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Part 4: Quantitative determination of constituents

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British Standards

National foreword

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Foreword

This document (CEN/TR 196-4:2007) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

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 supersedes ENV 196-4:1993.

This European Technical Report was drawn up by Technical Committee CEN/TC 51 "*Cement and building limes*" the Secretariat of which is held by NBN. It is based on a revision of the European Pre-standard ENV 196-4 of July 1993.

The main aim of this document is to quantitatively verify the compositions (analysis of the constituents) of all the cements included in EN 197-1:2000 (Cements – Part1: composition, specifications and conformity criteria for common cements) as set out in Table 1 “The 27 products in the family of common cements”.

Further to this objective, original methods of analysis were devised, firstly, for cements with 3 constituents and then a reference method for cements with more constituents. Following the progress of work on EN 197-1, cements with blastfurnace slag, siliceous fly ash and natural pozzolans have been successively studied. As a result the first draft of ENV 196-4 was published in December 1989, followed by the ENV 196-4 in July 1993.

The main aim of the revision of the Pre-standard was to adapt the reference method in such a way that it would be qualitative and quantitative whatever the constituent materials, including blastfurnace slag (which had not been included in the 1989 draft ENV 196-4). This entailed revising the analytical procedure and the calculation of the constituents.

The opportunity was taken at the same time to unify the presentation of the different methods, reference and alternative, endeavoring to standardize the notational symbols to eliminate all ambiguities in the interpretation of the formulae for calculations.

Table 1 of ENV 197-1:1992 introduced further new constituent materials. One of them, silica fume, could be routinely determined by the reference method, while calcareous fly ash and burnt shale, being composites of several minerals, react partially like other constituents capable of being determined by the reference method. Where these materials are constituents it has proved not to be possible to determine the mass composition of the cement but only to obtain an overall bulk analysis.

Almost all of the cements manufactured in Europe can be correctly characterized and quantified by the reference method. However, for cements containing burnt shale (CEM II/A-T and B-T) or calcareous fly ash (CEM II/A-W and B-W) it would be necessary to undertake further research in order to obtain an acceptable reference method.

For cements having constituents that can be analyzed by the current reference method as defined in section 1 “Scope” the method will be adequate. Where other constituents are known, or suspected, to be included it will be necessary to develop additional methods for the quantitative determination of those particular constituents.

The European Standard on the methods of testing cement comprises the following Parts:

EN 196-1 *Methods of testing cement — Part 1: Determination of strength*

EN 196-2 *Methods of testing cement — Part 2: Chemical analysis of cement*

EN 196-3 *Methods of testing cement — Part 3: Determination of setting times and soundness*

EN 196-5 *Methods of testing cement — Part 5: Pozzolanicity test for pozzolanic cement*

EN 196-6 *Methods of testing cement — Part 6: Determination of fineness*

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

EN 196-8 *Methods of testing cement — Part 8: Heat of hydration — Solution method*

EN 196-9 *Methods of testing cement — Part 9: Heat of hydration — Semi-adiabatic method.*

NOTE A previous Part, EN 196- 21: Methods of testing cement — Part 21: Determination of the chloride, carbon dioxide and alkali content of cement, has been revised and incorporated into EN 196-2

1 Scope

This European Technical Report describes procedures for determining the contents of most of the constituents of the cements that fall within the scope of EN 197-1.

In principle, the method described in Clause 6 applies to all cements, whatever the number and nature of their constituents, but in practice is limited to the cements identified in Table 1.

The method in clause 6 should be considered to be the method of choice and is based on a sequential selective dissolution of the cement's constituents, generally of an unknown number, where they are not available separately for analysis at the same time as the cement.

The method of choice enables the quantitative determination (by mass) of: Portland cement clinker, blastfurnace slag, siliceous fly ash, natural pozzolans, limestone, silica fume and set regulators in cements of the types identified in Table 1. Table 1 is derived from Table 1 of EN 197-1.

Table 1 — Common cement types specified in EN 197-1

Type of cement	Designation	Notation	Excluding (1)
CEM I	Portland cement	I	
CEM II	Portland-slag cement (with blastfurnace slag)	II/A-S II/B-S	
	Portland-silica fume cement	II/A-D	
	Portland pozzolana cement (with natural pozzolana)	II/A-P II/B-P	
	Portland-fly ash cement (with siliceous fly ash)	II/A-V II/B-V	
	Portland-limestone cement	II/A-L or LL* II/B-L or LL*	
	Portland-composite cement	II/A-M II/B-M	limestone Burnt shale
CEM III	Blastfurnace cement	III/A III/B III/C	
CEM IV	Pozzolanic cement	IV/A IV/B	
CEM V	Composite cement	V/A V/B	

*The method is incapable of distinguishing between limestones of type L and LL

NOTE 1 Where cements contain calcareous fly ash, burnt shale and/or constituents that partly contain mineral phases, similar to those of clinker, further investigation into the characteristics of those constituents will be necessary before the method can be applied.

The method of choice has limitations, as indicated earlier, and cannot be considered to be a means by which clinker content can simply be determined in isolation from any other constituent. Clinker content is determined ‘by difference’ and other constituents contain, in part, mineral phases similar to those present in clinker and can cause interferences that lead to difficulties in interpretation of the results.

Where apparently anomalous results are obtained, it is recommended that further investigations are undertaken in accordance with the procedure given in Section 6.2.5.4.

Any other method with the same objectives, and intended for use where the constituents are unavailable for separate analysis, can be considered to be an alternative to the method of choice when it is shown that, with appropriate statistical validity, it gives equivalent results.

In individual cases, where the laboratory has been formally advised that:

— the cement contains only two constituents, the method is greatly simplified because it is sufficient to determine the set regulator content (R) in order to be able to calculate the clinker content by difference;

— the cement contains only three constituents, i.e. a set regulator, clinker and one of the following three: slag, pozzolana or siliceous fly ash. Some of the methods in clause 7 are variations on the method of choice whereas others are based on physical separation of constituents and different analytical principles.

NOTE 2 This European Technical Report adopts the following use of terms for major constituents:

— ‘Portland cement clinker’ as defined in EN 197-1 is referred to as ‘clinker’;

— ‘granulated blastfurnace slag’ as defined in EN 197-1 is referred to as ‘slag’;

— ‘natural pozzolans’ as defined in EN 197-1 is referred to as ‘pozzolans’;

— ‘siliceous fly ash’ as defined in EN 197-1 is referred to as ‘fly ash’;

— ‘calcium sulfate’ as defined in EN 197-1 is referred to as ‘set regulator’.

2 Normative references

This European Technical Report incorporates by dated or undated reference provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Technical Report only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 196-2, *Methods of testing cement — Part 2: Chemical analysis of cements*

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

EN 197-1, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*

ISO 3534, *Statistics — Vocabulary and symbols*

3 General requirements for testing

3.1 Number of tests

To carry out the calculation for the contents of the cement constituents, two tests shall be made for each. The following analytes are determined:

- for the method of choice by selective dissolution (clause 6):
  sulfuric anhydride and carbon dioxide contents, residues after EDTA and nitric acid dissolution and sulfide contents in the cement and in the EDTA residue;
- for the methods of analysis for cements with three constituents (clause 7):
  sulfuric anhydride and carbon dioxide contents, loss on ignition, calcium oxide, magnesium oxide and manganese oxide contents, sulfide contents and insoluble residues. Depending on the method used, only some of these analytes can be determined.

