Standard Guide for
Pyrophoricity/Combustibility Testing in Support of Pyrophoricity Analyses of Metallic Uranium Spent Nuclear Fuel[1]

1. Scope

1.1 This guide covers testing protocols for testing the pyrophoricity/combustibility characteristics of metallic uranium-based spent nuclear fuel (SNF). The testing will provide basic data for input into more detailed computer codes or analyses of thermal, chemical, and mechanical SNF responses. These analyses would support the engineered barrier system (EBS) design bases and safety assessment of extended interim storage facilities and final disposal in a geologic repository. The testing also could provide data related to licensing requirements for the design and operation of a monitored retrievable storage facility (MRS) or independent spent fuel storage installation (ISFSI).

1.2 This guide describes testing of metallic uranium and metallic uranium-based SNF in support of transportation (in accordance with the requirements of 10CFR71), interim storage (in accordance with the requirements of 10CFR72), and geologic repository disposal (in accordance with the requirements of 10CFR60/63). The testing described herein is designed to provide basic data related to the evaluation of the pyrophoricity/combustibility characteristics of containers or waste packages containing metallic uranium SNF in support of safety analyses (SAR), or performance assessments (PA) of transport, storage, or disposal systems, or a combination thereof.

1.3 Spent nuclear fuel that is not reprocessed must be emplaced in secure temporary interim storage as a step towards its final disposal in a geologic repository. In the United States, SNF, from both civilian commercial power reactors and defense nuclear materials production reactors, will be sent to interim storage, and subsequently, to deep geologic disposal. U.S. commercial SNF comes predominantly from light water reactors (LWRs) and is uranium dioxide-based, whereas U.S. Department of Energy (DOE) owned defense reactor SNF is in several different chemical forms, but predominantly (approximately 80 % by weight of uranium) consists of metallic uranium.

1.4 Knowledge of the pyrophoricity/combustibility characteristics of the SNF is required to support licensing activities for extended interim storage and ultimate disposition in a geologic repository. These activities could include interim storage configuration safety analyses, conditioning treatment development, preclosure design basis event (DBE) analyses of the repository controlled area, and postclosure performance assessment of the EBS.

1.5 Metallic uranium fuels are clad, generally with zirconium, aluminum, stainless steel, or magnesium alloy, to prevent corrosion of the fuel and to contain fission products. If the cladding is damaged and the metallic SNF is stored in water the consequent corrosion and swelling of the exposed uranium enhances the chemical reactivity of the SNF by further rupturing the cladding and creating uranium hydride particulates and/or inclusions in the uranium metal matrix. The condition of the metallic SNF will affect its behavior in transport, interim storage or repository emplacement, or both, and therefore, influence the engineering decisions in designing the pathway to disposal.

1.6 Zircaloy[2] spent fuel cladding has occasionally demonstrated pyrophoric behavior. This behavior often occurred on cladding pieces or particulate residues left after the chemical dissolution of metallic uranium or uranium dioxide during fuel reprocessing of commercial spent fuel and/or extraction of plutonium from defense reactor spent fuel. Although it is generally believed that zirconium is not as intrinsically prone to pyrophoric behavior as uranium or plutonium, it has in the past ignited after being sensitized during the chemical extraction process. Although this guide primarily addresses the pyrophoricity of the metallic uranium component of the spent

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fuel, some of the general principles involved could also apply to zirconium alloy spent fuel cladding.

1.7 The interpretation of the test data depends on the characteristics of the sample tested and/or the usage to which the test results are put. For example, usage could include simple comparison of the relative ignition temperature of different sample configurations or as inputs to more complex computer simulations of spontaneous ignition. The type and the size of the SNF sample must be chosen carefully and accounted for in the usage of the data. The use of the data obtained by the testing described herein may require that samples be used which mimic the condition of the SNF at times far into the future, for example, the repository postcontainment period. This guide does not specifically address methods for 'aging' samples for this purpose. The section in Practice C1174 concerning the accelerated testing of waste package materials is recommended for guidance on this subject.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

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

C1431 Guide for Corrosion Testing of Aluminum-Based Spent Nuclear Fuel in Support of Repository Disposal

G86 Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments

2.2 *CFR Documents:*[4]

10CFR60, US Code of Federal Regulations Title 10, Part 60, Disposal of High Level Radioactive Wastes in a Geologic Repository

10CFR63, US Code of Federal Regulations Title 10, Part 63, Disposal of High Level Radioactive Wastes in Geologic Repositories at Yucca Mountain, Nevada

10CFR72, US Code of Federal Regulations Title 10, Part 72, Licensing Requirements for the Independent Storage of Spent Nuclear Fuel and High-Level Radioactive Waste

10CFR71, US Code of Federal Regulations Title 10, Part 71, Packaging and Transport of Radioactive Materials

40CFR191, US Code of Federal Regulations Title 40 Part 191, Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes

40CFR197, Code of Federal Regulations Title 40, Part 197. 2005 Protection of Environment: Public Health and Environmental Radiation Standards for Yucca Mountain, Nevada

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[3] 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.

[4] Available from Standardization Documents Order Desk, DODSSP, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, http://www.dodssp.daps.mil.

3. Terminology

3.1 *Definitions*—Terms used in this guide are as defined in Practice C1174 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 *attribute test, n*—a test conducted to provide material properties that are required as input to behavior models, but that are not themselves responses to the environment.

3.2.2 *characterization test, n*—in high-level radioactive waste management, any test conducted principally to furnish information for a mechanistic understanding of alteration.

3.2.3 *combustible, adj*—capable of burning or undergoing rapid chemical oxidation.

3.2.4 *design bases, n*—that information that identifies the specific functions to be performed by a structure, system, or component of a facility and the specific values or ranges of values chosen for controlling parameters as reference bounds for design (see 10CFR72).

