PD CEN/TS 16660:2015

BSI Standards Publication

Characterization of waste — Leaching behaviour test — Determination of the reducing character and the reducing capacity

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee B/508/3, Characterization of waste.

A list of organizations represented on this committee can be obtained on request to its secretary.

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ISBN 978 0 580 83659 6

ICS 13.030.01

Compliance with a British Standard cannot confer immunity from legal obligations.

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 May 2015.

Amendments issued since publication

Date	Text affected

TECHNICAL SPECIFICATION

SPÉCIFICATION TECHNIQUE

TECHNISCHE SPEZIFIKATION

CEN/TS 16660

May 2015

ICS 13.030.01

English Version

Characterization of waste - Leaching behaviour test - Determination of the reducing character and the reducing capacity

Caractérisation des déchets - Essais de comportement à la lixiviation - Détermination des propriétés réductrices et de la capacité de réduction

Charakterisierung von Abfällen - Untersuchung des Elutionsverhaltens - Bestimmung der Reduktionseigenschaft und der Reduktionsfähigkeit

This Technical Specification (CEN/TS) was approved by CEN on 21 March 2015 for provisional application.

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Ref. No. CEN/TS 16660:2015 E

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Foreword

This document (CEN/TS 16660:2015) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

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

This document has been developed primarily to support the requirements for leaching behaviour testing within EU and EFTA countries.

This document was elaborated on the basis of NEN 7348:2006.

To determine the various aspects of the leaching behaviour (the leaching characteristics) of solid earthy and stony building and waste materials a series of steps should be followed, in particular sampling, sample pretreatment, characterization tests, digestion and chemical analysis of the solid substance or the eluates. An umbrella standard (EN 16457) is developed that gives general instructions. In here the relationship is given between all the standards in each step, each with a specific scope. To determine the leaching characteristics, the general instructions or the specific standards to which reference is made shall be followed with good consistency.

This Technical Specification describes a test that can be used to determine whether or not the material to be tested possesses reducing properties. If this is the case, a next test is used to quantify the reducing capacity of this material or its eluates. Based on the results of this Technical Specification, it can be established whether leaching under practical conditions can differ (considerably) from leaching under standard aerobic laboratory conditions and whether there is justification for testing leaching under low-oxygen conditions (see Annex A, [16]).

The standards that characterize the various aspects of the leaching behaviour are produced and published in phases. This means that upon the publication of this Technical Specification, reference is not yet made in all relevant standards. For the missing aspects, users of this Technical Specification will have to make their own choice of the methods to be used. Annex A gives information on the validation and materials used. Annex B gives a further explanatory note on the reducing capacity. In addition to specifications provided in EN 15002, Annex C gives further guidance on sampling, sample pretreatment and sample storage. For more information, the standards and other publications included in the bibliography that have been published in this respect can be used.

The numbered clauses are normative with the exception of the passages marked with the heading 'NOTE'; the annexes are informative.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

This document specifies a set of three tests to assess if a material has reducing properties and subsequently to determine the reducing capacity of that material and the reducing capacity of an eluate produced at low liquid to solid ratio. For a proper performance special attention is given to minimize contact with the atmosphere before and during testing.

For the complete characterization of the leaching behaviour of waste under specified conditions the application of other test methods is required (see EN 12920).

Anyone dealing with waste and sludge analysis should be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples can contain hazardous (e.g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction.

Consequently these samples should be handled with special care. Gases which can be produced by microbiological or chemical activity are potentially flammable and will pressurize sealed bottles. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

In the different European countries, tests have been developed to characterize and assess the constituents which can be leached from waste materials. The release of soluble constituents upon contact with water is regarded as one of the main mechanism of release which results in a potential risk to the environment during life-cycle of waste materials (disposal or re-use scenario). The intent of these tests is to identify the leaching properties of waste materials. The complexity of the leaching process makes simplifications necessary. Not all of the relevant aspects of leaching behaviour can be addressed in one single standard. This Technical Specification addresses reducing properties of materials and the consequences to the test or test conditions to be applied in performing leaching tests.

Procedures to characterize the behaviour of waste materials can generally be divided into three steps, using different tests in relation to the objective. The following test hierarchy is taken from the Landfill Directive[1)] and the Decision on Annex II of this Directive[2)] for disposal of waste.

a) Basic characterization constitutes a full characterization of the waste by gathering all the necessary information for a safe management of the waste in the short and long term. Basic characterization may provide information on the waste (type and origin, composition, consistency, leachability, etc.), information for understanding the behaviour of waste in the considered management scenario, comparison of waste properties against limit values, and detection of key variables (critical parameters as liquid/solid (L/S) ratios, leachant composition, factors controlling leachability such as pH, redox potential, complexing capacity and physical parameters) for compliance testing and options for simplification of compliance testing. Characterization may deliver ratios between test results from basic characterization and results from simplified test procedures as well as information on a suitable frequency for compliance testing. In addition to the leaching behaviour, the composition of the waste should be known or determined by testing. The tests used for basic characterization should always include those to be used for compliance testing.

b) Compliance testing is used to demonstrate that the sample of today fits the population of samples tested before by basic characterization and through that, is used to carry out compliance with regulatory limit values. The compliance test should therefore always be part of the basic characterization program. The compliance test focuses on key variables and leaching behaviour identified by basic characterization tests. Parts of basic characterization tests can also be used for compliance purposes.

1) Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

2) Council Decision 2003/33/EC of 19 December 2002.

c) On-site verification tests are used as a rapid check to confirm that the waste is the same as that which has been subjected to characterization or compliance tests. On-site verification tests are not necessarily leaching tests.

The test procedure described in this document is a basic characterization test and falls in category a).

