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Nuclear energy — Standard method for testing the long-term alpha irradiation stability of matrices for solidification of high-level radioactive waste

Énergie nucléaire — Méthode d'essai normalisée de la stabilité à long terme à l'irradiation alpha des matrices de confinement des déchets radioactifs de haute activité

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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ISO 6962 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 6962:1982), which has been technically revised.

Introduction

It is generally agreed that a solid is the best form in which to store or dispose of highly radioactive waste (High Level Waste: HLW) from the first stage of a nuclear fuel reprocessing plant. This solid will usually be in the form of blocks having the mass of several hundred kilograms, cast or formed in a steel container. The solid will receive a large dose of radiation or every kind and it is important that this radiation should not significantly alter the properties of the solid for very long periods of time. Thus, proposed compositions must be tested to ensure their radiation stability.

Although the β-decays of the fission products will far out-number the α-decays of the incorporated actinides, most of the energy of the β particles (electrons) is dissipated by ionization of the atoms in their path and this will only have a transient effect. On the other hand, almost all the atom displacements in the solid will be caused by the α-decays, with the recoiling actinide nuclei being responsible for the great majority of these. Alpha-decays generates helium and helium atoms are a foreign body in solids. During long-term storage, helium pressure within the solids is built up to some atmospheres. Thus, it is the stability of the solid to α-decays that must be tested.

Nuclear energy — Standard method for testing the long-term alpha irradiation stability of matrices for solidification of high-level radioactive waste

1 Scope

This International Standard specifies a method designed to check the long-term stability of a solid to alpha disintegration by detection of all modifications in the properties of an irradiated sample.

The material favoured hitherto is a borosilicate glass, but possible alternatives include:

— ceramics or glass-ceramics,

— other glass compositions.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16797, *Nuclear energy — Soxhlet-mode chemical durability test — Application to vitrified matrixes for high-level radioactive waste*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
radioactive waste
any residue containing radioactive materials not currently considered useful or economically recoverable

3.2
package
waste package
product of conditioning that includes the waste form as well as any container(s) and internal barriers (e.g. shielding materials and liner), as prepared in accordance with requirements for handling, transportation, storage and/or disposal

3.3
waste form
waste in its physical and chemical form after treatment or conditioning prior to packaging and which is a component of the waste package

3.4
container
outer shell of a waste package

3.5
matrix
waste matrix
part of the waste form inside a waste package in which the radioactive substances are dispersed

4 Principle

Because most of the atom displacements are caused by the recoiling actinide nuclei, external radiation with α-particles is not considered a satisfactory simulation. A satisfactory simulation however is as follows: a sample of the candidate solid is made up in a realistic manner using the proper concentrations of the fission-product elements, although these can and, for convenience, usually will be the non-active nuclides. This sample is "doped" with a short half-life α-emitter so that it will receive the same number of α-decays per gram in few years as the actual storage medium will receive over a much longer time.

NOTE The difference of dose rate between real waste form and doped form includes the obligation to study this aspect.

The important properties of the sample can then be examined for changes.

It should be noted that it is the detection of any changes in sample properties with radiation that is important. The Soxhlet leach test, as described in ISO 16797, will adequately detect any significant changes and so is satisfactory in this context, although it has only limited environmental significance.

5 Test Method

5.1 Calculation of the necessary dose

The concentration of the actinides in the particular discharged fuel can be calculated using a computer program. The amount of these actinides that is or will be incorporated in the high-level waste stream of the reprocessing plant must then be ascertained. If this information is not available, it should be assumed that all the americium and curium and 0,5 % to 1 % of the plutonium left in the waste stream makes a significant contribution to the integrated radiation dose to the solid only after thousands of years. The age of the solid that is to be simulated must then be decided. It is recommended that this should be at least several thousand years (between 1 000 and 10 000 years, for instance). At short times, ^{238}Pu, ^{244}Cm and ^{241}Am are the most important nuclides. At long times, ^{239}Pu and ^{240}Pu contribute to the dose.

