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Metoda za ugotavljanje C3A v klinkerju na podlagi analize cementa

Method for the determination of C3A in the clinker from cement analysis

Verfahren für die Bestimmung des C3A-Gehalts im Klinker aus der Zementanalyse

Ta slovenski standard je istoveten z: **FprCEN/TR 17365**

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This draft Technical Report is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 51.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (FprCEN/TR 17365:2019) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

This document is currently submitted to the Vote on TR.

1 Scope

This document describes the analytical procedures used to determine the content of C_3A in the clinker starting from a chemical analysis on cement. The method can be applied to CEM type I and IV for the determination of the requirement of C_3A, as defined on EN 197-1.

This document describes two methods, traditional wet and XRF analysis (EN 196-2), which can be considered to be equivalent, in the scope of this CEN/TR 17365, for the determination of Al_20_3, Fe_20_3 and SO_3.

The same methods are described in EN 196-2, but for the scope of this document, the X-ray fluorescence (XRF) is the preferred method to be used for the determination of Al_20_3, Fe_20_3 and SO_3.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 196-2, *Method of testing cement — Part 2: Chemical analysis of cement*

EN 196-7, *Methods of testing cement — Part 7: Methods of taking and preparing samples of cement*

ISO 385, *Laboratory glassware — Burettes*

ISO 835, *Laboratory glassware — Graduated pipettes*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle of the method

The principle of the method is based on the calculation of the amounts of Al_20_3 and Fe_20_3 that may be occurring in the clinker by the chemical analysis of cement corrected for the oxide fraction resulting from materials other than clinker.

Once Al_20_3 and Fe_20_3 values are obtained, the amount of C_3A in the clinker is calculated according to Bogue.

The following assumptions should be made to determine the Al_20_3 and Fe_20_3 amounts in the clinker:

a) Any sulfate occurring in the cement is ascribable to $CaSO_4 \bullet 2H_20$; all determined CO_2 is $CaCO_3$. Moreover, the Al_20_3 and Fe_20_3 input from minor additional constituents and calcium sulfate is assumed to be zero;

b) The residue from the base-complexing agent treatment (BCR) is constituted by pozzolanic materials only (natural pozzolana, siliceous fly ash and microsilica) and the dissolution is selective and complete.

Based on the above assumptions and on the calculated quantities of $CaSO_4•2H_2O$ and $CaCO_3$, Al_2O_3 and Fe_2O_3 percentages in the clinker can be calculated by subtracting the oxide fraction in the cement and the BCR, corrected for the amount of gypsum and pozzolanic materials (see Figure 1).

