



EA NEN 7371:2004

LEACHING CHARACTERISTICS OF GRANULAR BUILDING AND WASTE MATERIALS

THE DETERMINATION OF THE AVAILABILITY OF INORGANIC COMPONENTS FOR LEACHING

'THE MAXIMUM AVAILABILITY LEACHING TEST'

Based on a translation of the

NETHERLANDS NORMALISATION INSTITUTE STANDARD

Version 1.0

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Foreword

This standard is for use with the Environment Agency's guidance on sampling and testing of wastes to determine acceptance at landfill¹. It relates to the determination of the maximum potential for leaching of inorganic components from granular waste materials and is often referred to as the maximum availability test.

The Environment Agency has issued a separate standard for the determination of the leaching of inorganic components from moulded or monolithic wastes.

The purpose of this availability test is to indicate the quantity of a particular component that may leach out from a granular waste material exposed to extreme conditions (for example, in the very long term, after disintegration of the material, full oxidation and/or loss of acid neutralising capacity), in an aerobic environment. The test conditions present a worst case leaching scenario rather than the conditions that might be expected to prevail in a landfill, and thus the test provides an upper limit to the leaching potential in a landfill environment. The results using this test are derived as the (cumulative) leaching of components, in mg per kg dry matter.

The acid neutralisation capacity values at pH7 and pH4 also can be determined from the test data.

This standard is based on a translation of the Dutch waste characterisation standards NEN 7341 (1995)² and NEN 7371 (2004)³. European standards for the characterisation of wastes are being developed under the auspices of CEN Technical Committee 292⁴, and this standard will be superseded in time by one or more of the CEN/TC 292-derived standards.

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¹ See also Agency Guidance on Sampling and Testing of Wastes to meet Landfill Waste Acceptance Procedures, 2005.

² Leaching characteristics of solid (earthy and stony) building and waste materials. Leaching tests. Determination of the availability of inorganic components for leaching.

³ Leaching characteristics – Determination of the availability of inorganic components for leaching – Solid earthy and stony materials.

⁴ Comité Européen de Normalisation (European Standards Organisation).

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1. Scope

This interim guidance describes a method for determining the availability for leaching of inorganic components from granular waste materials (availability test).

A list of materials for which the applicability of the method has been tested, and for which the precision in terms of repeatability and reproducibility has been determined, is given in Annex A.

2. Related standards

Reference is made to the following standards which should be adopted when using this standard. Alternatively, UK 'Blue book' methods, shown in brackets can be used. These are Methods for the Examination of Waters and Associated Materials, HMSO.

Draft prEN 14346:2004 Dry Matter Content

(The Conditionability, Filterability, Settleability and Solids Content of Sludges. Standing Committee of Analysts, HMSO, 1984).

ISO 10523:1994 Water Quality – Determination of pH

(The measurement of Electrical Conductivity and the Laboratory Determination of the pH value of Natural, Treated and Waste waters. Standing Committee of Analysts, HMSO, 1978).

ISO 7888:1985 Water Quality – Determination of electrical conductivity

(The measurement of Electrical Conductivity and the Laboratory Determination of the pH value of Natural, Treated and Waste waters. Standing Committee of Analysts, HMSO, 1978).

ISO 5667-3:2003 Water Quality – Sampling – Part 3: Guidance on the preservation and handling of water samples.

BS EN 13656:2002 Characterisation of waste – Microwave assisted digestion with hydrofluoric (HF), nitric (HNO₃) and hydrochloric (HCl) acid mixture for subsequent determination of elements in waste.

BS EN 13657:2002 Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements in waste.

3. Principle

The purpose of the availability test is to indicate the quantity of a particular component that may leach out from a granular waste material exposed to extreme conditions (for example, in the very long term, after disintegration of the material, full oxidation and/or loss of acid neutralising capacity), in an aerobic environment.

The availability for leaching is determined by twice consecutively extracting a sample of the finely ground material in a ratio between liquid and solid (L/S ratio) of 50 l/kg dry matter at a pH of 7 and 4 respectively. The quantities of the various inorganic components present in the material which are available for leaching may be calculated on the basis of the results of this availability test.

In addition, the acid neutralising capacity of the material can be calculated from the measurement data.