3.2.5 *design basis event (DBE), n*—(*1*) those natural and human-induced events that are expected to occur one or more times before permanent closure of the geologic repository operations area (referred to as Category 1 events); and (*2*) other natural and man-induced events that have at least one chance in 10,000 of occuring before permanent closure of the geologic repository (referred to as Category 2 events) (see 10CFR60).

3.2.6 *ignite, v*—to cause to burn and reach a state of rapid oxidation, which is maintained without requiring an external heat source.

3.2.7 *interim storage facility, n*—a facility for the storage of spent nuclear fuel for 20 years or longer, and which meets the intent of the requirements of an independent spent fuel storage installation (ISFSI) or a monitored retrievable storage facility (MRS) as described in 10CFR72.

3.2.8 *performance assessment (PA), n*—an analysis that identifies the processes and events that might affect the disposal system; examines the effects of these processes and events on the performance of the disposal system; and, estimates the cumulative releases of radionuclides, considering the associated uncertainties, caused by all significant processes and events. These estimates shall be incorporated into an overall probability distribution of cumulative release to the extent practicable (see 40CFR191.12).

3.2.9 *pyrophoric, adj*—capable of igniting spontaneously under temperature, chemical, or physical/mechanical conditions specific to the storage, handling, or transportation environment.

3.2.10 *safety analysis, n*—in high-level radioactive waste management, an analysis whose purpose is to determine the risk to the public health and safety associated with the reception, handling, treatment, packaging, storage, retrieval, transportation, or disposal of spent fuel or high-level waste. (see also Guide C1431)

3.2.11 *service condition test, n*—a test of a material conducted under conditions in which the values of the independent

variables characterizing the service environment are in the range expected in actual service.

3.2.12 *sibling sample, n*—one of two or more test samples that are nearly indistinguishable with respect to their chemical and physical properties.

3.2.13 *spent nuclear fuel, n*—nuclear fuel that has been irradiated in, and removed from a nuclear reactor.

3.2.14 *waste form, n*—the radioactive waste materials and any encapsulating or stabilizing matrix (see 10CFR63.2).

3.2.15 *waste package, n*—the waste form and any containers, shielding, packing, and other absorbent materials immediately surrounding an individual waste container (see 10CFR63.2).

4. Significance and Use

4.1 Disposition of SNF will involve isolation from the accessible environment, placement in a safe and environmentally-sound extended interim storage facility (ISFSI or MRS), and preparation for final disposal in a geologic repository. Disposition will be further complicated in the case of metallic uranium-based SNF if it is damaged/corroded.

4.2 Metallic uranium-based SNF has some unique physical and chemical characteristics, which must be considered in the design, safety analysis, and performance assessment of the planned U.S. geologic repository, that is, those of a reactive metal in a corroded condition. The metallic uranium SNF could be pyrophoric, or combustible, and determination of these characteristics is necessary for the development of EBS design bases and the safety and performance assessment analyses associated with those designs. In particular, repository preclosure design basis event (DBE) analyses and post-containment performance assessment analyses could require pyrophoricity/combustibility data.

4.3 The U.S. Nuclear Regulatory Commission (NRC) has licensing authority over the transportation in the public domain, and the repository emplacement, or interim dry storage, or both, in an ISFSI or MRS, of spent nuclear fuel and high level radioactive waste under the requirements set forth in 10 CFR Parts 71, 60/63, and 72, respectively. These requirements specifically include the following limitations:

4.3.1 10CFR60.135 requires that the waste form be in a solid form and that the waste package be free from significant amounts of liquid, powder, or particulate matter and not contain explosive, pyrophoric, or chemically reactive materials in an amount that could compromise the ability of the underground facility to contribute to waste isolation or the ability of the geologic repository to satisfy the performance objectives. It also requires that all combustible radioactive wastes shall be reduced to a noncombustible form unless it can be demonstrated that a fire involving the waste packages containing combustibles will not compromise the integrity of other waste packages, adversely affect any structures, systems, or components important to safety, or compromise the ability of the underground facility to contribute to waste isolation. The pyrophoricity constraint concerns the systems level performance of the repository, that is, the capability of the under-

ground facility to meet performance requirements, whereas, the waste form combustibility constraint concerns EBS component performance, that is, the effect of waste form combustion on other individual waste packages. A combustible waste form thus does not necessarily mean a pyrophoric waste package. The repository system performance assessment, however, must demonstrate that the assumed combustion of combustible waste forms in their waste packages will not adversely affect other (noncombustible-containing) waste packages, and ignition either will not occur or, if it does occur, will not adversely affect overall repository performance.

4.3.2 Section 43 of Part 71 (packaging and transport) requires that a package must be made of materials and construction, which assure that there will be no significant chemical, galvanic, or other reaction among the packaging components, or between the packaging components and package contents, including possible reaction from inleakage of water to the maximum feasible extent.

4.3.3 Section 122 of Part 72 (interim storage) requires that components important to safety must be designed so that they can continue to perform their safety functions effectively under credible fire and explosion exposure conditions. Noncombustible and heat-resistant materials must be used whenever practical throughout the ISFSI or MRS.

4.4 The metallic uranium SNF characterization activities described in this guide apply to the assessment of such issues as geologic repository disposal waste form combustibility under normal repository (post-closure) environment conditions. They also address waste package pyrophoricity under preclosure DBE or off-normal conditions, interim storage off-normal event consequence analyses, and public domain transportation safety analyses.