If, for each analyte, the difference between the two values obtained is less than twice the standard deviation for repeatability for this analyte, the value to take for further calculations is the arithmetic mean of the two values. If the difference between the two values is greater than twice the standard deviation for repeatability, a third test shall be carried out and the value to be taken for further calculations shall be the arithmetic mean of the two closest values.

Hence, for the method of choice by selective dissolution, only one calculation will need to be carried out for the quantitative determination of constituents, in particular for clinker.

Likewise, for the methods of analysis for cements with three constituents, a single calculation will enable the content of hydraulic or pozzolanic constituent to be determined.

The standard deviations for repeatability of the various analytes to be considered, most of which can be found in EN 196-2: 2005, are as follows:

Analyte	**Standard deviation for repeatability (s_r in % by mass)**
SO_3	0,07
CO_2	0,07
a (EDTA residue)	0,50
b (HNO_3 residue)	0,11
S^{2-}	0,02
CaO	0,18
MgO	0,15
MnO	0,003
insoluble residue	0,10
loss on ignition	0,04

3.2 Determination of constant mass

Constant mass shall be 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 weighing is less than 0,0005 g.

3.3 Expression of masses and results

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

Express the values for the analytes, given by the mean of two determinations (see 3.1) as the contents of constituents calculated in percentages, to one decimal place.

3.4 Repeatability and reproducibility

Repeatability - Precision under repeatability conditions where independent test results are obtained with the same method on identical test items (material) in the same laboratory by the same operator using the same equipment within short intervals of time.

Reproducibility - Precision under reproducibility conditions where test results are obtained with the same method on identical test items (material) in different laboratories with different operators using different equipment.

Repeatability and reproducibility in this document are expressed as repeatability standard deviation(s) and reproducibility standard deviation(s) in absolute percent and relate to clinker contents for the general method of determination of the constituents by selective dissolution and to hydraulic and pozzolanic contents for the methods of analysis of cement with three constituents

4 Preparation of a cement sample

Before analysis, the laboratory sample taken in accordance with the provisions of EN 196-7 shall be treated to obtain a test sample.

The details of this treatment of the sample differs according to the methods used and is specified at the start of each procedure (see 6.2.4.1, 7.2.1.4.1, 7.2.2.3.1, 7.3.1.4.1, 7.4.1.4.1 and 7.4.2.4.1).

5 Reagents

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

Unless otherwise specified, “%” 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, nitric acid (1+2) means that 1 volume of concentrated nitric acid has to be mixed with 2 volumes of water.

6 Determination of the contents of cement constituents

6.1 General

This method applies to cements with several constituents, i.e.:

- clinker;
- hydraulic, pozzolanic or inert constituents;

- set regulator(s).

The constituents determined by this method are classified as follows:

- set regulator;
- clinker;
- slag;
- (undifferentiated) calcareous constituents (i.e. combinations of any limestone, chalk, or materials derived from the clinker production process, etc);
- (undifferentiated) siliceous constituents (i.e. combinations of any flint, natural pozzolana, siliceous fly ash, silica fume, etc).

Their number is therefore five in principle, but

- some constituents, mainly calcareous or siliceous, can contain one or more components of the same nature although it may not be possible to identify them separately.
- these same (undifferentiated) calcareous or siliceous constituents, could contain one or more of each type, e.g. chalk can contain flint inclusions; some siliceous fly ashes and pozzolans have compositions similar to calcareous fly ashes. It is therefore not possible, using the method in this clause, to precisely identify the constituents of cement because of the possibility of the content of each type being modified by the other.

Should there be a need to determine (differentiate) the nature of the calcareous or siliceous constituents more precisely, further enquiries should involve the manufacturer of the cement as described in 6.2.5.4.

The results obtained from the application of this method are quantitatively valid, whatever the relative importance of the constituents identified.

6.2 Selective dissolution method

6.2.1 Principle

Following preparation, one fraction of the cement sample is treated with a solution containing triethanolamine (TEA), diethylamine (DEA) and EDTA.

Another fraction is treated with dilute nitric acid (see Table 2).

The results from these two selective dissolutions and the additional determinations of the sulfuric anhydride and carbon dioxide contents of the cement together with the sulfide contents of the cement and the residue from the dissolution in the EDTA solution enable the contents of the various constituents to be calculated.

Table 2 — Reagents and their effects

Reagent	Soluble	Insoluble
EDTA solution	Set regulator(s) Clinker Calcareous constituent(s)	Slag Pozzolana Fly ash Siliceous constituent(s) Silica fumes
Dilute nitric acid	Set regulator(s) Clinker Calcareous constituent(s) Slag	Pozzolana Fly ash Siliceous constituent(s) Silica fumes

6.2.2 Reagents

a) Triethanolamine (TEA) :	$N(CH_2CH_2OH)_3$ [p = 1,12 g/cm^3]
b) EDTA:	dihydrate of the disodium salt of ethylene-diamine-tetracetic acid $C_{10}H_{14}N_2Na_2O_8.2H_2O$
c) Diethylamine (DEA):	$(C_2H_5)_2NH$
d) Ethanol:	C_2H_5OH (ethyl alcohol)
e) Concentrated nitric acid:	HNO_3 [p (1,40 to 1,42) g/cm^3]

6.2.3 Apparatus

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

b) *Drying oven*, controlled at (105 ± 5) °C.

c) Apparatus, to check the *temperature at (20 ± 0,5) °C.*

d) *Electrically controlled stirrer*, fitted with a glass propeller.

e) *Glass microflbre filter papers,* with a porosity of the order of 1 µm to 2 µm and a maximum diameter of 9 cm that fits the funnel of the filtration system. Insert above and below the filter a ring of polytetrafluoroethylene (PTFE) obtained from the supplier in order to improve the collection of particles on the filter. The filter shall be resistant to alcohol and alkalis and shall be dried to constant mass at 105 °C.

f) *Filter paper*, capable of retaining particles between 4 µm and 12 µm to use in case of particularly fine filtration. If necessary, two superimposed glass microfibre filters can be used.

g) *Vacuum filtration system,* capable of being used with glass microfibre filter papers.

h) *Desiccator,* containing anhydrous magnesium perchlorate.

i) *Volumetric glassware*, of analytical accuracy,
i.e. class A as defined in ISO 385-1 and ISO 835-1.

j) *Ordinary glassware,* beakers, flasks, watch glasses, etc.

k) *Agate mortar*.

l) *Sieve,* with a mesh aperture of 75 µm.

6.2.4 Procedure

6.2.4.1 Preparation of the test sample

Treat the cement sample obtained in accordance with the provisions of EN 196-7: 1989 (see clause 4) as follows.

Prepare a laboratory sample of approximately 20 g using a sample divider or by quartering.

Do not remove the iron from the sample at any stage in the operations.

Grind the sample in the agate mortar (6.2.3 k)), then pass it through the 75 um sieve (6.2.3l)). If a residue remains, repeat the operation until all the sample passes through the 75 µm sieve.

Collect and blend all that has passed through the sieve into a single sample.

