
International Standard



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

Méthode normalisée d'essai de la stabilité à long terme à l'irradiation alpha des formes de déchets solidifiés de haute activité

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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 member 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, F. R.	Romania	

No member body expressed disapproval of the document.

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

0 Introduction

It is generally agreed that a solid is the best form in which to store or dispose of the highly radio-active 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 weighing several hundred kilograms, cast or formed in a steel container. The material favoured hitherto is a borosilicate glass, but possible alternatives include

- a) ceramics or glass-ceramics;
- b) a two-phase mixture of glass beads dispersed in a metal matrix.

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 β -decays of the fission products will far outnumber 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. Thus, it is the stability of the solid to α -decays that must be tested.

1 Scope and field of application

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.

2 References

ISO 6961, *Long-term leach testing of solidified radioactive waste forms.*¹⁾

ISO 6963, *Soxhlet leach test procedure for testing of solidified radio-active waste products.*¹⁾

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 "spiked" or "doped" with a short half-life α -emitter so that it will receive the same number of α -decays per gram in, say, one year as the actual storage medium will receive over a much longer time. 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 two ISO leach tests prescribed in 9.1 will adequately detect any significant changes and so are satisfactory in this context although they have only limited environmental significance.

4 Methods 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 will be incorporated in the glass. The amount of plutonium left in the waste stream only makes a significant contribution to the integrated radiation dose to the solid after thousands of years; at shorter times ²⁴¹Am is the most important isotope.

As an example, the number of disintegrations per gram of solid has been calculated for a particular set of conditions for Pressurized Water Reactor waste and this is presented in annex A and figure 1.

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.

1) At present at the stage of draft.

4.2 Choice of isotope to use

²³⁸Pu, ²⁴¹Am and ²⁴²Cm and ²⁴⁴Cm have all been used to spike simulated radio-active waste glasses. The one chosen will often depend on availability, but the following criteria must be considered :

- a) ²³⁸Pu is easier to handle than either curium isotope;
- b) the half-lives are :

²³⁸Pu 87,7 y
²⁴¹Am 433 y
²⁴²Cm 163 d
²⁴⁴Cm 18,1 y

Therefore, more Am and Pu must be added for a given dose-rate than when Cm is used. For this reason the use of ²⁴¹Am is not recommended.

- c) Plutonium oxide is not very soluble in complex borosilicate glasses¹⁾ and ²³⁸Pu is unsatisfactory in this respect. Autoradiography, 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. Some illustrative examples are presented in annex B and shown in figure 2.

5 Sample composition

The composition of the test samples should be as near as possible to that used in the industrial process.

In order to make the minimum alteration to the solids chemistry, Cm should be added to the simulated waste instead of a) other actinides and b) the rare earth elements on an atom for atom basis. Similarly, ²³⁸Pu should replace Ce or U first and then, if necessary, some of the rare earths.²⁾

Unspiked samples should also be prepared for comparison purposes.

6 Sample preparation

This 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 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.

7 Measurements before storage

The following measurements should be made on both spiked and unspiked samples as soon as possible after the specimens have been prepared.

- a) Density.
- b) Leach rate by a short-term method.
- c) Microscopic examination of a thin section.
- d) X-ray diffraction examination (for other than completely vitreous materials).
- e) Crushing properties (optional).

The techniques to be used are listed in clause 9.

8 Storage

The specimens shall be stored at room temperature for the pre-determined 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⁾

1) Usually less than 3 % by weight.

2) This comprises about 9 % by weight of the non-volatile fission products and about 22 % by weight of the rare earths. The concentration of U will vary depending on the efficiency of the reprocessing method used.

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 Measurements during and after storage

The most important of the solids properties in the storage context are 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 spiked and control samples.

9.1 Leach rate

An ISO standard leach test (see ISO 6961) shall be started as soon as the specimens have been prepared.

A repeat test will be carried out after the necessary storage period. If the latter is short, the two tests may overlap in time. Comparative tests should also be carried out on unspiked samples. A Soxhlet leach test (see ISO 6963) should be carried out before and after the storage period and the results compared, also for both spiked and unspiked samples.

9.2 Density measurements

Either an Archimedes or a flotation technique can be used. 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 unspiked samples should also be measured at the same times as a check on both the measurement techniques and the effect of storage. A minimum of four measurements is required in order to provide trend indication.

9.3 Stored energy

This can be measured by a differential thermal analysis or 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 unspiked batch, makes an ideal reference. Again, a minimum of four measurements is required.

9.4 Optical and crystallographic properties

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

If a diffraction pattern was observed on the freshly prepared samples, the exposure should 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.