4.5 Zirconium spent fuel cladding has also displayed pyrophoric behavior in the past. Pyrophoricity/ignition of zirconium has commonly been associated with cladding pieces and residues resulting from reprocessing operations. These cladding pieces and residues—left after the chemical dissolution of metallic uranium and/or uranium dioxide fuel element cores during fuel reprocessing or extraction of plutonium—have on occasion spontaneously ignited. Although it is generally believed that zirconium is not as intrinsically prone to pyrophoric behavior as uranium or plutonium [1] it has in the past spontaneously ignited after being sensitized by the chemical extraction of uranium, [2] as a result of an electrical spark or severe physical trauma, [3] or as the result of being wetted while fully exposed to air in a storage bin. [1] As with uranium metal, zirconium hydride inclusions form in the metal as a byproduct of corrosion and these hydride inclusions are believed to enhance the potential for pyrophoric behavior. Although this guide is focused on the pyrophoric behavior of the uranium in metallic uranium spent fuel, some of the general principles involved could also apply to zirconium spent fuel cladding.

5. Information Needs Related to Pyrophoricity for Interim Storage, Transport, and Disposal

5.1 SSNF characterization and/or accelerated testing should focus on those information needs most pertinent to the SNF

form and disposition pathway chosen. The disposal pathway could include continued wet storage in the reactor spent fuel pool,, interim dry storage (per 10CFR72, receipt (per 40CFR197) and emplacement (per 10 CFR60 and 10CFR63) in a geologic repository, and the transport (per 10CFR71) involved in these steps. This guide addresses certain information needs pertinent to the emplacement of metallic uranium-based SNF in an MRS/ISFSI, or geologic repository, or both, such as its pyrophoricity, and combustibility. Other characteristics of the SNF, such as oxidation kinetics, hydrogen/water content, geometric, or specific surface area of exposed uranium metal, uranium hydride content, and microstructural characteristics can affect these parameters. These information needs are addressed through tests whose environmental conditions represent those of the metallic SNF in the transport, storage, or disposal environment and which conform to the testing, data usage, and modeling logic of Practice C1174.

5.2 Information needs related to pyrophoricity/combustibility addressed by characterization, or service condition tests, or both, in accordance with Practice C1174. There are restrictions on the pyrophoricity of the waste package system and combustibility of the SNF within the interim storage container/cask (10CFR72.122). The potential for pyrophoric behavior must also be accounted for in meeting the performance objectives of (10CFR63.111, .112, .113). Metallic uranium particles, both unirradiated and irradiated, have in the past displayed pyrophoric behavior upon exposure to air in storage containers, ranging from smoldering to active burning with a flame. Ignition has been initiated thermally and by mechanical trauma, friction, sparks, or a combination thereof. Knowledge of the propensity towards pyrophoric behavior of the metallic uranium SNF, either as particles, in pieces, or in bulk, is therefore essential for waste package design, the evaluation of design basis air ingress events, and decisions concerning treatment of exposed uranium surfaces prior to interim storage or repository disposition, or a combination thereof.

5.2.1 *Ignition Temperature/Conditions*—The environmental conditions under which uranium metal SNF surfaces could ignite spontaneously can be inferred from carefully controlled and characterized ignition tests. Uranium metal and uranium metal SNF can be made to spontaneously ignite under mechanically quiescent conditions by external heating or by self-heating due to oxidation, and under conditions of mechanical trauma by the action of friction, sparks, or physical impact. Ignition testing can provide controlled thermal, oxidant exposure, and configuration conditions, and thus, can support analyses of the propensity of a given SNF condition toward pyrophoric behavior.

5.2.2 *Oxidation Kinetics*—The rate of oxidation of uranium in dry air, humid air, and oxygen-free water vapor may be enhanced by the extent to which the uraniummetal has corroded or undergone irradiation swelling, or both,. The degree of enhancement may vary with the nature of the damage and is not readily predictable for any particular fuel element. The rate of oxidation in oxygen-containing environments is an important factor in providing reaction heat input for waste container thermal analyses. The extent of corrosion also is important in

determining the condition of the SNF as it evolves, or 'ages', in the container in the interim storage, or repository environments, or both. Aging can result from long term reactions between the SNF and any oxygen or water not removed from the SNF or the storage container prior to emplacement.

5.3 Information needs related to pyrophoricity/combustibility addressed by attribute tests in accordance with Practice C1174.

5.3.1 *Hydrogen/Water Content*—Knowledge of the amount of hydrogen, or water, or both, included or trapped in the metallic uranium-based SNF is needed to evaluate both the criticality aspects of emplacement and the potential for further corrosion reactions during storage.

5.3.2 *Surface Area*—The surface area of exposed irradiated uranium metal is needed to evaluate the amount of material available to react with the oxidizing environment and the consequent heat generated by the reactions. The surface area to which the measured oxidation rate is to be normalized may be taken as the geometric surface area or the effective surface area for oxidation, but in either case, must be identified clearly.

5.3.3 *Uranium Hydride Content*—The amount and distribution (particulate size, location, etc.) of uranium hydride, which could act as an oxidation reaction initiator or accelerator should be characterized to interpret the results of oxidation, or ignition tests, or both (4).[5]

5.3.4 *Microstructure and Morphology*—Knowledge of the microstructure, chemical phases, such as uranium hydride distribution, and porosity of the surface SNF material exposed to the oxidizing environment would help in interpreting measured ignition temperatures and oxidation rates.

5.4 Alternative SNF disposition pathway development, such as processing or wet storage, could also involve these information needs. Various kinds of ignition, or oxidation tests, or both, could support the resolution of issues related to an alternative pathway if that pathway included at any point the exposure of metallic uranium SNF to oxidizing environments.

6. Sample Selection, Precharacterization, and Preconditioning Requirements

6.1 Documentation of the testing to be performed and justification of the testing should be provided in a test plan. The criteria used for sample selection, SNF sample type, size, and manner of emplacement within the test apparatus also should be documented.