4. Samples for analysis

To carry out a single availability test, a sample for analysis of (16 ± 2) g dry matter (m_0) is needed, for which the dry matter content ds is known and of which at least 95% (m/m) (dry matter) of the particles are smaller than 125 μm .

Where the dry matter content ds of the sample for analysis is not known, it must be determined on a separate sub-sample that is dried at $105 \pm 5^\circ\text{C}$ in accordance with prEN 14346.

Where the material needs to be pre-dried in order to prepare the sample for analysis, this may not be carried out at a temperature higher than 40°C in order to prevent components evaporating or chemical conversions taking place during the drying process, which might affect the leaching behaviour.

5. Reagents

5.1 1 molar nitric Acid

Nitric acid of analytically pure quality at a concentration $c(\text{HNO}_3)$ of 1 ± 0.1 mol/l.

5.2 0.2 molar nitric acid

Nitric acid of analytically pure quality at a concentration $c(\text{HNO}_3)$ of 0.2 ± 0.2 mol/l.

5.3 Demineralised water

Demineralised water with a maximum conductivity of 1 $\mu\text{S}/\text{cm}$.

6. Apparatus

The materials and equipment mentioned below must be checked before use to ensure their proper operation and absence of interferences which may affect the test results.

The equipment mentioned under 6.1, 6.6 and 6.7 must be calibrated.

6.1 Balances

Balances with a measurement range up to at least 100 and 1000 g respectively, and a measurement accuracy better than ± 10 mg and ± 1 g respectively.

6.2 Beaker

Glass or plastic beaker with a volume of at least 1 litre.

6.3 Collection bottles

Sealable plastic collection bottles.

6.4 Magnetic stirring rod

Magnetic stirring rod of inert material.

6.5 Magnetic stirring device.

Magnetic stirring device.

6.6 pH meter

pH meter with a measurement accuracy better than ± 0.05 pH units.

6.7 Burette

A burette fitted with automatic pH control (a titrator) is particularly suitable for this purpose.

6.8 Filtration apparatus

Filtration apparatus, suitable for filtration at increased or reduced pressure, rinsed consecutively with nitric acid (5.2) and demineralised water (5.3).

6.9 Membrane filters

Membrane filters for the filtration apparatus (6.8) which have not been used previously, with a pore size of $0.45 \mu\text{m}$.

6.10 Prefilters

Prefilters for the filtration apparatus (6.8) with a pore size of a maximum of $1.5 \mu\text{m}$, rinsed consecutively with nitric acid (5.2) and demineralised water (5.3).

6.11 Conductivity meter

Conductivity meter, calibrated in accordance with ISO 7888, with a measurement accuracy of better than $\pm 1\%$.

7. Procedure

The availability is determined by:

- determining the requirements of the eluate samples to be analysed in accordance with 7.1;
- carrying out the availability test in accordance with 7.2;
- analysing the eluate in accordance with 7.3;
- carrying out the calculation in accordance with Section 8.

7.1 Eluate samples

Determine the quantity of eluate needed to analyse the leached components and the way in which the eluate samples must be stored through the following steps:

- a) identify for what components, and by what methods, analyses are to be carried out;
- b) check for each component to be analysed whether the eluate will require preservation, and the requirements for this preservation;
- c) determine in the light of the above the minimum quantity of eluate necessary for each component to be analysed.

NOTES:

1. To prevent changes in the eluate through physical, chemical or biological reactions, the eluate samples must be preserved and stored as well as possible. Guidelines for surface water and wastewater samples have been developed in ISO 5667-3. It is recommended that these guidelines be followed for the conservation and storage of eluates.

2. If the quantity of eluate is not sufficient for the analysis of all components to be determined by the selected analysis methods, then the availability test should be repeated using further samples until sufficient eluate is generated.

7.2 The availability test

The availability test is carried out in 2 stages at a temperature which may vary between 18°C and 22°C.

7.2.1 Step 1

Rinse the beaker (6.2) consecutively with nitric acid (5.1) and demineralised water (5.3). Weigh the beaker to an accuracy of 10 mg. Transfer the sample for analysis (4) to the beaker and weigh again to an accuracy of 10 mg. The difference between the two is the quantity of solid material (m).

