is in-core, the internal gas will be released and water may enter into the fuel rod. Upon removal from the reactor, 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 and basin typically have tightly controlled water chemistries that may prevent or at least minimize fuel cladding damage.

5.8.1.2 The heat generated by the SNF during storage drops off predictably as the fission products decay. After a suitable cooling time that is dependent on the fuel burnup, decay heat output, system design, and applicable regulations (**11**), the SNF may be moved out of basin storage (wet storage) and placed into a dry storage system.

5.8.1.3 The thermal performance of a cask or package can be modeled to determine the expected temperature profile as a function of time (**12**). Design or regulatory requirements may establish short-term temperature limits for maintaining cladding integrity impacted by creep or by embrittlement, for example. The limits may depend on burnup, cladding design and fuel pressurization. Limits from 250 to 570°C (**13**) have been suggested. The evaluation of the limits should consider how cladding integrity is affected by hydride dissolution, reprecipitation, and reorientation, creep, delayed, hydride cracking, and thermal annealing of radiation damage. The impact of the hydrogen concentration and morphology on the cladding properties, such as the ductility transition temperature, will affect the temperature limits.

5.8.2 *Research and Non-commercial Reactor Fuels:*

5.8.2.1 Research reactors have irradiation temperatures and pressures that vary widely but are typically lower than those of a commercial power plant. Fuel lifetimes are also quite variable in 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. Production reactors may provide the opposite extreme as refueling scheduled to provide the optimum isotope abundances, and the total fuel irradiation time may be less than a year.

5.8.2.2 Conditions necessary for successful dry storage of research reactor SNF will depend on the total irradiation, fuel type, and decay heat output. The elimination of reprocessing in the U.S. essentially resulted in placing the vast majority of research and production reactor SNF into extended basin storage and a few dry storage systems. The primary considerations involved with movement of these fuels into interim dry storage include the lack of significant 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 prior damage to the fuel, any anticipated in-storage degradation would not compromise subsequent disposition options.

5.8.2.3 Two primary types of dry storage systems are currently in use for research reactor SNF: Underground well storage and 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 container because confinement is provided by the well or the facility itself. Exterior cask storage systems may be very similar to those used for commercial SNF even though the decay heat is insufficient to heat the cask significantly. The experience and expertise gained in operating the current dry storage systems for production reactor SNF should be carefully considered if the research reactor SNF is to be transferred to alternative dry storage systems for storage or disposition. The Irradiated Fuel Storage Facility at the Idaho Nuclear Technology and Engineering Center uses a forced ventilation system with high-efficiency particulate air filtration for dry storage of research reactor fuel in unsealed canisters (**14**).

5.8.2.4 Residual water in vented dry storage systems can evaporate or radiolyze over long times, so water can escape from the system. However, canisters containing cool fuels may also aspirate water from the external atmosphere. Water evaporation and aspiration during "dry" storage may significantly change the overall chemisorbed water content of the SNF, especially if it is badly damaged. Characterization of SNF behavior in such vented systems may provide insight into the probable behavior of SNF in alternative dry storage systems.

5.9 *Potential Effects of Residual Water on SNF and Containers*—Residual water in 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, although such degradation is not generally anticipated (**15**)..

5.9.1 *Radiolysis:*

5.9.1.1 Radiolysis occurs as a result of gamma, beta, neutron, or alpha particle interaction with residual water or oxyhydroxides. Radiolysis within a sealed spent fuel package releases free oxygen and hydrogen which may promote corrosion or produce a flammable atmosphere (**16, 17**). These radiolysis products, in the absence of residual air, recombine and persist at very low concentrations; however, as little as 0.1 % residual air can impede recombination and increase the concentration of radiolysis products. The specific concentration of radiolysis products depends temperature, time, and the amounts of residual air and water. One calculation for an SNF container with one litre of water (**17**) showed that the concentration of hydrogen remained well below the flammability limit for hydrogen/air mixtures after 300 years of storage.

5.9.1.2 Neutron radiolysis is important during reactor operation but diminishes rapidly after fuel removal from the active core, and is insignificant by the end of pool (basin or wet) storage.

5.9.1.3 Gamma interactions with water and hydroxyl groups may affect both the fuel and other hydrated compounds inside the cask. Gamma radiolysis of hydrated uranium oxides will occur in fields of 1000 Gy/h (**17**). Hydrogen production from dry (no free of physisorbed water) oxyhydroxides of aluminum has been reported (**18**). Gamma activity in SNF decreases over time, and the levels of hydrogen, oxygen, and nitric acid developed during storage are generally considered inconsequential even after 300 years (**17**).

5.9.1.4 Beta radiolysis of water occurs only in close proximity to the decay event because of the limited travel of the beta particle. However, if hydrated corrosion products are uniformly distributed in sludges or if sludges are in contact with fuel surfaces, the contribution by the beta emitting isotopes to water radiolysis could be significant.

5.9.1.5 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 known and additional work is needed (**19**).

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 flammable gas cannot be present in the event a welded canister needs to be opened, the hydrogen content in SNF containers is usually limited to below 4 %, the lower flammability limit for hydrogen in air (**20**). When the hydrogen-containing volume is otherwise inert, flammability will not be an issue, but hydrogen may cause embrittlement, and a flammable mixture may form when the container is breached or opened. This is especially true for non-intact fuel assemblies where, for example, the French Competent Authority has requested measurement of the hydrogen generation rate before transport of packages transporting at least one breached fuel rod (**20**). Hydrogen generation rates can be predicted with reasonable accuracy from the temperature, radiation levels, types of materials present, and water content (**17, 21**).