6.2 The test plan should describe any pre- and post-test characterization of samples required to adequately interpret the data. Since the interpretation of ignition test data in particular will be sensitive to the chemical nature and microscopic characteristics of the test samples as well as their configuration in the test apparatus, as much information as possible concerning these characteristics should be determined. Examples of such characterization (5) could be the exposed uranium metal surface area of the sample, sample shape and weight, condition

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

of exposed uranium surfaces, for example, corrosion product coverage, roughness, condition of cladding, degree of irradiation swelling, etc. Destructive chemical, or metallographic examinations, or both, of sibling samples to those tested may be required to obtain adequate precharacterization of these parameters. If practical, pre- and post-test visual, imaging, or other characterization records should be provided. If the sample is obtained by sectioning or otherwise extracting from a larger spent fuel element, its location within the element, sectioning requirements should be recorded (**6**). Sectioning of the uranium for the purpose of preparing test samples must be done in an inert atmosphere and the manner of sectioning, (for example, sawing, fracturing), should be described.

6.3 If detailed information concerning the microstructure of the sample is judged to be necessary for the proper interpretation of the test data, siblings of the test sample from the same area of the fuel element should be taken by the same sectioning/extraction method and retained for detailed metallographic, or chemical analysis, or both. Examples of such requirements might be the determination (**7**) of the amount and type of uranium hydride particulates, or inclusions, or both, (**4**) under the corrosion product on the exposed uranium metal surfaces or the degree of surface roughness of the uranium surface exposed to the test environment. Note that the irradiated uranium metal SNF may have highly localized zones of internal stresses, damage, or differences in microstructure that might lead to variability in the test results; therefore, several samples may be required from the same area of the fuel element.

6.4 The results of ignition and oxidation tests could depend on (among many other factors) the size and geometry of the test sample (**5**). For example, very small samples with high specific areas could ignite at lower temperatures than a sample of the same SNF with similar characteristics but also with lower specific area. In view of this, the interpretation of the test data should take into account for sample size and the degree to which the samples tested reflect the condition of the SNF in its storage configuration.

6.5 In order to evaluate the oxidation or combustibility characteristics of uranium metal SNF in its expected condition after extended wet or dry storage, it may be desirable to condition or "age" samples (see Practice C1174). The purpose of such conditioning would be to create a sample condition that as near as practical, mimics the actual condition of the spent fuel either during or after the storage period, or both, and prior to receipt at the repository. Conclusions concerning the extent to which the conditioning process actually simulates "aged" SNF, and decisions concerning the required extent of conditioning, will of necessity be qualitative and dependent upon expert judgement. An example of such conditioning might be to expose samples to a warm anoxic water vapor atmosphere for a period of time to simulate the long-term effects of corrosion, for example, formation of uranium hydride inclusions, on the sample surface.

7. Test Descriptions

7.1 Testing and analysis required to support the interim dry storage and repository disposal of metallic uranium-based spent nuclear fuels would include ignition testing (thermal ignition and spark/mechanical impact ignition tests), and oxidation kinetics testing. They also could include testing/measurement of SNF parameters, to which oxidation and ignition could be sensitive, such as moisture and uranium hydride content. Test methods could include, but may not be limited to, the following:

7.2 *Characterization and Service Condition Tests (see Practice C1174):*

7.2.1 *Ignition Testing*—Ignition potential tests and analyses would provide data related to the combustibility of the SNF in the moist air environment of the geologic repository, and the pyrophoricity of the SNF under potential accident of unanticipated event conditions. These could include static thermal ignition, spark source, or mechanical impact ignition tests.

7.2.1.1 *Thermal Ignition Tests*—Thermal ignition testing involves heating samples of the SNF in a furnace. Two basic methods can be used to obtain an ignition temperature: the sample can either be heated at a controlled rate (for example, burning curve test) or kept at a controlled temperature (for example, isothermal test). The atmosphere of the furnace should be typical of potential repository mixed water/air environments. Sample size must be compatible with the test apparatus. For small test furnaces samples would be commonly in the size range of a few grams or dimensions of several millimeters. Precharacterization of samples should include visual, or photographic records, or both, measurement of the geometric surface area of exposed uranium metal surfaces, and weight and dimensions. Since the heat dissipation characteristics of the sample in the test will influence the test result, the physical/geometric configuration of the test should be described in as much detail as possible and must be held constant during the test as much as practical. If multiple test samples from a single population (referred to as siblings) are available, metallographic examinations, or quantitative chemical analyses, or both, could be helpful in interpreting the test data. Such analyses could reveal microstructural aspects of the sample, which affect ignition such as the amount and location of uranium hydride inclusions, porosity, corrosion products, microcracking, and possible changes in these parameters during the test.

7.2.1.2 *Burning Curve Ignition*—In this method (**8,9,10**) for thermal ignition testing the sample is placed in a closed furnace and the temperature of the furnace raised at a controlled rate, commonly 5 to 50 K/min. A more detailed example protocol for a burning curve ignition test is given in Appendix X1. Both the furnace temperature and the sample temperature are monitored, usually by attached thermocouples. Thermocouple contact with the metal samples must be maintained during the test. As the sample is heated in the controlled (oxidizing) atmosphere the thermocouple traces are recorded. Self-supporting oxidation is indicated when the sample temperature trace shows thermal runaway as indicated in footnote (**8**). Ignition is indicated when the sample temperature increases much more rapidly than the furnace temperature. The ignition temperature is defined as the intersection of the sample temperature curves prior to and after self-sustained oxidation.

7.2.1.3 Since the furnace temperature in this type of ignition test is constantly increasing, the ignition temperature obtained must be interpreted in terms of a nonsteady state thermal analysis formulation (**8**). A disadvantage of this method is that the ignition temperature obtained cannot be directly equated to the true ignition temperature for the material in a different configuration than that of that tested. That is, it is very configuration dependent. Advantages of the method include that the ignition temperature obtained for sibling samples are relatively reproducible and that the test configuration is amenable to the benchmarking of more sophisticated nonsteady-state thermal analyses, for example, computer codes, used to analyze actual storage or disposal systems.