9.5 Crushing test (optional)

A crushing test will detect gross changes in the mechanical properties of the solid and also incipient cracking. At present there is no agreed standard test, but a method that has been used is described in annex C.

9.6 Helium release (optional)

If helium (from the α -particles) is released from the solid, it is possible, if little void space has been left above the solid in the container, for the container to pressurize. To investigate this, a specimen shall be stored in a helium tight capsule. At the end of the storage period the quantity of helium that has escaped from the sample into the capsule is measured, preferably by a mass spectrometric method.¹⁾

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 spike isotope.

10.2 Method of preparation

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

Temperature of melting.

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.

Where appropriate (for other than completely vitreous materials) :

- a) results of X-ray diffraction analysis;
- b) identification and proportion of any crystalline phase observed.

1) It seems improbable that a significant fraction of the helium will be released from glass stored at room temperature.

10.3 Storage period

Time of storage and graph of accumulated dose versus time.

Temperature of storage including any temperature variations.

10.4 Results of tests

The date of preparation of the specimens and the dates on which the tests were carried out shall be given.

The results should 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 6961 and ISO 6963.

10.4.2 Density measurements

Technique used :

a) Archimedes method :

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

b) flotation method :

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

10.4.3 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.

10.4.4 Crystallographic examination (for other than completely vitreous materials)

The results of the crystallographic examination carried out after the storage period shall be given and compared with that made on the freshly prepared specimen, noting particularly any changes in line breadths, profiles and intensities.

10.4.5 Crushing test (optional)

Dimensions of sample.

Diameter of die.

Pressure to rupture specimen and final pressure.

Mean particle diameter resulting.

10.4.6 Helium release (optional)

Sample size.

Details of capsule.

Temperature of storage.

Method of detection of helium.

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

Deduced fractional release.

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Annex A

Calculation of the number of α -disintegrations per gram of actual waste storage glass

The example taken here is for waste from a Pressurized Water Reactor (PWR) with uranium oxide fuel enriched to 3,2 % ^{235}U and irradiated to a total burn-up of 33 000 megawatt days/tonne of heavy metal. (MWd/t) at a mean fuel rating of 27 megawatts/tonne (MW/t).

The quantity of the various actinides produced in the fuel was calculated by a computer code. For the results below, HYLAS [1] was used but other codes such as ORIGEN [2] give similar results.

A given cooling time before processing is then assumed. The reason for this is of course to allow the short-lived fission products to decay and so reduce the amount of shielding and heat removal necessary at the reprocessing plant. As far as the actinides are concerned the main effects are

- a) ^{242}Cm decays to ^{238}Pu with a half-life of 163 days,
- b) ^{241}Pu (a β emitter) decays to ^{241}Am with a half-life of 15 years. The first of these effects reduces the dose to the glass, the latter increases it.

The assumptions made about the reprocessing plant are

- a) that all the actinides except Pu and U go into the high level waste and
- b) that 1 % of the Pu and U in the spent fuel also go into the waste (this is a very conservative and not very critical assumption as regards the dose to the glass in the first few thousands years).

The glass produced was assumed to contain 12,5 % by weight fission products — that is approximately 15,6 % by weight fission product oxides. The glass will also contain the actinides and other components of the waste for example corrosion products, neutron poisons and processing chemicals.

The number of α -decays per gram of solid is plotted against storage time in figure 1, for three assumed cooling times before reprocessing; 6 months, 2 years and 10 years. Solidification is assumed to have been done immediately after reprocessing. It can be seen that a short cooling time gives a higher dose to the solid initially, because of the decay of ^{242}Cm , but, at longer storage times, longer cooling times give the higher doses because of the greater amount of ^{241}Am in the waste.

The vertical line on the graph at 1 000 years show the spread of values obtained for 0,5 year and for 10 year cooled fuel by using various computer codes and nuclear data libraries.

Annex B

Dose to the specimens from the spike isotopes

The dose to the glass that would result from spiking the solid with some possible concentrations of ^{242}Cm , ^{244}Cm or ^{238}Pu are shown in figure 2.

As an example of using the two graphs, a solid containing 12,5 % by weight fission products from fuel cooled for 2 years

before processing and vitrification will receive $1,5 \times 10^{18}$ α -disintegrations per gram in the first 1 000 years. This can be simulated in about 6 months by spiking a sample with 0,1 % by weight ^{242}Cm , in about 1,5 years with 1 % by weight ^{244}Cm or in about 3,5 years with 2 % by weight ^{238}Pu .

