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Long-term leach testing of solidified radioactive waste forms

Essai de lixiviation de longue durée des formes de déchets radioactifs solidifiés

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Foreword

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0 Introduction

This International Standard is proposed to establish a testing and evaluation procedure for the resistance of radioactive waste solidification products to leaching under controlled conditions.

This testing procedure is intended to serve as a basis for an inter-laboratory comparison, which will be aimed at examination of the consistency of results obtained in leaching tests carried out in different laboratories, using as objects of the test samples representing various matrix compositions, various waste stream compositions, and various processing and solidification techniques. These samples will be subjected to exposure to leachant solutions of different compositions representing different conditions of salinity and pH, i.e., to deionized water, synthesized sea water, and other aqueous solutions, and leach resistance will be tested at various temperatures as specified in the procedure detailed below.

It should be emphasized that in its present form this test is restricted to evaluation and comparison of the resistance of solidification products to leaching under controlled laboratory conditions, and is not yet suitable for quantitative long-term extrapolations to determine the durability of these products in permanent repositories. The test is therefore not suitable in its present form for long-term hazard evaluation under service conditions.

The test procedure contains no reference to disposal sites or conditions, which may encompass a very wide range of temperatures, pressures and concentrations of solute ions present in the underground water of the disposal site. In particular, the present test procedures does not include tests carried out at high pressures and at correspondingly high liquid temperatures. Considerations concerning the use of the test are further detailed in annex A.

1 Scope and field of application

Processes are developed for the immobilization of radionuclides by solidification of radioactive wastes. The resulting solidification products are characterized by strong resistance to leaching aimed at low release rates of the radionuclides to the environment.

To measure this resistance to leaching of the solidified materials : glass, glass-ceramics, ceramics, bitumen, cement, concrete, plastics, a long-term leach test is presented.

The long-term leach test is aimed at :

a) the comparison of different kinds or compositions of solidified waste forms;

b) the intercomparison between leach test results from different laboratories on one product;

c) the intercomparison between leach test results on products from different processes.

The test temperatures will cover a sufficient range to give an indication of leaching behaviour at temperatures up to 90 °C. The test temperatures are chosen to be 313 K (40 °C), 343 K (70 °C) and 363 K (90 °C).

It is not required to carry out tests in all possible combinations of variables but one set of standard conditions should be met in order to assure interlaboratory comparability of the results. These conditions are :

A. HLW forms (see 3.1.1) and cement or concrete specimens (see 3.1.2); leaching in deionized water at 40 °C and 70 °C, for 1, 3, 7, 10, 14, 21 and 28 days. Three matrix elements and three waste constituents must be analysed.

B. Bitumen and plastic specimens (see 3.1.3); leaching in deionized water at 40 °C for bitumen and 40°C and 70 °C for plastics for 1, 3, 7, 10, 14, 21 and 28 days. At least three important waste constituents must be analysed.

2 Specimens, materials and apparatus

2.1 Specimen

The specimen is either prepared on a laboratory scale or can be taken from actual waste solidification products.

2.1.1 Laboratory scale specimens

The sample from which the test specimen is to be prepared is representative of the process material from the waste solidifying process stream :

a) the waste mixture can be taken as an average composition of the original waste or an average composition of non-radioactive simulated waste spiked with significant isotopes. Radioactive tracers should be used exclusively together with carriers. The carrier concentration should be given. For the simulation of high level waste the radioactive elements should be simulated according to annex B.

b) The average composition and the chemical form of the constituents of the waste and additives shall be the same for the laboratory scale specimen preparation.

c) The leaching rate of the sample is not only a function of the average composition, but also of the manufacturing process such as thermal history. Thus one shall try to duplicate the time and temperature sequences for the different phases of the solidification process in the laboratory scale specimen preparation as closely as possible.

2.1.2 Specimens from actual solidified waste forms

Test specimens shall be taken from actual solidified waste forms either as core-drilled or as by-pass samples.

2.2 Leachant

For reasons of comparison, the leachants will be as follows :

a) Test with deionized water.

b) Test with synthetized seawater having the composition given in the table.

c) Typical disposal site waters.

In all cases, the deionized water shall have a maximum conductivity of 150 μSm^{-1} before use.

2.3 Leachant container

The leachant container shall consist of a material which does not react with the leachant and is sufficiently resistant to the radiation dose received during the test. For determinations other than leached γ-activity the container shall not be sorbent towards those components extracted from the sample by the leachant which are to be monitored in the used leachant.

