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

[Revision of first edition (ISO 6962:1982)]

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

ICS 13.030.30; 13.280

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Foreword

Boilerplate text for ISO standards:

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

International Standard ISO 6962 was developed by Technical Committee ISO/TC 85, *Nuclear energy*, and was circulated to the member bodies in January 1980.

It has been approved by the members bodies of the following countries:

Austria	Hungary	South Africa, Rep. of
Belgium	Italy	Sweden
Brazil	Japan	Switzerland
Canada	Mexico	Turkey
Czechoslovakia	Netherlands	United Kingdom
Egypt, Arab Rep. of	New Zealand	USA
Finland	Philippines	USSR
France	Poland	
Germany	Romania	

No member body expressed disapproval of the document.

This document is a revised version (1997) of this international standard.

Introduction

It is generally agreed that a solid is the best form in which to store or dispose of the 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 of 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 βγ-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 ionisation of the atoms in their path and this will only have a transient effect. 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. α decay generates helium. 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 solidified high-level radioactive waste forms

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 reference(s)

IS 16797 - Chemical durability test - Soxhlet mode chemical durability test - Application to vitrified matrixes for high-level radioactive waste.[1]

ASTM C 1220-92 – Standard test method for static leaching of monolithic waste forms disposal of radioactive waste.

3 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 isotopes. 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 one year as the actual storage medium will receive over a much longer time[2]. 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 ISO 16797 leach test prescribed in sub-clause 9.1 will adequately detect any significant changes and so is satisfactory in this context although it has only limited environmental significance.

[1] Now at the Draft International Standard stage.

[2] The difference of dose rate between real waste form and doped form induces the obligation to study this aspect

4 Method of test

4.1 Calculation of the necessary dose

The concentration of the actinides in the particular discharged fuel can be calculated using a computer code. 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 1.0 % of the plutonium left in the waste stream only makes a significant contribution to the integrated radiation dose to the solid 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 1000 and 10000 years for instance), at shorter time, ^{244}Cm and ^{241}Am are the most important isotopes.

4.2 Choice of isotope to use

^{238}Pu, ^{241}Am and ^{242}Cm and ^{244}Cm have all been used to dope simulated radioactive waste glasses. The one chosen will often depend on availability, but the following criteria must be considered :

a) ^{238}Pu is easier to handle than either curium isotope.

b) the half-lives are :

^{238}Pu	87.7 y
^{241}Am	433 y
^{242}Cm	163 d
^{244}Cm	18.1 y

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

c) Plutonium oxide is not very soluble in some complex matrixes, preparation of sample might lead to indissolved plutonium oxide and 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.

Having decided on the required dose, the concentration of the chosen isotope 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.

5 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.

6 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 the 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 ionisation) 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.

7 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) Leach rate by a short-term method,

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 9.

8 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 a dry air. Optionally, a second set of specimens may be stored at some appropriate elevated temperature[3].

9 Measurements during and after storage

The most important of the solid properties in the storage context of 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 storage period and on both the doped and control samples.

9.1 Leach rate

An International Standard leach test (e.g. in clause 2) shall be carried out before and after the storage period and the results compared, also for both doped and undoped samples.

9.2 Density measurements

Either an Archimede's 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. A minimum of three measurements is required in order to provide trend indication.

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[3] 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.

9.3 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. Again, a minimum of three measurements is required.

9.4 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. Again, a minimum of four measurements is required.

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 localised, 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 :

a) to avoid repeating measurements on the same zones;

b) to use low-intensity beams of very short duration.

9.5 Heat release

The evolution of the thermal power in time is measured by calorimetry :

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.

9.6 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.).

9.7 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.

10 Test report

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

10.1 Details of the solid

- A comparative table of the composition of the actual waste and the simulates used.
- Time period and dose simulated.
- Concentration and activity of dopant isotope.

10.2 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:
  - i) Optical micrograph of the sample
  - ii) analysis of microscopic observations (SEM or microprobe).
- Where appropriate (for other than completely vitreous materials):
  - i) results of X-ray diffraction analysis,
  - ii) identification and proportion of any crystalline phase observed.

10.3 Storage period

- Time of storage and graph of accumulated dose versus time.
- Temperature of storage including any temperature variation.

10.4 Results of tests

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

10.4.1 Leach tests

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

10.4.2 Density measurements

Technique used :

a) Archimede's method :
   1) liquid used,
   2) density and temperature of liquid,