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)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Foreword

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 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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:

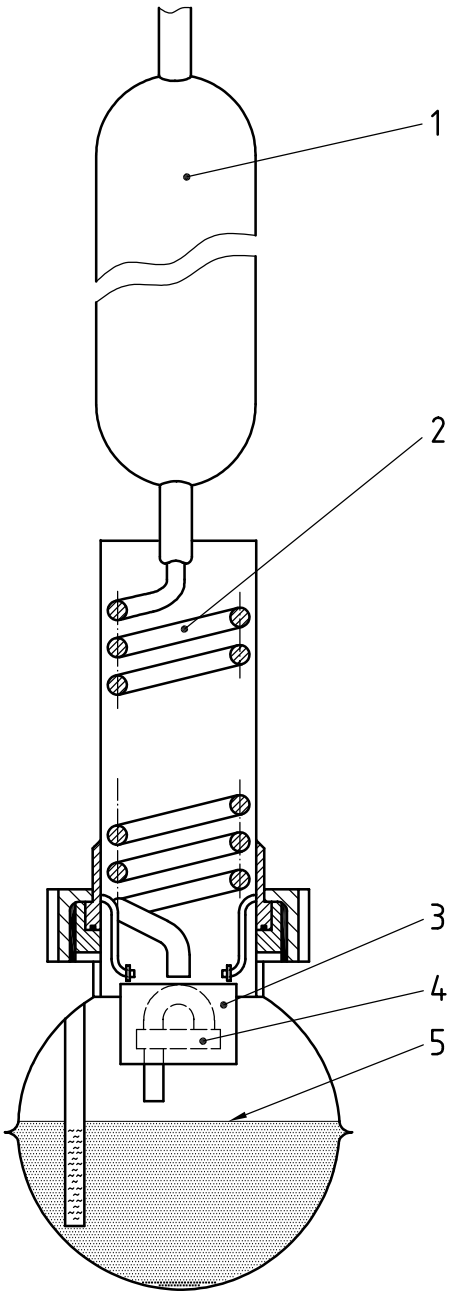
a) 5 % on major component elements;

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.

d) The time when the device heating system is started corresponds to the beginning of the test. Record the starting time and date, as well as the atmospheric pressure.

e) After the specified test duration, record the ending time and date, as well as the atmospheric pressure.

f) Remove the specimen. Separate the condenser from the boiler, plug the neck of the boiler and allow the device to cool. Dry the specimen at 105 °C until its mass remains constant. Record the mass.

g) Take an aliquot sample of the solution in the sample boat (optional); pour the solution from the sample boat into the boiler.

h) Measure and record the solution pH after it has cooled to room temperature; record the temperature.

i) Acidify the solution in the boiler to 1 N using concentrated nitric acid (4.2). Stir and allow to stand for 12 h, then check that the boiler contains no solid phases (precipitates). Acidify or dilute the solution, if necessary, to ensure this condition. For each type of material, and for each modification affecting the test device, a blank test [see item l)] shall be performed to ensure that this procedure is sufficient.

j) Measure the solution volume in the boiler. If the leaching solution volume loss exceeds 10 % of the initial volume, the test shall be repeated.

k) Take an aliquot of sufficient volume for solution analysis. Perform the analysis in accordance with the internal quality-assurance procedure.

l) Check the properties of the Soxhlet device by carrying out a 24 h blank test, i.e. without a material specimen. After the test, measure the solution pH (which should be within 0,5 unit of the initial pH) and analyse the solution (the measured “background” concentrations shall not exceed 10 % of the values determined during the actual test).

8.2 Measurements

The following measurements shall be performed during each test:

a) solution pH at the end of the test, after cooling to room temperature;

b) analysis of the solution in the sample boat (optional);

c) analysis of the solution in the boiler after acidification;

d) specimen mass loss.

8.3 Experimental matrix for determination of the initial alteration rate in pure water at boiling temperature

The alteration rate shall be measured at four or five intervals ranging from 1 day to 28 days (e.g. 1, 3, 7, 10 and 14 days). At least three of these intervals shall be specified to obtain the initial alteration rate (refer to Clause 9). The 1 day and 28 day test durations are merely indicative, and may be modified for glass compositions or vitrification products that are either very soluble or very durable. The objective is to obtain quantifiable element concentrations in solution for the first test interval, and to limit the specimen dissolution to no more than 10 % of the initial mass after the last test interval.

8.4 Solution renewal rate in the sample boat

In measuring the “initial dissolution rate of a material in pure boiling water”, it is important to avoid excessively high concentrations in the sample boat of elements dissolved from the specimen. At high concentrations, the alteration rate may be observed to diminish between solution renewals as a result of a drop in the dissolution affinity of the material. It is thus advisable to ensure that this is not a possibility, by dividing the concentrations measured in the sample boat during the first test by the number of solution renewals. If such a risk exists, the solution renewal rate in the sample boat shall be increased, or the ratio of the specimen surface area to the solution volume in the sample boat shall be reduced (e.g. by diminishing the specimen surface area).

The solution renewal rate (or leaching-solution flow rate) shall be measured at least whenever the experimental configuration is modified (test device, environmental conditions, heating system, thermal insulation, etc.).

9 Expression of results

9.1 Specimen mass loss

The normalized mass loss, NML, is the ratio of the specimen mass loss during the test to its initial geometric surface area; the result is generally expressed in grams per square centimetre or grams per square metre, and qualifies the overall material durability. However, since an alteration film may develop on the specimen surface, containing elements that precipitate or elements not involved in the alteration process (residual network), the normalized mass loss does not correspond to the total altered glass mass.

$$\text{NML} = \frac{m_\text{i} - m_\text{f}}{A}$$

where

m_i is the initial specimen mass;

m_f is the final specimen mass;

A is the initial specimen geometric surface area.

