INTERNATIONAL STANDARD

ISO 16797

First edition
2004-04-15

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

Énergie nucléaire — Test de durabilité chimique en mode Soxhlet — Application aux matrices vitrifiées des déchets radioactifs de haute activité

Reference number
ISO 16797:2004(E)

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Published in Switzerland

Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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 16797 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Introduction

Any material submitted to the action of water is subject to alteration. Numerous leach tests have been developed to measure this alteration. One of these, the Soxhlet test, is routinely used to assess the chemical durability of nuclear glasses, and is now widely applied to other types of glass, to materials resulting from vitrification processes, or even to other nonporous solids intended for containment of non-radioactive toxic wastes. This is a short-term test designed to obtain a quick assessment of the chemical durability of a material in deionized water at about 100 °C.

In a static environment without water renewal, the concentration of dissolved material in solution increases, and the alteration rate subsequently diminishes. Conversely, the maximum alteration rate is observed in continuously renewed deionized water, or in a complexing medium that consumes elements from solution and prevents saturation from occurring.

This approach has several advantages: shorter test duration, higher element concentrations in solution in the boiler (well above the detection limits), assessment of the potential durability of the material under extreme conditions.

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

1 Scope

This International Standard describes the Soxhlet-mode parameter test to assess the chemical durability of materials by measuring the initial dissolution rate in pure water. The measurement is performed at the boiling point of water, at which the dissolution rate is considerably higher than at room temperature. In most cases, the alteration phenomena are therefore significantly accelerated.

The test described in this International Standard is intended to measure the initial dissolution rate; it is thus applicable only to nonporous materials (or materials with small, closed porosity) for which the primary alteration phenomenon is a surface reaction mechanism (diffusion mechanisms are involved in the dissolution of porous media). The test results can therefore be compared only with findings obtained for nonporous materials if serious errors of interpretation are to be avoided.

The resulting “initial dissolution rate in pure boiling water at atmospheric pressure” can be used to compare materials of the same type (e.g. oxides), provided their initial dissolution is governed by the same mechanism (e.g. surface reactions).

This parameter test cannot be used to assess the long-term behaviour of a material, which generally requires several tests, modelling and validation, as described, for example, in Standard ENV 12920.

This test is applicable to any glass, vitrified material (i.e. material resulting from a vitrification process) or nonporous oxide material with a morphology that allows the preparation of monolithic test coupons of known surface area. It determines the initial dissolution rate of the material in deionized water at the boiling point (approximately 100 °C) by analysis of the leaching solution and by measurement of the specimen mass loss.

2 Terms and definitions

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

2.1
alteration
superficial chemical modification of a material due to surrounding agents

2.2
alterability
susceptibility to alteration

NOTE Alterability depends on the material itself and on its environment.

2.3
durability
ability of a material to exist for a long period of time while retaining its original qualities and properties

2.4
chemical durability
ability to withstand chemical attack

NOTE This characteristic may be an inherent material property if the environment is duly specified and established (e.g. chemical durability in pure water at 100 °C).

2.5
leaching
extraction of one or more elements from solid elements by a solvent

NOTE By extension, the term commonly designates any operation in which a specimen is exposed to the action of a solvent.

2.6
dissolution
dispersal of a substance into a solution

2.7
corrosion
gradual destruction or slow degradation of a substance or surface by a chemical effect

2.8
source term
flow of chemical species transferred from a given surface under the conditions specified by the test scenario

2.9
long-term behaviour
evolution of the “source term” and the material properties over time, up to the end of the relevant scenario

NOTE The investigation of long-term behaviour covers the progress of the alteration and the release of elements (source term) over a specified time interval.

2.10

scenario
a time horizon and a list of factors (including risk factors) affecting the conditions of disposal or utilization of a material, specified for the purpose of assessing its long-term behaviour

3 Principle

The test temperature is the boiling point of water, which depends on the atmospheric pressure and therefore on the altitude of the laboratory in which the test is performed. The difference in the boiling temperature between a laboratory at sea level and a laboratory at an altitude of 1 000 m is about 5 °C; this may have a significant effect on the test results (by a factor of almost 2 for a reaction mechanism activation energy of 60 kJ · mole^{-1}).