Dry the sample for 2 h in the oven (6.2.3 b)) and allow it to cool in the desiccator (6.2.3 h)).

6.2.4.2 Preparation of the EDTA solution

Mix 250 ml of triethanolamine (TEA) (6.2.2 a)) with 500 ml water in a 2000 ml beaker. Dissolve (93,00 ± 0,02) g of EDTA (6.2.2 b)) in this mixture and allow to cool to ambient temperature. Transfer to a 1000 ml graduated flask.

Place the flask under a fume-hood, add rapidly 173 ml of diethylamine (DEA) (6.2.2 c)), stopper and allow to cool.

Make up to the mark with water.

Promptly transfer the solution so obtained to a dark brown glass bottle fitted with an air-tight closure. The solution shall not be stored for more than one month.

WARNING Diethylamine (DEA) is a very volatile material which can be toxic if inhaled in a concentrated form. Hence the need to prepare this solution under a fume-hood, away from any source of heat or flame, while wearing safety glasses and gloves, and carrying out all operations as quickly as possible.

Additionally, during dissolution of the cement, the beaker should be covered in order to prevent any risk of inhalation and to avoid the loss of volatile constituents which can affect the buffering action of the EDTA solution. If an unpleasant smell escapes from the covered beaker, it is recommended that work be carried out under a fume-hood, including the filtration procedures.

6.2.4.3 Dissolution using the EDTA solution

Using a pipette fitted with a filler, transfer 50 ml of the EDTA buffered solution (6.2.4.2) to a 1000 ml beaker and dilute with water to approximately 800 ml.

Using the stirrer (6.2.3 d)) stir the solution at approximately 300 r/min.

Check that the temperature of the solution is (20 ± 0,5) °C (6.2.3 c)).

Spread onto the surface of the solution (0,5000 ± 0,0200) g of dry cement accurately weighed to the nearest 0,0001 g (m). The addition shall be progressive during stirring in order to avoid formation of agglomerates which are difficult to disperse.

After 5 min interrupt the stirring and check that no lumps of cement remain. If they do, break them up using the flattened end of a glass rod.

Cover the beaker.

Continue stirring for (120 ± 5) min, while maintaining the temperature of the solution at (20 ± 0,5) °C.

The filter paper should be prepared before filtration in order to avoid any errors due to loss of glass microfibres during subsequent handling. In order to do this, it is necessary to wash the filter paper with water, dry it in the oven, allow it to cool in a desiccator until ambient temperature is reached and weigh it to the nearest 0,0001 g (m_1).

Place the weighed filter paper flat on the vacuum filtration apparatus (6.2.3 g)) and, before fixing the upper part of the funnel, moisten it with water.

Filter the extract solution through the moist filter paper or the conical filter paper (6.2.3 f)) moisten as well, by applying suction such that the pressure in the filter flask is never less than 33,5 kPa (250 mm Hg).

Wash the stirrer and the beaker with water and if necessary use a glass rod with a rubber end to detach any adhering solids and transfer the total solid residue to the filter funnel. Rinse the sides of the funnel with water so that the solid residue collects on the filter paper and then wash the residue five times with 10 ml of water, allowing the water to pass through completely between each rinsing. Finally rinse with ethanol (6.2.2 d)).

Carefully remove the filter paper from the funnel and place it on a weighing dish (6.2.3 j)). Dry the filter paper in the dish in the oven (6.2.3 b) for 1 h.

After cooling in the desiccator (6.2.3 h)) for 15 min, weigh the filter paper plus the residue to the nearest 0,0001 g (m_2).

Retain the filter paper plus residue in a sealed container so that, if required (see 6.2.4.7), the sulfide content of the residue can be determined.

6.2.4.4 Dissolution using dilute nitric acid

Pour 120 ml distilled water into a 400 ml beaker. Stir using the stirrer (6.2.3 d)). During stirring, add gradually (1,000 ± 0,0200) g of dry cement weighed to the nearest 0,0001 g (m_3). The addition shall be progressive in order to avoid the formation of agglomerates which are difficult to disperse. Stir for 5 min. Check that no lumps of cement remain. If they do, break them up using the flattened end of a glass rod. Continue to stir and whilst stirring, slowly add 80 ml of dilute nitric acid (1+ 9).

Continue stirring for 30 min.

If hydrogen sulfide (H_2S) is evolved, carry out this procedure under a fume-hood.

Filter through a pre-weighed glass microfibre filter paper (m_4) (6.2.3 e)).

The preparation of the filter paper, the filtration procedures and washing of the residue are identical to those described in order to obtain the EDTA residue (see 6.2.4.3).

Dry the filter paper and the residue for 1 h in the oven (6.2.3 b)). After cooling in the desiccator for 15 min, weigh the filter paper plus residue to the nearest 0,0001 g (m_5).

6.2.4.5 Sulfuric anhydride content

Determine the sulfuric anhydride content of the cement by the method described in clause 8 of EN 196-2.

6.2.4.6 Carbon dioxide content

Determine the carbon dioxide content of the cement by the method described in clause 15 of EN 196-2.

6.2.4.7 Sulfide content

Determine the sulfide contents of the cement (S_1) and of the residue obtained from the EDTA dissolution (S_2) by the method described in clause 11 of EN 196-2.

NOTE In order to improve the accuracy of the determination of sulfide content, it is necessary that:

- S_1 is determined by taking a quantity of cement of (0,5000 ± 0,0200) g weighed to the nearest 0,0001 g for the measurement;
- S_2 is determined by taking the residue from the EDTA dissolution, including the filter paper (see 6.2.4.3) and placing it all in a reaction flask for the measurement. The sample mass involved is then given as ($m_2 - m_1$);
- the use of a larger test portion of cement, as suggested in the note to sub-clause 11.2 of EN 196-2, is recommended when the sulfide content is low.

6.2.5 Calculation of the contents of cement constituents

6.2.5.1 General

During the experimental work carried out prior to the preparation of this European Technical Report it became clear that the calculated contents for set regulator and calcareous constituents, based on exact stoichiometric relationships using sulfuric anhydride and carbon dioxide values respectively, did not correspond to the actual contents in the cements. It should be appreciated that, on the one hand, set regulators can be mixtures of materials more or less dehydrated during the course of manufacture and that other constituents besides clinker can contain a fraction of sulfuric anhydride that is not negligible. On the other hand, calcareous constituents are rarely pure products. Accordingly, the coefficients used in the calculations have been obtained empirically from experimental results.

The coefficients also take account of the fact that siliceous constituent is partially soluble in nitric acid and that slag is not completely soluble in EDTA.

6.2.5.2 Calculation of contents of insoluble residues

Express all calculated values as percentages (%) of dry material. Calculate the content of insoluble residue, *a*, obtained from the EDTA dissolution from the formula:

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

where

m is the mass of cement;

m_1 is the mass of the filter paper;

m_2 is the combined mass of the dried residue plus filter paper.

Calculate the content of insoluble residue,*b,* obtained from the nitric acid dissolution from the formula:

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

where:

m_3 is the mass of cement;

m_4 is the mass of the filter paper;

m_5 is the combined mass of dried residue plus filter paper.

6.2.5.3 Calculation of contents of constituents

Calculate the set regulator content, R, from the formula:

$$R = 1{,}6 \cdot s \qquad (3)$$

where:

s is the sulfuric anhydride content of the cement.