7.2.1.4 *Isothermal Ignition*—In this method (**11**) of thermal ignition testing, the sample is heated in a closed furnace to a preset temperature in an inert gas (typically argon) atmosphere. When the desired furnace temperature is reached, the predetermined oxidizing atmosphere is introduced to the furnace. The temperatures of the sample and furnace are monitored with thermocouples for a predetermined period of time. Ignition is indicated if and when the sample temperature increases rapidly and maintains a temperature well in excess of the furnace temperature. In this type of test, ignition may occur after some period of incubation in the furnace. The ignition temperature is defined as the lowest preset furnace temperature at which ignition occurs.

7.2.1.5 Since the furnace temperature is held constant in this type of ignition test, the system is isothermal and the ignition temperature is taken as the lowest furnace temperature that leads to thermal runaway of the sample. Some advantages of this method are that the ignition temperature is directly determined as the lowest preset furnace temperature which results in ignition, and the time after introduction of the oxidizing atmosphere can be used to determine the total heat deposition required for ignition. Potential disadvantages of this method are that experience has shown that nominally sibling samples can give ignition temperatures, which vary by as much as 100K. Several tests may be required before the minimum furnace temperature for ignition can be determined, and since several tests may be required to obtain ignition, a large number of samples (including siblings) may be required (**12**).

7.2.2 *Thermogravimetric Analyzer (TGA) Ignition*—The basic types of burning curve ignition and isothermal ignition testing described above also can be performed using a TGA-type apparatus instead of a furnace (**11**). This apparatus can be operated essentially the same as the furnace above, but also has the further advantage of continuously monitoring the weight gain of the sample up to the point of ignition. After ignition the potential relocation of particles resulting from the sample burning makes the weight measurement problematical. In an isothermal test this weight gain due to oxidation, that is, the reaction rate at the fixed furnace temperature, and the enthalpy of the oxidation reaction can be used along with the ignition temperature to calculate the heat generation rate in the sample required to cause ignition. In a burning curve ignition test, the weight gain trace can be used to obtain the kinetic oxidation rates at the self-sustaining oxidation temperature just prior to

ignition. In either case the data could be used in the development or benchmarking of ignition prediction algorithms (**13**) or computer codes.

7.2.2.1 A potential disadvantage in using a TGA-type apparatus for ignition testing is that ignition generally could involve the generation, entrainment in the gas stream, and transport of combustion product fine particulates in the equipment. This negates the usefulness of the weight gain/loss data after ignition, and also can require extensive decontamination/cleanup efforts on the sensitive equipment between test runs.

7.2.3 *Spark Ignition*—Spark ignition testing (**3**) consists of directing a spark generated by a tesla coil, DC arc, or other appropriate spark source on a sample of the SNF in an enclosed container with a controlled atmosphere and temperature. The sample is observed visually for evidence of ignition, such as smoldering, glowing, flames, or flashes of light. The size, shape, and physical condition of the sample should be characterized in detail. The total energy deposited in the sample by the spark also should be characterized (**14**). Test temperatures should start in the lower range of anticipated repository waste package temperature. The lowest test temperature at which the sample ignites and maintains a self-sustained burn then could be regarded as the ignition temperature under mechanical friction or impact waste package accident conditions.

7.2.4 *Mechanical Impact Ignition*—Mechanical impact tests (see Test Method G86) would be designed to expose spent fuel samples to a controlled mechanical impact in the presence of air. Testing could consist of a drop of an SNF sample on a flat, hard surface from a set height, or a controlled energy impact on the sample by a hard pointed impacter. The size, shape, and physical condition of the sample, along with the shape and configuration of the impacter, should be characterized in detail. The total energy deposited in the sample by the mechanical impacter also should be characterized. The tests would be performed on samples under controlled atmosphere and temperature. Any ignition would be observed and interpreted visually in the same way as the spark source test data.

7.3 *Oxidation Kinetics*—Oxidation kinetics tests would be used to measure the rate of oxidation of the exposed uranium metal surfaces in the SNF. The rate of oxidation then would be used with the known heat of reaction to provide heat input data for the calculation of waste form/package temperature rise due to the oxidation of the fuel when it is exposed to water saturated air. This information is necessary to predict waste package heating due to chemical energy input, and thus, the proximity of the SNF to ignition under air exposure scenarios. Examples of test methods that could be used to investigate oxidation kinetics include the following:

7.3.1 *Thermogravimetric Analysis-Mass Spectrographic (TGA/MS) Testing* (**15**)—The SNF sample is enclosed in a chamber and heated under repository relevant conditions. The weight change would be continuously recorded. The change due to the loss of water and volatile products would be monitored by the MS system, which identifies species in the off-gas system of the TGA and measures their quantity. This weight change due to volatilization of water, etc. would be combined with the overall weight change to obtain the oxygen weight gain of the sample, and thus, its rate of oxidation during

the test. The weight gain then can be analytically converted to a measure of the thermal input to the system.

7.3.1.1 This type of test has the advantage of being capable of generating a significant amount of temperature-related oxidation rate data in a short period of time for generating oxidation rate models. It is, however, a procedure that would require close surveillance, for example, instrument stability, for the duration of the test.

7.3.2 *Isothermal Furnace Oxidation Testing (9,16)*—In one way of performing this type of test the SNF sample is heated in a sealed furnace at a constant temperature in the oxidizing atmosphere for a given time. During heating the consumption of oxygen is measured and recorded as a change in pressure in the furnace. The change in pressure can be converted algebraically by the ideal gas law to an amount of oxygen consumed as a function of time, and thus, the rate of oxidation of the sample. After the test the sample may be weighed/examined for amount of corrosion product produced to verify the total extent of sample oxidation. Portions of the sample may be examined by X-ray diffraction or other means to determine the stoichiometry of the resulting uranium oxide.