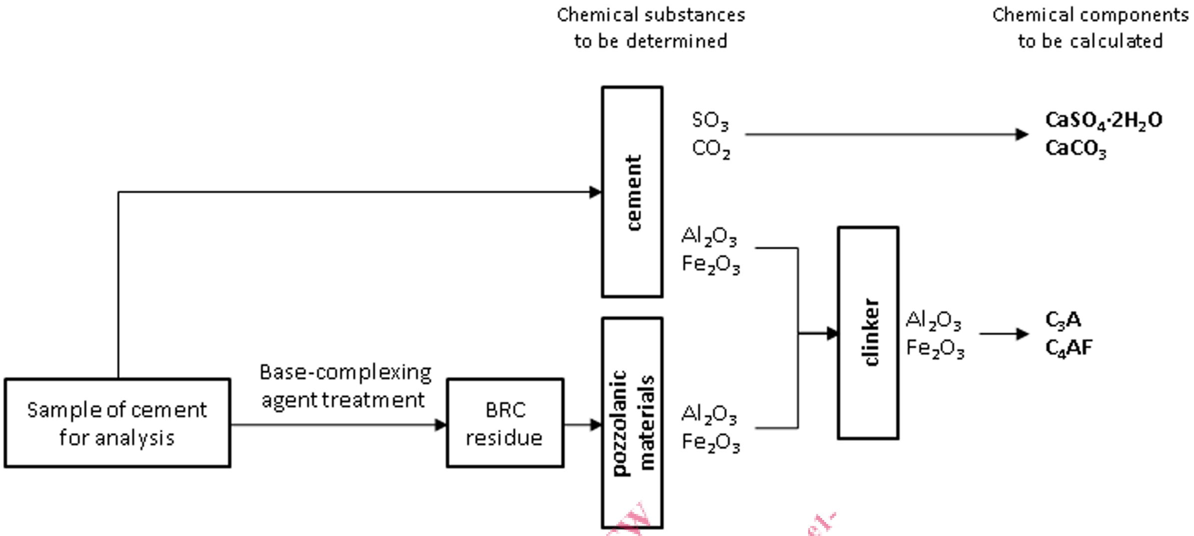

Figure 1 — General outline of the analytical procedures and the chemical substances to be determined

5 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0,0001 g and volumes from burettes in millilitres to the nearest 0,05 ml.

Express the factors of solutions, given by the mean of three measurements, to three decimal places.

Express the results, where a single test result has been obtained, as a percentage generally to two decimal places.

Express the results, where two test results have been obtained, as the mean of the results, as a percentage generally to two decimal places.

The results of all individual tests shall be recorded.

6 Ignitions

Carry out ignitions as follows.

Place the filter paper and its contents into a crucible which has been previously ignited and tared. Dry it, then incinerate slowly in an oxidising atmosphere in order to avoid immediate flaming, while ensuring complete combustion. Ignite the crucible and its contents at the stated temperature then allow to cool to the laboratory temperature in a desiccator. Weigh the crucible and its contents.

7 Determination of constant mass

Determine constant mass by making successive 15 min ignitions followed each time by cooling and then weighing. Constant mass is reached when the difference between two successive weighings is less than 0,0005 g.

8 Preparation of a test sample of cement

Before chemical analysis, treat the laboratory sample, taken in accordance with EN 196-7, as follows to obtain a homogeneous test sample.

Take approximately 100 g of the laboratory sample by means of a sample divider or by quartering. Sieve this portion on a 90 µm sieve until the residue remains constant. Remove metallic iron from the material retained on the sieve by means of a magnet (see Note). Then grind the iron-free fraction of the retained material so that it completely passes the 90 µm sieve. Transfer the sample to a clean dry container with an airtight closure and shake vigorously to mix it thoroughly.

Carry out all operations as quickly as possible to ensure that the test sample is exposed to ambient air only for the minimum time.

NOTE Where the analysis is one of a series subject to statistical control and the level of the metallic iron content has been shown to be insignificant in relation to the chemical properties to be determined then it is not necessary to remove metallic iron.

9 Reagents

Use only reagents of analytical quality. References to water mean distilled or de-ionized water having an electrical conductivity ≤ 0,5 mS/m.

Unless otherwise stated percent means percent by mass.

Unless otherwise stated the concentrated liquid reagents used in this document have the following densities (ρ) (in g/cm^3 at 20 °C):

hydrochloric acid	1,18 to 1,19	perchloric acid	1,60 to 1,67
acetic acid	1,05 to 1,06	ammonium hydroxide	0,88 to 0,91

The degree of dilution is always given as a volumetric sum, for example: dilute hydrochloric acid 1 + 2 means that 1 volume of concentrated hydrochloric acid is to be mixed with 2 volumes of water.

9.1 Triethanolamine (TEA): $[N(CH_2CH_2OH)_3]$ (d = 1,12 g/cm3).

9.2 EDTA - dihydrated disodium salt of ethylenediaminetetra-acetic acid.

9.3 0,025M EDTA solution

In a litre flask, dissolve 9,3060 g of EDTA, previously dried in an oven at a temperature of 80 ± 2°C for 4 days, add distilled water up to the calibration mark and blend.

9.4 Diethylamine (DEA): $[(C_2H_5)2NH]$.

9.5 Ethanol 95°: $[C_2H_5OH]$.

9.6 Anhydrous sodium carbonate (Na_2CO_3).

9.7 Perchloric acid, $(HClO_4)$.

9.8 Acetic acid, glacial (CH3COOH)

9.9 Hydrochloric acid, (HCl)

9.10 Hydrochloric acid 12 % (HCl)

Dilute 100 ml of concentrated HCl (9.9) with 250 ml of distilled water.

