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English version

Methods of testing cement; Quantitative determination of constituents.

Méthodes d'essais des ciments; Détermination quantitative des constituants.

Prüfverfahren für Zement; Quantitative Bestimmung der Bestandteile.

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CEN

European Committee for Standardization
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Europäisches Komitee für Normung

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BRIEF HISTORY

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

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

Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom

Foreword

The 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

Part 21. Determination of the chloride, carbon dioxide and alkali content of cement.

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1 Object and field of application

This European Prestandard lays down the procedures for determining the contents of the constituents of cements that fall within the scope of ENV197 [1)].

The first method given in clause 6, entitled 'Determination of the constituent content of cements with more than three constituents' applies to all cements, whatever the number and nature of their constituents.

In the case where the operator is certain that the cement contains only, over and above the clinker and set regulator, blastfurnace slag, fly ash or pozzolana, the other methods given in clause 7 can be applied.

2 Normative references

EN 196-2 Methods of testing cement - Chemical analysis of cement

EN 196-7 Methods of testing cement - Methods of taking and preparing samples of cement

EN 196-21 Methods of testing cement - Determination of the chloride, carbon dioxide and alkali contents of cement

ENV 197 Cement : Composition, specifications and conformity criteria 1)

ISO 3534-1977 Statistics - Vocabulary and symbols.

3 General requirements for testing

3.1 Number of tests

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

3.2 Determination of constant mass

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

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1) At present at the draft stage.

3.3 Expression of masses and results

Express masses in grams to the nearest 0,0001 g.

Express the results of the tests, given by the mean of two determinations, as a percentage to one decimal place.

If the difference between two determinations is greater then 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 time interval)[2)]

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 laboratories and/or different times)[2)].

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

4 Preparation of a cement sample

Take a sample by the method described in EN 196-7. Dry the test sample in an oven at 105 ± 5 °C for 2 h.

5 Reagents

Use only reagents of analytical quality and distilled water or water of equal purity during the analysis.

Unless otherwise stated, % means % by mass.

The density ρ of liquids is given at 20 °C. The densities of concentrated liquid reagents are expressed in g/cm^3.

The degree of dilution is always given in the form of a volumetric sum, for example, hydrochloric acid 1 + 2 means 1 volume of concentrated hydrochloric acid has to be mixed with 2 volumes of water.

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2) Definitions taken from ISO 3534-1977.

6 Determination of the constituent content of cements with more than three constituents

6.1 Field of application

The purpose of the method is to determine the constituent content of cements.

It applies to cements having several constituents, i.e. clinker, hydraulic, pozzolanic or inert constituents and set regulator(s).

The results can be considered quantitatively valid if one of the two following conditions is obtained:

- zero slag content;
- clinker content greater than 60 %.

In all other cases, the results allow the type of cement to be identified qualitatively.

6.2 Selective dissolution method

6.2.1 ***Principle***. After drying at 105 ± 5 °C, the cement sample is attacked by a solution containing sodium hydroxide, triethanolamine and EDTA.

The clinker and the set regulator(s) as well as calcium carbonate are in principle dissolved, whereas the other constituents are not.

The cement is attacked by dilute hydrochloric acid. Pozzolanas, fly ashes and siliceous fillers are the only constituents which, in principle, are not dissolved during this attack.

The result of these two selective dissolutions and the additional determinations of sulphuric anhydride and carbon dioxide contents of the cement enable the various constituent contents to be calculated.

6.2.2 ***Reagents***

Sodium hydroxide NaOH.

Sodium hydroxide solution. Dissolve 40 g of sodium hydroxide in water and make up to 1000 mL. This is a concentrated solution of about 1 mol/L. Store in a polythene flask.

EDTA, disodium dihydrogen salt of ethylenediaminetetra-acetic acid.

EDTA Solution. Dissove 4 g of sodium hydroxide and 18,6 g of EDTA in water and make up to 1000 mL. This solution contains about 0,05 mol/L of EDTA and 0,1 mol/L of sodium hydroxide.

Triethanolamine $N(CH_2CH_2OH)_3$, (ρ = 1,12 g/cm^3).

Triethanolamine solution 1 + 1.

Ethanol C_2H_5OH, (concentrated ethyl alcohol).

Concentrated hydrochlorie acid HCl (ρ = 1,18 g/cm^3 to 1,19 g/cm^3)

Dilute hydrochloric acid 1 + 10.

Dilute hydrochloric acid 1 + 50.

6.2.3 ***Apparatus***

Balance, capable of weighing to the nearest 0,0001 g.

Drying oven, controlled at 105 ± 5 °C.

Magnetic stirrer with PTFE covered bar.

Electrically controlled propeller stirrer.

Glass membrane filter with a porosity of the order of 1 µm to 2 µm and a diameter of at least 9 cm, resistant to alcohol and alkalis and that can be dried at 105 °C to constant mass.

pH meter.

Desiccator, containing dried magnesium perchlorate.

6.2.4 ***Procedure***

6.2.4.1 ***Attack by EDTA solution***. Add successively to a 600 mL beaker, 250 mL of the EDTA solution, 250 mL of water and 25 mL of the triethanolamine solution. Adjust the pH to 11,6 ± 0,1 with the sodium hydroxide solution.

Add progressively 0,500 ± 0,020 g of the cement (m) while stirring with the magnetic stirrer. The addition should be made progressively during stirring to avoid the formation of a mass which would be difficult to disperse. Continue stirring for 1 h and then allow to stand for 15 min to decant.

Preparation of the filter prior to filtration is recommended in order to avoid any error due to loss of glass microfibres in handling. This is done by washing the filter with water, drying it in the oven, then allowing it to cool in the desiccator to ambient temperature and weighing (m_1).