7.3.2.1 This method of oxidation rate testing has the disadvantage of requiring several tests of significant duration at each environmental condition and at different temperatures to provide enough data to generate an oxidation rate model. This type of test, if desired, could run for relatively long times without interference. It has the advantage of being able to indicate changes in the mechanism of oxidation as oxidation products buildup during the test.

7.3.3 *Oxidation Reaction Energetics Testing*—Differential scanning calorimetry could help in estimating the hydride, oxide, and metallic uranium components of the sample and the heat of oxidation of the material. This data would enable calculation of the chemical thermal heat input under air exposure conditions in waste package performance analyses.

7.4 *Attribute Tests per Practice C1174:*

7.4.1 *Hydrogen/Water Content*—These tests would measure the total quantity of hydrogen, or water, or both, in the SNF at any point in the disposal cycle, and the amount of hydrogen/water evolved from the SNF as a function of time, temperature, and process atmosphere. These tests could involve heating the samples to above 1100 K. Examples of methods that could be used include the following:

7.4.1.1 *Thermogravimetric Analysis/Mass Spectrometry (TGA/MS)*—Representative samples of the SNF are enclosed in a chamber and heated in an inert atmosphere until all the hydrogen or water in the sample is driven off. The weight of the sample is recorded continuously and the gas evolved (off-gas) during heating is channeled into a mass spectrometer or gas chromatograph to measure the amount of each chemical species evolved from the sample.

7.4.2 *Furnace Drying Tests*—Samples are dried in air and the water in the off-gas measured, for example, by a LECO-type or capacitance probe-type moisture analyzer. The samples would be weighed before and after drying or oxidation.

7.5 *Metallographic Examinations (7,17)*—Polishing and etching techniques could be used on sectioned samples of the SNF to reveal microstructural features and highlight uranium hydride and other inclusions in the uranium metal matrix. Uranium hydride inclusions generally are identified after mechanical polishing, heat tinting, and acid etching as needles/stringers (light brown or silver under bright field light or gray under polarized light) in the uranium matrix. This technique enables an estimate of the quantity of uranium hydride within the uranium metal fuel matrix, as well as, a determination of the location of hydride concentrations, for example, near the corrosion layer, underneath cladding, etc.

7.6 *Exposed Uranium Metal Surface Area Measurements*—The surface area of the SNF samples to which the oxidation reaction rate is to be normalized may be taken either as the geometric surface area or the effective uranium metal surface area available for oxidation. The type of surface area, geometric or effective, and its method of determination, should be identified clearly. Geometric surface area generally is determined through sample dimensional measurements. Effective surface area may be determined by such techniques as BET analysis, laser profilometry (roughness), optical image analysis, etc.

8. Test Data Usage

8.1 Data obtained from ignition tests may be used either qualitatively or quantitatively. A logic diagram indicating one potential usage of oxidation and ignition test data for the analysis of pyrophoric behavior is shown in Fig. 1. This diagram shows how qualitative ignition test data can be used for comparisons of the relative pyrophoric behavior of different materials and how quantitative oxidation and ignition test data can be used for calculational code/algorithm benchmarking. The ignition test data also may be used to verify that the oxidation rate models used in pyrophoricity analyses is conservative.

8.1.1 The calculational algorithms which the data support can be used to determine if the SNF is pyrophoric in its storage environment and configuration. The results of the pyrophoricity testing could provide part of the technical basis for judging the acceptability or unacceptability of the SNF with respect to repository acceptance criteria; however, the extrapolation of ignition experiments on small SNF samples to assess the behavior of large SNF-containing packages should be done with caution. The oxidation of uranium is exothermic, providing heat at the reacting surface. This heat can in turn, if not dissipated, further accelerate the oxidation reaction. Ignition generally occurs when the heat of the oxidation reaction on the exposed uranium surfaces cannot be dissipated quickly enough to prevent the reaction from becoming self-sustaining. The oxidation—and consequent heat generation rates—of the uranium can be enhanced through one or a combination of several possible factors, such as, *(1)* the provision of heat from an outside source raising the temperature and thus increasing the oxidation rate; *(2)* the further exposure of uranium surface area and consequent effective quantity of metal available for reaction; *(3)* the sudden removal, for example, spallation, of protective surface oxide layers exposing previously unreacted metal; and, the presence of chemical species or phases, such as uranium hydrides.
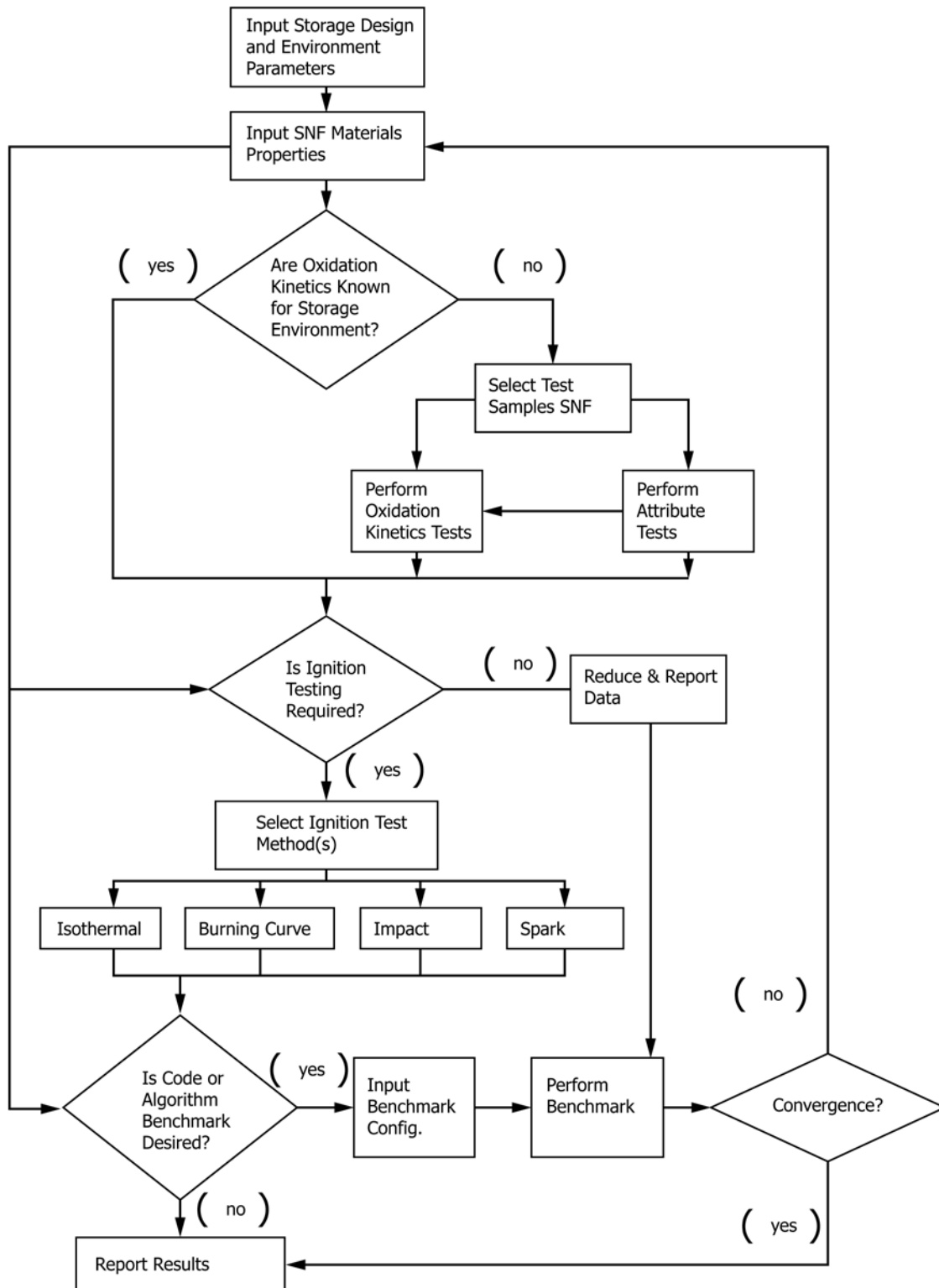
FIG. 1 Logic Diagram for a Potential Usage of Pyrophoricity-Related U-Metal Test Results