5.9.2.2 Hydrogen may be a problem for SNF container materials over long storage times, although analysis has shown (**17**) that after 300 years of storage in a container with one litre of residual water, the hydrogen concentration reaches only 2.3 %. Hydrogen tends to collect in steels at locations of high stress and surface discontinuity, and it may embrittle certain steels, especially high strength ferritic and martensitic steels. The effects of hydrogen in steels are fairly well established, and numerous ASTM test methods are available for evaluating hydrogen effects (**22**). Hydrogen may also be absorbed by zirconium-alloy cladding and make it more susceptible to fracture. In general, these effects increase with increases in the hydrogen concentration or in the strength of a metal. Hydrogen content increases with increasing hydrogen fugacity, which is generally greater at a surface during corrosion by aqueous environments than during exposure in gaseous atmospheres (**23**). Hydrogen entry into fuel or container materials may also be driven by galvanic corrosion. High-pressure hydrogen effects data, in general, should not be used to predict the impact of hydrogen on SNF storage containers.[5] 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 concentration in a sealed container depends on the extent of reaction of water with fuel and container materials. Assuming that free and physisorbed water are removed by drying, the issue of adequate dryness may relate directly to:

(1) The 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 chemisorbed water is released from the compounds,

(4) The hydrogen diffusion, venting, corrosion, gettering, and recombination rates during interacting with the system,

(5) Free 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 gettering may be an effective technique to mitigate hydrogen buildup in storage containers if the radiation levels are low and the hydrogen is not radiolyzed from the getter material. However, effective gettering may require high temperatures, so getters may have limited utility for long-term storage.

5.9.3 *Water Corrosion Reactions:*

5.9.3.1 The expected quantities of residual water expected after drying are typically small relative to the substantial internal surface area of typical dry storage containers and the mass of the fuel and cladding, so water corrosion damage to the structural materials and SNF should not be significant in establishing adequate dryness. However, there are potential exceptions to the anticipated lack of corrosion damage, including:

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[5] 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 that required to cause fracture unless the material was highly stressed.

(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) Fuels that would be expected to release aggressive fission products and reach a temperature sufficient to allow corrosion cracking of container welds, and

(4) Fuels with significant chloride contamination.

5.9.4 *Fission Product Reactions:*

5.9.4.1 Some fission products could be released from fuel during storage. These could react with residual water and increase the corrosiveness of the storage environment. Cesium, rubidium, and iodine are the fission products of primary concern. Krypton and Xenon may add to internal container pressures, and decay of krypton to rubidium may help spread rubidium 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 similarly to chlorine in attacking stainless steel packaging components if sufficient residual tensile stress and ion concentrations are present. Fission product interactions are not expected to present major problems, but they should not be overlooked when criteria 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 components if residual is present. Large quantities of stainless steel are typically present in storage containers, and galvanic coupling between the stainless steel and aluminum can occur if sufficient electrolyte is present. Galvanic coupling will result in accelerated corrosion of the aluminum components. This process is especially important with relatively cold aluminum clad fuel in vented storage systems where water ingress is possible.

5.9.6 *Carbide Fuel—Water Reactions:*

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 carbide fuels are coated spheres of uranium carbide, thorium carbide, or both, that are dispersed in a carbonaceous matrix. The coating 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 is penetrated, the reaction of the fuel with moisture may be quite rapid.

5.9.6.2 The intrinsic rate of hydrolysis of ThC_2 and UC_2 in moisture proceeds at a penetration rate as fast as 24 μm/day. Bulk samples of ThC_2 powder hydrolyzed completely in ambient laboratory air within 12 hours (**24**). Uranium and thorium carbides react with water or water vapor to form hydrogen and low molecular weight hydrocarbons:

$$(Th, U)C_2 + H_2O \rightarrow (Th, U)O_2 + H_2 + hydrocarbons$$
$$(Th, U)C + H_2O \rightarrow (Th, U)O_2 + H_2 + hydrocarbons$$
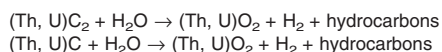
5.9.6.3 The low molecular weight hydrocarbons are primarily methane (CH_4), ethylene (C_2H_4), and ethane (C_2H_6), with minor amounts of acetylene (C_2H_2) and the C_3H_x to C_6H_x alkanes, alkenes, and alkynes (**2, 25-30**). The reported product distributions vary substantially and reflect the effects of impurities in the carbides and variations in analysis techniques. 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 produces hydrogen, CO, and CO_2 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 (**31-33**).

5.9.6.5 Silicon carbide reacts with water vapor to form silica (SiO_2), carbon dioxide, carbon monoxide, and hydrogen at temperatures above 600°C, and silica, methane, hydrogen, carbon dioxide, and carbon monoxide below 600°C (**34, 35**). However, the reaction is extremely slow at temperatures below 500°C (**21**) and is therefore not considered to be important.