The atmospheric pressure of the laboratory shall be recorded, and shall be taken into account in any comparison with the results obtained by other laboratories: the data may be used to calculate the actual boiling temperature.

The water flow rate on the test coupon is determined by the heating power supplied to the water by the boiler and by the efficiency of the reflux condenser.

4 Reagents

4.1 Water

Alteration tests shall be conducted using high-purity water in equilibrium with air [at least 2 h to ensure stabilization of carbon dioxide (CO_2) concentration].

4.2 Concentrated nitric acid (HNO_3), to acidify the solution before analysis.

5 Apparatus

5.1 Soxhlet device

The Soxhlet alteration device (see Figure 1) comprises the following:

a) a stainless-steel distillation flask with a volume of at least 500 ml;

b) a suitable regulated heater with controlled thermal power dissipation;

c) an overflow-type sample boat (see Figure 1); in some cases it may be preferable to provide for upward flow of the alteration solution to ensure adequate renewal; the surface area of the sample boat shall not exceed 5 % of the total specimen surface area, and shall allow optimum solution flow conditions around the test coupon with at least 5 mm clearance between the coupon and the sides of the boat or the surface of the solution;

d) a stainless-steel condenser;

e) a water coil to return the solution to the sample boat.

The following requirements shall be met.

a) The flow of the alteration solution into the sample boat, controlled by the setting of the flask heater, shall be constant (± 10 % of the specified flow rate) and shall ensure at least two renewals per hour of the sample-boat volume.

b) The length of the water coil and the sample-boat design shall ensure that, when they are exposed to the steam from the boiling solution, the temperature of the solution in the boat is maintained within 1 °C of the boiling point.

c) Provision shall be made for measurement of the temperature in the sample boat, to ensure that it is within ± 1 °C of the boiling point of water.

A washing procedure shall be strictly implemented on both new and previously used devices:

a) to prevent contamination between tests or when a new device is used for the first time;

b) to recover all the elements that were dissolved during the test and precipitated or adsorbed on the device; the dissolution shall be exhaustively quantified.

5.2 Precision balance, to measure the solution mass (± 0,25 %) and to weigh specimens before and after testing (± 0,1 mg maximum).

5.3 Graduated flasks, **pipettes** or **burettes**, for solution volume measurement (accuracy: ± 1 %).

5.4 Solution analysis

Regardless of the analysis method, the following accuracy may be required:

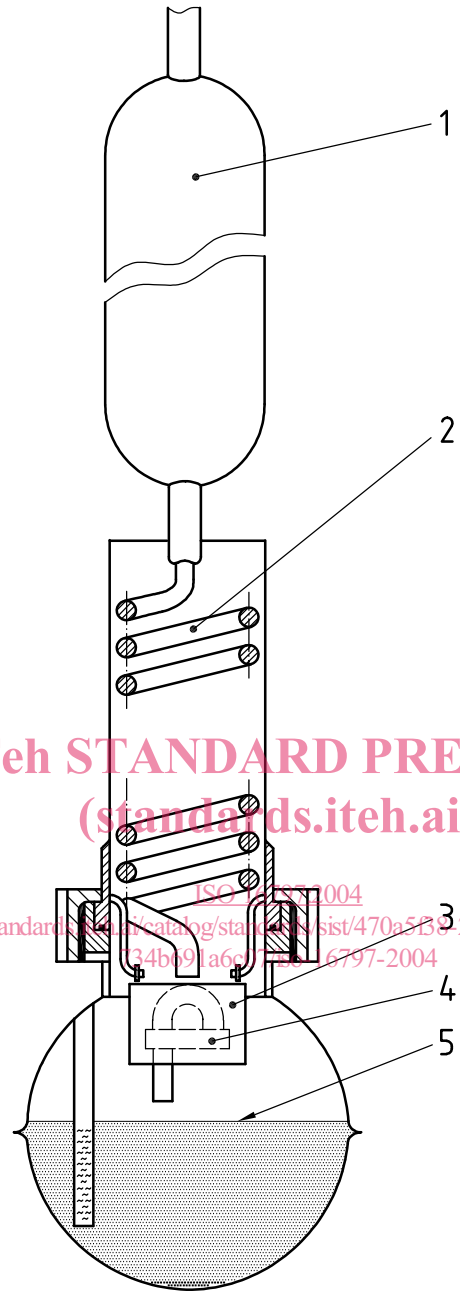
a) 5 % on major component elements;