1 Scope

This Technical Specification specifies three laboratory tests to determine the reducing character and the reducing capacity of construction products, waste materials and the eluate resulting from exposure of these solids to a leachant. Reducing species released from the product are titrated to quantify the reducing capacity.

For a specification of the materials with which experience has been acquired with the execution of the tests according to this Technical Specification see Annex A and [16].

NOTE Materials with reducing properties can in practice under both oxidizing and anoxic (isolated) conditions show completely different leaching behaviour than obtained with the leaching tests specified in EN 16457. This may seriously hamper the interpretation of the leaching tests, if this condition is not taken into consideration.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 14346, *Characterization of waste - Calculation of dry matter by determination of dry residue or water content*

EN 15002, *Characterization of waste - Preparation of test portions from the laboratory sample*

EN ISO 10523, *Water quality - Determination of pH (ISO 10523)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply. Additional terms and definitions are given in EN 13965-2.

3.1
eluate
solution obtained by a leaching test

3.2
laboratory sample
sample or sub-sample(s) sent to or received by the laboratory

[SOURCE: IUPAC, 1990]

Note 1 to entry: When the laboratory sample is further prepared (reduced) by subdividing, cutting, sawing, coring, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis. The laboratory sample is the final sample from the point of view of sampling but it is the initial sample from the point of view of the laboratory.

Note 2 to entry: Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

3.3
leaching test
test during which a material is put into contact with a leachant and some constituents of the material are extracted

[SOURCE: EN 12457-1:2002]

3.4
liquid to solid-ratio
L*/*S
ratio between the amount of liquid (*L*) and of solid (*S*) in the test

Note 1 to entry: *L*/*S* is expressed in l/kg dry matter.

3.5
reducing capacity
potential for a material to impose reducing conditions

Note 1 to entry: Reducing capacity is expressed in mmol O_2/kg.

3.6
redox potential
value that indicates reducing or oxidized state of a material

Note 1 to entry: Redox potential is expressed in mV.

3.7
sample
portion of material selected from a larger quantity of material

3.8
test portion
amount or volume of the test sample taken for analysis, usually of known weight or volume

[SOURCE: IUPAC, 1990]

3.9
test sample
sample, prepared from the laboratory sample, from which test portions are removed for testing or for analysis

[SOURCE: IUPAC, 1990]

4 Principle

The purpose of the tests described in this Technical Specification is to:

— establish whether or not a material has reducing properties;

— establish where necessary the reducing capacity of this material or its eluates in quantitative terms.

The reducing character of a material is determined by bringing the material into contact with demineralized water at a low L/S value in an airtight sealed vessel (24 h contact time) and then measuring the redox potential with respect to the redox potential in water with the same pH.

The reducing capacity of a material or its eluates is determined by carrying out a redox titration. In the titration an excess Ce(IV) is used to oxidize the reducing components. Then by back titration the oxidant demand is determined.

NOTE Sulphide is often the major reducing component.

5 Preparation of the test portion

The test consists of three parts which in principle can be carried out separately. For the single execution of the test to determine the reducing character according to this Technical Specification (8.2) a test portion A_1 of (50 ± 5) g dry matter is necessary, of which the dry matter content w_{dm} is known and of which at least a mass percentage of 95 % (dry matter) of the particles is smaller than 4 mm.

For the single execution of the test to determine the reducing capacity of the solid material according to this Technical Specification (8.3) a test portion A_2 of (2 ± 0,002) g dry matter is necessary, of which the dry matter content w_{dm} is known and of which at least a mass percentage of 95 % (dry matter) of the particles is smaller than 125 µm.

For the single execution of the test to determine the reducing capacity of the eluates according to this Technical Specification (8.4) a test portion A_3 of (20 ± 0,02) g dry matter is necessary, of which the dry matter content w_{dm} is known and of which at least a mass percentage of 95 % (dry matter) of the particles is smaller than 4 mm.

The dry residue of the sample shall be determined from a subsample which is dried at 105 °C ± 3 °C according to EN 14346.

The dry residue expressed as a percentage of the mass fraction is calculated as follows:

$$w_{dr} = 100 \times \frac{m_d}{m_r} \quad (1)$$

where

w_{dr} is the dry residue of the sample, expressed as percentage (%);

m_d is the mass after drying, in grams (g);

m_r is the mass before drying, in grams (g).

Calculate the undried mass of the test portion Mw in grams to be used for the test as follows:

$$M_w = \frac{M_d}{W_{dr}} \times 100 \quad (2)$$

where

M_w is the total mass of the test portion, in grams (g);

M_d is the dry mass of the test portion, in grams (g);

w_{dr} is the dry residue of the sample, expressed as percentage (%).

For the sampling of solid earthy and stony building and waste materials for leaching tests no standards are yet available that are aimed at preserving the reducing capacity of the material to be tested. It is recommended to use the procedures described in EN 14899, taking into account the instructions to limit contact with the outside air (see Annex C).

If the sample from which the test portions are obtained has to undergo pretreatment, use the procedures described in EN 15002, taking into account the instructions to limit contact with the outside air as much as technically feasible (see Annex C).

6 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

6.1 Demineralized water, with a conductivity of max. 1 mS/cm.

6.2 Hydrochloric acid, $c(HCl)$ = (1 ± 0,1) mol/l.

6.3 Sulphuric acid, $c(H_2SO_4)$ = (1 ± 0,01) mol/l.

6.4 Sodium hydroxide solution, $c(NaOH)$ = (1 ± 0,1) mol/l.

6.5 Cerium(IV) sulphate solution, $c(Ce(SO_4)_2)$ = (0,1 ± 0,001) mol/l in (1 ± 0,01) mol/l sulphuric acid.

6.6 Iron(II) sulphate solution, $c(FeSO_4)$ = (0,1 ± 0,001) mol/l in (0,1 ± 0,001) mol/l sulphuric acid.

6.7 Standard redox solutions, suitable for the calibration of a redox electrode, with an inaccuracy of max. 1 mV.

NOTE A buffer solution with E_H = 439 mV (E_{meas} = 220 mV) and pH 7 will usually suffice.