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

5.9.7.1 Cladding damage may lead to water ingress into the fueled fords and subsequent water retention. Residual water may oxidize the fuel pellets toward a low density UO_3 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. For example, the hydrated compound $UO_3 \cdot 2H_2O$ has a volume 2.6 times that of the starting UO_2. Evaluations of the reaction process indicate that UO_2 begins to form hydrated phases within six weeks if exposed to moisture at fuel storage temperatures (**36**). Additionally, sintered UO_2 forms metaschoepite when reacted with deionized water. The peroxide phases, studtite and meta-studtite, may form if radiolysis of residual water produces hydrogen peroxide (**37**). The formation of low-density hydrated compounds and resulting cladding rupture may impact the handling and transport of SNF.

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 and by failure of cladding and the subsequent release of gas from spent fuel. However, reaction of these gases with constituents inside the storage container can decrease the pressure build up. 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) Free volume of the 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) Decrease in temperature as decay heat output declines,

(9) Initial pressure and composition of the fill gas,

(10) Container and basket materials corrosion rates,

(11) The number of damaged fuel rods and the fission product content of the rods, and

(12) Corrosion, including galvanic corrosion, of fuel cladding and assembly materials.

5.9.8.2 The inability to accurately predict pressure and hydrogen concentration within a sealed system affects the design criteria for the container. Regulators and designers typically assume that only reactions that increase pressure are occurring. Such calculations yield pressures up to 0.35 MPa (50.8 psi) for a commercial fuel container with 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 pressurization 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 Trapped water and fuel displacement/geometric re-arrangement of fuel assemblies can have an impact on criticality evaluations. Although criticality must be considered, the mass of water in a properly dried container is expected to be low enough that criticality will not be an issue (**15**). The removal of residual fuel pool water from casks also results in removal of soluble neutron absorbers (boron) in the case of borated pool 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 (for example, Reference (**38**)). 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 8.1-1998 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 amount and type (unbound, chemisorbed, trapped, etc.) of water to be removed. The kinetics of drying will depend on the geometric configuration and materials of the storage and drying system, the chemical composition of the phases (such as $UO_2(OH)_2$, $UO_2(OH)_2 \cdot H_2O$, $Al(OH)_3$, etc.) 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 The time required for unbound water removal is primarily limited by the geometry of the system, the physical location of the water in the system, and the operating speed of the water removal system. If vacuum drying technologies are used, the local temperature and the conductance of the path from 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 (**39**). However, two drying steps with a thermal homogenization by He-backfilling were needed to fully remove the unbound water in the rod.

6.1.2 *Prevention of Ice Formation:*

6.1.2.1 Staged increases in the vacuum level and hold cycles with or without helium backfill are typically used in commer-cial 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, specialized vacuum-backfill-vacuum cycles, or operation at pressures well above the triple point to prevent ice formation.

6.1.3 *Removing Physisorbed Water:*

6.1.3.1 Physisorbed water may be removed by circulating heated gas under turbulent flow conditions to promote convective heating of surfaces being dried. The principal drying conditions, including temperature, pressure, and flow rate can be adjusted to maximize moisture removal from the system.

6.1.3.2 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 masses, thin layered materials, and "wet" materials of a small particle size, first-order desorption kinetics generally apply. Desorption of physisorbed water from metal surfaces typically occurs at temperatures well below room temperature (**40**). Dry air at 50°C should desorb the superficial physisorbed water layers in 10 to 30 hours. Less desorption time is required to vacuum dry at 20°C. However, surface water that has physisorbed onto wetted UO_2 powders has been shown to require higher temperatures; desorption begins at about 150°C, and the reaction is essentially complete at 230°C (**41**).

6.1.4 *Removal of Chemisorbed Water:*

6.1.4.1 Removal of chemisorbed water depends on the chemical species present and purity of those species involved. The water removal temperatures for some compounds(**42**) are discussed in Annex A1. However, energy input from ionizing radiation may reduce the temperatures required.

6.1.4.2 Because of practical limits to the drying temperature, some chemisorbed water may be present inside a dried SNF container. This water may be released to the container environment by the combination of thermal energy and ionizing radiation. If a drying temperature higher than the storage temperature can be used the release of water through thermal decomposition may be avoided. Release of water may occur regardless of the drying temperature, but the rate will depend on SNF storage temperature, dehydration kinetics, and the rate of radiolytic decomposition reactions. Radiolytic decomposition can also generate other products, including 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 controlled; fuel decay heat output determines the drying temperature. The temperature of the SNF will generally rise during vacuum drying, so care should be taken to keep temperatures below some maximum level. Commercial processes typically have minimal flexibility, but the following operational adjustments may be made to decrease the time required to achieve final dryness or reduce the amount of water retained:

(1) Removal of unbound water by slightly tilting the cask toward the drain tube.

(2) Use of a vacuum lance to aspirate unbound water from the bottom of the cask.

(3) Repetition of the vacuum drying cycle, with inert gas backfill between cycles to obtain effective thermal equilibration.

(4) Hot gas purging of the cask (used especially on fuels with low decay heat output).

6.2.2 Research and 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 of the SNF may impose restrictions that make the drying processes less effective than those used for commercial fuels.

6.2.3 Commercial SNF has been dried using hot gas drying systems. The hot circulated gas is controlled and monitored to promote water boiling and evaporation in the system while maintaining fuel and cladding temperatures within regulatory limits (**43**).