Filter through the previously weighed filter (m_1) which is placed flat on a vacuum filtering apparatus, the suction of which shall always be above 35 kPa (about 250 mm Hg).

Wash the beaker with water to transfer any remaining residue to the filter. Wash the filter and the residue seven times in water then three times in ethanol.

Filtration should be rapid under these conditions. If the filtration time exceeds 30 min, including washing, start the test again and carry out the filtration on a larger diameter filter.

Dry in the oven to constant mass. Allow to cool in the desiccator to ambient temperature and weigh (m_2).

6.2.4.2 ***Attack with dilute hydrochloric acid***. Add successively to a 250 mL beaker 1 g ± 0,02 g of cement (m_3) and 100 mL of water.

Stir for 5 min with the electrically controlled propeller stirrer. Check that no lumps of cement remain. If there are any lumps break these down with a flat-ended glass stirrer and continue stirring. While continuing stirring, slowly add 40 mL of dilute hydrochloric acid 1 + 10 and then 60 mL of water. Continue stirring for 30 min.

Filter through the previously weighed filter (m_4). Wash with 50 mL of dilute hydrochloric acid 1 + 50 at 70 °C. Wash three times with water then twice with ethanol.

Dry in the oven to contant mass. Allow to cool in the desiccator to ambient temperature and weigh (m_5).

6.2.4.3 ***Sulphuric anhydride content***. Determine the sulphuric anhydride content of the cement by the method described in clause 8 of EN 196-2.

6.2.4.4 ***Carbon dioxide content***. Determine the total carbon dioxide content of the cement by the method described in clause 5 of EN 196-21.

6.2.5 ***Calculation of the constituent content of the cement***. Calculate the content of insoluble material after attack by EDTA from the formula:

$$a = \frac{(m_2 - m_1)}{m} \times 100 \qquad (1)$$

where

m is the mass of cement
m_1 is the mass of the filter
m_2 is the mass of the dried sum (residue + filter).

Calculate the content of insoluble material after attack by hydrochloric acid from the formula:

$$b = \frac{(m_5 - m_4)}{m_3} \times 100 \qquad (2)$$

where

m_3 is the mass of cement
m_4 is the mass of the filter
m_5 is the mass of the dried sum (residue + filter).

Calculate the set regulator(s) content from the formula:

$$R = 1,81 \times S_c \qquad (3)$$

where

S_c is the sulphuric anhydride content of the cement

Calculate the calcareous filler content from the formula:

$$D = 2,27 \times D_c \qquad (4)$$

where

D_c is the carbon dioxide content of the cement

Calculate the pozzolana, fly ash and siliceous filler content from the formula:

$$P + S = (1,07 \times b) - 1,3 \qquad (5)$$

Calculate the clinker content from the formula:

$$C = 101,63 - 1,23 \times a + 0,14 \times (P + S) - 1,01 \times (D + R) \qquad (6)$$

Calculate the slag content from the formula:

$$L = 100 - D - R - (P + S) - C \qquad (7)$$

If the total of the values calculated exceeds 100, the slag content is zero and each value has to be calculated proportionally in relation to 100.

To obtain the contents of the different constituents expressed as a ratio of the cement less set regulator(s) multiply the values obtained above by the factor

$$\frac{100}{100 - R}$$

6.2.6 ***Repeatability and reproducibility***. The standard deviation for repeatability is 0,4 %.

The standard deviation for reproducibility is 4 %.

These standard deviations are valid if the slag contents are zero and/or the clinker contents are greater than 60 %.

6.2.7 ***Qualitative determination of the type of cement***. The type of cement examined is determined by comparing the values obtained with the ranges shown in the table defining the different categories of cement in ENV 197 .1)

7 Determination of the constituent contents of cements with three constituents

7.0 General

Three constituent cements can contain, apart from the clinker and set regulator(s), blastfurnace slag, fly ash or pozzolana.

7.1 Determination of the blastfurnace slag content

7.1.1 ***Field of application***. The purpose of the methods is to determine the blastfurnace slag content of cements.

They apply to cements having three constituents i.e. clinker, slag and set regulator(s).

Two methods are given: dense liquid separation and microscopy.

The dense liquid separation method is the reference method.

7.1.2 Dense liquid separation method

7.1.2.1 ***Principle***. Fractions of clinker and of slag are separated as cleanly as possible by means of dense liquids from a size fraction of cement.

The concentrations of tracers present in the cement and in the fractions of clinker and slag are determined.

The slag content of the cement is then calculated.

7.1.2.2 ***Reagents***

Di-iodomethane[3] CH_2I_2 (ρ = 3,31 g/cm³ to 3,32 g/cm³).

Dibutyl phthalate $C_6H_4(COOC_4H_9)_2$, (ρ = 1,04 g/cm³).

Bromoform[3] $CHBr_3$, (ρ = 2,88 g/cm³ to 2,89 g/cm³).

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1) see page 5

3) This reagent is toxic and shall be handled with the greatest care using safety gloves in a fume cupboard fitted with an extractor.

Ethanol C_2H_5OH, (absolute ethyl alcohol).

Diethyl ether, $C_2H_5OC_2H_5$.

7.1.2.3 Apparatus

Balance, capable of weighing to the nearest 0,0001 g.

Drying oven, controlled at 105 ± 5 °C.

Sintered glass filter with mean pore diameter less than 4 µm.

Electric centrifuge capable of at least 1000 r/min.

Sieve with a minimum mesh aperture of 32 µm and maximum of 40 µm.

Sieve with a mesh aperture of 80 µm.