Polytetrafluoroethylene, polymethylpentene and polypropylene are recommended as leachant containers for their chemical inertness. The dimensions of the leach test container shall be such that the value of the ratio

$$\frac{\text{Volume of leachant}}{\text{Exposed "geometric" surface area of specimen}}$$

shall be in the range 0,1 to 0,2 m. The "geometric" surface area is the area calculated from measurements of the over-all macroscopic dimensions of the specimen. If for any reason the dimensions used in a test deviate from those specified, the dimensions used shall be reported along with the reasons for the deviation.

During each leach test period the container has to be closed by a cap such that the loss of leachant by vaporization and/or radiolysis is less than 10 % of the total volume.

A blank must be run in parallel to the sample and treated in the same way.

2.4 Temperature of leach test

The leach tests shall be conducted at the following three temperatures. At each temperature, the vessel temperature must be kept constant and within ± 1 K of the specified value. Temperatures specified are :

a) 313 K (40 °C),

b) 343 K (70 °C),

c) 363 K (90 °C).

These temperatures were selected for general testing. However, some of the solidification samples will not withstand the higher temperatures.

Under special circumstances, additional tests may be carried out at higher temperatures in an autoclave, or at lower temperatures such as room temperature, ground water and/or sea water temperatures.

3 Method of test

3.1 Specimen preparation

The dimensions for the specimens have to be taken such that the apparent geometric surface area exposed to the leachant does not change by more than 5 % over the whole leaching time.

3.1.1 Glass, glass-ceramic or ceramic specimens

The specimens shall be monolithic and have a cut, non-polished surface, (use 200 grit saw blade). The geometric surface area shall be $0,5 \times 10^{-2}$ to 1×10^{-4} m^2. The shape shall be cubic or cylindrical. (Diameter and height should be about equal.)

3.1.2 Cement or concrete specimens

Cement-waste or concrete-waste mixtures shall be filled into cylindrical plastic containers and treated for the elimination of air bubbles in the same way as the actual sample. When the mixture has become set, the cement or concrete block is withdrawn from the container and cured in a water-vapour-saturated atmosphere, preferably at (65 ± 5) % relative humidity and a temperature of 298 ± 5 K (23 ± 5 °C) for at least 28 d. The upper and lower surfaces of the cylindrical block are polished with 200 grit paper, cleaned from dust particles with pressurized air to achieve a well-defined smooth surface, before starting the leach test. The surface area shall be $5 \times 10^{-1} - 1 \times 10^{-3}$ m^2 (diameter to height ratio shall be about equal).

3.1.3 Bitumen and plastic specimens

As the distribution and grain sizes of the hydrophilic waste materials to be incorporated into the hydrophobic organic matrix are closely dependent on the fixation process technology, the specimens have to be prepared from larger samples. The specimen preparation is done either by casting or by taking an appropriately-shaped part from a larger sample by core-drilling or by cutting with a 200 grit saw. The surface area shall be 5×10^{-1} to 1×10^{-3} m^2. The shape shall be as described in 3.1.2.

3.2 Leachant container preparation

The specimen is suspended by a suitable inert device. Polytetrafluoroethylene tubing or polytetrafluoroethylene-covered inert wires are recommended. The proper volume of the leachant is introduced into the leachant container, such that the specimen is surrounded by at least 1 cm of leachant in all directions for the smallest and by 10 cm for the largest samples. The leachant containers should be thoroughly cleaned with deionized water prior to use, and there shall not be any stirring device.

3.3 Changing the leachant

After certain intervals (see 3.4) the specimen is withdrawn from the leachant container and immediately transferred to a new leachant container filled with fresh leachant. The specimen shall not dry out during the transfer. The used leachant container containing all leached material is carefully closed including dissolved, suspended, deposited and absorbed substances.

3.4 Changing frequency

The changing frequency which may not be identical with the analytical frequency depends on both the material and its activity concentration.

3.4.1 Initially the leachant shall be changed after 1, 3, and 7 days from the start of the test.

3.4.2 After the conditions of 3.4.1 have been met, changing frequency shall be twice per week for the second week and once a week for the third, fourth, fifth and sixth week, and monthly thereafter.

3.4.3 If for any reason the changing frequency deviates from the specified one, it shall be reported along with the reasons for the deviation.

3.4.4 The leach test is terminated not before the leaching rate has become virtually constant within the analytical error limit. The test shall not be terminated before 6 months at 313 K (40 °C).