6.8 Nitrogen gas, N_2, of a purity of 99,999 %, O_2 contamination < 3 ppm.

It shall be possible to supply the nitrogen gas as a constant stream.

NOTE Argon gas can be used instead of nitrogen gas also. The use of nitrogen gas is more cost effective and therefore prescribed in this Technical Specification.

7 Equipment

Check the equipment and requisites listed below before use for proper operation and absence of disrupting elements that may affect the result of the test.

Calibrate and/or check the equipment listed under 7.1, 7.2, 7.5, 7.9 and 7.10 before use.

7.1 E_H electrode with reference electrode, standard combination of an E_H platinum electrode with a reference electrode of Ag/AgCl or calomel (Hg_2Cl_2).

NOTE No standards are available for the calibration and measurement of the redox potential on a laboratory scale. The guidelines of the electrode manufacturer can be followed for this.

7.2 pH meter, with a measurement accuracy of at least ± 0,1 pH units and calibrated according to EN ISO 10523.

7.3 Erlenmeyer, sealable 100 ml glass Erlenmeyer or glass pot, with a neck that is wide enough to pass a pH electrode or E_H electrode (7.1) through it.

7.4 Vibrating table, with a travel of at least 5 cm and orbital shaking motion.

7.5 Titration set-up with burette, titration set-up with burette, with an inaccuracy of max. 0,02 ml, and fitted with an electrode for measuring the redox potential via an mV read-out (7.1).

7.6 Filtering device, either a vacuum filtration device (between 30 kPa and 70 kPa) (300 mbar to 700 mbar) or a high-pressure filtration apparatus (<0,5 MPa) (5 bar). Rinsing is compulsory.

NOTE An alternative is the use of vacuum filtration, provided a continuous stream of nitrogen gas (6.8) is passed over the solution to be filtered to prevent oxidation.

7.7 Membrane filters, for the filtration equipment (7.6) with a pore size of 0,45 µm that have been rinsed with demineralized water (6.1).

7.8 Prefilters, with a pore size of max. 1,5 µm.

7.9 Analytical balance, with a measurement range up to 300 g and an accuracy of at least 10 mg.

7.10 Analytical balance, with a measurement range up to 100 g and an accuracy of at least 0,1 mg.

7.11 Thermometer, for temperature measurement in air and liquid.

8 Procedure

8.1 General

The reducing character and/or the reducing capacity of the material to be tested or its eluates shall be determined by respectively:

— carrying out the test according to 8.2 for the reducing character;

— carrying out the test according to 8.3 for the reducing capacity of the solid;

— carrying out the test according to 8.4 for the reducing capacity of the eluates;

— carrying out the calculations according to Clause 9.

All tests shall be carried out at a temperature between 19 °C and 23 °C.

8.2 Determination of the reducing character

De-aerate minimal 500 ml demineralized water (6.1) by bubbling nitrogen gas (6.8) through it for at least 18 h.

Less than 18 h is also possible, provided the redox potential of the water does not change anymore. If the de-aerated water has to be stored, this should be done in gas-tight packaging.

Weigh (50 ± 5) g (dry matter) of the available sample with an analytical balance (7.9) and place this in an Erlenmeyer (7.3). This is the test portion A_1.

Add to the Erlenmeyer containing the test portion (50 ± 5) ml of the de-aerated water. Drive the remaining air out of the Erlenmeyer by blowing nitrogen gas (6.8) over the solution for at least 1 min. After all remaining air is driven out seal the Erlenmeyer airtight and shake for 24 h (7.4).

Some samples may absorb a lot of moisture (for example dried sludge), which makes the execution of the test more difficult. In that case more than 50 ml of de-aerated water may be added. In this case a note shall be made in the test report stating that more than 50 ml of de-aerated water was added to the sample.

If reducing conditions arise as a result of decomposition in the material (for example anaerobic breakdown of organic matter in materials containing a high amount of organic matter), a contact time of 24 h is possibly too short. If there are indications that such reactions can be significant, the contact time may be extended up to four weeks. A note should be made in the test report if the contact time was more than 24 h.

Check the platinum electrode of the standard redox combination (7.1) against the standard redox solution (6.7). Then measure the redox potential of the solution produced in the Erlenmeyer after 24 h ($E_{measured}$ of the solution produced) with the platinum electrode while constantly blowing nitrogen gas (6.8) over it.

Measure the pH of this solution with the pH meter (7.2) with an accuracy of 0,1 pH unit.

Adjust the pH of a quantity of de-aerated water in an Erlenmeyer at the same pH (with an accuracy of 0,1 pH unit) as measured in the solution obtained after 24 h from the test portion A_1, by adding a volume of hydrochloric acid (6.2) or sodium hydroxide (6.4). Then measure the redox potential of this water with the platinum electrode ($E_{measured}$ of the demineralized water) while constantly blowing nitrogen gas (6.8) over it.

NOTE Particularly in the neutral pH range it is not easy to set the pH exactly with acid and base. In that case a titration of the water which spans the relevant pH range, can be carried out where the E_H is measured for different pH values. By plotting the pH and E_H data in a graph form, the corresponding E_H can be determined for the desired pH.

8.3 Determination of the reducing capacity of the solid material

8.3.1 Calibration procedure

Prepare fresh Ce(IV) sulphate solution (6.5) and Fe(II) sulphate solution (6.6).