Polarizing microscope with source for transmitted light with a minimum magnification of 100.

Desiccator, containing dried magnesium perchlorate.

7.1.2.4 Procedure

7.1.2.4.1 ***General***. About 2 kg of cement are required for the determination of slag content.

The method comprises:

- the separation by sieving of a size fraction of cement,
- the separations of this fraction using dense liquids to obtain fractions of clinker and of slag (see figure 1),
- the chemical analysis of tracers in the cement and in the clinker and slag fractions.

Make each chemical analysis in duplicate and use the mean result in the calculations.

It is necessary in order to carry out the chemical analyses that each of the final fractions of clinker (c_4) and of slag (c_7) weighs at least 4 g (see figure 1).

If these amounts are not obtained, it is necessary to carry out enough separations so that the sum of each of the individual fractions of clinker and slag weighs at least 4 g.

7.1.2.4.2 ***Separation of the clinker and slag fractions***.
Separate by dry seiving a sufficient quantity of cement to obtain at least 15 g of material in the size fraction 32 µm to 80 µm or 40 µm to 80 µm.

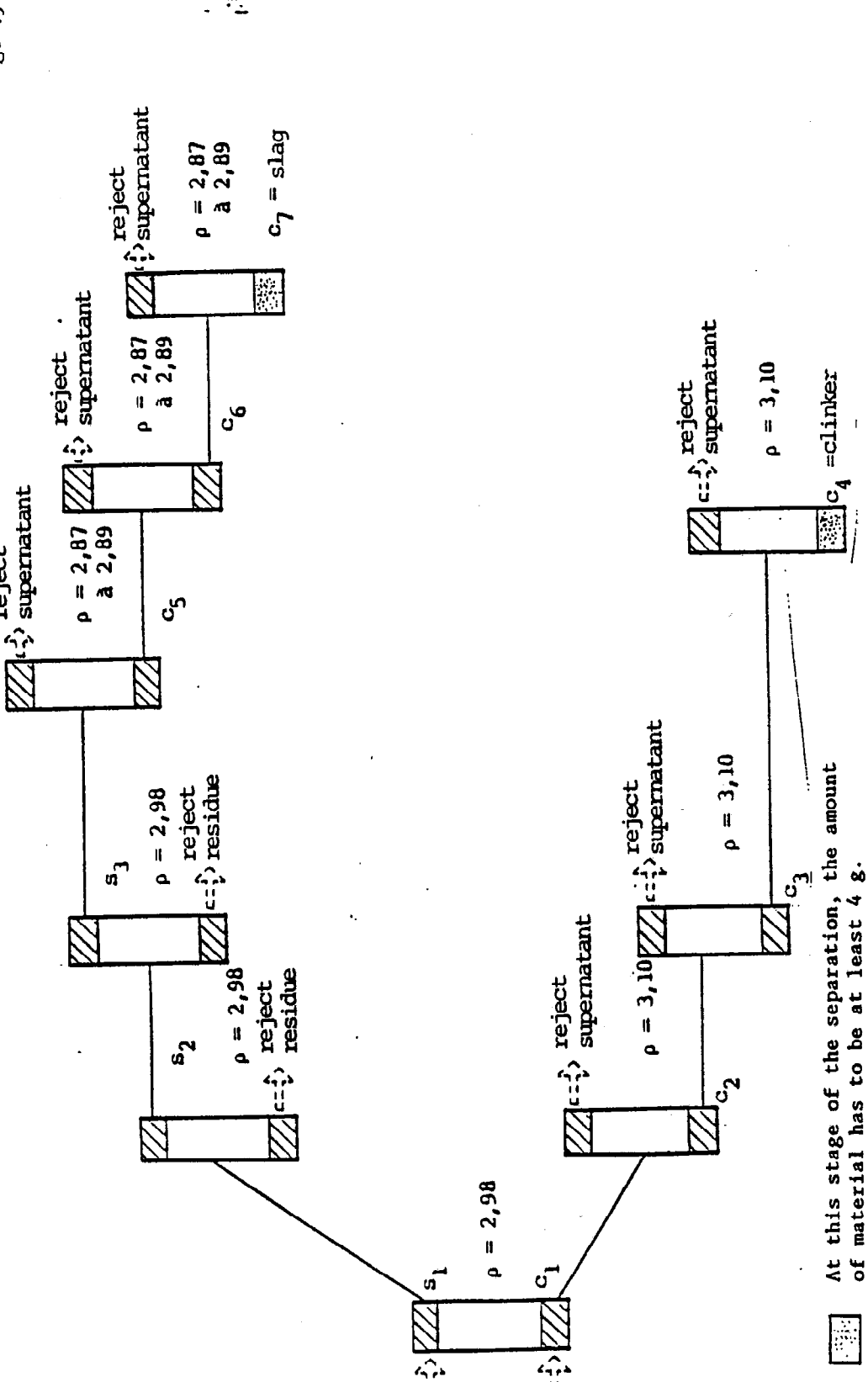

Figure 1 – Scheme for the dense liquid separation

Re-sieve this last fraction with ethanol on the finer sieve in order to remove fine particles which would adhere to the larger grains. Dry the residue for 30 min in the oven. Allow to cool in the desiccator to ambient temperature.

Weigh the size fraction obtained and bring it into suspension in a liquid with a density of 2,98 g/cm^3 (a mixture of di-iodomethane and dibutyl phthalate or bromoform) at a concentration not exceeding 4 g of material per 100 mL of dense liquid.