7. Confirmation of Adequate Dryness

7.1 *Establishing the Requirements for Drying:*

7.1.1 Quantitative criteria for drying are currently being evaluated and are not yet available for inclusion in this standard. For interim dry storage of commercial SNF some conditions or drying criteria have been adopted. These eliminate enough water to preclude gross damage to fuel cladding during storage (for example, see 10 CFR 72 and References (**1**) and (**44**)).

7.1.2 Dry storage canisters for research and production reactor fuels are expected to contain the SNF through interim storage, transport, and repository packaging. The objectives of drying processes used on this fuel are to remove sufficient water to preclude:

7.1.2.1 Geometric reconfiguration of the packaged fuel,

7.1.2.2 Damage to the canister from over-pressurization or corrosion,

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

7.1.2.4 Any adverse impact on criticality safety.

7.2 *Confirming Dryness:*

7.2.1 *Evaluating Adequate Dryness:*

7.2.1.1 An evaluation of dryness must consider the starting system, the types of water, and the water inventory, and then determine if appropriate techniques have been applied through the drying process to ensure that transportation and storage 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), and the adequacy of water removal should be evaluated by techniques such as pressure rebound measurements or monitoring the moisture content in gas removed from the dried container.

7.2.1.3 Chemisorbed water may still be present after standard drying process, especially for SNF in Fuel Conditions 3 through 6. The amount of residual water must be determined with enough accuracy to show that its effects will not violate the system requirements. Such determinations involve estimation of:

(1) Amount and location of hydrated compounds,[6]

(2) Temperature history and temperature profile 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 drying,

(4) Rates for recombination of radiolyzed species or for reaction with other materials,

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

(6) Hydrogen generation or pressurization of the container by reaction of the water with the fuel and cask components.

7.2.2 *Measurement:*

7.2.2.1 *Pressure Measurement – Pressure Rebound Test*—A pressure rebound check performed in connection with the drying process is one method currently being used to show compliance with dryness requirements. Pressure rebound measurements consist of showing that an evacuated container loaded with SNF will retain vacuum for a specified period without a pressure rise greater than a specified limit. For commercial SNF, the typical acceptance criterion is maintaining a 4×10^{-4} MPa (3 torr) pressure for 30 minutes; compliance has been used to suggest that less than one mole of residual gas is inside the container (**45**). This criterion was developed for cask licensing; however, regardless of the storage period, the change in pressure or in pressure rise with time is an indicator of the residual moisture. System variables such as container size, drying temperature, potential for ice formation, locations in the fuel and container that could trap moisture, and the 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 A2.3).

7.2.2.2 *Other Measurement Options*—Other measurement techniques may be used to show drying adequacy. Application of these techniques and the metrics for dryness would need concurrence from the applicable regulatory agency.

8. Keywords

8.1 chemisorbed water; corrosion; drying; hydrates; physisorbed water; radiolysis; spent nuclear fuel

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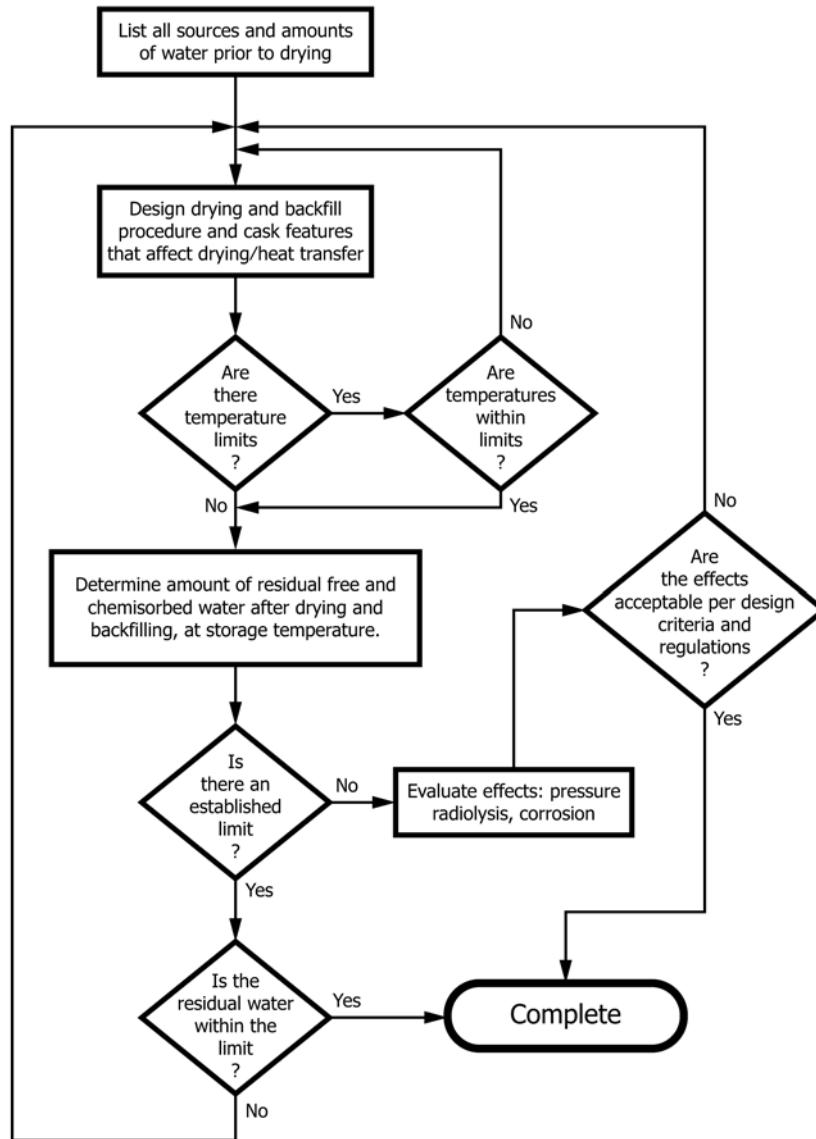[6] This estimation relates directly to the SNF, the fuel damage, and the corrosion products and sludge carried into the package.