Calibrate/titrate the Fe(II) sulphate solution (6.6) against (10 ± 0,02) ml Ce(IV) sulphate solution (6.5). Register the volumes of used Fe(II) sulphate solution ($V_{Fe(II)}$) and Ce(IV) sulphate solution ($V_{Ce(IV)}$).

The Fe(II) sulphate solution is subject to oxidation and should therefore be prepared shortly before the test.

NOTE The solution can be kept sealed from the air for no more than a few days. The procedure described above serves to determine the strength of the Fe(II) solution prior to the test ($M_{Fe(II)}$). For the titration of 10 ml Ce(IV) solution approximately 10 ml Fe(II) sulphate solution will be necessary.

8.3.2 Determination of the reducing capacity of the solid material

It may be that a slight pressure will build up in the Erlenmeyer during the equilibrium time as a result of gas formation. From a safety point of view the (glass) stoppers in the Erlenmeyers shall not be fixed too tightly.

Weigh (2 ± 0,002) g (dry matter) (m_0) of the available sample with an analytical balance (7.10) and place this in an Erlenmeyer (7.3). This is the test portion A_2.

Add to the Erlenmeyer containing the test portion (30 ± 0,02) ml ($V_{Ce(IV)}$) of the Ce(IV) sulphate solution (6.5). Drive the remaining air out of the Erlenmeyer by blowing nitrogen gas (6.8) over the solution for at least 1 min. After all remaining air is driven out close the Erlenmeyer with the stopper and shake for 24 h (7.4).

It is possible that for extreme reducing materials 30 ml Ce(IV) sulphate solution is not sufficient for fully oxidizing the sample. In that case a bigger volume than 30 ml shall be added. In this case a note shall be made in the test report stating that more than 30 ml of Ce(IV) sulphate solution was added to the sample.

Titrate (7.5) the suspension produced with the Fe(II) sulphate solution (6.6) back until the transition point is reached. Read off the quantity of Fe(II) sulphate solution added to an accuracy of 0,02 ml ($V_{Fe(II)}$). During the

titration constantly measure the redox potential. The transition point is reached when the redox potential changes from approximately 1 200 mV to 600 mV.

NOTE The change in redox potential is accompanied by a barely perceptible colour change from yellow to colourless. The transition point is reached as soon as the end point is reached of the reaction: $[Fe^{2+}]/[Fe^{3+}] = [Ce^{4+}]/[Ce^{3+}]$. The validation (Annex A) showed that the colour change does not always take place at the same time as the change in the redox potential. Titration based on the change in the redox potential is a more objective method and is therefore more accurate than titration based on colour change. The validation of this part and 8.4 has not yet been carried out in all cases based on the measurement of the change in the redox potential. It is expected that the results of the validation of 8.3 and 8.4 (see Annex A) will be improved with this procedure.

8.4 Determination of the reducing capacity of the eluates

8.4.1 Calibration procedure

Carry out the calibration procedure as described under 8.3.1.

8.4.2 Determination of the reducing capacity of the eluates

De-aerate minimal 500 ml demineralized water (6.1) by bubbling nitrogen gas (6.8) through it for at least 18 h.

Less than 18 h is also possible, provided the redox potential of the water does not change anymore. If the de-aerated water has to be stored, this should be done in gas-tight packaging.

Weigh (20 ± 0,02) g (dry matter) (m_0) of the laboratory sample with an analytical balance (7.10) and place this in an Erlenmeyer (7.3).

Add (20 ± 0,02) ml (V_{add}) of the de-aerated water to the test portion in an Erlenmeyer (7.3). Drive out the remaining air from the Erlenmeyer by blowing nitrogen gas (6.8) over the solution for at least 1 min, seal it so that it is airtight and shake for 24 h (7.4).

Some samples may absorb a lot of moisture (for example dried sludge), or already contain a lot of moisture (undried sludge). In that case the quantity of de-aerated water added may differ from the 20 ml specified. In the calculation in 9.3 this shall be taken into account by using V_{add} for the adjusted volume.

Filter (7.6) the solution produced through a membrane filter (7.7), if necessary fitted with a prefilter (7.8). First blow nitrogen gas (6.8) through the filter holder and filter the solution by pressurizing the holder with nitrogen gas (6.8) up to the maximum permitted value. Collect the filtrate in an Erlenmeyer (7.3) while constantly blowing nitrogen gas (6.8) through it.

Since eluates are generally poorly buffered due to the absence of solid matter, it is recommended to carry out the filtration and the titration of the eluates in a glove bag under increased nitrogen pressure. This is particularly recommended for samples from oxygen-free environments.

Add to a known volume of the filtered solution (V_{filtr}) (10 ± 0,01) ml of the Ce(IV) sulphate solution (6.5) ($V_{Ce(IV)}$) and titrate (7.5) with the Fe(II) sulphate solution (6.6) back until the transition point is reached as described in 8.3.2. Read off the quantity of Fe(II) sulphate solution added to an accuracy of 0,02 ml ($V_{Fe(II)}$).

Because eluates may have a relatively low reducing capacity, it is recommended for the titration to use Ce(IV) sulphate solution (6.5) and Fe(II) sulphate solution (6.6) diluted with de-aerated water. A dilution with a factor 10 seems to be sufficient for the materials that are used in the validation (see Annex A).

To determine the reducing capacity of eluates, coming from leaching tests according to EN 12457 (all parts), CEN/TS 14405, EN 14429, EN 14997, EN 15863, or CEN/TS 15864 a similar titration procedure can be followed to that described here (see also [19]). Since these tests are carried out under aerobic conditions, oxidation may occur particularly in the fractions with a longer duration (>1 d to 2 d). If fractions of a longer

duration are significant, one should start from the collection of the fractions under a nitrogen atmosphere and/or carry out the test entirely under oxygen-free conditions.