Remove iron particles by stirring with a magnet. Transfer the suspension into centrifuge tubes and centrifuge for 5 min. Separate the residue from the supernatant by pouring the latter (s_1) into another centrifuge tube (the use of a narrow necked tube may simplify this operation). Reserve the residue (c_1) for the purification of the clinker.

Repeat the separation operation at least twice, restoring the supernatant (s_1) to suspension in a liquid with the same density and centrifuging for 5 min. Reject the residues.

Pour the last supernatant obtained (s_3) into a sintered glass filter, wash twice in diethyl ether, dry for 30 min in the oven, and allow to cool in the desiccator to ambient temperature.

Weigh the fraction s_3.

7.1.2.4.3 ***Purification of the clinker fraction***. Wash, on a sintered glass filter, the residue (c_1) from the first centrifuging operation twice with diethyl ether. Dry for 30 min in the oven, and allow to cool in the desiccator to ambient temperature.

Weigh the fraction c_1.

Bring the powder into suspension in a liquid with a density of 3,10 g/cm^3 (a mixture of di-iodomethane and dibutyl phthalate or bromoform) and at a concentration not exceeding 4 g of material per 100 mL of dense liquid. Transfer into centrifuge tubes and centrifuge for 5 min.

Reject the supernatant and, using a sintered glass filter, recover the liquid from the centrifuge tubes. Centrifuge the residue at least twice more for 5 min after having again suspended it in the liquid with a density of 3,10 g/cm^3. Reject the supernatants. Pour the last residue obtained (c_4) into a sintered glass filter, wash twice with diethyl ether.

Dry for 30 min in the oven and allow to cool in the desiccator to ambient temperature.

Weigh the fraction c_4.

7.1.2.4.4 ***Purification of the slag fraction***. To obtain the slag fraction, restore the supernatant (s_3) to suspension in a liquid with a density of 2,87 g/cm³ to 2,89 g/cm³ (a mixture of di-iodomethane and dibutyl phthalate or bromoform) at a concentration not exceeding 4 g of material per 100 ml of dense liquid.

When the quantity of slag collected is small, however, the use of a liquid with lower density is permitted but the latter may never have a value below 2,84 g/cm³.

Transfer into centrifuge tubes. Centrifuge for 5 min. Reject the supernatant and, using a sintered glass filter, recover the liquid from the centrifuge tubes. Centrifuge the residue at least twice more for 5 min after having again suspended it in the liquid of the same density as that used for the first separation. Reject the supernatants and pour the last residue obtained (c_7) into a sintered glass filter and wash twice with diethyl ether. Dry for 30 min in the oven and allow to cool in the desiccator to ambient temperature.

Weigh the fraction c_7.

7.1.2.4.5 ***Checking the purity of the clinker and slag fractions***. The operator can ascertain the purity of the phases by observing them under a microscope.

For this purpose, arrange a few milligrams of powder on a slide, disperse in a drop of immersion oil, cover the sample with a cover slip and examine the sample using the microscope (magnification 100).

The slag grains are bright, homogeneous, with a glassy fracture and they remain faint between crossed nicols.

The clinker grains are dark, granular with irregular contours and the facets reflect in polarized light when the microscope table is rotated.

If one of these phases is not considered sufficiently pure, carry out a further separation.

7.1.2.4.6 ***Determination of the tracer content***. Determine the contents of sulphuric anhydride, calcium oxide and other tracers (sulphide, magnesium oxide or manganese (II) oxide) which are not present in the set regulator(s), in the cement dried in the oven, as well as in the slag c_7 and in the clinker c_4 fractions.

Carry out analyses according to the methods described in EN 196-2.

If the final result of the analysis has to be expressed on calcined materials it is necessary to determine the loss on ignition of the cement and of the slag and clinker fractions by the method described in clause 7 of EN 196-2.

7.1.2.5 ***Calculation of the slag content of the cement.***
Calculate the sulphuric anhydride content, S_s, in the set regulator(s) from the formula:

$$S_s = \frac{(S_k \times X) + (A_k \times Y) - (C_k \times Z)}{X - 0{,}7\ Z} \qquad (8)$$

where

$$X = (C_c - C_l)\ (A_l - A_k) - (A_c - A_l)\ (C_l - C_k) \qquad (9)$$

$$Y = S_c\ (C_l - C_k) + S_k\ (C_c - C_l) \qquad (10)$$

$$Z = S_c\ (A_l - A_k) + S_k\ (A_c - A_l) \qquad (11)$$

where

S_c is the sulphuric anhydride content of the cement

S_k is the sulphuric anhydride content of the clinker fraction

A_c is the content of the second tracer in the cement

A_l is the content of the second tracer in the slag fraction

A_k is the content of the second tracer in the clinker fraction

C_c is the calcium oxide content of the cement

C_l is the calcium oxide content of the slag fraction

C_k is the calcium oxide content of the clinker fraction

The sulphuric anhydride content in the set regulator(s) shall be within limits corresponding to the extreme values existing under industrial conditions. These limits are considered as being equal to:

maximum : S_s = 58 % (sulphuric anhydride content of anhydrite)

minimum : S_s = 32 % (sulphuric anhydride content of gypsum containing 30 % impurities).

If the calculated value of S_s is not within these limits, repeat the determination.

Among the tracers meeting the foregoing conditions, that which leads to the most precise final result is that for which the term f defined as follows is a minimum:

$$f = \frac{\sigma}{(A_1 - A_k)} \qquad (12)$$

where σ is the standard deviation for reproducibility of the analytical determination of this tracer content.

