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English version

Methods of testing cement;
Pozzolanicity test for pozzolanic cements

Méthodes d'essais des ciments;
Essai de pouzzolanicité des
ciments pouzzolaniques

Prüfverfahren für Zement;
Prüfung der Puzzolanität
von Puzzolanzementen

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CEN

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BRIEF HISTORY

This European Standard was drawn up by the Technical Committee CEN/TC 51 "Cement" the Secretariat of which is held by IBN.

According to the Common CEN/CENELEC Rules, following countries are bound to implement this European Standard:

Belgium, Denmark, France, Germany, Greece, Italy, Netherlands, Norway, Sweden.

FOREWORD

The European Standard EN 196 on methods of testing cement consists of the following Parts :

Part 1 : Determination of strength

Part 2 : Chemical analysis of cement

Part 3 : Determination of setting time and soundness

Part 4 : Quantitative determination of constituents

Part 5 : Pozzolanicity test for pozzolanic cements

Part 6 : Determination of fineness

Part 7 : Methods of taking and preparing samples of cement

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1 SCOPE AND FIELD OF APPLICATION

This European Standard describes the method of measuring the pozzo-
lanicity of pozzolanic cements conforming to the definition in
EN 197-1. This standard does not apply to Portland pozzolana cements
or to pozzolanas.

This method constitutes the reference procedure.

2 REFERENCES

EN 196-2   Methods of testing cement - Chemical analysis of cement[1]

EN 196-7   Methods of testing cement - Sampling[2]

EN 197-1   Definitions and specifications for cements -
            Definitions and terminology[1]

ISO 3534 - 1977   Statistics - Vocabulary and symbols

3 GENERAL REQUIREMENTS FOR TESTING

3.1 Expression of masses, volumes and factors

Express masses in grams to the nearest 0,0001 g and volumes from the
burette in millilitres to the nearest 0,05 ml. Express the factors
of solutions, given by the mean of three determinations, to three
places of decimals.

3.2 Number of tests

The number of tests shall be two (see also 3.3).

3.3 Expression of results

Express the results of the determinations in millimoles
per litre to the nearest 0,1 mmol/l

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1) At present at the stage of draft.

2) At present at the stage of draft proposal.

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Give the final result as the mean of two determinations to one place of decimals.

If the difference between two determinations is more than twice the standard deviation for repeatability, repeat the test and take the mean of the two closest values.

3.4 Repeatability and reproducibility

The standard deviation of repeatability gives the closeness of agreement between successive results obtained with the same method on identical material tested under the same conditions (same operator, same apparatus, same laboratory and short intervals of time[3]).

The standard deviation of reproducibility gives the closeness of agreement between individual results obtained with the same method on identical material but tested under different conditions (different operators, different apparatus, different laboratory and/or different time[3]).

The standard deviations of repeatability and reproducibility are expressed in absolute %.

4 PREPARATION OF A CEMENT SAMPLE

Take a sample by the method described in EN 196-7. Treat this laboratory sample as described in clause 6 of EN 196-2: 1985.

5 PRINCIPLE

The pozzolanicity is assessed by comparing the quantity of calcium hydroxide present in the aqueous solution in contact with the hydrated cement, after a fixed period of time, with the quantity of calcium hydroxide capable of saturating a solution of the same alkalinity. The test is considered positive if the concentration of calcium hydroxide in the solution is lower than the saturation concentration.

Experiment has shown that a mixture of 20 g of cement and 100 ml of water at 40 °C achieves equilibrium after a period of 8 or 15 days[4].

To evaluate the results it is therefore necessary to know the solubility at 40 °C of calcium hydroxide in a solution of which the alkalinity varies from 35 to about 100 mmol OH⁻ per litre.

6 REAGENTS

Use only reagents of recognised analytical quality and freshly boiled water, distilled or of equivalent purity, during the analysis.

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[3] Definitions taken from ISO 3534.

[4] 8 days are sufficient if the test is positive at this stage (see 10.2).