8.1.1.1 Caution, therefore, should be used in directly extrapolating the ignition temperature obtained from an ignition test to more complex spent fuel storage configurations. In some cases, the ignition test results only may be qualitatively interpreted, but may nevertheless provide an understanding of why certain materials or configurations are more likely to ignite than others.

8.2 An example of qualitative use of the data would be the comparison of the static thermal ignition results for the SNF samples with static ignition results in the literature for similar experimental configurations on similar metals, such as unirradiated or uncorroded uranium metal, or both. For example, a direct comparison of the test data for the thermal ignition temperature of metallic uranium SNF samples with literature data for similarly sized and configured unirradiated uranium could indicate the relative propensity toward pyrophoric behavior of these materials. Such a comparison could be helpful in designing and evaluating SNF handling methods and systems by giving an initial indication of the potential pyrophoricity of the material.

8.3 An example of quantitative use of the data would be the benchmarking (13) of waste package thermal analysis algorithms, or computer codes, or both, to the experimental configuration as a method of code validation. The environmental and geometric parameters of the ignition test, such as size of sample, gas flow rate, exposed uranium surface area, temperature ramp rate, etc., would be input into the code/algorithm along with the assumed oxidation kinetics behavior. The ignition temperature of the sample then is calculated by the algorithm. The predicted ignition temperature then would be compared with the experimentally measured value. In this way, code input assumptions, such as uranium oxidation rates or effective exposed oxidizing surface area, would be verified if the test and calculated values are similar. If dissimilar, the input assumptions could be modified to enable the code to reproduce the observed ignition temperature. The code validation could be further aided by using the results of the oxidation tests to provide oxidation rates and consequent chemical oxidation heat inputs into the code evaluation.

8.4 Thermal ignition test data could be used to evaluate whether the SNF waste package is pyrophoric with respect to the performance objectives of 10CFR63.111 and the integrated safety analysis (10CFR63.112) of the repository operations area. This could be done by comparing the experimental temperature at which the SNF ignites in humid or dry air with credible temperature estimates for the expected post-containment period repository environment. If, within a prescribed safety margin, the ignition temperature obtained from the static ignition tests is lower than the credible temperature of the SNF in the repository, then the SNF would be considered to be pyrophoric under mechanically quiescent conditions. Impact or spark ignition test data could be used to evaluate whether the waste package is pyrophoric under potential postclosure conditions of mechanical trauma or disturbance.

8.5 If the design basis for the repository containment period involves allowances for breached waste packages under off-normal or design basis event (DBE) conditions, the thermal ignition test and impact/spark ignition test data could be used to evaluate whether the SNF waste package is pyrophoric with respect to the safety analysis requirements of 10CFR60.111 and .112. SNF ignition under mechanical impact or sparking considered credible under the expected waste package DBE scenario limits would indicate the material to be pyrophoric.

8.6 Ignition test data would be used to evaluate whether the SNF waste package is pyrophoric with respect to the requirements of 10CFR63.112 and 10CFR63.135 by comparing the static ignition temperature data, or the temperature at which a spark or physical impact induces ignition, or both, to bounding temperature estimates for the SNF in the waste package during post-containment air exposure circumstances. Air and moisture exposure would be the expected condition of the waste package during the post-containment period of the repository. If either the static ignition temperature or the spark ignition temperature is, within a prescribed safety margin, below the expected bounding temperature, then the SNF would be regarded as pyrophoric.