Calculate the calcareous constituent content, C, from the formula:

$$C = 2{,}0 \cdot c \quad \text{if} \quad c > 1 \qquad (4a)$$

$$C = 0 \quad \text{if} \quad c \leq 1 \qquad (4b)$$

where:

c is the carbon dioxide content of the cement.

Calculate the siliceous constituent content, P, from the formula:

$$P = \text{l}, 05 \cdot b \quad \text{if } b > 2 \qquad (5a)$$

$$P = 0 \quad \text{if } b \leq 2 \qquad (5b)$$

where:

b is the content of insoluble residue obtained from the nitric acid dissolution.

Calculate the slag content, L, from the formula:

$$L = 0 \quad \text{if } (a - b) \leq 1 \qquad (6a)$$

$$L = 1{,}05\,(a - b) \quad \text{if } 1 < (a - b) < 30 \qquad (6b)$$

$$L = \max\,(L_l, L_2) \quad \text{if } (a - b) \geq 30 \qquad (6c)$$

where

$$L_1 = 1{,}05\ (a - b) \qquad (7)$$

$$L_2 = 100 \cdot \frac{S_1(a - b)}{S_2 \cdot a} \qquad (8)$$

This equation is valid if the condition 100 $S_1 \geq a \cdot S_2$ is satisfied.

If this is not the case, carry out a new determination of S_1, S_2 and a.

where:

S_1 is the sulfide content of the cement;

S_2 is the sulfide content of the residue obtained from the EDTA dissolution.

Calculate the clinker content, K, from the formula:

$$K = 100 - R - C - P - L \qquad (9)$$

NOTE 1 To obtain the contents of the various constituents expressed in relation to cement on the “set regulator free" basis, it is necessary to multiply the values obtained above by the factor: 100/(100-R)

NOTE 2 Clinker content, taking into consideration that it is the principal constituent present in all types and classes of cement, is in effect always calculated as the difference between 100 % and the sum of the other constituents.

6.2.5.4 Further investigations

If results are anomalous, i.e. when:

- some of the constituents quantified are different from those which should be present on the basis of the designated type and/or class declared by the supplier;
- the content measured for some constituents normally present in the cement leads to its identification within a type and/or class other than those declared by the supplier;
- the use of a new constituent for which experience of the quantitative determination by the present method is considered as yet insufficient;

an inspection body or, failing this, any independent body commissioned by the interested parties to carry out the analyses should proceed, prior to issuing a report of the analysis, to additional investigations with the cement manufacturer.

6.2.6 Repeatability and reproducibility

Precision estimates for repeatability and reproducibility have been determined for clinker content only because clinker is present in all types and classes of cement.

Where

$(a-b) < 30$; or

$(a-b) \geq 30$ and $L = L_1$

the standard deviation for repeatability is 1 %;

the standard deviation for reproducibility is 2 %.

Where

$(a\text{-}b) \geq 30$ and $L = L_2$

the standard deviation for repeatability is 2 %;

the standard deviation for reproducibility is 4 %.

6.2.7 Qualitative determination of cement type

Determine the type of cement under investigation by comparing the values obtained with the ranges given in table 1 of EN 197-1 defining the different cement types.

7 Determination of the contents of constituents for cements with three constituents

7.1 General

The different methods described in this clause apply only to cements with three constituents, i.e.:

- clinker
- a single hydraulic or pozzolanic constituent (slag, pozzolana, siliceous fly ash);
- set regulator(s).

Therefore, they can only be used if an inspection body or, failing this, any independent body commissioned by the interested parties to carry out the analyses has a document from the cement producer certifying the absence of any constituent other than those listed above.

Some of the methods in clause 7 are variations on the methods of choice whereas others are based on physical separation of constituents and different analytical principles.

7.2 Determination of the slag content

7.2.1 Dense liquid separation method

7.2.1.1 Principle

Fractions of clinker and of slag are separated as cleanly as possible by means of dense liquids from a size fraction of cement (see Figure 1).

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

The slag content of the cement is then calculated.