5.2 Choice of nuclide to use

Short half-lived alpha emitters, principally ^{238}Pu, ^{241}Am, ^{242}Cm and ^{244}Cm, should be used to dope the simulated waste form. The one chosen will often depend on availability, but the following criteria must be considered:

a) ^{238}Pu is the easiest short-lived nuclide to handle.

b) The half-lives are

   — ^{238}Pu 87,7 years,

   — ^{241}Am 433 years,

   — ^{242}Cm 163 days,

   — ^{244}Cm 18,1 years.

   Therefore, more Am and Pu must be added for a given dose-rate than when curium is used.

c) Plutonium oxide is not very soluble in some complex matrixes; thus, the preparation of a sample might lead to undissolved plutonium oxide, and the actinides will partition unequally in different phases of the sample. Autoradiography and microscopic examination on a sample cut from the interior of the specimen should be used to check that there is no gross segregation.

Once the required dose is decided, the concentration of the chosen nuclide needed to produce it in a reasonable time can be determined. Again, this must be calculated in each case, since the isotopic purity of the actinide available will vary.

6 Sample composition

The composition of the test samples shall be as near as possible to that used in the industrial process. In order to make the minimum alteration to the solids chemistry, curium shall be added to the simulated waste instead of a) other actinides, and b) the rare earth elements, on an atom for atom basis. Similarly, ^{238}Pu shall replace cerium or uranium first and then, if necessary, some of the rare earth elements. Undoped samples shall also be prepared for comparison purposes.

7 Sample preparation

The sample preparation can be checked by, for example, auto-radiography and microscopic examination. It is essential to verify the uniform distribution of the alpha-dopant in the material. Also, for non-vitreous material, the distribution of actinides in the crystal phases must be known and the dopant must distribute in the same way. Otherwise, a realistic picture of damage may not be obtained. This is true because alpha particles (which cause ionization) can penetrate into phases adjacent to the one in which the decay takes place. Recoil nuclei, which cause atomic displacements, travel very short distances (approximately 100 Å) and only result in damage to the phases in which the decay takes place.

8 Measurements before storage

The following measurements should be made on both doped and undoped samples as soon as possible after the specimens have been prepared:

a) initial leach rate,

b) density,

c) optical and microscopic examination of a sample,

d) X-ray diffraction examination,

e) heat emission,

f) mechanical properties (optional).

The techniques to be used are listed in Clause 10.

9 Storage

The specimens shall be stored at room temperature for the predetermined period; this will often be a year or more. The storage shall be in dry air or in an inert atmosphere such as argon. Optionally, a second set of specimens may be stored at some appropriate elevated temperature.

NOTE If waste that has been cooled for several years is to be solidified in large-diameter cylinders, then the cooling rate of the solid near the centre of the cylinder will be very slow and holding a sample at some elevated temperature may be appropriate. It seems likely, however, that most of the effects of radiation will decrease with increasing temperature, so that storing samples at the minimum temperature to be experienced by the solid is the crucial consideration.

10 Measurements during and after storage

10.1 General

The most important properties of a solid relative to its storage or solidified high-level radioactive waste forms are initial leach-rate, density, stored energy and structural integrity. In some instances, the release of helium may be important.

In the present context, it is most important to detect changes due to radiation and, consequently, the same procedure must be followed before, during and after the storage period and on both the doped and undoped samples. For each property studied, the number of measurements must be sufficient to describe correctly their evolution according to the integrated dose.

10.2 Initial leach rate

An International Standard leach test (e.g. in ISO 16797) shall be carried out for both doped and undoped samples before and after storage period and the results.

10.3 Density

Either an Archimedes' or a flotation technique can be used for the measurement of the density. The density of the same specimen shall be measured before and after storage and at intervals during the storage period. Again, the densities of the undoped samples shall also be measured at the same times as a check on both the measurement techniques and the effect of storage.

10.4 Stored energy

The stored energy can be measured by a differential thermal analysis or a differential scanning calorimeter technique, from the storage temperature up to a temperature close to the softening point. A sample of the same composition, either after annealing or from an undoped batch, makes an ideal reference.

10.5 Optical, microscopic and crystallographic examinations

Optical microscopy shall be performed to detect micro cracking. The micrographs shall be prepared of the same area before, during and after irradiation.