FIG. 1 Flowchart for Evaluation of Spent Fuel Drying Procedures

ANNEXES

(Mandatory Information)

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

11

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 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 observation is noted. The environmental history of some fuels may have impacted the mineralogical form of the compounds present, and may have resulted in synthetic compounds which have their own distinct decomposition characteristics.

A1.1 Hydrates of Uranium Oxides

A1.1.1 *Uranium Trioxide Hydrates:*

A1.1.1.1 The formation of UO_3-based hydrates in systems related to SNF has been documented by a number of authors (**46-52**). Review of these reports identified three forms of UO_3-based hydrates: $UO_3 \cdot 2H_2O$, $UO_3 \cdot H_2O$, and $UO_3 \cdot 0.5H_2O$. Table A1.1 lists some of the characteristics of these hydrates.

A1.1.1.2 The structural formula for the mineral, schoepite is $(UO_2)_6O_2(OH)_{12}](H_2O)_{12}$ (**46**). The mineral phase, paraschoepite, with a corresponding composition of $UO_{2.86} \cdot 1.5H_2O$ was identified on the surface of metallic uranium fuel elements from N-Reactor (**53**). The phase paraschoepite is a modified form of schoepite ($UO_3 \cdot 2H_2O$) and may have been inadequately described as a new mineral although it is not actually a different mineralogical species (**54**). Other modified forms of the uranium-containing hydrates that have different dehydrating kinetics may also exist. Wheeler et. al. (**47**) acknowledged the possibility of modified forms of the schoepite while Hoekstra and Siegel (**48**) suggest two forms of the dihydrate and four forms of the monohydrate (α-, β-, γ-$UO_3 \cdot H_2O$, and α-$UO_3 \cdot 0.8H_2O$).

A1.1.1.3 The thermal decomposition of these uranium-containing hydrates have been studied in detail (**55, 56**) and reviewed by Hoekstra and Siegel (**57**). Thermogravimetric and Differential Thermal Analysis (DTA) experiments showed the following reactions:

$UO_3 \cdot 2H_2O \rightarrow UO_2(OH)_2$
~100°C < T < ~160°C
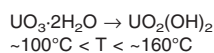
(*1*) The decomposition of $UO_2(OH)_2$ then follows at higher temperatures:

$UO_2(OH)_2 \rightarrow UO_3$
~250°C < T < ~260°C
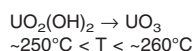
(*2*) $UO_2(OH)_2$ can also decompose to $UO_3 \cdot 0.5H_2O$. The decomposition reaction of $UO_3 \cdot 0.5H_2O$ is represented as:

$UO_3 \cdot 0.5H_2O \rightarrow UO_{3-x}$
~500°C < T< ~550°C
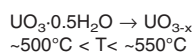
A1.1.2 *Uranium Peroxide Hydrates:*

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 crystallic forms of the hydrates were developed:
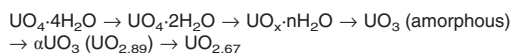
$UO_4 \cdot 4H_2O$ at temperatures below 50°C, and
$UO_4 \cdot 2H_2O$ above 70°C

A1.1.2.2 The natural analogue of the UO_4-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 (**58-61**). 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

TABLE A1.1 Hydrates of Uranium Oxides

Compound	Volume Relative to UO$_2$	Structure	Formation Conditions
$UO_3 \cdot 2H_2O$ 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
$UO_3 \cdot 0.8H_2O$ 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
$UO_2(OH)_2$ or $UO_3 \cdot H_2O$ Monohydrate	1.84	Orthorhombic, consists of pseudo hexagonal sheets of UO$_2$(OH)$_2$	
$UO_3 \cdot 0.5H_2O$ Hemi-hydrate	1.73	Triclinic	Hydrothermally at 300 to 400°C

pool **(62)** 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 the K-Basin starts at a temperature of 100°C and a complete removal of waters of hydration occurred at about 400°C although some weight loss was observed at higher temperatures. The weight loss 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 **(63)** indicates the following thermal decomposition sequence for studtite:

$$UO_4 \cdot 4H_2O \rightarrow UO_4 \cdot 2H_2O \rightarrow UO_x \cdot nH_2O \rightarrow UO_3 \text{ (amorphous)}$$
$$\rightarrow \alpha UO_3 (UO_{2.89}) \rightarrow UO_{2.67}$$

where $3.0 \leq x \leq 3.5$ 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 **(63)**.

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 Selected aluminum hydroxide compounds are listed in Table A1.2.