Calculate the slag content of the cement (1 or 1') from the following formulae:

On dry cement

$$1 = \frac{(C_c \times a) - (C_k \times b) - 0,7\ (S_s \times c)}{(C_1 \times a) - (C_k \times S_s) + 0,7\ (S_s \times S_k)} \times 100 \qquad (13)$$

where

$$a = S_s - S_k \qquad (14)$$

$$b = S_s - S_c \qquad (15)$$

$$c = S_c - S_k \qquad (16)$$

On calcined cement

$$1' = \frac{(100 - P_1)}{(100 - P_c)} \times 1 \qquad (17)$$

The slag content related to the sum of the slag and clinker (L or L') is:

on dry cement

$$L = \frac{100\ a \times 1}{100\ b - S_k 1} \qquad (18)$$

on calcined cement

$$L' = \frac{100a \times 1\ (100 - P_1)}{100\ (100\ b - S_k\ 1) - 1\ (a\ p_1 - S_s\ P_k) - 100\ b\ p_k} \qquad (19)$$

where

p_1 is the loss on ignition of the slag fraction

P_c is the loss on ignition of the cement

P_k is the loss on ignition of the clinker fraction

Express these values as percentages by mass rounded to the nearest 0,1 %.

7.1.2.6 ***Repeatability and reproducibility***. The standard deviation for repeatability is 1 %.

The standard deviation for reproducibility is 3 %.

These values are valid whatever the slag content.

7.1.3 Microscope method

7.1.3.1 ***Principle***. The slag content is measured by microscope counting. The sample, taken from a particular cement size fraction, is examined in transmitted or reflected light.

After counting a sufficient number of grains, ignoring the set regulator(s), the ratio is calculated:

$$L_v = \frac{\text{number of slag grains}}{\text{total number of slag and clinker grains}} \times 100 \qquad (20)$$

The slag content of the cement is calculated using two corrections, for density (by calculation) and for distribution (by chemical analysis).

7.1.3.2 ***Apparatus and materials***

Air jet or mechanical siever with a sieve of mesh aperture 32 µm.

Sieve with a mesh aperture of 40 µm.

Polarizing microscope with source for transmitted light with a magnification of 100.

Microscope with source for reflected light with a magnification from 200 to 400.

Canada balsam.

Equipment for preparing sections.

Synthetic resin.

7.1.3.3 ***Procedure***

7.1.3.3.1 ***Sieving the 32 µm to 40 µm fraction***. Using the air jet or mechanical siever, first separate by sieving the fraction of grains larger than 32 µm. Next, with the hand sieve, separate by sieving the fraction of grains larger than 40 µm. Remove the iron particles by means of a magnet. The 32 µm to 40 µm fraction shall be at least 2 g.

7.1.3.3.2 ***Preparation of the fraction for examination and microscope counting***

(a) Examination in transmitted light

Disperse a sample of about 0,02 g of the fraction in Canada balsam. For this purpose, melt the Canada balsam on a microscope slide at a temperature of 130 °C to 150 °C. Cover with a cover slip. Examine the sample in transmitted light at a magnification of 100. Count at least a total of a thousand slag and clinker grains. Do not take account of the set regulator(s).

The grains of slag are clear, homogeneous, with a glassy fracture, and they remain faint between crossed nicols.

The grains of clinker are dark, granular, with irregular contours, and the facets reflect in polarized light when the microscope table is rotated.

The grains of the set regulator(s)(gypsum and anhydrite) are not very distinct in natural light but the facets reflect in polarized light when the microscope table is rotated.

The observation is made easier by using a mica quarter wave plate.

(b) Examination in reflected light

Disperse a sample of about 1 g of the sieved fraction in the synthetic resin. Wait until the synthetic resin has solidified.

Grind the surface of the sample, polish and etch with water for about 30 s.

Take care to ensure that the sample is not damaged when placed under the microscope. Count at least a thousand clinker and slag grains under the microscope in reflected light. Do not take account of the set regulator(s).

After etching, the ferrite phase (C_4AF) of the clinker appears white and the other clinker minerals (C_3S, C_2S and C_3A) appear dark in colour while the slag grains are light grey in colour which makes it easy to distinguish them from the clinker grains.

7.1.3.3.3 ***Determination of the tracer content.*** Determine the contents of the tracers calcium oxide and sulphuric anhydride and the loss on ignition in the cement and in the fraction examined by microscope, after removing the iron by means of a magnet.

Carry out these determinations in accordance with the methods described in EN 196-2. The calcium oxide and sulphuric anhydride contents are expressed on calcined material.

7.1.3.4 ***Calculation of the slag content of the cement.***
Calculate successively:

the result of the count:

$$L_V = 100 \times \frac{n_l}{n_l + n_k} \qquad (21)$$

the correction for density:

$$L_m = \frac{100\ d_l \times L_V}{100\ d_k - (d_k - d_l)L_V} \qquad (22)$$

The densities of the slag and clinker can be estimated at 2,87 g/cm^3 and 3,15 g/cm^3 respectively, hence:

$$L_m = \frac{287\ L_V}{315 - 0{,}28\ L_V} \qquad (23)$$

the correction for distribution:

$$C_m = \frac{100\ (C_c - 0{,}7\ S_c)}{100 - 1{,}7\ S_c - p} \qquad (24)$$

$$C_f = \frac{100\ (C_{f'} - 0{,}7\ S_{f'})}{100 - 1{,}7\ S_{f'} - p'} \qquad (25)$$

the slag content on calcined cement (L'):

$$L' = L_m - 100\ \frac{C_m - C_f}{23} \qquad (26)$$

In this formula, it is assumed that the difference between the calcium oxide contents of the clinker and slag is 23 %.