3.4.5 All the material remaining in the leachant container after transfer of the specimen shall be included in the analytical determination of the leachant. If this is not possible in all cases the reasons shall be reported.

4 Analyses

4.1 The various elements in the waste may leach out at different rates. Therefore, in the case of low level waste, the concentrations of all relevant radionuclides shall be determined both in the initial sample and in the leachant solution. Matrix elements should be chemically analyzed as well.

4.2 In the case of high level waste, the concentration of all relevant radionuclides shall be determined both in the initial sample and in the leachant solution. Matrix elements shall be determined as in 4.1.

4.3 The pH of each used or blank leachant solution is determined immediately after the sample has been removed and the leachant is allowed to cool to room temperature. The blank is treated in the same way.

5 Test report

5.1 Report on test specimen

5.1.1 A report shall be given on the sampling procedure from actual solidification products or on laboratory scale specimen preparation respectively. Supplementary information should be given on special pretreatment of the specimen such as thermal treatment or irradiation and on homogeneity of the specimen. Possible swelling or cracking of the samples in the leachant during or after the experiment shall be reported.

5.1.2 Type and composition of the solidified material

a) glass, glass-ceramics and ceramics : chemical compositions of the base material, the waste ratio in the final product;

b) cement and concrete : chemical composition of the base material including water content and type as well as function, composition and proportion of any additives and the waste ratio in the final product;

c) bitumen : type of bitumen, dried waste to bitumen ratio, softening point, water content, and maximum temperature reached during processing;

d) plastics : type and composition, relevant physical properties, catalysts and promoters, polymerization type, maximum temperature reached during processing and the ratio of dried waste and water content in the final product.

5.1.3 Type and composition of the waste incorporated in the specimen

As specific as possible. The chemical composition of the waste shall be given. For high level waste the specific α-, β-and γ-activity.

5.1.4 Significant physical properties of the specimen.

5.1.5 Density and weight of the specimen before the test.

5.1.6 Dimensions, geometric surface and volume of the test specimen before and after the leaching test.

5.2 Report on leachant

5.2.1 The pH-value and buffer used if different from those specified and if necessary other physical properties such as conductivity and redox potential for each leachant solution, before and after test and for each blank solution.

5.2.2 If the ratio

$$\frac{\text{Volume of leachant}}{\text{Exposed surface area of specimen}}$$

deviates from the recommended range of 0,1 to 0,2 m, the ratio shall be reported along with the reasons for deviation.

5.2.3 Any deviations from the specified changing frequency shall be reported along with the reasons for the deviation.

5.2.4 Temperature of test in kelvins.

5.3 Report on analytical determinations

A detailed description of the analytical methods used shall be given. The method of counting used for each nuclide together with its accuracy and precision shall be reported.

5.4 Report on leach test results

5.4.1 All data acquired in the test shall be given in the form of tables. The results shall be expressed for each constituent by a plot of incremental leaching rates, R^i_n, as a function of time, t, of leaching :

$$R^i_n = \frac{a^i_n}{A^i_o \times F \times t_n}$$

where

R^i_n is the incremental leaching rate, in kg per m^2 per second for the i-th constituent;

a^i_n is the radioactivity, per second, or weight in kilograms, of each constituent leached during each leaching interval;

A^i_o is the specific radioactivity, per second kilogram, or concentration in weight fraction initially present in the specimen;

F is the exposed surface area of the specimen, in square metres;

t_n is the duration of the nth leaching period, in seconds;

t is the cumulative leaching time, in seconds.

A^i_o and a^i_n are to be corrected for decay time.

n is the time increment.

5.4.2 For suitable waste forms, the leaching rate, R_n, becomes constant after a certain time of leachant renewal periods as indicated by the plot of R_n as a function of t. The mean value of R_n together with the accuracy shall be reported for the virtually constant range.

Annex A

Considerations concerning the use of the test

The following considerations have to be taken into account when performing the test.

The test is intended to serve as a basis for comparing the leaching behaviour of solidified waste products under controlled conditions. It is not :

a) suitable for providing data for mathematical models that predict long-term (hundreds or thousands of years) leach rates;

b) defining leaching behaviour at conditions representative of a deep geologic repository.

Nevertheless, because of the flexibility permitted in leachant compositions and temperature, the test provides a good preliminary indication of probable leach behaviour, on a relative basis. Thus it can be valuable as part of a waste solidification product selection process.