Determine the dry weight of the analysis sample as:

$$m_0 = m \times d_s \quad (1)$$

where:

m_0 is the dry weight of the analysis sample in the beaker, in g;

m is the weight of material weighed into the beaker, in g;

d_s is the dry matter content (m/m) determined in accordance with prEN 14346; if the sample is pre-dried then $d_s = 1$.

Place the stirring rod (6.4) in the beaker and add a quantity of demineralised water (5.3) of $50 \times m_0 \pm 10$ g (m_w). Weigh to an accuracy of 1 g and note the total mass of the beaker, solid material, stirring rod and demineralised water (m_{tot}).

Stir the mixture with the aid of the magnetic stirrer (6.5). Set the rotation speed such that all the material is brought into suspension, but avoid intensive stirring as this could cause aeration with consequent absorption of CO₂.

With the aid of the pH meter (6.6) read off the instantaneous pH of the contact fluid (pH_A) after one minute and the stabilised pH (pH_B) after 10 minutes. Classify the material on the basis of the pH_A and pH_B measured according to the following plan:

pH _A > 10	:alkaline reactive;
pH _A < 10 and pH _B >	:neutral reactive;
4 < pH _B < 7	:weak acid reactive;
pH _B < 4	:acid reactive.

Continue to stir.

Where the material is neutral reactive, and it is known to contain more than 5% carbonate, add 0.2M nitric acid (5.2) from the burette (6.7) until a pH value of 7.0 is achieved.

Where the material is alkaline and/or the analysis sample contains more than 5% carbonate, add 1M nitric acid (5.1) from the burette (6.7) until a pH value of 7.0 is achieved.

Maintain the pH at 7.0 ± 0.5 for three hours.

Note the molarity (5.1 or 5.2) and the added quantity of nitric acid (V_1) to an accuracy of 0.1 ml.

In the event of weak acid to acid reacting material, whereby the pH settles at a lower value than 7, no acid or base is added. In this case, the pH is determined by the material itself.

NOTES:

- 1 The accuracy of the pH control is dependent, amongst other things, on the arrangement of the titrator and the concentration of the acid used. In Step 1 the pH must not vary by more than 0.5 pH units from the set value of 7.0. In order to achieve the required accuracy, it is advisable to place the point of the burette in the solution.
- 2 It is advisable to note the pH periodically during the test, so that the conduct of the test can be validated afterwards.

Filter the suspension within 1 hour from the end of acid dosing over a membrane filter (6.8 and 6.9). Where the particle size of the analysis sample is such that the membrane filter (6.9) may clog, a prefilter (6.10) must be added.

NOTES:

1. If a prefilter is used to prevent clogging, pressure filtration is advisable in preference to vacuum filtration.
2. Filtration can be accelerated by first allowing the suspension to settle for 15 minutes. Subsequently, decant the liquor over the membrane filter, then pour over the rest of the suspension.

Store the filtered eluate in a sealed bottle (6.3).

7.2.2 Step 2

Transfer the residue, including the membrane filter and stirring rod, to the beaker (6.2). Rinse the filtration apparatus (6.8) with demineralised water (5.3) and transfer the rinsing fluid to the beaker. Then add sufficient demineralised water for the total mass of the beaker, residue, filter(s), stirring rod and water to return to m_{tot} (to an accuracy of 1 g).

Keep stirring.

Where the material is weak acid reactive and it is known that the analysis sample contains more than 5% carbonate, add 0.2M nitric acid (5.2) from the burette (6.7) until a pH value of 4.0 is achieved.

Where the material is alkaline and/or the analysis sample contains more than 5% carbonate, add 1M nitric acid (5.1) from the burette (6.7) until a pH value of 4.0 is achieved.

Maintain the pH at 4.0 ± 0.5 for three hours.

Note down the molarity (5.1 or 5.2) and added quantity of nitric acid (V_2) to an accuracy of 0.1 ml.

In the event of an acid reacting material, where the pH settles at a value lower than 4, no acid or base is added. In this case, the pH is again determined by the material itself.

Filter the material through the membrane filter in the same way as described in step 1. Add the filtered eluate to the eluate obtained according to step 1.

Pour the quantities of the combined eluates intended for analysis into suitable bottles (6.3), filling each bottle with at least 10 ml of eluate.