The slag content on the dry cement (L):

$$L = L' \times \frac{100 - p}{100} \qquad (27)$$

The values of L and L' are expressed as a percentage of the sum of the slag and clinker constituents.

where

L_v is the slag content by volume of the fraction examined by microscope

n_l is the number of slag grains

n_k is the number of clinker grains

L_m is the slag content of the slag and clinker mixture of the fraction examined by microscope, on dry cement

d_l is the density of the slag

d_k is the density of the clinker

C_m is the calcium oxide content of the clinker and slag mixture

C_f is the calcium oxide content of the fraction examined by microscope related to the calcined sample free of set regulator(s)

C_c is the calcium oxide content of the cement

S_c is the sulphuric anhydride content of the cement

C_f' is the calcium oxide content of the fraction examined by microscope

S_f' is the sulphuric anhydride content of the fraction examined by microscope

p is the loss on ignition of the cement

p' is the loss on ignition of the fraction examined by microscope

7.1.3.5 ***Repeatability and reproducibility***. The standard deviation for repeatability is 1 %.

The standard deviation for reproducibility is 3 %.

These standard deviations are valid whatever the slag content.

7.2 Determination of fly ash content

7.2.1 ***Field of application***. The purpose of the method is to determine the fly ash content of cements.

It applies to cements having three constituents, i.e. clinker, fly ash from coal or fly ash of similar composition and set regulator(s).

7.2.2 ***Selective dissolution method***

7.2.2.1 ***Principle***. After drying at 105 ± 5 °C, the cement is attacked by a solution of hydrochloric acid in methanol containing salicylic acid.

This solution dissolves the clinker minerals and, partially, the set regulator(s).

Weighing the residue obtained and also the determination of its sulphuric anhydride content and that of the cement allow the fly ash content of the cement to be calculated.

7.2.2.2 ***Reagents***

Methanol CH_3OH (anhydrous methyl alcohol) (ρ = 0,79 g/cm^3).

Concentrated hydrochloric acid HCl (ρ = 1,18 g/cm^3 to 1,19 g/cm^3).

Salicylic acid $C_6H_4(OH)COOH$.

Acid solution. Put 800 mL of the methanol into a graduated 1000 mL flask. Add 41,7 mL of hydrochloric acid and 50 g of salicylic acid. Mix until the salicylic acid is completely dissolved. Make up to 1000 mL with methanol.

7.2.2.3 ***Apparatus***

Balance, capable of weighing to the nearest 0,0001 g.

Drying oven, controlled at 105 ± 5 °C.

Filters with a mean pore diameter less than 4 µm.

Desiccator, containing dried magnesium perchlorate.

7.2.2.4 ***Procedure***

7.2.2.4.1 ***Determination of the insoluble residue***. Put 200 mL of the acid solution into a 400 mL beaker. Stir using an electrically controlled glass stirrer. Slowly add 2,0 ± 0,1 g of cement (m). Continue stirring for 30 min. Allow the solution to settle for 5 min.

Filter through a weighed filter (m_1). Wash the insoluble residue six times with approximately 100 mL of methanol allowing it to evaporate after each washing.

Dry the filter and insoluble residue for 2 h in the oven. Allow the filter and the insoluble residue to cool in the desiccator to ambient temperature and weigh (m_2).

7.2.2.4.2 ***Determination of the sulphuric anhydride content.*** Determine the sulphuric anhydride content of the insoluble residue (7.2.2.4.1) and also of the cement by the method described in clause 8 of EN 196-2.

7.2.2.5 ***Calculation of the fly ash content of cement.*** Calculate the fly ash content of the dry cement from the formula:

$$v = \frac{(m_2 - m_1)}{m} \times (100 - 1{,}813\ S_r) \qquad (28)$$

Calculate the fly ash content of the sum of the clinker and fly ash from the formula:

$$V = \frac{100 \times v}{100 - 1{,}813\ S_c} \qquad (29)$$

where

m is the mass of the cement

m_1 is the mass of the filter

m_2 is the mass of the filter and the insoluble residue

S_c is the sulphuric anhydride content of the cement

S_r is the sulphuric anhydride content of the insoluble residue

7.2.2.6 ***Repeatability and reproducibility.*** The standard deviation for repeatability is 0,5 %.

The standard deviation for reproducibility is 2 %.

These standard deviations are valid whatever the fly ash content.

7.3 Determination of pozzolana content

7.3.1 Field of application

The purpose of the methods is to determine the pozzolana content of cements.

They apply to cements having three constituents, i.e. clinker, pozzolana and set regulator(s).

These methods are: selective dissolution and dense liquid separation.

The selective dissolution method is the reference method.

7.3.2 Selective dissolution method

7.3.2.1 ***Principle***. After drying at 105 ± 5 °C, the cement sample is attacked by a solution of hydrochloric acid in methanol containing salicylic acid.

This solution dissolves the clinker minerals and partially dissolves the alkaline earth carbonates which may be present in certain pozzolanas: it also partially dissolves the set regulator(s).

Weighing the residue obtained and the determination of its sulphuric anhydride content, as well as the carbon dioxide content and sulphuric anhydride content of the cement, allow the pozzolana content of the cement to be calculated.

7.3.2.2 ***Reagents***

Methanol CH_3OH (anhydrous methyl alcohol) (ρ = 0,79 g/cm^3).

Concentrated hydrochloric acid HCl (ρ = 1,18 g/cm^3 to 1,19 g/cm^3).

Salicylic acid $C_6H_4(OH)COOH$.

Acid solution. Put 800 mL of the methanol into a graduated 1000 mL flask. Add 41,7 mL of the hydrochloric acid and 50 g of salicylic acid. Mix until the salicylic acid is completely dissolved. Make up to 1000 mL with methanol.

