
**Metode za preskušanje gostih ognjevdzdrhnih izdelkov ņ Navodila za preskušanje
odpornosti ognjevdzdrhnih materialov proti koroziji zaradi tekoč in**

Methods of test for dense refractory products - Guidelines for testing the corrosion of
refractories caused by liquids

Prüfverfahren für dichte feuerfeste Erzeugnisse - Leitlinien zur Prüfung von durch
Flüssigkeiten hervorgerufene Korrosion an feuerfesten Erzeugnissen

Méthodes d'essai pour produits réfractaires denses - Lignes directrices pour la conduite
sur réfractaires d'essais de corrosion provoquée par des liquides

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English Version

Methods of test for dense refractory products - Guidelines for testing the corrosion of refractories caused by liquids

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Lignes directrices pour la conduite sur réfractaires d'essais
de corrosion provoquée par des liquides

Prüfverfahren für dichte feuerfeste Erzeugnisse - Leitlinien
zur Prüfung von durch Flüssigkeiten hervorgerufene
Korrosion an feuerfesten Erzeugnissen

This Technical Specification (CEN/TS) was approved by CEN on 25 March 2006 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

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Foreword

This Technical Specification (CEN/TS 15418:2006) has been prepared by Technical Committee CEN/TC 187 "Refractory products and materials", the secretariat of which is held by BSI.

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

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1 Scope

These guidelines introduce the principles, testing and assessment of corrosion of refractories by liquids (molten metals, metallurgical slags, glasses, fluxes etc.) and describe four commonly used test methods.

- Method A: Corrosion testing by the crucible test;
- Method B: Corrosion testing by the finger-dip test;
- Method C: Corrosion testing by the rotary slag test;
- Method D: Corrosion testing by the induction crucible test.

2 Normative references

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

EN 1402-5 *Unshaped refractory products — Preparation and treatment of test pieces*

EN ISO 12677 *Chemical analysis of refractory products by XRF— Fused cast bead method (ISO 12677:2003)*

ISO 3611 *Micrometer callipers for external measurement*

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3 General

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3.1 Principles

Industrial refractories are mainly used for the inner linings of operational units in combustion, chemical, metallurgical and materials manufacturing processes. Because of the thermal, chemical, mechanical and physical gradients encountered in these refractory linings, their service life is limited by corrosion phenomena, which often involve a combination of different mechanisms such as dissolution, invasive penetration, oxidation-reduction reactions, mass transport, acid-base reaction and spalling of reacted layers.

Because of the complexity of the phenomena, a simple, all-encompassing, general theory of corrosion of refractory materials does not exist, but some basic principles can be applied.

A fundamental and long considered principle is the acid-base relationship between the refractory and the corroding liquid so that an acid refractory such as silica is chosen for an acidic liquid and a basic refractory such as magnesia or doloma for a basic liquid. For example, commonly used acid-base ranking of various compounds are:

most acidic < N_2O_5 (g) < SO_3 (g) < SO_2 (g) < CO_2 (g) < B_2O_3 (g or l) < V_2O_5 (g or l) < SiO_2 (s) < TiO_2 (s) < ZrO_2 (s) < Fe_2O_3 (s) < Cr_2O_3 (s) < Al_2O_3 (s) < FeO (s) < NiO (s) < MnO (s) < MgO (s) < CaO (s) < Na_2O (s or g) < K_2O (s or g) < most basic.

However, whilst this approach provides a starting point for refractory selection, it has limited value in comparing actual behaviour.

A second approach is to make appropriate thermodynamic calculations for the thermal stability of each constituent (free energy of formation); red-ox potentials and possible reactions (free energy change) between reactants (solid, liquid and gas) with the help of the Ellingham diagrams; and the volume changes caused by phase transformations inducing microcracks in the matrix.

Finally, the kinetics of the corrosion are also governed by several other phenomena:

- wetting or non-wetting behaviour of the liquid reactant on a solid surface and the capillary forces controlling its penetration in the porous volume of the refractory (slag penetration inducing structural spalling);
- dissolution of the solid into the liquid;
- condensation of a gas to form a liquid or a solid into the pores that may react chemically and create a thermal-expansion mismatch (for instance, alkali vapours causing the formation of high thermal expansion aluminosilicates).

In practice, for porous solids such as refractories, with open porosity and with fine and highly reactive matrix materials, both dissolution and penetration occur. Hence, most corrosion situations involve chemical attack of the matrix or low-melting constituent phases, which disrupts the structure and allows the coarse-grained aggregates to be carried away by movement of the liquid.

When penetration is more important than dissolution, another mechanism of degradation, structural spalling, needs to be considered.

NOTE Structural spalling is the general term for the cracking or fracture caused by stress produced between the altered (e.g. slag impregnated) zone and the original zone in a refractory under service.