6.1 Concentrated hydrochloric acid (HCl), approximately 12 mol/l (ρ = 1,18 g/cm^3 to 1,19 g/cm^3).

6.2 Dilute hydrochloric acid : about 0,1 mol/l.
Using the 50 ml precision burette (7.8), add 8,5 ml of concentrated hydrochloric acid (6.1) to a 1 litre volumetric flask (7.10) containing about 500 ml of water. Then make up the volume with water.

6.3 Dilute hydrochloric acid (1+2) : add 250 ml of concentrated hydrochloric acid to 500 ml water.

6.4 Methyl orange (dimethylaminoazobenzene p-sodium sulphonate).

6.5 Methyl orange indicator : dissolve 0,02 g of methyl orange in water and make up to 1000 ml.

6.6 Sodium hydroxide (NaOH).

6.7 Sodium hydroxide solution : dissolve 100 g of sodium hydroxide in water and make up to 1000 ml.

6.8 Calcium carbonate (CaCO$_3$) : dried at 110 °C.

6.9 Potassium chloride (KCl) : dried at 110 °C.

6.10 Murexide (ammonium purpurate).

6.11 Murexide indicator : grind and mix 1 g of murexide with 100 g of dry potassium chloride.

6.12 EDTA (disodium dihydrate salt of ethylenediaminetetra-acetic acid).

6.13 EDTA solution about 0,025 mol/l : dissolve 9,306 g of EDTA in water and make up to 1000 ml.

6.14 Sodium carbonate (Na$_2$CO$_3$) : dried at 260 °C.

7 APPARATUS

7.1 500 ml cylindrical polyethylene container of about 70 mm diameter with a pressure seal-plug locked by a screw plug.

7.2 Wide stem funnel.

7.3 Porcelain Buchner funnel of 60 mm inner diameter.

7.4 Filter paper with low porosity (mean pore diameter of about 2 μm)

7.5 250 ml vacuum flask.

7.6 250 ml and 400 ml beakers.

7.7 50 ml and 100 ml precision pipettes (ISO class A).

7.8 50 ml precision burette (ISO class A).

7.9 Uniform temperature enclosure controlled thermostatically at 40 ± 0,5 °C.

7.10 500 ml and 1000 ml volumetric flasks.

7.11 250 ml conical flask.

8 STANDARDIZATION OF SOLUTIONS

8.1 Standardization of the EDTA solution

Weigh approximately 1 g of calcium carbonate (6.8) to the nearest 0,0001 g and introduce into the 250 ml beaker (7.6). Add approximately 100 ml of water and, very carefully, 50 ml of dilute hydrochloric acid (6.3) keeping the beaker covered with a watch glass.

Stir with a glass rod and ensure that dissolution is complete . Then transfer the solution into the 500 ml volumetric flask (7.10), wash the beaker and watch glass carefully with water, adding the washings to the solution and make up the volume with water.

Pipette (7.7) 50 ml of the solution into the 400 ml beaker (7.6), dilute with approximately 150 ml of water and add the quantity of sodium hydroxide solution (6.7) necessary to achieve pH 13 (check the pH by means of a pH meter or by indicator papers).

Add approximately 50 mg of murexide indicator (6.11) and titrate by means of the burette (7.8) against the EDTA solution (6.13) until there is a steady colour change from purple to violet. From the volume of EDTA solution used, calculate the factor f_1 of the EDTA solution by the formula :

$$f_1 = \frac{m_1}{100,09} \times \frac{1000}{10 \times 0,025 \times V_1} = \frac{m_1}{V_1} \times 39,96 \qquad (1)$$

where

m_1 is the mass of calcium carbonate

V_1 is the volume of EDTA solution used for the titration

100,09   is the molecular mass of calcium carbonate.

8.2   Standardization of the 0,1 mol/l solution of hydrochloric acid

Weigh approximately 0,2 g of sodium carbonate (6.14), add it to the
250 ml flask (7.11) and dissolve it in 50 ml to 75 ml of water . Add
five drops of the methyl orange indicator (6.5) to the solution
and titrate with the 0,1 mol/l dilute hydrochloric acid (6.2) until the colour
changes from yellow to orange.