7.3.2.3 *Apparatus*

Balance, capable of weighing to the nearest 0,0001 g.

Drying oven, controlled at 105 ± 5 °C.

Sintered glass filters with a mean pore diameter from 5 µm to 15 µm.

Desiccator, containing dried magnesium perchlorate.

7.3.2.4 *Procedure*

7.3.2.4.1 ***Determination of the insoluble residue.*** Put 200 mL of the acid solution into a 400 mL beaker. Stir using an electrically controlled glass stirrer. Slowly add 2,0 ± 0,1 g of cement (m). Continue stirring for 30 min. Allow the solution to settle for 5 min.

Filter through a weighed filter (m_1). Wash the insoluble residue six times with approximately 100 mL of methanol allowing it to evaporate after each washing.

Dry the filter and the insoluble residue for 2 h in the oven. Allow the filter and the insoluble residue to cool to ambient temperature in the desiccator and weigh (m_2).

7.3.2.4.2 ***Determination of the sulphuric anhydride content.*** Determine the sulphuric anhydride content (SO_3) on the insoluble residue and also on the cement by the method described in clause 8 of EN 196-2.

7.3.2.4.3 ***Determination of the carbon dioxide content.*** Determine the carbon dioxide content (CO_2) of the cement by the method described in clause 5 of EN 196-21, using however, as the solution for attacking the cement, the acid solution described in 7.3.2.2 and the quantities of cement and acid solution previously specified.

7.3.2.5 ***Calculation of the pozzolana content of the cement.*** Calculate the calcium carbonate content of the dry cement from the formula:

$$D = 2{,}273 \times D_c \qquad (30)$$

The pozzolana content of the dry cement is:

$$b = \frac{(m_2 - m_1)}{m} \times (100 - 1{,}813\ S_r) + D \qquad (31)$$

The pozzolana content of the sum of the clinker and pozzolana constituents is:

$$B = \frac{100 \times b}{100 - 1{,}813\ S_c} \qquad (32)$$

where

D_c is the carbon dioxide content of the cement

m is the mass of cement

m_1 is the mass of the filter

m_2 is the mass of the filter and insoluble residue

S_r is the sulphuric anhydride content of the insoluble residue

S_c is the sulphuric anhydride content of the cement.

7.3.2.6 ***Repeatability and reproducibility***

The standard deviation for repeatability is 1 %.

The standard deviation for reproducibility is 1,5 %.

These standard deviations are valid whatever the pozzolana content within the range 0 % to 40 % of this material.

7.3.3 Dense liquid separation method

7.3.3.1 ***Principle***. After drying at 105 ± 5 °C the cement sample is attacked by a solution of salicylic acid in methanol. This solution dissolves the clinker silicates but not the aluminates or aluminoferrites. It is assumed that the pozzolanas used in the cement are practically insoluble in this reagent.

The clinker is isolated by separating a size fraction of the cement using dense liquids. Possible contamination of this clinker can be corrected by attack by a dilute acid. The clinker is selectively dissolved by a solution of salicylic acid in methanol enabling the clinker content to be determined and the pozzolana content to be calculated.

7.3.3.2 *Reagents*

Di-iodomethane[3] CH_2I_2, (ρ = 3,31 g/cm³ to 3,32 g/cm³).

Bromoform[3] $CHBr_3$, (ρ = 2,88 g/cm³ to 2,89 g/cm³).

Methanol CH_3OH, absolute methyl alcohol (ρ = 0,79 g/cm³).

Ethanol C_2H_5OH (absolute)

Salicylic acid $C_6H_4(OH)COOH$.

Concentrated hydrochloric acid HCl (ρ = 1,18 g/cm³ to 1,19 g/cm³).

Dilute hydrochloric acid 1 + 100.

Dilute hydrochloric acid 1 + 500.

Diethyl ether $C_2H_5OC_2H_5$, (ρ = 0,71 g/cm³).

Acid solution. Put 800 mL of the methanol into a graduated 1000 mL flask. Add 170 g of salicylic acid. Mix until the salicylic acid is completely dissolved. Made up to 1000 mL with methanol.

7.3.3.3 *Apparatus*

Balance, capable of weighing to the nearest 0,0001 g.

Drying oven, controlled at 105 ± 5 °C.

Electric centrifuge, capable of at least 1000 r/min.

Sieve with a minimum mesh aperture of 32 µm and maximum of 40 µm.

Sieve with a mesh aperture of 80 µm.

Sintered glass filters with mean pore diameters from 5 µm to 15 µm.

Desiccator, containing dried magnesium perchlorate.

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3) This reagent is toxic and shall be handled with the greatest care using safety gloves in a fume cupboard fitted with an extractor.

7.3.3.4 ***Procedure***

7.3.3.4.1 ***Determination of the cement residue insoluble in salicylic acid solution***. Put 100 mL of the salicylic acid solution into a 200 mL beaker. Stir using an electrically controlled glass stirrer. Slowly add 1,0 ± 0,1 g of cement (m). Continue stirring for 60 min. Allow the solution to settle for 5 min.

Filter through a sintered glass filter previously dried in the oven and weighed (m_1). Wash the insoluble residue six times with approximately 100 mL of methanol allowing it to evaporate after each washing. Wash once in diethyl ether.

Dry the filter and the insoluble residue for 2 h in the oven. Allow the filter and the insoluble residue to cool to ambient temperature in the desiccator and weigh (m_2).

7.3.3.4.2 ***Determination of the sulphuric anhydride content***. Determine the sulphuric anhydride content (S_c) of the cement by the method described in clause 8 of EN 196-2.