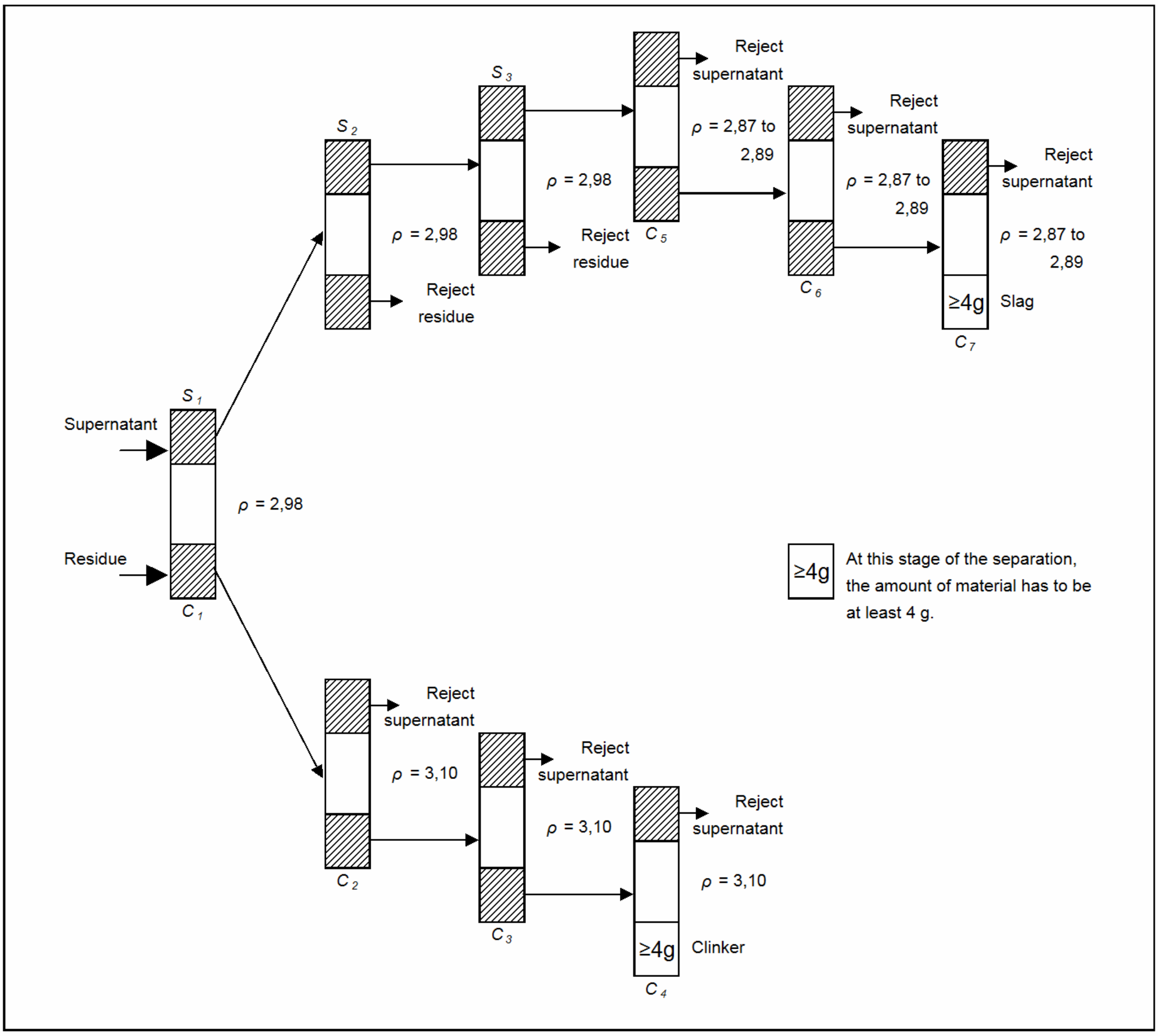

Figure 1 — Scheme of the separation using dense liquids

7.2.1.2 Reagents

a) Di-iodomethane[1] :	CH_2I_2	(p = 3,31 to 3,32 g/cm^3)
b) Dibutyl phthalate:	$C_6H_4\ (COOC_4H_9)_2$	(p = 1,04 g/cm^3)
c) Bromoform[1]:	$CHBr_3$	(p = 2,88 to 2,89 g/cm^3)
d) Ethanol:	C_2H_5OH	(absolute ethyl alcohol)
e) Diethyl ether:	$C_2H_5OC_2H_5$	

7.2.1.3 Apparatus

a) *Balance*, as 6.2.3 a).

b) *Drying oven*, as 6.2.3 b).

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

d) *Centrifuge*, capable of at least 1000 r/min.

e) *Sieve*, with a minimum mesh aperture of 32 µm and maximum of 40 µm.

f) *Sieve*, with a mesh aperture of 75 µm as 6.2.3 l).

g) *Polarising microscope*, fitted with source for transmitted light with a minimum magnification of 100.

h) *Desiccator*, as 6.2.3 h).

i) *Volumetric glassware*, see 6.2.3 i).

j) *Ordinary glassware*, see 6.2.3 j).

7.2.1.4 Procedure

7.2.1.4.1 Preparation of the test sample

The cement sample obtained (approximately 2 kg) in accordance with the provisions of EN 196-7 (see clause 4) shall be treated as follows.

Separate by dry sieving a sufficient quantity of cement to obtain at least 15 g of material in either the size fraction 32 µm to 75 µm or 40 µm to 75 µm.

Re-sieve this fraction with ethanol on the finer sieve (32 µm or 40µm) in order to remove fine particles, which would adhere to the larger grains.

Wash once in diethyl ether and then dry the sample for 2 h in the oven (7.2.1.3 b)) and allow it to cool in the desiccator (7.2.1.3 h)).

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[1] WARNING This reagent is toxic and shall be handled with the greatest care using safety gloves in a fume cupboard fitted with an extractor.

7.2.1.4.2 Separation of the clinker and slag fractions (see Figure 1)

Bring the size fraction 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 in 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 twice, restoring the supernatant (s_2) to suspension in a liquid with the same density and centrifuging it for 5 min. Reject the residues.

Pour the latest supernatant obtained (s_3) into a sintered glass filter (7.2.1.3 c)), wash twice in diethyl ether, dry for 30 min in the oven and allow to cool in the desiccator to ambient temperature.

7.2.1.4.3 Purification of the clinker faction (c_4) (see Figure 1)

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

Bring the powder so obtained into suspension in a liquid with a density of 3,10 g/cm^3 (a mixture of di-iodomethane and dibutyl phthalate or bromoform) at a concentration not exceeding 4 g of material in 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. Remove the supernatants. Pour the last residue obtained (c_4) 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.

In order for the chemical analyses to be carried out, the final clinker fraction (c_4) shall weigh at least 4 g.

If this quantity has not been obtained, sufficient separations shall be carried out so that the sum of each of the individual clinker fractions weighs at least 4 g.

7.2.1.4.4 Purification of the slag fraction (c_7) (see Figure 1)

To obtain the slag fraction, restore the supernatant (s_3) to suspension in a liquid with a density of 2,87 g/cm^3 to 2,89 g/cm^3 (a mixture of di-iodomethane and dibutyl phthalate or bromoform) at a concentration not exceeding 4 g of material in 100 ml of dense liquid.

When the quantity of slag collected is small, however, the use of a liquid with a lower density is permitted, but the latter shall never have a value below 2,84 g/cm^3.

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 of the same density as that used for the first separation. Reject the supernatants.

Pour the last residue obtained (c_7) into a sintered glass filter and wash twice in diethyl ether.

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

In order to carry out the chemical analyses, the final slag fraction (c_7) shall weigh at least 4 g.

If this quantity has not been obtained, sufficient separations shall be carried out so that the sum of each of the individual slag fractions weighs at least 4 g.

7.2.1.4.5 Checking the purity of the clinker and slag fractions.

The purity of the fractions can be checked by the operator by observing them under a microscope (7.2.1.3 g)).

For this purpose, place a few milligrams of powder on a slide, disperse in a drop of immersion oil, cover the sample with a cover slide and examine 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 fractions is not considered sufficiently pure, carry out a further separation.

7.2.1.4.6 Determination of the contents of the tracer analytes

Determine, in mass %, the contents of sulfuric anhydride (s_s), calcium oxide and other tracer analytes (S^{2-}, MgO or MnO), which are not present in the set regulator, in the oven-dried cement as well as in the fractions of slag and clinker, (c_7) and (c_4) respectively.

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 in accordance with the method described in clause 7 of EN 196-2.

7.2.1.5 Calculation of the slag content of cement

Calculate the sulfuric anhydride content, s_s, in the set regulator(s) from the formula:

$$s_s = \frac{s_k \cdot X + A_k \cdot Y - C_k \cdot Z}{X - 0,7 \cdot Z} \tag{10}$$

where

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

$Y = s(C_l - C_k) + s_k(C_c - C_l)$

$$Z = s(A_l - A_k) + s_k(A_c - A_l)$$

where

s_s is the sulfuric anhydride content of the set regulator(s);

s is the sulfuric anhydride content of the cement;

s_k is the sulfuric anhydride content of 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;

A_c is the tracer content of the cement (S^{2-}, MgO or MnO);

A_l is the tracer content of the slag fraction (S^{2-}, MgO or MnO);

A_k is the tracer content of the clinker fraction (S^{2-}, MgO or MnO).

The calculated sulfuric anhydride content of the set regulator(s) shall be within the limits corresponding to the extreme values existing under industrial conditions. These limits are considered to be equal to:

Maximum: $s_s = 58\ \%$ (SO_3 content of anhydrite);

Minimum: $s_s = 32\ \%$ (SO_3 content of gypsum containing 30 % impurities)

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

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

$$f = \frac{S_r}{(A_l - A_k)}$$

where S_r is the standard deviation for repeatability of the analytical determination of this tracer analyte (see 3.1).