9 Calculations

9.1 Determination of the reducing character

Deduce the redox potentials measured according to 8.2 of the solution obtained in the Erlenmeyer from the test portion A_1 and from the de-aerated demineralized water, brought to the same pH, to the standard potential for hydrogen according to:

$$E_H = E_{Measured} + E_{ref} \quad (3)$$

where

E_H is the measured value corrected to the standard potential for hydrogen, in mV;

$E_{Measured}$ is either the potential measured in the sample solution or in the demineralized water brought to pH, in mV;

E_{ref} is the difference between the standard potential of the reference electrode and that for hydrogen, in mV.

Compare the E_H values thus calculated from the two separate measurements and establish whether the difference is greater or smaller than 50 mV.

NOTE 1 For the correct value of E_{ref} consult the manual for the electrode used. For a reference electrode of Ag/AgCl, E_{ref} in Formula (3) is usually equal to 244 mV; for calomel E_{ref} is usually equal to 225 mV.

NOTE 2 A measurement of the redox potential in eluates has a reasonable accuracy of around 50 mV.

A redox potential of the solution obtained from the test portion A_1 that is 50 mV lower than in de-aerated demineralized water indicates a reducing character such that significant changes in the leaching behaviour of the material are possible upon exposure to air.

9.2 Calculation of the reducing capacity of the solid material

Deduce from the calibration procedure according to 8.3.1 what is the molarity of Fe(II) in the Fe(II) sulphate solution (6.6) according to the formula:

$$M_{Fe(II)} = \frac{V_{Ce(IV)}}{V_{Fe(II)}} \times M_{Ce(IV)} \quad (4)$$

where

$M_{Fe(II)}$ is the molarity of Fe(II) in the Fe(II) sulphate solution, in mol/l;

$V_{Ce(IV)}$ is the volume of the Ce(IV) sulphate solution, in ml (10 ml ± 0,02 ml, see 8.3.1);

$V_{Fe(II)}$ is the volume of the Fe(II) sulphate solution added during the titration, in ml;

$M_{Ce(IV)}$ is the molarity of the Ce(IV) sulphate solution, in mol/l (0,1 mol/l ± 0,001 mol/l, see 6.5).

Then calculate from the quantity of Fe(II) sulphate solution added during the test according to 8.3.2 the reducing capacity of the solid material according to the formula:

$$RV_{\text{solid}} = \frac{(V_{\text{Ce(IV)}} \times M_{\text{Ce(IV)}}) - (V_{\text{Fe(II)}} \times M_{\text{Fe(II)}})}{m_0 \times 4} \quad (5)$$

where

RV_{solid} is the reducing capacity of the solid, in mmol O_2 per kg dry matter;

$V_{\text{Ce(IV)}}$ is the volume of the Ce(IV) sulphate solution in 8.3.2, in ml;

$M_{\text{Ce(IV)}}$ is the molarity of the Ce(IV) sulphate solution, in mol/l (0,1 mol/l ± 0,001 mol/l, see 6.5);

$V_{\text{Fe(II)}}$ is the volume of the Fe(II) sulphate solution that is added in 8.3.2, in ml;

$M_{\text{Fe(II)}}$ is the calculated molarity of the Fe(II) solution according to Formula (4), in mol/l;

m_0 is the dry mass of the test portion A_2, in kg.

NOTE The factor 4 in Formula (5) arises from the fact that 1 mmol of Ce(IV) consumed corresponds to 0,25 mmol O_2 (g).

9.3 Calculation of the reducing capacity of the eluates

Deduce from the calibration procedure according to 8.3.1 what is the molarity of Fe(II) in the Fe(II) sulphate solution (6.6) in the way described in 8.3.

Then calculate from the quantity of Fe(II) sulphate solution added during the test according to 8.4.2 the reducing capacity of the eluates according to the formula:

$$RV_{\text{eluates}} = \left(\frac{V_{\text{add}} + w}{V_{\text{filtr}}} \right) \times \frac{(V_{\text{Ce(IV)}} \times M_{\text{Ce(IV)}}) - (V_{\text{Fe(II)}} \times M_{\text{Fe(II)}})}{m_0 \times 4} \quad (6)$$

where

RV_{eluates} is the reducing capacity of the eluates, in mmol O_2 per kg dry matter;

V_{add} is the volume of de-aerated water added, in ml (the standard quantity is 20 ml);

w only if field-moist analysis samples are used in the test (for example wet sludge) the quantity of moisture in the analysis sample shall be entered here (in g), to be deduced from the determination of the dry matter content determined according to EN 14346. In other cases no value shall be entered for w;

$V_{\text{Ce(IV)}}$ is the volume of the Ce(IV) sulphate solution in 8.4.2, in ml;

$M_{\text{Ce(IV)}}$ is the molarity of the Ce(IV) sulphate solution (6.5) taking into account any dilution, in mol/l;

$V_{\text{Fe(II)}}$ is the volume of the Fe(II) sulphate solution that is added in 8.4.2, in ml;

$M_{\text{Fe(II)}}$ is the calculated molarity of the Fe(II) solution according to Formula (4), taking into account any dilution, in mol/l;

V_{filtr} is the volume of the filtrate that is processed, in ml;

m_0 is the dry mass of the test portion A_3, in kg.

NOTE It is possible to determine the reducing capacity of the eluates for different pH values, which may be important if the conditions in which the material will be used in practice differ from those during the test according to 8.4.

10 Test report

The report shall contain at least the following data:

— reference to this Technical Specification;

— the date of the test;

— the data necessary for the identification of the sample used for the analysis samples (origin and specifications);

— the parts of the test carried out;

— dry matter content of the samples;

— relevant notes on the conditions under which work is carried out (for example the way oxidation is prevented in 8.4.2);

— the temperature range within which the tests were carried out;

— whether or not the material tested is reducing;

— the amount of sample used;

— the pH values measured, rounded to 0,1 pH unit;

— the redox potentials measured, rounded to 1 mV;

— the volumes of the solutions used, rounded to 0,02 ml;

— the titration quantities used, rounded to 0,02 ml;

— the result of the calculations carried out;

— any deviation from the test method and the reason of this deviation together with all circumstances that may have influenced the results.