Calculate the factor f_2 of the hydrochloric acid solution by the formula :

$$f_2 = \frac{2 \cdot m_2}{105,989} \times \frac{1000}{0,1 \times V_2} = \frac{m_2}{V_2} \times 188,70 \qquad (2)$$

where

m_2 is the mass of sodium carbonate

V_2 is the volume of hydrochloric acid used for the titration

105,989 is the molecular mass of sodium carbonate.

9 PROCEDURE

9.1 Storage and filtration

Pipette (7.7) 100 ml of freshly boiled water into the polyethylene
container (7.1) and place the sealed container in the thermostatic
enclosure (7.9) until equilibrium is reached (about 1 h). Remove

the container from the thermostatic enclosure . Pour 20 ± 0,01 g
of the cement to be examined into it, using the wide stem funnel
(7.2). Seal the container immediately.

Shake vigorously for about 20 s to avoid formation of cement lumps.
A horizontal rotary motion has to be used to prevent any part of the
sample or liquid being thrown up and remaining separated from the rest
of the solution.

Replace the container in the thermostatic enclosure, making sure
that its base is perfectly horizontal so that the deposited layer
of cement has a uniform thickness. Perform all operations outside the
thermostatic enclosure as quickly as possible (in 1 min
maximum) to avoid any appreciable lowering in temperature of the
contents of the container.

After a period of 8 or 15 days[4] in the thermostatic enclosure,
remove the container and filter the solution immediately under
vacuum through the Buchner funnel (7.3) into the vacuum flask (7.5)
using dry double filter paper (7.4) in less than 30 s (to avoid
absorption of atmospheric carbon dioxide and any appreciable
lowering in temperature of the solution). Seal the
vacuum flask immediately and let the filtrate cool to room temperature.

[4] 8 days are sufficient if the test is positive at this stage (see 10.2

9.2 Determination of the hydroxyl ion concentration

Shake the vacuum flask (7.5) to homogenise the filtrate and pipette (7.7) 50 ml of the solution into the 250 ml beaker (7.6). Add five drops of methyl orange indicator (6.5) and determine the total alkalinity with the dilute hydrochloric acid (6.2). The titration end-point corresponds to the colour change from yellow to orange.

Calculate the hydroxyl ion concentration $[OH^-]$ by the formula :

$$[OH^-] = \frac{1000 \times 0,1 \times V_3 \times f_2}{50} = 2 \times V_3 \times f_2 \quad (mmol\ OH^-/l) \qquad (3)$$

where :

V_3 is the volume of 0,1 mol/l hydrochloric acid solution used for the titration

f_2 is the factor of 0,1 mol/l hydrochloric acid solution.

9.3 Determination of the calcium oxide concentration

To the same solution remaining after completing 9.2, add 5 ml of sodium hydroxide solution (6.7), approximately 50 mg of murexide indicator (6.11) and titrate the calcium oxide with EDTA solution (6.13) by means of the burette (7.8) until there is a steady colour change from purple to violet.

Before and after titration, the pH value of the solution should be at least 13, if not, add the requisite amount of sodium hydroxide solution.

Calculate the calcium oxide concentration $[CaO]$ by the formula :

$$[CaO] = \frac{1000 \times 0,025 \times V_4 \times f_1}{50} = 0,5 \times V_4 \times f_1 \quad (mmol\ CaO/l) \qquad (4)$$

where :

V_4 is the volume of EDTA solution used for the titration.

f_1 is the factor of the EDTA solution.

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10 RESULTS

10.1 Expression of results

Plot the mean concentrations (see 3.3) of hydroxyl ions and calcium oxide in the solution, obtained in accordance with 9.2 and 9.3, as a point on figure 1 which shows the saturation concentration of calcium oxide in the solution as a function of the hydroxyl ion concentration at 40 °C.

10.2 Assessment of results

The cement satisfies the pozzolanicity test when the point plotted is under the curve of calcium oxide saturation concentration shown on figure 1.