7.3.3.4.3 ***Separation of the clinker fraction***. The clinker fraction obtained after separation by dense liquids shall weigh at least 3 g in order to carry out the determination of its salicylic residue. If this amount is not obtained, repeat the separation operations in order to obtain the required amount.

Separate by dry sieving a sufficient amount of cement to obtain at least 15 g of material in the size fraction 32 µm to 80 µm or 40 µm to 80 µm. Remove iron particles using a magnet. Re-sieve this last fraction with ethanol on the finest sieve to remove the fine particles which would adhere to the larger grains. Wash once in diethyl ether. Dry the residue for 2 h in the oven. Allow to cool to ambient temperature in the desiccator.

Add the size fraction to a dense liquid with a density of 3,05 g/cm^3 (a mixture of di-iodomethane and bromoform) at a concentration not exceeding 4 g of material per 100 mL of dense liquid. Transfer the suspension into centrifuge tubes. Centrifuge for 5 min at not less than 1000 r/min. Separate the supernatant from the residue and reject the supernatant.

Repeat the separation operation at least twice putting the residue back into suspension in a liquid with the same density and centrifuging for 5 min. Reject the supernatants. Rinse the last residue obtained, twice in methanol and once in diethyl ether, dry for 2 h in the oven and allow to cool to ambient temperature in the desiccator.

Suspend the powder obtained in a dense liquid of density 3,25 g/cm^3 (mixture of di-iodomethane and bromoform) at a concentration not exceeding 4 g of material per 100 mL of dense liquid. Transfer the suspension into centrifuge tubes and centrifuge for 5 min at not less than 1000 r/min. Separate the residue from the supernatant by pouring the supernatant into a new centrifuge tube. Reject the residue.

Repeat the separation operation at least twice putting the supernatant back into suspension in a liquid of the same density and centrifuging for 5 min. Reject the residues. Rinse the last supernatant obtained, twice in methanol and once in diethyl ether, dry for 2 h in the oven and allow to cool to ambient temperature in the desiccator.

7.3.3.4.4 ***Determination of the clinker residue insoluble in salicylic acid solution***. Put 100 mL of the salicylic acid solution into a 200 mL beaker. Stir using an electrically controlled glass stirrer. Slowly add 1,0 ± 0,1 g of the clinker fraction prepared according to 7.3.3.4.3 and weighed (m_3). Continue stirring for 60 min. Allow the solution to settle for 5 min.

Filter through a sintered glass filter previously dried in the oven and weighed (m_4). Wash the insoluble residue six times with approximately 100 mL of methanol allowing it to evaporate after each washing. Wash once in diethyl ether.

Dry the filter and the insoluble residue for 2 h in the oven. Allow the filter and the insoluble residue to cool to ambient temperature in the desiccator and weigh (m_5).

7.3.3.4.5 ***Determination of the clinker residue insoluble in hydrochloric acid.*** Put into a 250 mL beaker 1,0 ± 0,1 g of the clinker fraction prepared according to 7.3.3.4.3 and weighed (m_6). Add 100 mL of water and disperse. Pour in 40 mL of dilute hydrochloric acid 1 + 100 and 60 mL of water and stir for 30 min.

Filter through a sintered glass filter previously dried in the oven and weighed (m_7). Wash the insoluble residue with 50 mL of dilute hydrochloric acid 1 + 500 previously heated to 70 °C. Rinse with 10 mL of water then with methanol and with diethyl ether.

Dry the filter and the insoluble residue for 2 h in the oven. Allow the filter and the insoluble residue to cool to ambient temperature in the desiccator and weigh (m_8).

7.3.3.5 ***Calculation of the pozzolana content of the cement.*** Calculate successively:

$$R_c = 100 \times \frac{(m_2 - m_1)}{m} \qquad (33)$$

$$R_g = 100 \times \frac{(m_5 - m_4)}{m_3} \qquad (34)$$

$$I_f = 100 \times \frac{(m_8 - m_7)}{m_6} \qquad (35)$$

$$R_{kp} = 100 \times \frac{(R_c - 1{,}7\ S_c)}{100 - 1{,}7\ S_c} \qquad (36)$$

$$R_k = 100 \times \frac{(R_g - I_f)}{100 - I_f} \qquad (37)$$

Calculate the pozzolana content of the sum of the clinker and pozzolana constituents of the dry cement from the formula:

$$B = 100 \times \frac{(R_{kp} - R_k)}{(99 - R_k)} \qquad (38)$$

In this formula, it is assumed that the pozzolana residue insoluble in salicylic acid solution is 99 %.

where

R_c is the cement residue insoluble in salicylic acid solution
R_g is the insoluble residue of the fraction 3,05 to 3,25 in salicylic acid solution
I_f is the insoluble residue of the fraction 3,05 to 3,25 in hydrochloric acid solution
R_{kp} is the cement residue free from set regulator(s) insoluble in salicylic acid solution
R_k is the clinker residue insoluble in salicylic acid solution corrected for any pollution
S_c is the sulphuric anhydride content of the cement
m is the mass of the cement
m_1 is the mass of the filter
m_2 is the mass of the filter and the insoluble residue
m_3 is the mass of the clinker
m_4 is the mass of the filter
m_5 is the mass of the filter and the insoluble residue
m_6 is the mass of the clinker
m_7 is the mass of the filter
m_8 is the mass of the filter and the insoluble residue

All the values m to m_8 are expressed in grams by mass of material dried in the oven.

7.3.3.6 ***Repeatability and reproducibility***. The standard deviation for repeatability is 1,5 %.

The standard deviation for reproducibility is 3 %.

These standard deviations are valid whatever the pozzolana content within the range 0 % to 40 % of this material.