Annex A
(informative)

Validation of the provisions of the reducing capacity

A.1 General

In a ring test based on the procedure according to ISO 5725-2 the precision is determined of the test for reducing character and reducing capacity in terms of repeatability and reproducibility. For the execution of the ring test the procedure described in this Technical Specification was used.

The validation test is carried out on the basis of the participants volunteering. The scope of the validation test was therefore somewhat limited by the input that can reasonably be asked of the participants (number of samples and measurements), and the readiness of the participants.

The ring test was carried out with four laboratories on three types of materials that are known to have a reducing character. These are blast furnace slag, steel slag and Malburg harbour sludge.

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

— the sample pretreatment (variations in the preparation of the test portion for the leaching test);

— the test components themselves.

When establishing the precision of the test for the reducing capacity the aim was to limit the errors that were not the result of the test itself, by centralising the pretreatment. In addition to the variation between laboratories the variation between the different measurements was determined. The tests were therefore carried out in duplicate by each laboratory.

A preliminary test showed that in particular for 'wet' materials the sample pretreatment is an important factor that can affect the value of the reducing capacity to be measured. A small preliminary test showed that freeze drying this material, before size-reducing it, gives the most consistent results. The Malburg harbour sludge was therefore freeze-dried, size-reduced (crushed) and packed under nitrogen for dispatch.

The choice of the samples is based on the good measurability of the reducing character and the reducing capacity of the solid. This is also the case for the third sample, Malburg harbour sludge, this sample was consciously chosen because of the sensitivities in (pre)treatment of the sample and a possible bigger dispersion in the results.

In the following the results of the validation test are discussed for each paragraph of the standard.

A.2 Validation results 9.1 'Determination of the reducing character'

The material has a reducing character if the E_H measured in the suspension of the material is at least 50 mV lower than the E_H measured in de-aerated demineralized water for the same pH (see 9.3). Although the absolute values show some dispersion, the difference between E_H measured in demineralized water and E_H measured in the suspension for three of the four laboratories is a few hundred millivolts. This shows that the materials are reducing (see Table A.1).

Table A.1 — Difference in E_H between demineralized water and suspension

Material	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4
	ΔE_H mV	ΔE_H mV	ΔE_H mV	ΔE_H mV
Blast furnace slag sand (A)	282	185	390	55
Blast furnace slag sand (B)	230	267	363	313
Steel slag (A)	191	265	420	−45
Steel slag (B)	223	322	383	72
Malburg harbour sludge (A)	–	−83	345	–
Malburg harbour sludge (B)	–	96	377	371

For one laboratory the results showed some variation and did not always lead to the conclusion that the materials were reducing (laboratory 4, see Table A.1). Although the precise cause of this is not known, it is noted that it is not generally easy to measure the redox potential in poorly buffered systems. A general cause for unstable values of the redox potential is the possibility of oxygen entering the system. In addition, the participants pointed out that it was not easy to adjust the pH of the demineralized water exactly to the pH of the suspension, particularly in the neutral pH range. This may also be one cause of the changing values and the difference between E_H in the demineralized water and in the suspension.

The problem is overcome in the text of the standard by stating that in that case a titration of the water has to be carried out that bridges the relevant pH range, where in case of different pH values the E_H is measured. By setting out the pH and E_H data in graph form, for the desired pH the corresponding E_H can be determined (see note in 8.2). For one material (Malburg harbour sludge) most of the laboratories obtained no reliable values because the material absorbed too much moisture. This makes the measurement difficult. The problem is overcome by including a note in the text of the standard that in that case it is also possible to add more de-aerated water (see 8.2).

A.3 Validation results 9.2 'Calculation of the reducing capacity of the solid material'

The reducing capacity of the solid was in all cases high (a few hundred mmol O_2 per kg dry matter). The values for the relative standard deviation in respectively the repeatability (CV_r) and reproducibility (CV_R) that were obtained in the ring test for the materials mentioned in Table A.1 are set out in Table A.2.

Table A.2 — Mean values

Material	Total mean value ± standard deviation	CV_r	CV_R
	mmol O_2/kg d.m.	%	%
Malburg harbour sludge	436 ± 41	1,0	9,5
Blast furnace slag sand	308 ± 38	2,3	12,3
Steel slag	186 ± 76	8,6	41,4

Both the repeatability and reproducibility can in general be termed good. The value for the reducing capacity for three of the four laboratories is based on change in the redox potential instead of on the colour change; for one laboratory no values were available for the redox potential and the measurements were based on colour

change. The reproducibility of the measurements on steel slag was distorted by the measurements of one laboratory, where the measurements came out considerably higher due to an unknown cause.

During the validation it was found that measurements based on redox potential (from +1 200 mV to +600 mV, a good measurable difference) were the most objective measurements because colour change is usually poorly visible and does not occur at precisely the same time as the change in the redox potential. With reference to the validation the measurement of the redox potential during the titration is therefore specified as normative in 8.3 and 8.4.

A.4 Validation results 9.3 'Calculation of the reducing capacity of the eluates'

The measurement results of the reducing capacity are set out in Table A.3.