Major factors like chemical reaction rate, viscosity, diffusion constant are highly temperature dependent.

Information about the maximum service temperature for normal durability as a function of refractory materials and corrosion reactants can be found in the literature (see e.g. [1]).

3.2 Corrosion testing

Corrosion resistance data, obtained in a laboratory environment rarely simulate the actual conditions that prevail in service. The size and geometry, thermal gradient and cycling, mechanical load, as well as operation time are difficult to scale down to laboratory conditions. Moreover, accelerated tests in more severe conditions to reduce testing time can lead to erroneous predictions of service performance.

As full-size testing in industrial conditions or at the scale of small panels are more costly and not always possible to perform, numerous laboratory test procedures have been developed but only a few of these have reached the status of an international standard because each industrial application requires specific conditions.

Nevertheless, there is a need for corrosion test standards, describing general procedures and reasonable expectations in terms of data and reliability, leaving full freedom for the choice of the temperature and the nature of the reactant.

On the other hand, when the reactant is a pure chemical compound, acting under readily definable conditions, a standard has already been developed (for instance, the CO attack procedure in the EN ISO 12676 [2]).

In the case of liquid corrodent (e.g. molten metal, molten salt, slag), different approaches have been adopted for corrosion testing in the laboratory:

— Static

The crucible test, the immersion test or the pill test deal with the thermodynamic aspect for the appraisal of chemical attack.

— Dynamic

The drip test and the finger-dip test with movement and/or rotation add a kinetic aspect; for immersion and finger-dip tests, weight changes can be recorded. More application oriented tests are the basin test,

the rotary slag test and the induction crucible test, which are performed on a larger scale, closer to the service conditions but, as a consequence, involve a high degree of setting up and expense.

Finally, it is emphasised that corrosion resistance is not an intrinsic material property, but that of a "three-component" system (i.e. material-corrodent-environment). Accordingly, the results will be largely dependent upon the test method used and any comparison between results obtained by different methods should be done with great care.

3.3 Assessment of the extent of corrosion

The extent of chemical attack may be ascertained using a number of simple criteria:

- Depth of penetration and formation of an altered layer;
- Change of mass (gain or loss);
- Change of cross-section (contraction or expansion);
- Change of mechanical strength;
- Change in the chemical composition of the corroding medium.

In addition, microscopic examination and microanalysis techniques can be used to study the nature of the attack.

3.4 Overview

An overview of the main characteristics of the 4 methods covered by the present guidelines is shown in Table 1 and is meant to assist in the selection of the most pertinent method for a given practical situation.

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Table 1 — Overview of the various test methods

Factors		Crucible	Finger-dip	Rotary slag	Induction furnace
Technical (Materials)	Metals (M)	X	X	-	X
	Slags (S)	X	X	X	-
	M + S	X	X	(X)	X
	Glasses	X	X	(X)	-
Technical (Parameters)	Static	X	X	-	-
	Dynamic	-	X	X	X
	Isothermal	X	X	-	-
	Temp. gradient	-	-	X	X
	$\frac{Vol_{corrodent}}{Surf_{refrac}}$	low	high	medium	medium
	Renewal of corrodent	-	-	X	X
	Possible interaction between samples	-	X	X	X
Technical (Assessment)	Control of the atmosphere	X	X	X	X
	Visual/Microscopy	X	X	X	X
	Dimensional	X	X	X	X
	Change of composition	possible	possible	possible	possible
Economical	Mechanical	-	-	-	-
	Scale	small	medium	large	large
	Ease	++++	+++	++	+
	Cost	low	medium	high	high

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4 Method A: Crucible test

4.1 Scope

This clause describes a method of determining the relative resistance of refractory products to a given liquid corrodent under static conditions when heated to specified temperatures, by melting the corrodent in crucibles formed from the products to be tested.

It is applicable to fired or unfired products and to monolithic materials including concrete, gun mixes, ram mixes, plastics, etc. A variation of the test allows assessment of jointing material.

The method enables the relative resistance of various refractory products to a specified corrodent to be established by comparing the erosion and penetration occurring under static conditions and a uniform temperature.

4.2 Principle

Crucibles together with lids are cut or fabricated from the products to be tested. The crucibles are filled with a quantity of the corrodent and heated to the test temperature for a specified period.

The test conditions (temperature and corrodent composition) may reflect expected service conditions, but in some situations, a more aggressive corrodent and/or high temperature may be used to speed up the attack to determine the resistance of the refractory to the corrosive liquid in a relatively short time.

After cooling the crucibles are cut open, examined and measured for penetration or erosion and photographed if required.

4.3 Advantages/disadvantages

4.3.1 Advantages

The method is an easy and simple test to perform, merely a standard furnace and a crucible of the refractory being the principle requirements.