Preserve the eluate samples according to the procedure described in 7.1. Where more than 1 ml of preservation fluid is needed per 250 ml of eluate, the concentrations determined according to 8.1 must be corrected for this.

7.3 Analysis

Analyse the eluate samples obtained in accordance with the requirements set out in ISO 5667-3.

8. Calculation

8.1 Availability

Calculate for each component separately the quantity available for leaching (availability) by the formula:

$$U_{avail} = c \times \frac{(2V_0 + V_1 + V_2)}{m_0 \times f_1} \quad (2)$$

where:

- U_{avail} is availability of a component, in mg/kg dry matter;
 c is the concentration of that component in the eluate, in $\mu\text{g/l}$;
 V_0 is the volume of demineralised water added in the first step, in ml (the numerical value of m_w);
 V_1 is the added volume of nitric acid in the first step, in ml;
 V_2 is the added volume of nitric acid in the second step, in ml;
 m_0 is the dry weight of the analytical sample, in g;
 f_1 is a dimensionless factor: 1000 $\mu\text{g/mg}$.

The concentration c , referred to in equation (1) is the concentration originally present in the eluate. The measured value determined in accordance with 7.2 must be corrected for the quantity of preservation fluid added in 7.1 where this is more than 1 ml per 250 ml of eluate.

Where the concentration of a component in the eluate is below the lower detection limit, for that component the upper limit of the availability may be calculated by making c in formula (2) equal to the lower detection limit.

NOTE:

- 1 From the availability of a component calculated above, and the original content of that component in the sample for analysis, the "relative availability" can also be calculated. See Annex B.
- 2 The volume V_o is the volume corresponding with m_w and not with m_o .

8.2 Acid neutralising capacity

In addition to the availability, the acid neutralising capacity (ACN) of the material can be calculated from the measured data by the formulas:

$$ACN_7 = (V_1 \times c_1^{HNO_3}) \times f_2 / m_0 \quad (3)$$

$$ACN_4 = (V_1 \times c_1^{HNO_3} + V_2 \times c_2^{HNO_3}) \times f_3 / m_0 \quad (4)$$

where:

- ACN_7 is an indication for the acid neutralising capacity of the material under investigation at pH=7, in mol/kg dry matter;
 ACN_4 is an indication for the acid neutralising capacity of the material under investigation at pH=4, in mol/kg dry matter;
 V_1 is the added volume of nitric acid in the first step of the availability test, in ml;
 V_2 is the added volume of nitric acid in the second step of the availability test, in ml;
 m_0 is the weight of the analytical sample, in g;
 $c_1^{HNO_3}$ is the molarity of the nitric acid added in the first step, in mol/l;
 $c_2^{HNO_3}$ is the molarity of the nitric acid added in the second step, in mol/l;
 f_2 is a conversion factor: 1 l x g/ml x kg;
 f_3 is a conversion factor: 1 l x g/ml x kg.

9. Report

The report must contain at least the following data:

- a reference to this standard indicating: "in accordance Environment Agency standard, EA NEN 7371:2004";
- the data needed to identify the sample for analysis;

- the origin and specifications of the sample for analysis;
- the nature and dry matter content *ds* of the analysed sample;
- the means by which the eluates have been preserved and stored prior to analysis;
- the components which are analysed and the lower detection limits of these components in the eluate;
- all measured concentrations, rounded to a maximum of 2 significant figures;
- the quantity of preservation fluid added in accordance with 7.1 where this is more than 1 ml per 250 ml eluate;
- the calculated availabilities in mg per kg dry matter, rounded to a maximum of 2 significant figures; for analysis results below the lower limit of detection, the upper limit of the availability of the component concerned must be calculated;
- the calculated acid neutralising capacity at pH=4 and pH=7, in mol per kg;
- the date of the test.

Where the availability test is not carried out fully in accordance with this standard, all deviations from the prescribed procedures must be indicated in the report, giving the reasons.

Annex A

Validation of the Availability Test

In developing the Dutch Standard, NEN 7371, a round-robin test was undertaken with 10 laboratories on 6 types of solid (earthy and stony) building materials and wastes to establish the precision of the availability test in terms of repeatability and reproducibility. The following is taken from the discussion presented in NEN 7371.