8.7 Oxidation kinetics data would be used in waste package thermal analyses to determine the self-heating of the SNF due to chemical reaction upon exposure to the ambient air of the repository environment, or the unsaturated air in an off-normal event in the MRS/ISFSI environment. This data also could be used to predict the extent of SNF degradation while in the storage environment. The data would thus support thermal analyses of the waste package and waste form condition predictions in MRS/ISFSI or repository emplacement.

9. Keywords

9.1 combustion; ignition; pyrophoricity; spent nuclear fuel; spontaneous ignition; uranium metal; uranium metal oxidation; zirconium pyrophricity; zirconium oxidation

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE PROTOCOL FOR BURNING CURVE IGNITION TESTING

X1.1 Purpose

X1.1.1 The purpose of this example protocol is to describe a possible configuration for ignition testing of metallic uranium-based spent nuclear fuel (SNF) specimens in a controlled temperature and atmosphere. This is not a detailed procedure for performing the testing. The spent nuclear fuel samples would be obtained by sectioning from larger fuel elements under inert conditions to preserve as much as possible the as-received characteristics of the SNF. The test specimens used in this example procedure could range from approximately 10 to 50 g. The basic components of the test system would be a clean dry air source with a maximum flow capability of 1000 cc/min, a water bubbler with controlled temperature up to 373 K, a thermocoupled furnace tube, sample holder, and sample inside a clamshell furnace, and a gas chromatograph/hydrogen analyzer, all connected through a sealed gas train. A dedicated test equipment control and data acquisition computer could be part of the system.

X1.2 Sample and Furnace Preparation

X1.2.1 Characterize the sample by taking several photographs at various orientations, measuring dimensions, and weighing them before loading in the furnace. If sibling samples are to be taken for attribute testing also take photographs and weights, describe the location of the fuel elements from which they were sectioned, and identify the test samples to which they are sibling. Store the siblings in inerted containers.

X1.2.2 Place sample holder containing the sample into the furnace in the resistively heated furnace located in a hotcell.

X1.2.3 Verify that the furnace tube inlet gas line is connected to the dry air supply through the water bubbler.

X1.2.4 Ensure the air flow controller is installed and that it and the appropriate channel of the data acquisition system on the computer are both connected to a data recorder.

X1.2.5 Verify that the data acquisition system is properly calibrated for the flow controller. Check by setting the flow controller to 50 % and ensuring that the appropriate channel on the computer reads approximately 500 cc/min. Hold the dry air flow at 500 cc/min with the furnace at 300 K. Heat the bubbler to its preset temperature and reconfigure the air line to flow for at least 10 minutes through the bubbler.

X1.2.6 Mount the specimen in the sample holder such that the sample is in the center of the heated zone when loaded into the furnace. Ensure that the sample is in contact with the specimen thermocouple. Record the method used to ensure thermocouple contact.

X1.2.7 Carefully load the sample holder into the furnace tube, and assemble the rest of the system (the air supply components and the effluent gas analytical components).

X1.2.8 Check for system leakage by pressurizing it and monitoring the pressure.

X1.2.9 Set data acquisition system to record temperature and gas outlet data.

X1.3 Perform Ignition Test

X1.3.1 The sample will be heated to the point of ignition in an atmosphere of flowing air saturated at 300K, and then, quenched by purging the system with high purity argon. The sample temperature will be recorded via an attached thermocouple, and the gas flow rate monitored by the gas controller. The moisture content of the off-gas will be detected by a moisture analyzer. Hydrogen in the off gas stream will be monitored by a gas chromatograph.

X1.3.1.1 Open the dry air supply valve and establish a dry air flow rate of 500 cc/min into the bubbler.

X1.3.1.2 Activate the heating tapes and maintain at 100°C during the testing.

X1.3.1.3 Set the over-temperature protection to an indicated temperature of 50°C above maximum furnace set-point.

X1.3.1.4 Heatup furnace at rate of 5°C/min until ignition of the sample is indicated or a maximum sample temperature of 973 K is reached. If 973 K is reached without indicating sample ignition hold for 15 minutes before allowing the furnace to cool to ambient temperature.

X1.3.1.5 After the specimen temperature exceeds 423 K and until the furnace tube has been purged with argon after the test, closely monitor the furnace and sample thermocouple readings.

X1.3.1.6 If and when the sample thermocouple reading rapidly increases over the furnace thermocouple reading, switch the gas supply from saturated air to high purity argon at a flow of 1000 cc/min to quench the reaction. Turn off the furnace heaters and allow the furnace to cool to 373 K. Reduce the argon flow to 100 cc/min.

X1.3.1.7 If and when the sample thermocouple reading increases slowly over the furnace thermocouple reading, allow the furnace temperature to increase to 973 K. After the sample has reached 973 K, hold at this temperature for 10 minutes, then turn off the furnace heaters and switch the gas supply from saturated air to argon at a flow rate of about 500 cc/min. Allow the furnace to cool to 373 K and reduce the argon flow to 20 to 200 cc/min.

X1.3.1.8 Allow the furnace to cool to ambient.

X1.3.1.9 Open the furnace and carefully remove the sample.

X1.3.1.10 Visually inspect the specimen and take photographs. If possible, identify the location on the specimen at which ignition initiated.

X1.3.1.11 Weigh the specimen and compare with the initial weight. Qualitatively identify the amount and visual characteristics of any particulate matter generated from the sample during the test.

X1.4 Interpret Data

X1.4.1 The method for using the temperature trace from the burning curve test to generate an ignition temperature is explained in Ref (**8**), and basically consists of drawing tangents to the pre- and post-ignition temperature traces and taking the temperature ordinate of their intersection point as the ignition temperature. This tangent generation could be done by approximation, for example, visually, or by detailed statistical treatment, such as linear-least-squares fitting, of the pre- and post-ignition temperature traces or data points. The method of fitting the tangents should be described in the data reporting and the precision of the ignition temperature determination estimated.

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