There is no temperature profile over the refractory, so the reaction of the corrodent and refractory is over the complete thickness of the crucible. The advantage is that the corrodent attack is measured at the test temperature. The test can be performed at different temperatures and in this way the temperature dependence of the attack is obtained (no corrodent attack temperature, moderate corrodent attack temperature and high corrodent attack temperature).

4.3.2 Disadvantages

A disadvantage is that the test is under static conditions, so no flow of the corrodent along the crucible takes place. A second drawback is that the ratio of corrodent to refractory is relatively small so that as the refractory is dissolved, the chemical composition and aggressiveness of the corrodent can be changed.

4.4 Apparatus

4.4.1 Balance, capable of determining the weight of the crucibles and corrodent, to the nearest 1 g.

4.4.2 Furnace, either electric or gas-fired, capable of heating the crucibles under controlled defined conditions and maintaining the test temperature for the required time.

NOTE The use of an electric furnace is recommended, but a gas-fired furnace may be used provided that the furnace atmosphere is continuously oxidising and there is a provision for monitoring this condition.

4.4.3 Drill, with a diamond core bit of typically 55 mm outside diameter. The drill bit and machine shall be capable to give a smooth drilled surface.

4.4.4 Vernier callipers, in accordance with ISO 3611.

4.4.5 Microscope, a binocular or travelling, allowing measurement of the depth of penetration of the corrodent in the test sample, or the dimensional changes of the latter.

4.5 Test materials

The test can be applied to a wide range of fired refractory materials and corrosive liquids, including metals, slags, metal/slag combinations and glasses.

4.6 Test pieces

The shape of the crucible used in the test is typically a 100 mm square by 76 mm high block, cut or formed from the test material and having a 55 mm diameter by 55 mm deep hole drilled in its centre. The test crucible is fitted with a 100 mm square by 15 mm thick lid.

NOTE Different sizes of crucible and central hole may be used depending on the original product shape. The latter may affect the results.

For unshaped refractory products EN 1402-5 gives a description for the preparation and treatment (curing, drying and firing) of test pieces (shape A) from unshaped refractory materials.

In some cases it may be desirable to prefire the crucible and lids before adding the corrodent. The procedure to be employed should be agreed between the parties.

4.7 Test conditions

Test temperature, heating rate and corrodent composition shall be agreed between the parties. It is essential that the chosen temperature is sufficiently high to melt the corrodent. The test period is five hours unless agreed otherwise.

4.8 General procedure

The test crucible and lid are dried in the oven at $110\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ to constant mass (minimum 8 hours).

The crucible is then weighed, the hole is packed with the corrodent and the crucible is re-weighed to determine the amount of corrodent used.

If more than one crucible is used, the same weight of corrodent should be used for each crucible.

The crucible with its lid in place is mounted in the furnace and protected from direct radiation in an electrically heated furnace or from flame impingement in a gas-fired furnace. If more than one crucible is used, they should be separated from each other by a distance of not less than 20 mm and at a distance of not less than 50 mm from the furnace walls to allow free circulation of hot gases.

The furnace is heated to the test temperature at a rate typically of between $1^{\circ}\text{C}/\text{min}$ and $4^{\circ}\text{C}/\text{min}$. After holding at this temperature for the agreed test period, the furnace is switched off and allowed to cool naturally together with the crucible.

NOTE 1 Other heating rates may be used (e.g. higher heating rates for approaching the chosen test temperature and/or limiting interaction between sample and corrodent below this test temperature) upon agreement between parties; the exact heating cycle adopted should be reported in detail as it may affect the results.

After cooling in the furnace, the crucible is sectioned vertically through the axis of the drilled hole, so that the corrodent penetration and/or erosion of the refractory material can be measured with the vernier callipers and photographed. If it is found that the corrodent has not melted (e.g. sintered), the crucible is packed with fresh corrodent and the test is repeated at a higher temperature.

NOTE 2 It is common to perform the test with several test crucibles and a reference refractory. In this way the test conditions of the crucibles are similar and direct comparison between the test materials can be made.

NOTE 3 If aluminium or other easily oxidising metals are used as corrodent, the metal should be melted in a separate crucible and poured in the hot (temperature above the melted temperature of the metal) test crucible. If the metal is placed in the hole of the test crucible at room temperature and then heated, an oxidising film will be formed around the melt during heating. This film will prevent attack of the refractory by the metal.

4.9 Assessment of results

The result of this test is reported as the depth of penetration of the refractory material in mm, the type and amount of erosion in mm occurring during the test.

In some cases it may be desirable to photograph the sectioned crucibles so a visual appraisal of the test can be included in the report. The photograph shall show two sides of the test crucible at not less than half their actual size.

Differences in the nature of corrosion can be assessed by optical or scanning electron microscopy.

The following classification is used for reporting the condition of the crucible:

- a) Unaffected (U), no visible attack;
- b) Lightly attacked (LA), minor attack;