The error in the end result of a leaching test is composed of contributions from:

- the origin of the material (variation in production processes);
- the method of sample taking (differences in representativeness);
- the sample pre-treatment (variations in the preparation of the test piece for the leaching test);
- the leaching test itself;
- the chemical analysis (error in the determination of concentration in the leachates).

To establish the precision of the availability test, the contribution of these sources of error were minimized through the experimental design. Therefore, in the validation study the following starting points were used:

- components which can be very inhomogeneous in certain materials were not included in determining the precision;
- the samples were all taken from one batch and the sample pre-treatment was performed in one session;
- all chemical analyses were carried out by one laboratory;
- the precision was only determined for components for which the error in the chemical analysis was sufficiently small (relative standard deviation in repeatability nominal less than 5%). For larger errors in the concentration measurement the precision of the analysis would dominate the precision of the leaching test result too much.

The materials examined covered all grain size classes to which the test applies: powdered materials and sludges (0 mm to 125 μm), fine-grained materials (0 mm to 4 mm) and coarse-grained materials (0 mm to greater than 4 mm) and formed materials.

Table A.1 below gives a summary of the materials used and their components tested.

The results of the round robin test were used to assess the performance of the test with respect to repeatability (S_r) and reproducibility (S_R). The following values were obtained for the relative standard deviation for these parameters:

	Median value	Range
S_r in the determination of U_{avail}	4%	1% to 17%
S_R in the determination of U_{avail}	8 %	1% to 24%

No unambiguous dependence of S_r and S_R on the type of material and/or component was found in general.

NOTES:

For the median value and range of S_r and S_R indicated:

- A correction is made for the contribution of the analytical error.
- The values of S_r and S_R indicated only relate to the material-component combinations for which:
 - the contribution of the relative standard deviation of the concentration determinations is less than 5%;

- the leaching during the column test is not so strongly pH-dependent that the cumulative leaching at LS = 10 l/kg is dominated by the quantity which has leached in the first fraction.

All material-component combinations from Table A.1 for which the components are not placed in brackets and not marked with a * meet these two conditions.

Table A.1: Materials and components tested

Grain size class	Material tested	Components tested¹
Powdered	MSWI fly ash	Na, (Cd), Cl, Pb, (SO ₄), Zn, F, Br
Fine-grained	PC bottom ash	(Na), As, Zn
Coarse-grained	MSWI bottom ash	Na, Ca, Cl, Cu*, Pb*, SO ₄ , F
Moulded	Fly ash/cement mix	Na, Ba, (Cu), (Mo), SO ₄ , V
Moulded	Limestone with PC fly ash	Na, As, (Ni), SO ₄ , V, Se
Moulded	Brick	(Na), As, V
¹ The components in brackets or marked * were tested but were not included in the determination of the median and ranges, because: <ul style="list-style-type: none"> - the error in the determination of the concentration was too large - the inhomogeneity of the material was too large (marked *) 		

The median value and range for S_r and S_R in the determination of U_{avail} are indicative values of the attainable precision, if the test is performed in accordance with this standard and the requirements mentioned in topic 2 of the notes are met. In particular, accuracy may be poorer in very heterogeneous materials and/or which show strongly pH-dependent leaching behaviour in the pH range of this test.

Annex B

Determination of the relative availability

From the availability of a component, as calculated in 8.1 and the original content of that component in the sample for analysis, the "relative availability" can be calculated with the formula:

$$UP_{avail} = \frac{U_{avail}}{S_0} \times 100\%$$

where:

UP_{avail} is the relative availability referred to the quantity of component present in the solid, in % (m/m) dry matter;

U_{avail} is availability of a component, in mg/kg dry matter;

S_0 is the original content of that component in the sample of analysis, in mg/kg dry matter. This content must be determined by total digestion, for example according to:

BS EN 13657:1996 Characterisation of waste – Digestion for subsequent determination of *aqua regia* soluble portion of elements in waste.

BS EN 13656:1996 Characterisation of waste – Microwave assisted digestion with hydrofluoric (HF), nitric (HNO₃) and hydrochloric (HCl) acid mixture for subsequent determination of elements in waste.