The precision and bias of the test have not been established. Experience with similar tests has shown that while, in laboratories, precision may be quite good, the inter-laboratory precision and bias is likely to be much larger, thus comparison of test results between laboratories should be done with great caution until there is more experience with the test. Interlaboratory testing of specially-prepared reference waste solidification products is recommended.

The value of results obtained by means of the present test procedure for long-term extrapolations by mathematical models is limited because, being based upon estimations of the geometric surface area alone, long-term changes in the roughness and texture of the exposed surface are not allowed for. Even more seriously, it has been observed that measured leach rates depend not only on the total exposure time from the beginning of the test but also on the time elapsed since the most recent change of leachant. In general, shorter time between leachant changes will yield higher apparent leach rates.

In addition, it may not always be possible to conduct the leaching tests under the specified volume-to-surface ratio of 0,1 ± 0,02 m, whether because the achievement of sufficiently high sensitivity in the detection of leached components will require a reduction of this ratio or because of limitations of the size of highly radioactive samples used in the test procedure. In these cases, direct normalization of the leaching results for purposes of comparison with leaching rates measured with the specific volume-to-surface ratio will not be possible because the volume-to-surface ratio is known to have a considerable effect on leaching rates, and this effect has not yet been quantitatively and fully characterized.

The test results do not apply directly to geologic repository conditions for obvious reasons : high pressures, high temperatures, and high solute concentrations can prevail to differing degrees in a repository depending on its location and the time elapsed after emplacement of the solidified waste products. The different oxygen fugacities and dissolved CO_2 content which can prevail at repository depths may also have significant effects on leach rate. The present test is not designed to study these geologic repository parameters. They must be studied with other tests.

The present test can be utilized for study of radioactive samples of waste solidification products, and in some cases the sensitivity of the test will be significantly increased if radioactive samples are used. Several considerations must be taken into account when radioactive samples are used, however. The plastic leachant containers are subject to radiation-induced degradation. It must be ascertained that their degradation does not introduce contaminants in the leachant that will affect the test results. Radiation can also affect the leachant, by converting dissolved N_2 to HNO_3, for instance, and making the leachant more acidic. In addition, significant changes may be induced on the leaching surface, such as the generation of H_2O_2. In porous materials, radiation-induced gases may prevent access of the leachant to the pores and actually decrease the apparent leach rate. Although radiation can introduce special considerations, such as those listed here and others, which must be understood, the use of the radioactive samples with this test is strongly recommended whenever practicable, since ultimately it will be the leach rate of the radionuclides in the waste that is of most interest.

Annex B

Radioactive elements and their simulation

Radioactive element	Substitute elements				
	French glasses	German glass ceramics	German glasses	UK glasses	USA glasses
Tc	Mo	Mn	Mn	Mo	Mo
Ru	—	—	—	—	Fe
Rh	Pd	—	—	Pd	Co
Pm, Sm, Eu, Gd	Nd	Nd	Nd	Nd	RE1)
Np, Pu, Am, Cm	U	U	U	U	RE1)
U	—	—	—	—	RE1)

1) A commercial rare earth mixture nominally containing 0,2 % by weight Y_2O_3, 24 % by weight La_2O_3, 48,0 % by weight CeO_2, 5,0 % by weight Pr_6O_{11}, 17,0 % by weight Nd_2O_3, 3,0 % by weight Sm_2O, 0,8 % by weight Eu_2O_3 and 2,0 % by weight Gd_2O_3.

Artificial seawater is made from pure inorganic compounds (mostly salts) and pure water, the aim being to produce solutions having the same chlorinity and salinity as standard seawater. For may physico-chemical measurements it is even more important that the ionic strength should have the correct value of about 0,71 mol/kg. A formula which largely satisfies these requirements is given in column I of the table[1].

Table — Formula for artificial seawater

Compound	I	II	III
NaCl	23,497 g	23,538 g	23,538 g
$MgCl_2$	4,981	4,985	5,934
Na_2SO_4	3,917	4,087	4,087
$CaCl_2$	1,102	1,108	—
KCl	0,664	0,665	0,665
$NaHCO_3$	0,192	—	—
KBr	0,096	0,096	0,096
Total	34,449	34,379	34,321

NOTE — Make up to 1 000 g with H_2O.

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[1] See Fichtner — Handbook, Hömig, H. E., *Seawater and seawater distillation*, Vulkan-Verlag, Essen.