From the normalized mass loss calculated at the final time interval, a mean rate, v_m, is calculated such that

$$v_\text{m} = \frac{\text{NML}}{\Delta t}$$

where

Δt is the duration of the test, in days;

v_m is generally expressed in grams per square centimetre per day or grams per square metre per day.

9.2 Analysis of leaching solution in the boiler

The normalized mass loss for element i, NML (i), is the quantity of glass that shall be dissolved to obtain the concentration of element i actually measured in solution for a given surface. This quantity is used to assess the durability of the glass matrix (assuming element i is a mobile element) and the containment properties of the material with respect to less mobile elements [by comparing different NML (i) values]. It is given by

$$\text{NML}\,(i) = \frac{c_i \cdot V}{w_i \cdot A}$$

where

c_i is the concentration of element i in the solution;

V is the volume of solution;

w_i is the mass percentage of element i in the glass;

A is the initial specimen geometric surface area.

The result is generally expressed in grams per square centimetre or grams per square metre.

Consider four separate elements in the specimen: a soluble element, A, that is not incorporated in the dissolution products (referred to here as a “mobile element”); another mobile element, B; a third element, C, that is partially retained, and an element D that is completely retained in the dissolution products. Hence:

$\text{NML}\,(\text{A}) = \text{NML}\,(\text{B})$

$\text{NML}\,(\text{B}) > \text{NML}\,(\text{C})$

$\text{NML}\,(\text{C}) > \text{NML}\,(\text{D})$

and $\text{NML}\,(\text{D}) = 0\ \text{g} \cdot \text{m}^{-2}$

In this example, NML(A) and NML(B) both express the total specimen alteration.

In order to ensure that NML(A) and NML(B) are in fact indicative of the initial alteration rate, it is indispensable to check that elements A and B are not incorporated in an alteration film or gel layer on the specimen surface, or in precipitates that were not dissolved when the solution was acidified.

For a given element i, during the time interval in which c_i and $\text{NML}\,(i)$ vary in a linear manner, the initial corrosion rate of the material at the boiling temperature $v_0\,(i)$ may be calculated as follows:

$$v_0\,(i) = \frac{\text{dNML}\,(i)}{\text{d}t}$$

where $\text{dNML}\,(i)$ is the variation of $\text{NML}\,(i)$ during the time $\text{d}t$.

The initial corrosion rate is calculated by linear regression from the normalized element mass losses for the most highly mobile elements, i.e. those with the highest $\text{NML}\,(i)$ values.

Ideally, the five normalized mass-loss values calculated for a given element from the five Soxhlet tests conducted on a material sample should be found along a straight line when plotted as a function of time. In fact, these points may not actually be aligned for a variety of reasons:

a) the first point may deviate from the straight line if the specimen surface finish inhibits or catalyses the alteration reaction (the process stabilizes only after a few micrometres have been dissolved from the material surface);

b) the last one or more points may be situated beneath the theoretical straight line when an alteration film develops on the specimen surface, forming a diffusion barrier.

These deviant points should not be used to calculate $v_0\,(i)$. At least three points are required, however. The correlation coefficient on the slope of the straight line connecting at least these three points shall also be indicated.

One or more additional Soxhlet tests will be necessary to determine the initial alteration rate of the material in the following cases:

— When three straight-line points are not obtained on the $c_i = f\,(t)$ curve.

— When $v_0 < 0{,}95\ v_{\text{M}}$, i.e. when the initial rate obtained is less than 95 % of the mean rate calculated from the mass loss. If $v_0 < 0{,}95\ v_{\text{M}}$, this means that element i was not correctly determined, that it precipitated and was not redissolved, or that a more mobile element than element i was not determined in solution. Under such conditions, v_0 is underestimated.

— When the concentration c_{0i} (where i is the element used to measure v_0) calculated from the Y-intercept of $c_i = f\,(t)$ exceeds 0,2 times the difference Δc_i between the initial and final concentrations of i: i.e. $c_{0i} > 0{,}2\ \Delta c_i$. This means that the operating conditions do not correspond to the initial rate phase of material dissolution. In this case, the test shall be repeated with fewer sampling intervals.

10 Test report

The following information shall be indicated in the test report:

a) Specimen characteristics
   1) specimen description;
   2) sampling representativity;
   3) specimen surface finish and estimated reactive surface area (and error factor);
   4) element composition (and error factor);
   5) homogeneity;
   6) specimen mass.

b) Test conditions
   1) description of test equipment:
      i) method of solution renewal in sample boat;
      ii) solution renewal rate;
      iii) solution temperature in sample boat;
   2) atmospheric pressure at beginning of test and specimen temperature;
   3) test duration;
   4) initial solution volume;
   5) solution volume recovered after testing;
   6) blank test background solution composition.

c) Results
   1) specimen mass loss:
   2) pH at end of test;
   3) solution analysis results;
   4) mean rate v_{m};
   5) initial alteration rate (with error factor, number of data points used, correlation coefficient, v_0/v_{m} ratio and $c_{0i}/\Delta c_i$ ratio).

Bibliography

[1] ASTM C1220-98, *Standard test method for static leaching of monolithic waste forms for disposal of radioactive waste*

[2] ASTM C1285-97, *Standard test methods for determining chemically durability of nuclear, hazardous, and mixed waste glasses: The Product Consistency Test (PCT)*

[3] ENV 12920:1997, *Characterization of waste — Methodology for the determination of the leaching behaviour of waste under specified conditions*

ICS 13.030.30; 27.120.99

Price based on 10 pages