If a diffraction pattern was observed on the freshly prepared samples, the exposure shall be repeated, and the pattern examined for changes, especially of diffraction line profiles, which might be indicative of increased strain, and line intensities, which might indicate phase instabilities.

Scanning electron microscope (SEM) or microprobe examinations should be considered during storage to assess the evolution of the sample homogeneity. Two aspects must be considered in this type of measurement:

a) the measurements are highly localized, and must therefore be repeated on a sufficient number of zones to ensure statistical representativeness;

b) these techniques use particle beams (notably electron beams); care must be taken to avoid disturbances in time resulting from the measurement procedure (e.g. increased diffusion of alkali metals under irradiation).

It is therefore preferable

— to avoid repeating measurements on the same zones;

— to use low-intensity beams of very short duration.

10.6 Heat release

The evolution of the thermal power during the storage time is measured by calorimetry. This measure is made

a) to corroborate data on the radionuclide composition of the material by comparing the experimental values obtained at the outset of the storage period with the results calculated from the composition;

b) to assess the thermal environment to which the irradiation-induced defects will be exposed.

10.7 Mechanical properties

The evolution of the mechanical properties with time will be optionally assessed by measuring the inherent material parameters (Young's modulus, K1c, etc.).

10.8 Helium release

The quantity of occluded helium released in time will be optionally assessed for a doped specimen. The specimen geometry has a decisive effect on the measured results, and must be taken into account.

11 Test report

11.1 General

The following information shall be included in the report, using SI units throughout.

11.2 Details of the solid

— A comparative table of the composition of the actual and simulated wastes used.

— Time period and dose simulated.

— Concentration and activity of dopant nuclide.

11.3 Method of preparation

— Feed materials used both in the plant and for the specimens.

— Temperature of melting/sintering or ceramic consolidation.

— Cooling cycle after preparation, again both for the real material and for the specimens.

— Autoradiograph of the sample.

— Optionally also:

  — optical micrograph of the sample;

  — analysis of microscopic observations (SEM or microprobe).

— Where appropriate (for other than completely vitreous materials):

  — results of X-ray diffraction analysis;

  — identification and proportion of any crystalline phase observed.

11.4 Storage conditions

— Time of storage and graph of accumulated dose versus time.

— Temperature of storage including any temperature variation.

11.5 Results of test

11.5.1 General

The date of preparation of the specimens and the date on which the test was carried out shall be given. The results shall be displayed graphically as a function of α-dose (Gy), or, optionally, as displacements per atom (dpa), or number of disintegration per volume or mass unit. The precision of the results shall be given. The model used to convert dose to dpa must be referenced.

11.5.2 Leach tests

The results of the leach tests mentioned previously shall be reported as specified in ISO 16797.

11.5.3 Density measurements

Technique used:

a) Archimedes' method:

- liquids used;
- density and temperature of liquid;
- mass of specimen in air and in liquid;
- resultant density.

b) Flotation method:

- liquids used;
- temperature;
- proportions of liquids used;
- resultant density.

11.5.4 Stored energy

- Technique used.
- Calibration method.
- Sample size and method of preparing the sample for test.
- Graph of energy released versus temperature.
- Total energy stored.

11.5.5 Crystallographic and microscopic examination

- Crystallographic examination of materials other than fully vitreous materials. The results of examinations performed after storage shall be compared with the results of tests performed on the freshly prepared specimen, with particular attention to any changes in the line breadth, profile and intensity.
- Microscopic examinations. The results of examinations performed after storage shall be compared with the results of tests performed on the freshly prepared specimen.

11.5.6 Mechanical properties

For each measured quantity, the following should be specified:

— technique used;

— interpretation method;

— environmental conditions under which the sample was stored (relative humidity, temperature, etc.).

11.5.7 Helium release

— Measurement methodology.

— Details of experimental set-up.

— Sample size.

— Temperature of storage.

— Method of detection of helium.

— Quantity of helium detected or limit of detection if no helium is detected.

11.5.8 Heat release

— Technique used.

— Calibration method.

— Sample size and method of preparing the sample for test.

— Heat release versus time.

Bibliography

[1] ASTM C 1220-98, *Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste*

[2] ASTM C 1285-97, *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)*

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