

BRITISH STANDARDS 4550 : Part 2 : 1970

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METHODS OF TESTING CEMENT

Part 2. Chemical Tests

**Amendment No. 3
published and effective from 29 July 1988
to BS 4550 : Part 2 : 1970**

**Methods of testing cement
Part 2. Chemical tests**

Revised text

Contents list. After the reference to table 1, insert the following.

- '2. Solutions for checking purity of calcium solution**
- 3. Solutions for calibrating flame photometer**
- 4. Precision estimates'.**

Clause 7.2.2.6 (as amended by Amendment No. 2). In line 2 delete 'Grade No. 4' and substitute 'Grade P16'.

Clause 17. Chloride (method recommended for UK internal purposes) Delete the existing clause entirely and substitute the following.

'17. CHLORIDE

17.1 PRINCIPLE

The sample is boiled with dilute nitric acid to decompose it and to remove sulphides. The chloride is precipitated by adding a measured excess volume of standard silver nitrate solution. The precipitated silver chloride is coagulated by boiling and, together with other insoluble material, is filtered off. The excess silver nitrate is titrated with standardized ammonium thiocyanate solution in the presence of iron (III) indicator.

17.2 REAGENTS

Prepare reagents by the following methods and store in well stoppered containers. Ensure that the water, reagents, filters and glassware used are chloride free.

(1) *Dilute nitric acid (1 + 2)*. Measure 200 ml of concentrated analytical reagent grade nitric acid (relative density 1.42) into a 1000 ml glass beaker, add 50 ml of water and boil gently until the solution is colourless. Add 350 ml water, cool and store in a glass vessel.

(2) *Dilute nitric acid (1 + 100)*. To 15 ml of the dilute nitric acid (1 + 2) add 490 ml of water and store in a glass vessel.

(3) *Standard silver nitrate solution (0.05 mol/l)*. Dry analytical reagent grade silver nitrate at a temperature of $150 \pm 10^\circ\text{C}$ for 2 h and then cool in a covered dish in a desiccator. Weigh 8.494 g of the dried silver nitrate, dissolve in water and dilute to 1000 ml in a volumetric flask. Store the solution in an opaque glass bottle and protect from prolonged exposure to light.

(4) *Ammonium thiocyanate solution (approx 0.05 mol/l)*. Dissolve 3.8 g of ammonium thiocyanate in water and dilute to 1000 ml. At least once a week, or whenever a chloride determination is being made if the test is infrequently used, standardize the ammonium thiocyanate solution by the following procedure.

Measure 50 ml of the dilute nitric acid (1 + 2) into a 500 ml conical flask, add 50 ml of water and 5.00 ml of standard silver nitrate solution using the same pipette or burette as used in 17.3. Heat to boiling, boil for 1 min and cool to below 25°C in subdued light or in the dark. Add 100 ml of dilute nitric acid (1 + 100) and 1 ml of the iron (III) indicator and titrate with the ammonium thiocyanate solution until the suspension has the first discernible faintly pink colouration which does not disappear on shaking. Record the volume, V_1 , of ammonium thiocyanate used in the titration to the nearest 0.01 ml. Carry out the standardization twice and use the average of the values of V_1 provided they do not differ by more than 0.1 ml. If the two values of V_1 differ by more than 0.1 ml repeat the standardization.

(5) *Iron (III) indicator solution*. To 50 g of ammonium ferric sulphate add 60 ml of water and warm to dissolve. Add 10 ml of dilute nitric acid (1 + 2), cool and store in a glass bottle.

NOTE. A crystalline deposit sometimes occurs during storage of this reagent. In these cases either warm the supernatant liquid to redissolve the precipitate before use, or prepare a fresh reagent.