9.11 Hydrochloric acid, dilute (1 + 1)

9.12 Hydrochloric acid, dilute (1 + 100)

9.13 Acetic anhydride (CH_3COOCH_3)

9.14 Sulfo-5-salicylic acid dehydrate

9.15 Sulphosalicylic acid indicator:

Dissolve 5 g of sulphosalicylic acid dihydrate (9.14) in 100 ml of H_2O.

9.16 Anhydrous sodium acetate (CH_3COONa).

9.17 Acetic buffer solution at pH 4,7-4,8

On a magnetic stirrer, dissolve 82,0 g of CH_3COONa (9.16), 57 ml of glacial acetic acid (9.8) in 1000 ml of distilled water, blend and store in a plastic spray bottle.

9.18 Ammonium chloride (NH_4Cl).

9.19 Ammonium hydroxide (NH_4OH)

9.20 buffer solution, ammoniacal

Dissolve 540,0 g of ammonium chloride (NH_4Cl) (9.18) and 6,00 ml of 25 % concentrate ammonium hydroxide (9.19) in 4 l of distilled water.

9.21 Potassium hydroxide (KOH),

9.22 Potassium hydroxide solution 4N,

Dissolve 250,0 g of potassium hydroxide (KOH) (9.21) in 900 ml of distilled water.

9.23 Methylthymol blue complexone indicator

9.24 Methyl orange indicator

9.25 Potassium Nitrate (KNO_3)

9.26 Methylthymol blue mix complexone indicator

Mix and grind together 0,15 g of Methylthymol blue (9.23), 0,0165 g of methylorange and 15 g of dried KNO_3.

9.27 Hydrous copper sulfate ($CuSO_4•5H_2O$)

9.28 Copper complexonate solution

In a 250 ml volumetric flask, dissolve 2,0 g of $CuSO_4 \bullet 5H_2O$ (9.27) and fill to the calibration mark.

Pipette 10,0 ml of this solution into 400 ml beaker and dilute with 200 ml of distilled water.

Adjust the pH to 10,2 with the ammoniacal buffer solution (9.20), add a spatula-tip of murexide indicator (9.24), then titrate with a 0,025M solution of EDTA until the colour changes from green to violet: let *n* be number of millilitres of EDTA used. Take exactly 100 ml of the copper solution, add n.10 ml of 0.025M EDTA and blend thoroughly the copper complexonate solution thus obtained.

9.29 PAN indicator solution [1(-pyridine) - 2 naphthol] **0,1 % in ethanol at 95 °.**

9.30 Murexide indicator

Prepare by grinding (1,0 ± 0,1) g of murexide (ammonium purpurate, $C_8H_4N_5O_6.NH_4$) with (100 ± 1) g of sodium chloride (NaCl).

9.31 Copperchloride (Cu_2Cl_2).

9.32 Copper chloride ($CuCl_2 \bullet H_2O$)

9.33 Reagent for determination of carbon dioxide

Dissolve 1,50 g of cuprous chloride and 2,50 g of copper chloride in 350 ml of 12 % hydrochloric acid (9.10).

10 Apparatus

10.1 Balance(s), capable of weighing to an accuracy of ± 0,0005 g.

10.2 Laboratory oven(s), capable of being set at (150 ± 5) °C.

10.3 Electric furnace or Bunsen burner for temperatures up to 950 °C

10.4 Electromagnetic stirrer

10.5 Membrane filters, preferably made from polycarbonate, 47 mm or 90 mm in diameter, with maximum pore size of 1µ.

10.6 Vacuum filtration device

10.7 Vacuum pump, for vacuum filtration at negative pressures of approximately 700 mmHg.

10.8 Silica gel desiccator, with indicator.

10.9 Rod with rubber tip, to facilitate removal of any particles that stick to the sides of the apparatus.

10.10 Platinum crucibles, 10 to 20 cm^3 capacity, with lids

10.11 Hot plate (or sand bath) capable of being set to temperatures up to 350°C.

10.12 Sand bath set to a temperature of 105 ± 5°C (or bain-marie).