Table A.3 — Measured values of the reducing capacity of the eluates

Material	Reducing capacity mmol O_2/kg			
	Laboratory 1	Laboratory 2	Laboratory 3	Laboratory 4
Blast furnace slag sand (A)	0,77	0,65	0,23	0,18
Blast furnace slag sand (B)	0,44	0,49	0,24	1,04
Steel slag (A)	0,18	1,92	0,03	0,48
Steel slag (B)	0,18	0,10	0,004	0,77
Malburg harbour sludge (A)	–	2,80	2,57	3,23
Malburg harbour sludge (B)	–	2,16	2,21	8,51

The measurements show a great deal of dispersion between one laboratory and another and between samples. In particular the measurements on steel slag show great dispersion. The eluates of this material are probably the most poorly buffered and very susceptible to the entry of oxygen.

For Malburg harbour sludge the measurement was made difficult by absorption of water (see A.1), but the values for the reducing capacity of the eluates were higher than for the other samples and so can be better measured. In the text of the standard a revision was made for materials that may contain a lot of water, namely by increasing the *L/S* value used in the test (see 8.4.2).

Laboratory 3 and laboratory 4 carried out the titrations with diluted solutions because of the poor reducing capacity of the eluates. This gives greater accuracy. Laboratory 1 based the measurements on colour change and did not have available measured values of the redox potential. Particularly for poorly buffered systems this may lead to differences with respect to measurements of the change in the redox potential. Laboratory 3 has used a glove bag for the filtration step in the test to minimize oxygen entry.

In general it may be expected that the measurements are considerably affected by the method of excluding the entry of oxygen, as a few participants indicated. It is likely that the results are more repeatable and reproducible when the titration is carried out under strict anoxic conditions in a 'glove bag'.

Annex B
(informative)

Explanatory note

B.1 Cause of reducing material behaviour

The reducing properties of a material or solution that has been in contact with this material, are largely determined by the presence of sulphide (S^{2-}), bivalent iron (Fe^{2+}) and/or bivalent manganese (Mn^{2+}). If these chemical species are available to a sufficient degree, a macroscopic effect such as change in the redox potential can come about. The redox-determining species S^{2-}, Fe^{2+} and Mn^{2+} usually only become available if increased mobility has occurred as a result of leaching.

The leaching behaviour of the redox-determining species S^{2-}, Fe^{2+} and Mn^{2+} is very greatly dependent on the prevailing pH. For Fe^{2+} and Mn^{2+} only in an acidic to slightly acidic environment there is any question of imposing reducing conditions on the environment, because the leachability of these elements decreases considerably in a neutral to slightly alkaline environment.

For sulphide the redox effect takes place over the whole pH range, though with an increase in a strongly alkaline environment. In blast furnace slag and phosphorus slag sulphide is the dominant redox-determining species; these slags contain sufficient sulphide to bring about reducing conditions over the whole pH range. The reducing behaviour of steel slag, on the other hand, is mainly determined by the presence of reduced Fe and Mn oxides, because the capacity relating to sulphides is relatively quickly exhausted. Other metal slags, such as lead slag and zinc slag, contain so little redox-determining species that the reducing capacity can be ignored.

Also for materials with a high organic matter content sulphide, derived from biological decomposition (sulphate reduction), is often the dominant redox-determining species. In addition microorganisms can also reduce iron and manganese.

B.2 Set-up of the tests to determine the reducing capacity

A common method for obtaining an idea of the reducing capacity of a material, is to determine the biological oxygen demand (BOD) or the chemical oxygen demand (COD). Both determination methods were developed for wastewater. The BOD method when applied to solids results in great variations in the results because of the slow and poorly reproducible reaction with oxygen. The COD determination gives a measure of the total reducing capacity of a material, after complete pulverization and long term exposure to strongly oxidising conditions (dichromate, increased temperature). Both methods are therefore less suitable for relating the leaching behaviour of materials to practical conditions.

A more direct and absolute measure of the reducing capacity is derived from the measured concentrations of sulphide, bivalent iron and bivalent manganese in the material to be tested or its eluates. The sum of the reducing components measured gives, after conversion based on electron demand (equivalents/l), the actual reducing capacity as a function of the *L/S* value for a specific pH value.

Actual reducing capacity = $[S^{2-}] + [Fe^{2+}] + [Mn^{2+}]$

This variable can be converted again for the actual reducing capacity, expressed in mmol O_2 per kg.

In this Technical Specification a determination method is described that is mid-way between a BOD and a COD determination: the 'cerimetric' method. This method, that can be used both for the solid and for the

eluates, is based on addition of an excess Ce(IV) in 0,5 mol/l H_2SO_4 and back titration with Fe^{2+}. The determination is not carried out at increased temperature and keeps the (silicate) matrix of the material intact. The results of the test are expressed in mmol O_2 per kg solid that has been in contact with the leaching fluid.

The results of the Ce(IV) titration method seem to be well in line with those of the direct chemical analysis of sulphide, bivalent iron and bivalent manganese, although this has not yet been checked over the whole pH range [20]. The Ce(IV) titration method is therefore preferable for routine determinations.

B.3 Limitations of the cerimetric determination method

Values for the reducing capacity of less than 2 mmol O_2 per kg solid fall within the scope of the method.

With the cerimetric method described in this test an instantaneously imposed reducing capacity is determined. For materials of which the occurrence of reducing conditions show very slow kinetics, for equilibrium in the extract a longer contact time is necessary than specified according to 8.4. Such materials will in the test for the solid according to 8.3 lead to a measurable value, while in the test for the extract according to 8.4 no measurable response is obtained, unless the contact time is considerably lengthened.

The content of 'inert' carbon in the test portion may lead to an overestimation of the calculated reducing capacity. In slags from smelting processes the carbon content is usually negligible (<1 %), but in other combustion residues the fraction of unburned carbon, in combination with the specific area of the material, makes a correction to the calculation necessary. This is the case if the inert carbon content is greater than 5 %. This can be corrected by taking into account a reduction in the measured reducing capacity of 16,4 mmol O_2/kg material per % inert carbon in the material.