Calculate the slag content of the cement from the following formulae:

From the dry materials:

$$L = 100\ \frac{(C_c \cdot a') - (C_k \cdot b') - (0{,}7 \cdot s_s \cdot c')}{(C_i \cdot a') - (C_k \cdot s_s) + (0{,}7 \cdot s_s \cdot s_k)} \qquad (11)$$

where

$a' = s_s - s_k$

$b' = s_s - s$

$c' = s - s_k$

From the calcined materials:

$$L' = L\,\frac{(100 - p_1)}{(100 - p)} \tag{12}$$

The slag content related to the sum of the slag and clinker is given by:

From the dry materials:

$$l = \frac{100 \cdot a' \cdot L}{(100 \cdot b'\,) - (s_k \cdot L)} \tag{13}$$

From the calcined materials:

$$l' = \frac{100 \cdot a' \cdot L\,(100 - p_1)}{100(100 \cdot b' - s_\mathrm{k} \cdot L) - L\,(a' \cdot p_1 - s_\mathrm{s} \cdot p_\mathrm{k}) - 100 \cdot b' \cdot p_\mathrm{k}} \tag{14}$$

where

L is the slag content of the cement;

L' is the slag content of the calcined cement;

l is the slag content of the (clinker + slag);

l' is the slag content of the calcined (clinker + slag);

p_1 is the loss on ignition of the slag fraction;

p is the loss on ignition of the cement;

p_k is the loss on ignition of the clinker fraction.

7.2.1.6 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.

7.2.2 Microscope method

7.2.2.1 Principle

The blastfurnace 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), calculate the ratio, L_v, as a percentage from the formula:

$$L_v = \frac{Number\ of\ grains\ of\ slag}{Total\ number\ of\ grains\ (slag + clinker)} \text{ x } 100 \qquad (15)$$

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

7.2.2.2 Apparatus and materials

a) *Air jet*, or *mechanical sieve apparatus*, with a sieve of mesh aperture 32 µm.

b) *Sieve*, with a mesh aperture of 40 µm.

c) *Polarizing microscope*, as 7.2.1.3 g).

d) *Microscope*, with source for reflected light with a magnification from 200 to 400.

e) *Canada balsam*.

f) *Equipment for preparing sections*.

g) *Synthetic resin*.

h) *Volumetric glassware*, see 6.2.3 i).

i) *Ordinary glassware*, see 6.2.3 j).

7.2.2.3 Procedure

7.2.2.3.1 Preparation of the test sample

The cement sample obtained in accordance with the provisions of EN 196-7 (see clause 4) shall be treated as follows.

Using the air jet or mechanical sieve apparatus (7.2.2.2 a)), first separate by sieving the fraction of grains larger than 32 µm. Next, with the hand sieve (7.2.2.2 b)), 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.

a) Examination in transmitted light

Disperse a sample of approximately 0,02 g of the fraction in Canada balsam (7.2.2.2.e)). For this purpose, melt the Canada balsam on a microscope slide at a temperature of 130 °C to 150 °C. Cover with a cover slide.

b) Examination in reflected light.

Disperse a sample of approximately 1 g of the sieved fraction in the synthetic resin. Wait until the synthetic resin (7.2.2.2.g)) has solidified.

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

7.2.2.3.2 Microscope counting

Take care to ensure that the sample is not damaged when placed under the microscope.

a) In transmitted light

Examine the sample in transmitted light (magnification 100). Count at least one thousand clinker and slag grains in all ignoring the set regulator.

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 (gypsum and anhydrite) are not very distinct in natural light, but the facets reflect in polarized light when the microscope table is rotated.

NOTE 1 The observation is made easier by using a mica quarter wave plate.

b) In reflected light

Count at least one thousand clinker and slag grains in all under the microscope in reflected light ignoring the set regulator.

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 granulated blastfurnace slag grains are light grey in colour, which makes it easy to distinguish them from the clinker grains.

NOTE 2 $C_4AF = (CaO)_4 . Al_2O_3 . Fe_2O_3$, tetracalcium aluminoferrite;

$C_3S = (CaO)_3 . SiO_2$, tricalcium silicate;

$C_2S = (CaO)_2 . SiO_2$, dicalcium silicate;

$C_3A = (CaO)_3 . Al_2O_3$, tricalcium aluminate.

7.2.2.3.3 Determination of the contents of the tracers

Determine the contents of the tracers, CaO, SO_3 and the loss on ignition, in the cement and in the fraction examined by microscope, in accordance with the methods described in EN 196-2.

Express the CaO and SO_3 contents on the calcined material.

7.2.2.4 Calculation of the slag content of cement

Calculate successively:

- the result of the count:

$$L_\mathrm{v} = 100 \frac{n_1}{n_1 + n_\mathrm{k}} \tag{16}$$

— the correction for density:

$$l_\mathrm{m} = \frac{100 \cdot d_1 \cdot L_\mathrm{v}}{100 \cdot d_\mathrm{k} - (d_\mathrm{k} - d_1) \cdot L_\mathrm{v}} \tag{17}$$

The densities of the slag and clinker can be estimated as 2,87 g/cm^3 and 3,15 g/cm^3 respectively hence equation 17 can be written:

$$l_\mathrm{m} = \frac{287 \cdot L_\mathrm{v}}{315 - 0{,}28 \cdot L_\mathrm{v}} \tag{18}$$

the correction for distribution:

$$C_\mathrm{m} = \frac{100 \cdot (C_\mathrm{c} - 0{,}7 \cdot S)}{100 - 1{,}7 \cdot S - P} \tag{19}$$

$$C_\mathrm{f} = \frac{100 \cdot (C_{f'} - 0{,}7 \cdot s_{\mathrm{f}'})}{100 - 1{,}7 \cdot s_{\mathrm{f}'} - p'} \tag{20}$$

The slag content, l’, on calcined (slag + clinker) is then given by:

$$l' = l_\mathrm{m} - 100 \frac{(C_\mathrm{m} - C_\mathrm{f})}{23} \tag{21}$$

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

The slag content, *l*, on dry (slag + clinker) is then given by:

$$l = l' \frac{(100 - P)}{100} \tag{22}$$

where

L_v	is the slag content by volume of the fraction examined by microscope, in %;
n_1	is the number of slag grains;
n_k	is the number of clinker grains;
d_1	is the density of the slag (in g/cm^3);
d_k	is the density of the clinker (in g/cm^3);
C_c	is the calcium oxide content of the cement;
C_m	is the calcium oxide content of the slag and clinker mixture;
$C_{\mathrm{f}'}$	is the calcium oxide content of the fraction examined by microscope;
C_f	is the calcium oxide content of the fraction examined by microscope related to the

calcined sample free of set regulator(s).

S is the sulfuric anhydride content of the cement;

s_{f}' is the sulfuric 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;

l is the slag content of the slag and clinker mixture;

l' is the slag content of the calcined slag and clinker mixture;

l_m is the slag content of the slag and clinker mixture of the fraction examined by microscope, on dry material, in %.

7.2.2.5 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.

7.3 Determination of the siliceous fly ash content

7.3.1 Selective dissolution method

7.3.1.1 Principle

After drying in the oven, the cement is treated with a solution of hydrochloric acid in methanol containing salicylic acid.

The clinker and a fraction of the set regulator(s) are, in principle, dissolved.

The siliceous fly ash and the fraction remaining from the set regulator(s) are not, in principle, dissolved.

Weighing the residue obtained and also the determination of its sulfuric anhydride content and that of the cement allows the siliceous fly ash content of the cement to be calculated.