Annex C

Crushing test

This test detects strain and incipient cracking by measuring the particle size resulting when a solid sample is crushed in a semi-reproducible manner: if strain was present or cracks had occurred, the sample would crush to a finer powder. Use of the test is described in reference [3].

A cylindrical- or cube-shaped specimen, as cast or cut from a larger sample, is inserted into the testing device, which is similar to a pelleting die. The dimensions of the cylindrical specimen shall be such that the ratio of the height to the diameter shall be about 1 and the ratio of the area of the press die to the cross-sectional area of the specimen shall be

about 10. The specimen and the press die are exposed to a pressure that shall be ten times larger than the pressure necessary for rupture of the specimen. A sieve analysis is performed on the crushed specimen and evaluated utilizing the Rosin-Rammler-Sperling (RRS) grain size distribution. For the intercomparison of different types of specimen, the average grain diameter has to be standardized to a $1 \times 10^{-6} \text{ m}^3$ volume for each specimen since the crushing of the specimen pieces after rupture is dependent on the total particle volume. Hence it is desirable that the dimensions of the specimens for the before-and-after storage tests shall be identical. The average grain diameter after the test is a measure of the rupture properties of the material.

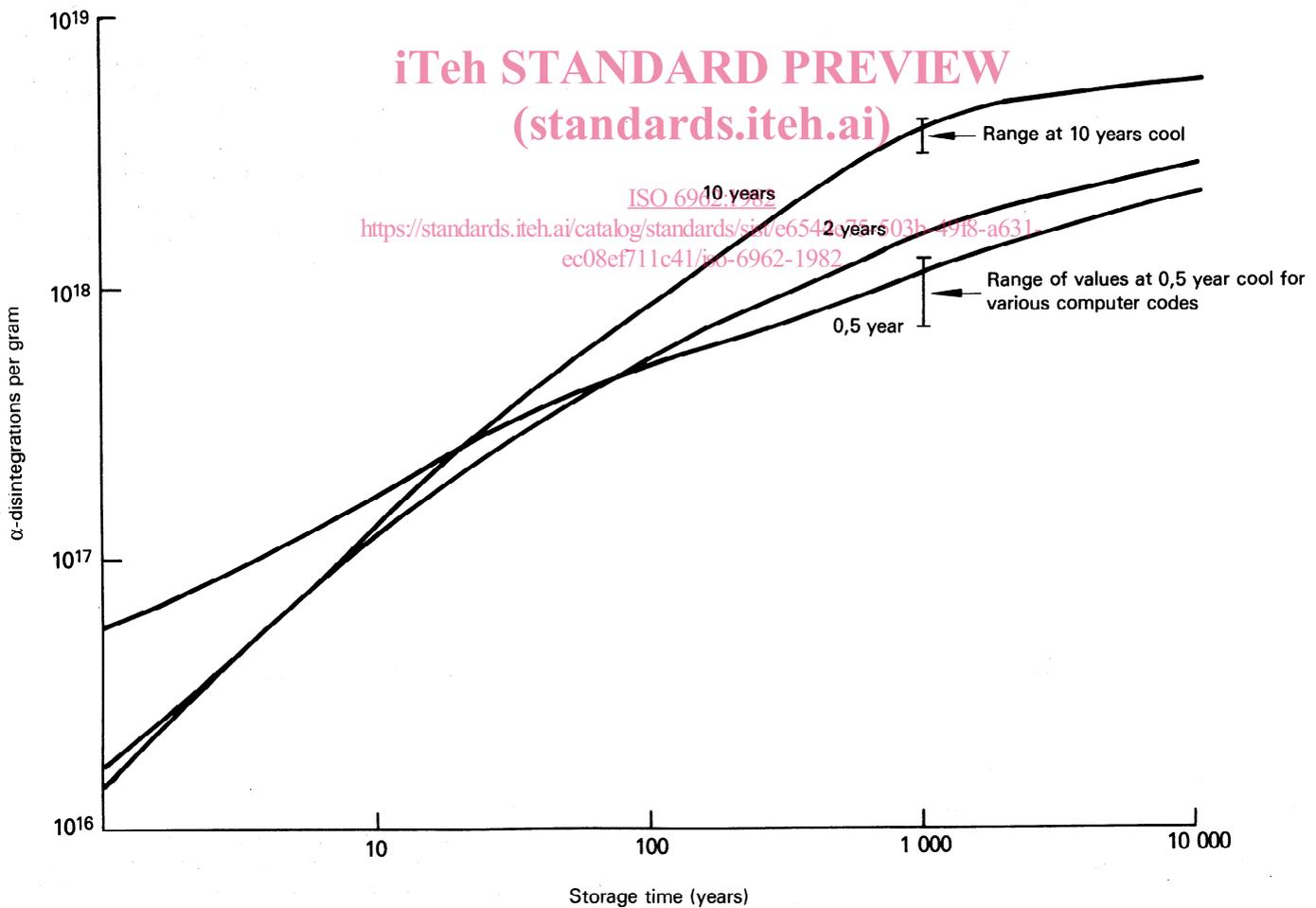


Figure 1 — α -disintegrations per gram versus storage time for various cooling times