B.4 Materials with reducing properties

Examples of materials with reducing properties are:

— industrial slags from smelting processes, such as steel slag, blast furnace slag and phosphorus slag and some coal gasification residues;

— sulfur-containing waste materials;

— immobilised residues that contain organic or inorganic sulphides;

— materials with decomposable organic material.

When processing residues 'containment' (sulphide deposition) of metals among other things is obtained in a strong alkaline environment (cement stabilization) or by imposing reducing conditions by adding sulphide based additives.

Materials with decomposable organic material, such as natural sediments and sewage treatment sludges, are reducing due to biological decomposition in the very short-term, unless they are stored in a dry environment and with a limited layer thickness.

Depending on the way in which the above-mentioned materials are used, the conditions will be or become oxidising, or reducing. Table B.1 gives an outline of this.

Table B.1 — Outline of the conditions that may occur for a few frequently occurring applications of reducing materials

Material	Oxidising conditions (exchange with the atmosphere)	Reducing conditions (sealed from the atmosphere)
Oxidized materials	For all normal applications	Only upon contact with reducing material
Immobilised waste with sulphide	For application in contact with air [a]	For isolated applications
Steel slag, blast furnace slag, phosphorus slag	Open applications with good flowing surface water and air contact	Isolated applications with limited air contact
Sulfur-containing waste materials	For application in contact with air	For isolated applications
Materials with decomposable organic matter (sludges)	Only with intensive aeration	After a short time reducing in closed applications
[a] This applies in any case for the outer layer of the material. For application in thick layers it may take a very long time before the whole layer is oxidized. This shall be assessed for each situation.		

If the anticipated application situation is such that the material is or will become reducing, the leaching behaviour in practice can only be reasonably well predicted in the very short-term based on the current aerobic leaching tests (CEN/TS 14405, EN 14429, EN 15863 and CEN/TS 15864), provided this is carried out on a sample of the fresh (reducing) material.

If however the conditions are oxidising, the leaching behaviour will change in character considerably within a very short time. It is recommended for these conditions to use a fully oxidized sample for the test [21, 22].

If an estimate has to be made of the leaching of reducing materials in the longer term and/or in an isolated application, adapted leaching tests will be necessary, to be carried out under low-oxygen conditions. A column test under low-oxygen conditions has been developed. This test was published as CEN/TS 16660 (this Technical Specification). For further information, see [16], [21] and [22].

On the basis of earlier measurements an estimate was made that the transition point for the development of reducing behaviour should lie in the region of 10 mmol O_2/kg for the solid [16]. For a reducing capacity of the solid that is greater than this value the material should perhaps be tested with adapted leaching tests. There are however still too few data available to be able to state this with certainty.

Annex C
(informative)

Sampling, storage and pretreatment

For potentially reducing materials for which the intention is to determine the reducing character and reducing capacity according to this Technical Specification, it should be taken into account that oxidation may occur at every stage of the characterization due to contact with oxygen from the air. Whether measures should be taken to prevent oxidation of the material, very much depends on the situation in which the material is found. If materials are produced, processed or temporarily stored in contact with the atmosphere, no special precautions are necessary. If samples come from oxygen-less practical applications, it is recommended that contact with oxygen be avoided as far as possible.

In the first place the duration of exposure to the air should be kept as short as possible. A number of recommendations are made below that arise from the studies [16], [20] and [22]. It should be noted that there are still a number of uncertainties in the elaboration or operation of these recommendations.

When sampling (potential) reducing materials it should be noted that the outer layer in direct contact with the air is not representative of the bulk of the material. Particularly because of this property, layered sampling is important, or at least a sample should be obtained that is that representative of the whole batch. Sometimes it may already be apparent due to a colour difference whether this involves reduced or partly oxidized material. Reducing sediment is black (iron sulphide), while oxidized sediment is of a light colour. The oxidized surface of slags can often be identified from brown oxidized iron on the surface.

When sampling in practical situations it is recommended that the samples be transported in vessels that are as airtight as possible. If necessary, this can be in the sampling tube with which the sample was taken (if used), as far as possible vacuum extracted or under nitrogen. Of course, it is preferable to do this already in the field.

Also when taking a sub-sample for analysis in the laboratory (test portion) a key issue is to prevent oxidation. In the last case, it is recommended that the sample be taken from the middle of the vessel or the pot and to ensure that the outer layer (against the wall or on top) is not further processed.

When sampling (fresh or size-reduced) potential reducing materials, EN 15002 is generally sufficient. Although care should be taken at all times to minimize exposure of the sample to the atmosphere to the extent technically and practically feasible. Where this largely concerns organic materials (sludge, sediments), the samples should be stored under refrigeration until they are used for further analysis.

When size-reducing or sieving the sample (sample pretreatment) the contact time with the air is relatively short, as a result of which only in extreme conditions oxidation shall be taken into account. For reduced or moist samples (e.g. sediments) the storage method very soon becomes determinant. If these are relatively dry materials (e.g. slags), the method of size reduction is not very critical (manual, crushing jaws). Moist, largely inorganic materials (sulphide containing) may, if necessary, first be gently dried at 40 °C before being size reduced/sieved.

A modest preliminary test shows that when using ‘wet’ sediment (with no further pretreatment) significant oxidation occurs before and during the test. Significant oxidation also occurs when the sediment sample is first dried before being further processed. For moist (moisture content > 10 % of the mass percentage), largely organic materials (e.g. sediments, sludges), it is therefore recommended to freeze dry the sample before sieving or crushing. This gave the highest reducing capacity and (within the margins of uncertainty (n = 4), the most reproducible result.

An alternative for the above-mentioned methods is to carry out the pretreatment under cryogenic conditions.

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