A1.2.2.2 Studies have been performed to establish 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 place **(62)** is approximately 1.7 L, based on a conservative 0.0034 cm film thickness and the following calculations:

TABLE A1.5 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 A1.6 Iron Hydroxides

Mineral Name	Chemical Compound	Crystallographic Designation	Crystal Structure
Geothite	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)$_3$	

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 cm^2
Boehmite properties: density 3.01 g/cm^3, 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 *Zirconium Hydroxides:*

A1.2.3.1 Hydrolysis of zirconium oxides may generate hydroxides of Zr, including: *(a)* $ZrO_2 \cdot xH_2O$, *(b)* $Zr(OH)_4$, and *(c)* $ZrO(OH)_2$. The $ZrO(OH)_2$ is known to decompose at about 120°C for ZrO_2.

A1.2.4 *Iron Hydroxides:*

A1.2.4.1 The hydroxides of iron that will contribute to bound water are $Fe(OH)_3$, $Fe_5HO_8 \cdot 4H_2O$ and $FeOOH$. These iron based corrosion products are listed in Table A1.3.

A1.2.4.2 Geothite, the most common form of iron oxyhydroxide, may exist in a synthetic or mineral form. These two forms of Goethite are both α-FeOOH but decompose differently with the synthetic form, decomposing over two different temperature ranges while the mineral form decomposes at a single temperature. The decomposes reaction for either form is:

$$2FeOOH \rightarrow Fe_2O_3 + H_2O$$
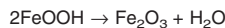
A1.2.4.3 Bakker et al. **(63)** have studied decomposition of the iron hydroxide lepidocrocite and concluded from spectroscopic and magnetic studies that a molecular level prereactional dehydroxylation begins at a temperature between 150 and 170°C and that the overall conversion to Fe_2O_3 starts at about 200°C.

A1.2.4.4 The decomposition of the ferrihydrite **(64)** starts at 400°C and is not completed until the temperature reaches of about 475°C. The decomposition reaction is:

$$2Fe_5HO_8 \cdot 4H_2O \rightarrow 5Fe_2O_3 + 5H_2O$$
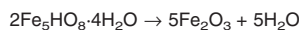
A1.2.4.5 Naturally occurring hydroheamatite usually contains 5.4 to 8 % H_2O **(65)** and shows characteristic dehaydration with temperatures over the range of about 129 to 150°C. The weight loss is observed until a temperature of 877°C with a inflection at 447°C. The decomposition reactions are:

$$Fe(OH)_3 \rightarrow FeOOH + H_2O, \text{ and}$$
$$2FeOOH \rightarrow Fe_2O_3 + H_2O$$
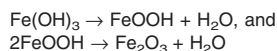
A1.3 Summary

A1.3.1 The literature data shows that thermal treatments may be possible for the removal of water from most hydrated

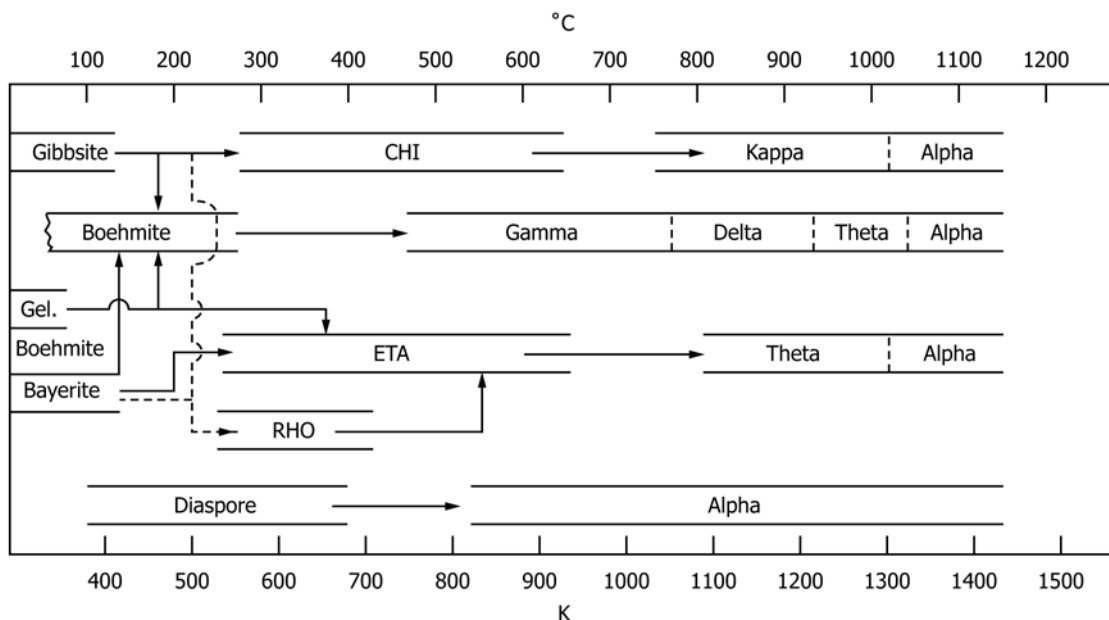**FIG. A1.1 Transformation Sequence Al(OH)$_3$ → Al$_2$O$_3$**

species associated with oxides and hydroxides. The kinetics of the 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:	
$UO_2(OH)_2 \cdot H_2O \rightarrow UO_2(OH)_2 + H_2O$	$\leq 150°C$
$UO_4 \cdot 4H_2O \rightarrow UO_4 \cdot 2H_2O + 2H_2O$	$25–100°C$
Metal Hydroxyls:	
$UO_2(OH)_2 \rightarrow UO_3 + H_2O$	$>250°C$