10.3 Repeatability and reproducibility

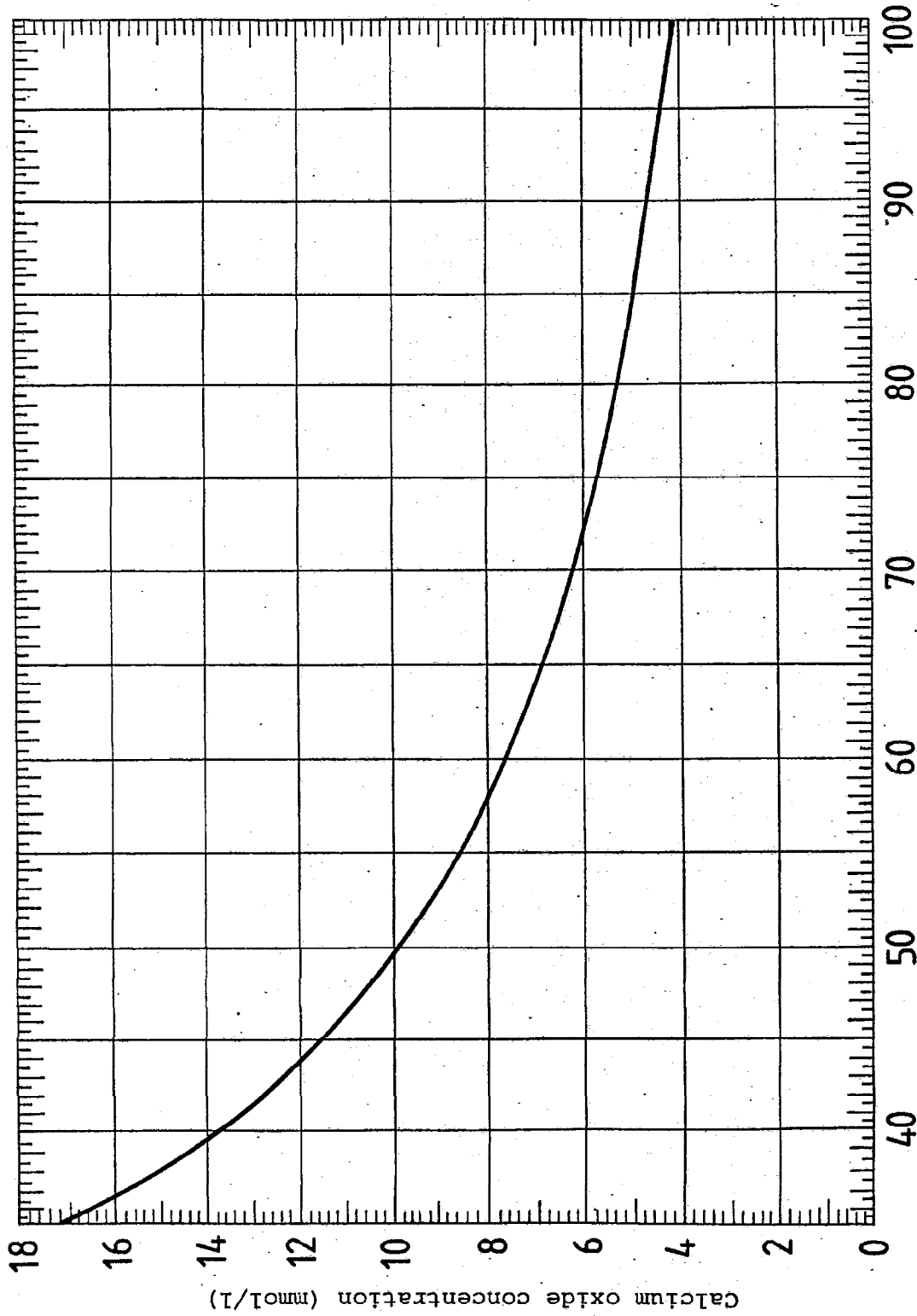The standard deviation for repeatability is :

for calcium oxide : 0,2 mmol/1
for hydroxyl ion : 0,5 mmol/1

The standard deviation for reproducibility is :

for calcium oxide : 0,5 mmol/1
for hydroxyl ion : 1,0 mmol/1.

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Hydroxyl ion concentration (mmol/l)

Fig. 1 Diagram for assessing pozzolanicity

Calcium oxide concentration (mmol/l)