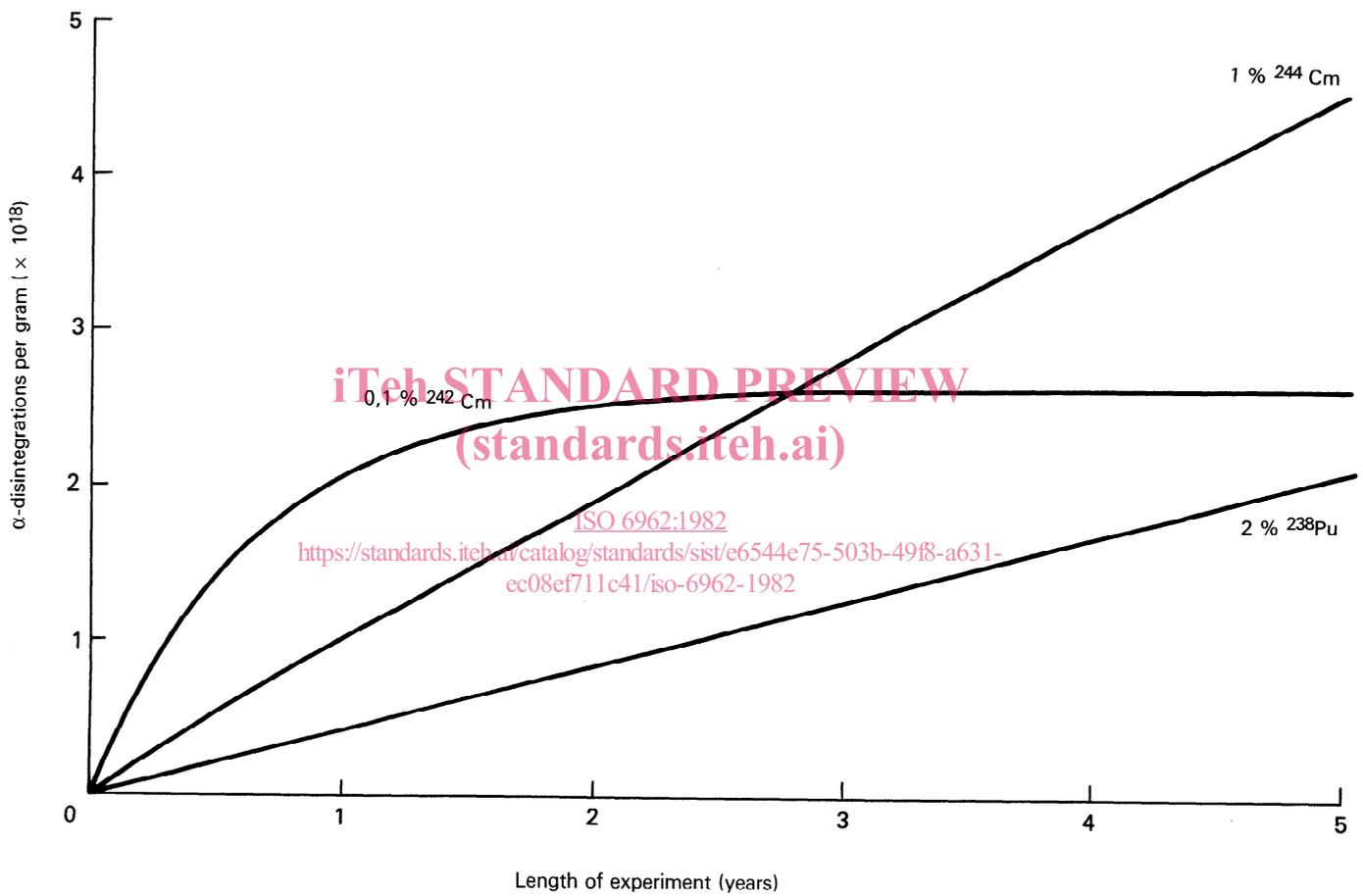


Figure 2 — α -disintegrations per gram versus time of experiment for various dopants (in % by weight)