b) 10 % to 15 % on other elements.

Such an accuracy may not be reached for elements found in solution at concentrations near the detection limit. The analytical results shall therefore always be stated together with the corresponding detection limits.

5.5 pH Measurement

The pH shall be measured to within ± 0,1 unit.



Key

1 condenser
2 water coil
3 soxhlet sample boat
4 glass coupon
5 leachate level

Figure 1 — Schematic diagram of the Soxhlet leaching device

6 Specimen preparation

Test specimens may be fabricated individually or cut from a larger sample. If a sample is cut into coupons, the use of adhesives or compounds to maintain the sample shall be avoided; if such use is unavoidable, the coupon surfaces shall be thoroughly cleaned. If a sample is cut into coupons, the use of water to cool the blade shall be strictly limited.

Cut or individually fabricated specimens shall be such that the surface area of each face can be measured with maximum precision. A specimen with polished surfaces is therefore preferable to as-cut surfaces, provided the polished finish does not pollute the surface or affect the reactions. An accurate determination of the specimen surface area is indispensable in comparing different specimens, since the quantity of dissolved elements must be normalized with respect to the reactive surface area.

The specimen dimensions shall be determined to ensure that it is fully immersed at all times in the leaching solution contained in the sample boat.

The specimen shall be carefully washed before testing in order to eliminate all adhering particles or external pollution. Ultrasonic cleaning for 5 min in absolute ethyl alcohol is advisable.

After cleaning, the specimen shall be handled only with clips.

The specimen shall then be maintained for 1 h at 105 °C, and allowed to cool before weighing. The same heating/cooling/weighing cycle shall be repeated. If the results of the two mass measurements are identical (within 0,1 mg), the specimen may be assumed to be correctly dried, and shall be placed at room temperature in a desiccator until it is required for use. If the results of the two mass measurements diverge, the specimen shall again be dried for 1 h at 105 °C. The cycle shall be repeated until the specimen mass has stabilized.

The specimen shall then be characterized as described in Clause 7.

7 Specimen characterization

The elemental chemical composition of the specimen shall be accurately known.

Where possible, the specimen shall be characterized by optical microscopy, or by scanning electron microscopy, to determine the extent of cracking and microcracking, the degree of porosity, the component phases, their concentrations and homogeneity.

If the test coupon is to be used to characterize the durability of the material sample from which it was cut, the specimen shall be representative of the material. In the case of a heterogeneous or multiphase specimen, the distribution of the heterogeneity or of the phases in the specimen shall be representative of the original sample. Moreover, with certain multiphase materials, some phases may be represented by large inclusions. In order to ensure that the size of these inclusions does not skew the results obtained for a given specimen, the specimen dimensions may be assigned so that the largest dimension of any grain or inclusion does not exceed half the smallest dimension of the specimen. Moreover, the surface area of any given grain or inclusion shall not exceed 10 % of the total geometric surface area of the specimen.

8 Procedure

8.1 Testing of prepared specimens

The following procedure shall be followed:

a) Place the specified volume of high-purity water (4.1) in the boiler.

b) Place the weighed specimen in the sample boat.

c) Assemble the Soxhlet device (5.1); start the condenser cooling system and apply the heating power required to ensure the desired solution renewal.