Compound/Reaction	Drying Temperature
$2UO_4 \cdot 2H_2O \rightarrow 2UO_3 + O_2 + 4H_2O$	~150°C (pure >425°C)
$Al(OH)_3 \rightarrow AlOOH + H_2O$	120–300°C[A]
$2AlOOH \rightarrow Al_2O_3 + H_2O$	>350°C
$Fe(OH)_3 \rightarrow FeOOH + H_2O$	>120°C
$2FeOOH \rightarrow Fe_2O_3 + H_2O$	250°C
$2Fe_5HO_8 \cdot 4H_2O \rightarrow 5Fe_2O_3 + 5H_2O$	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 or below, kinetics indicates that about 85 % of the decomposition will occur in about one hour at temperature.

A2. CURRENT DRYING PROCESSES[7]

INTRODUCTION

Drying technologies have been developed to preserve the integrity of SNF and fuel storage systems while the nuclear industry awaits government decisions concerning used fuel deposition. Documentation of the drying technologies is extensive and includes an annotated bibliography for drying nuclear fuel (**66**). Numerous helpful resources are listed in that bibliography, and reference to those resources is recommended as technologies and practices for drying SNF are currently being developed and refined.

A2.1 Typical Commercial Fuel Vacuum Drying Process[8]

A2.1.1 The following sequence is an example of a process in use for drying commercial SNF for cask storage:

(1) Load container with commercial SNF in the water pool basin.

(2) Install the lid.

(3) Remove container from the water pool basin. Water may or may not be drained before lifting the container out of the pool.

(4) Seal weld the canister lid or bolt the lid in place (for a bare fuel cask). Drying and backfill can't take place until the pressure boundary is established. Welding and lid bolting would preferably take place with water still in the fuel cavity for shielding purposes.

(5) Remove some amount of water to allow for thermal expansion of the water for sealing the lid. Seal the lid by welding or bolting.

(6) Complete draining of water; most commercial containers do not have bottom drains, so they are drained by pumping or pressurizing with a gas, often called blowdown.

(7) 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 aspirated out.

(8) 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 output.

(9) 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.

(10) Reduce container internal pressure to less than 4×10^{-4} MPa (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 4×10^{-4} MPa (3 torr).

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

(a) The recommended practice **(11)** is 30-minute hold time "maintaining a constant pressure" < 4×10^{-4} MPa (<3 torr) to verify adequate water removal.

(b) Stricter requirements may be specified for some systems or some Fuel Conditions.

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

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

NOTE A2.1—The duration of vacuum cycles may be limited because of system conductance reduction. Inert backfill gas is required to protect the cladding from oxidation. Increased temperatures during the vacuum drying process will certainly improve drying and heat transfer by radiation across gaps. Use of helium as the inert gas will significantly enhance heat transfer across gaps between the various components by as much as a factor of eight as compared to nitrogen. Vacuum times may be limited to maintain cladding and component temperatures below the appropriate allowable temperatures. Straightforward operational procedures permit multiple vacuum cycles if needed. The initial blowdown with helium provides a reasonably conductive medium even when the helium is at low pressures **(67)**.

NOTE A2.2—Hold times during the helium backfill between cycles may be useful to allow more water to evolve before the helium is evacuated. 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. Such approaches generally increase operational times and worker radiation exposure and are not used routinely.

A2.2 Forced Gas Dehydration

A2.2.1 The Forced Gas Dehydration (FGD) process removes residual moisture in a fuel storage container after all of the water that can practically be removed by inert gas blowdown has been expelled. Fuel drying by the FGD process is effectuated by circulating dry heated non-reactive gas (for example helium or nitrogen) through the storage container loaded with Spent Nuclear Fuel (SNF). The fuel is demoisturized initially by water evaporation and subsequently more vigorously by boiling due to concomitant heating of the fuel and elevation of the vapor pressure of water above the operating pressure of the canister in the drying process.

A2.2.2 The FGD system is schematically illustrated in Fig. A2.1. The system is defined by series connected gas conditioning modules as follows: (*1*) the condensing module, (*2*) the demoisturizer module, (*3*) the gas circulator module, and (*4*) the pre-heater module. The condensing module serves to cool the gas/vapor mixture exiting the fuel storage container to a temperature well below its dew point such that water may be extracted from the gas stream. The demoisturizer module, engineered to receive partially cooled gas exiting the condensing module, progressively chills the recirculating gas to a temperature that is well below the temperature corresponding to the partial pressure of water vapor at 4×10^{-4} MPa (3 torr).

A2.2.3 In a classical system of the FGD genre, moisture removal operation occurs in two discrete phases. In Phase 1, the FGD is configured to remove bulk moisture by operating the pre-heater module to heat the circulating gas and condensing module to remove the evaporated moisture from the fuel storage container. Phase 1 ends when all of the bulk water in the container cavity is vaporized. At this point, Phase 2 operation commences by starting the demoisturizer module and monotonically lowering the vapor pressure of gas in the fuel storage container to at or below the 4×10^{-4} MPa (3 torr) criteria. The demoisturizer module is equipped with a facility to chill dry the circulating gas and plays the principal role in Phase 2 dehydration.