7.3.1.2 Reagents

a) *Methanol*: CH_3OH (anhydrous methyl alcohol) ($\rho = 0,79$ g/cm^3)

b) *Concentrated hydrochloric acid*: HCl ($\rho = 1,18$ to $1,19$ g/cm^3)

c) *Salicylic acid*: $C_6H_4(OH)COOH$

d) *Acid solution*: Place 800 ml of the methanol into a graduated 1000 ml flask. Add 41,7 ml of hydrochloric acid and (50,00 ± 0,02) g of salicylic acid. Mix until the salicylic acid is completely dissolved. Make up to 1000 ml with methanol.

7.3.1.3 Apparatus

a) *Balance*, as 6.2.3 a).

b) *Drying oven*, as 6.2.3 b).

c) *Electrically controlled stirrer*, as 6.2.3 d).

d) *Filters*, with a mean pore diameter less than 4 µm.

e) *Desiccator*, as 6.2.3 h).

f) *Volumetric glassware*, as 6.2.3 i).

g) *Ordinary glassware*, as 6.2.3 j).

7.3.1.4 Procedure

7.3.1.4.1 Preparation of the test sample

The cement sample obtained in accordance with the provisions of EN 196-7 (clause 4) shall be treated as follows:

Take 20 g of the sample using a sample-divider or by quartering.

Dry the sample for 2 h in the oven (7.3.1.3 b)) and allow to cool in the desiccator (7.3.1.3 e)).

7.3.1.4.2 Dissolution using acid solution

Place 200 ml of the acid solution, (7.3.1.2 d)), into a 400 ml beaker. Stir using the stirrer, (7.3.1.3 c)). Slowly add (2,0 ± 0,1) g of dry cement weighed to the nearest 0,0001 g (m). The addition shall be progressive whilst stirring in order to avoid formation of lumps which are difficult to disperse. After 5 min interrupt the stirring and check that no lumps of cement remain. If they do, break them up using the flattened end of a glass rod.

Continue stirring for 30 min. Allow the solution to settle for 5 min.

Filter through a pre-weighed filter (m_1). Wash the insoluble residue six times with approximately 100 ml of methanol, allowing it to dry completely 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).

7.3.1.4.3 Determination of the sulfuric anhydride content

Determine the sulfuric anhydride content of the insoluble residue, s_i, (7.3.1.4.2) and also of the cement, s_c, as described in clause 8 of EN 196-2.

7.3.1.5 Calculation of the fly ash content of cement

Calculate the fly ash content, V, of the dry cement from the formula:

$$V = \frac{(m_2 - m_1)}{m}(100 - 1{,}813 \cdot s_i) \qquad (23)$$

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

$$v = \frac{100 \cdot V}{100 - 1{,}813 \cdot s_c} \qquad (24)$$

where

V is the fly ash content of dry cement;

v is the fly ash content of dry (clinker + fly ash);

m is the mass of the cement;

m_1 is the mass of the dried filter;

m_2 is the mass of the dried filter plus insoluble residue;

s_i is the sulfuric anhydride content of the insoluble residue;

s_c is the sulfuric anhydride content of the cement.

7.3.1.6 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.

7.4 Determination of the natural pozzolana content

7.4.1 Selective dissolution method

7.4.1.1 Principle

After drying in the oven, the cement sample is treated with a solution of hydrochloric acid in methanol containing salicylic acid.

The clinker and a fraction of the set regulator(s) and the alkaline earth carbonates of certain pozzolanas are, in principle, dissolved.

The natural pozzolanas (except the alkaline earth carbonates of some of them) and the remaining fraction from the set regulator(s) are not, in principle, dissolved.

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

7.4.1.2 Reagents

a) *Methanol*: as 7.3.1.2 a).

b) *Concentrated hydrochloric acid*: as 7.3.1.2 b).

c) *Salicylic acid*: as 7.3.1.2 c).

d) *Acid solution*: as 7.3.1.2 d).

7.4.1.3 Apparatus

a) *Balance*, as 6.2.3 a).

b) *Drying oven*, as 6.2.3 b).

c) *Electrically controlled stirrer*, as 6.2.3 d).

d) *Sintered glass filter*, with a mean pore diameter from 5 µm to 15 µm.

e) *Desiccator*, as 6.2.3 h).

f) *Volumetric glassware*, see 6.2.3 i).

g) *Ordinary glassware*, see 6.2.3 j).

7.4.1.4 Procedure

7.4.1.4.1 Preparation of the test sample

Treat the cement sample obtained in accordance with the provisions of EN 196-7 (see clause 4) as follows:

Take approximately 20 g of the sample using a sample-divider or by quartering.

Dry the sample for 2 h in the oven (7.4.1.3 b)) and allow to cool in the desiccator (7.4.1.3 e)).

7.4.1.4.2 Dissolution using acid solution

Place 200 ml of the acid solution into a 400 ml beaker. Stir using the stirrer (7.4.1.3 c)). Slowly add (2,0 ± 0,1) g of dry cement weighed to the nearest 0,0001 g (m). The addition shall be progressive whilst stirring in order to avoid formation of agglomerates which are difficult to disperse. After 5 min interrupt the stirring and check that no lumps of cement remain. If they do, break them up using the flattened end of a glass rod.

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 dry completely 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).

7.4.1.4.3 Determination of the sulfuric anhydride content

Determine the sulfuric anhydride content of the insoluble residue (s_i) and of the cement (s_c) according to the method described in clause 8 of EN 196-2.

7.4.1.4.4 Determination of the carbon dioxide content

Determine the carbon dioxide content, *c,* of the cement by the method described in clause 15 of EN 196-2, using however, as the solution for dissolving the cement, the acid solution 7.4.1.2 d) and the quantities of cement and acid solution previously specified.

7.4.1.5 Calculation of the pozzolana content of cement

Calculate the calcium carbonate content of the cement, C', from the equation:

$$C' = 2{,}273 \cdot c \qquad (25)$$

The pozzolana content of the cement, P_o, is given by:

$$P_o = \frac{(m_2 - m_1)}{m}(100 - 1{,}813 \cdot s_i) + C' \qquad (26)$$

The pozzolana content of the sum of the clinker and pozzolana, p_o, is given by:

$$p_o = \frac{100 \cdot P_o}{100 - 1{,}813 \times s} \qquad (27)$$

where

P_o is the pozzolana content of the cement:

p_o is the pozzolana content of the sum of the clinker and pozzolana;

C' is the calcium carbonate content of the cement;

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 the insoluble residue;

s_i is the sulfuric anhydride content of the insoluble residue;

s is the sulfuric anhydride content of the cement.

7.4.1.6 Repeatability and reproducibility

The standard deviation for repeatability is 1 %.

The standard deviation for reproducibility is 1,5 %.

These standard deviations are valid for pozzolana contents of cement within the range 0 % to 40 %.

7.4.2 Dense liquid separation method

7.4.2.1 Principle

After drying in the oven, the cement sample is dissolved in a solution of salicylic acid in methanol. The clinker silicates are, in principle, dissolved. The clinker aluminates and aluminoferrites as well as the pozzolanas are not, in principle, dissolved.

The clinker is isolated by separating a size fraction of the cement using dense liquids. Possible contamination of the clinker can be corrected by dissolving it in 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.