A2.3 A Production Reactor (N-Reactor) Fuel Drying Process

A2.3.1 The Hanford Site in the U.S. 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
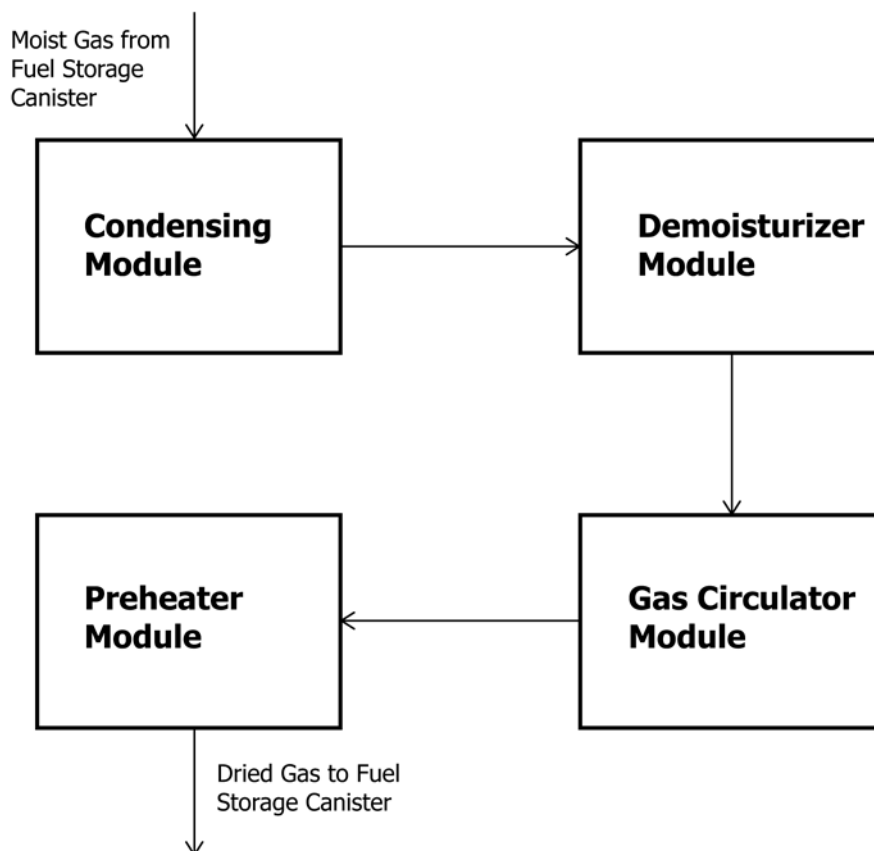
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[7] Recommended current practice.
[8] This is for illustrative purposes and does not constitute a recommendation by ASTM.

FIG. A2.1 Block Flow Diagram of the Forced Gas Dehydration Process

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 ~120 kPa (~3 psig or 17.7 psia) 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.

A2.3.2 The major process steps at the drying facility may be as follows:

(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 ~0.0425 m^3/min (~1.5 scfm) is maintained until pressure in the MCO drops to below 10×10^{-4} MPa (7.5 torr), after which it is secured while the vacuum pump continues to run.

(6) Upon reaching a pressure below 0.67×10^{-4} MPa (0.5 torr), the MCO is isolated and a pressure rebound test is performed. The MCO pressure must remain below 3.1×10^{-4} (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.

(a) If the rebound test is unsatisfactory, steps 5 – 7 are repeated.

(8) The cask/MCO is cooled using the tempered water at ~15°C to lower the system temperature for the helium backfill.

(9) A final helium backfill to a pressure of 179 kPa (11.25 psig or 25.95 psia) is performed.

(10) The MCO is sealed and moved to the interim storage location.

APPENDIX

(Nonmandatory Information)

X1. SAMPLE CALCULATION

X1.1 The following sample calculation provides an example of uranium oxyhydrate ($UO_3 \cdot H_2O$) corrosion product pressurization of a container assuming worst case conditions (no back reactions):

X1.1.1 One kg of $UO_3 \cdot 2H_2O$ (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:

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

where:

P_1 = 1 atm (helium),
V_1 = 500 L,
R = 0.08206 atm · litre/mol K, and
T_1 = 298.15 K.

X1.1.2 Solving for the He:

n_1 = (1 atm) (500 L) / (0.08206 atm L/mol K) (298.15 K) = 20.436 moles of He

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

$P_2/P_1 = n_2 T_2 / n_1 T_1$ or $P_2 = (P_1) (n_2) (T_2) / (n_1) (T_1)$

P_2 = (1 atm) (20.436 moles He + 6.212 moles H_2O) (523.15 K) / (20.436 moles He) (298.15 K) = 2.289 atm (33.639 psia or 231.4 kPa)

X1.1.4 However, if the water is radiolytically decomposed to hydrogen and oxygen ($H_2O \rightarrow H_2 + \frac{1}{2} O_2$) we have one mole of steam going to 1.5 moles of gas (Note: It is also possible to have $H_2O \rightarrow \frac{1}{2} H_2 + \frac{1}{2} H_2O_2$) 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.

X1.3 This sample calculation is for a container with 500 litres of free volume. Most commercial SNF containers will have free volumes in the range of 2000 to 7000 litres (**1, 15, 44**).

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