7.4.2.2 Reagents

a) *Di-iodomethane*$^{1)}$: as 7.2.1.2 a).

b) *Bromoform* $^{1)}$: as 7.2.1.2 c).

c) *Methanol*: as 7.3.1.2 a).

d) *Ethanol*: as 7.2.1.2 d).

e) *Salicylic acid*: as 7.3.1.2 c).

f) *Concentrated hydrochloric acid*: as 7.3.1.2 b).

g) *Dilute hydrochloric acid*: HCl (1+100).

h) *Dilute hydrochloric acid*: HCl (1+500).

i) *Diethyl ether*: $C_2H_5OC_2H_5$ (ρ = 0,71 g/cm^3).

j) *Acid solution*: Place 800 ml of the methanol into a graduated 1000 ml flask. Add (170,00 ± 0,02) g of salicylic acid. Mix until the salicylic acid is completely dissolved. Make up to 1000 ml with methanol.

7.4.2.3 Apparatus

a) *Balance*, as 6.2.3 a).

b) *Drying oven*, as 6.2.3 b).

c) *Electrically controlled stirrer*, as 6.2.3 d)

d) *Centrifuge*, as 7.2.1.3 d).

e) *Sieve*, as 7.2.1.3 e).

f) *Sieve*, as 7.2.1.3 f).

g) *Sintered glass filters*, with mean pore diameters of 5 µm to 15 µm.

h) *Desiccator*, as 6.2.3 h).

i) *Volumetric glassware*, see 6.2.3 i).

j) *Ordinary glassware*, see 6.2.3. j).

7.4.2.4 Procedure

7.4.2.4.1 Preparation of the test sample

Treat the cement sample obtained in accordance with the provisions of EN 196-7 (see clause 4) as follows for, 7.4.2.1 a), the determination of insoluble residue in the salicylic acid solution and, 7.4.2.4.1 b), the separation of the clinker fraction:

a) take approximately 20 g of the sample using a sample-divider or by quartering, dry it for 2 h in the oven (7.4.2.3 b)) and allow to cool in the desiccator (7.4.2.3 h)).

b) take a sample of approximately 2 kg, separate by dry sieving a sufficient amount of cement to obtain at least 15 g of material in either the size fraction 32 µm to 75 µm or 40 µm to 75 µm, re-sieve this fraction with ethanol on the finest sieve to remove the fine particles which would adhere to the larger grains, wash once in diethyl ether and then dry the sample for 2 h in the oven (7.4.2.3 b)) and allow to cool in the desiccator (7.4.2.3 h)).

7.4.2.4.2 Determination of the cement residue insoluble in the salicylic acid solution

Place 100 ml of the salicylic acid solution into a 200 ml beaker. Stir using the stirrer (7.4.2.3 c)). Slowly add (1,0 ± 0,1) g of dry cement weighed to the nearest 0,0001 g (m).

The addition shall be progressive whilst stirring in order to avoid formation of agglomerates which are difficult to disperse. After 5 min, interrupt the stirring and check that no lumps of cement remain. If they do, break them up using the flattened end of a glass rod.

Continue stirring for 60 min. Allow the solution to settle for 5 min.

Filter through a sintered glass filter (7.4.2.3 g)) previously dried in the oven and weighed (m_1). Wash the insoluble residue six times with approximately 100 ml of methanol in all, allowing it to dry completely after each washing. Wash once in diethyl ether.

Dry the filter and insoluble residue for 2 h in the oven (7.4.2.3 b)). Allow the filter and the insoluble residue to cool in the desiccator (7.4.2.3 h)) to ambient temperature and weigh (m_2).

7.4.2.4.3 Determination of the sulfuric anhydride content

Determine the sulfuric anhydride content(s) of the cement according to the method described in clause 8 of EN 196-2.

7.4.2.4.4 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 residue insoluble in the salicylic acid solution. If this amount is not obtained, repeat the separation operations in order to obtain the required amount.

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 in 100 ml of dense liquid.

Remove the metal particles using a magnet.

Transfer the suspension into centrifuge tubes and 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 (a mixture of di-iodomethane and bromoform) at a concentration not exceeding 4 g of material in 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.

7.4.2.4.5 Determination of the clinker residue insoluble in the salicylic acid solution

Place 100 ml of the salicylic acid solution into a 200 ml beaker. Stir using the stirrer (7.4.2.3 c)). Slowly add (1,0 ± 0,1) g of clinker fraction prepared in accordance with 7.4.2.4.4 and weighed to the nearest 0,0001 g (m_3). Continue stirring for 60 min. Allow the solution to settle for 5 min.

Filter through a sintered glass filter (7.4.2.3 g)) previously dried in the oven and weighed (m_4). Wash the insoluble residue six times with approximately 100 ml of methanol, allowing it to dry completely after each washing. Wash once in diethyl ether.

Dry the filter and insoluble residue for 2 h in the oven (7.4.2.3 b)). Allow the filter and the insoluble residue to cool in the desiccator (7.4.2.3 h)) to ambient temperature and weigh (m_5).

7.4.2.4.6 Determination of the clinker residue insoluble in hydrochloric acid

Place in a 250 ml beaker (1,0 ± 0,1) g of clinker fraction prepared according to 7.4.2.4.4 and weighed to the nearest 0,0001 g (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 (7.4.2.3 g)) 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 (7.4.2.3 b)). Allow the filter and the insoluble residue to cool to ambient temperature in the desiccator (7.4.2.3 h) and weigh (m_8).

7.4.2.5 Calculation of the pozzolana content of cement

Calculate successively the insoluble residue as percentages from the formulae:

$$R_\mathrm{c} = 100\,\frac{(m_2 - m_1)}{m} \qquad (28)$$

$$R_\mathrm{g} = 100\,\frac{(m_5 - m_4)}{m_3} \qquad (29)$$

$$I_\mathrm{f} = 100\,\frac{(m_8 - m_7)}{m_6} \qquad (30)$$

$$R_\mathrm{kp} = 100\,\frac{(R_c - 1{,}7 \cdot S)}{(100 - 1{,}7 \cdot S)} \qquad (31)$$

$$R_\mathrm{k} = 100\,\frac{(R_\mathrm{g} - I_\mathrm{f})}{(100 - I_\mathrm{f})} \qquad (32)$$

The pozzolana content of the sum of the clinker and pozzolana, p_o, is given by:

$$p_\mathrm{o} = 100\,\frac{(R_\mathrm{kp} - R_\mathrm{k})}{(99 - R_\mathrm{k})} \qquad (33)$$

NOTE In this formula, it is assumed that the insoluble residue of the pozzolana in salicylic acid solution is

99 %.

Where

R_c	is the cement residue insoluble in salicylic acid solution;
R_g	is the residue of the 3,05 to 3,25 fraction insoluble in salicylic acid solution;
I_f	is the residue of the 3,05 to 3,25 fraction insoluble 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 contamination;
S	is the sulfuric anhydride content of the cement;
m	is the mass of the cement;
m_1	is the mass of the filter;
m_2	is the combined 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 combined 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 combined mass of the filter and the insoluble residue;
p_o	is the pozzolana content of the sum of the clinker and pozzolana constituents of the cement.

7.4.2.6 Repeatability and reproducibility

The standard deviation for repeatability is 1,5 %.

The standard deviation for reproducibility is 3 %.

These standard deviations are valid for pozzolana contents of cement within the range 0 % to 40 %.

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