17.3 PROCEDURE

Weigh out 5 ± 0.05 g of the sample and record the mass, m , to the nearest 0.001 g. Place in a 400 ml tall form glass beaker, add 50 ml of water and disperse by stirring with a glass rod. While stirring, add 50 ml of dilute nitric acid (1 + 2) and heat to boiling (in a fume cupboard for samples containing or consisting of slag) with occasional stirring and boil for 1 min avoiding loss of liquid. Remove from the source of heat and add exactly 5.00 ml of the standard silver nitrate solution using either a pipette or a burette. Return the beaker to the source of heat, cover with a watch glass, return to the boil and boil for not less than 1 min and not more than 2 min. Immediately rinse the watch glass into the beaker and filter*, using vacuum filtration, into a 500 ml conical flask. Wash the beaker, glass rod, and residue on the filter paper five times with dilute nitric acid (1 + 100) using approximately 25 ml of the dilute acid for each washing.

*Filter media can contain chloride and handling them can introduce further contamination. It is strongly advised, therefore, to wash filters well before use and to discard the washings. Any filter paper or filtration system that gives a solution clear enough to ensure a precise end point may be used. Glass microfibre filter media of 1 μm particle size retention has been found satisfactory.

[AMD 5713]

Cool the filtrate plus washings to below 25 °C in subdued light or in the dark.

Add 1 ml of the iron (III) indicator and titrate with the ammonium thiocyanate solution until the suspension has the first discernible faintly pink colouration which does not disappear on shaking. Ensure that the end-point indicator colour is similar to that obtained during the standardization of the ammonium thiocyanate.

Record the volume, V_2 , of ammonium thiocyanate used in the titration, to the nearest 0.01 ml. If V_2 is less than 0.5 ml, repeat the procedure with half the sample mass.

Carry out this determination twice.

17.4 CALCULATION OF RESULTS

Calculate the chloride content of the sample as a percentage to the nearest 0.001 % from the equation:

$$\text{Cl} = \frac{1.773 (V_1 - V_2)}{2 V_1 m}$$

where

V_1 is the volume of 0.05 mol/l ammonium thiocyanate required to titrate 5.00 ml of the standard silver nitrate in the standardization (in ml)

V_2 is the volume of 0.05 mol/l ammonium thiocyanate required in the titration of the sample (in ml)

m is the mass of the sample (in g).

17.5 REPORTING

Report the results of both determinations of chloride content. Also report the mean of the two results to the nearest 0.005 %.

17.6 PRECISION

Estimates for repeatability, r , and reproducibility, R , of chloride content are given in table 4.

TABLE 4. PRECISION ESTIMATES

Range of chloride content	r	R
%	%	%
From 0.01 to 0.08	0.005	0.010

Repeatability, r , is defined as the value below which the absolute difference between two single test results obtained with the same method using different test portions of the same laboratory sample under the same conditions (same operator, same apparatus, same laboratory, and a short interval of time) may be expected to lie with a probability of 95 %.

Reproducibility, R , is defined as the value below which the absolute difference between two single test results obtained with the same method using different laboratory samples from the same bulk sample under different conditions (different operators, different apparatus, different laboratories and/or different time) may be expected to lie with a probability of 95 %.

NOTE 1. The above definitions have been modified from those given in BS 5497: Part 1: 1979 to recognize that identical material cannot be tested by this method for determining chloride content.

NOTE 2. The precision data were determined from an experiment conducted in 1984 involving 12 operators and 2 cements and from a separate experiment conducted in 1982 involving 9 operators and 2 cements.'

Amendment No. 4
published and effective from 15 July 1992
to BS 4550 : Part 2 : 1970

Methods of testing cement
Part 2. Chemical tests

Deletions

Page 2 (as amended by Amendments No. 1 and No. 2). At the end of the list of reference standards insert the following.

'BS EN 196. Methods of testing cement

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

Contents list (as amended by Amendments No. 1 and No. 3). Delete the entries for clauses 16 and 17 and substitute the following.

'16. } *Text deleted.*'
17. }

Delete the entries for tables 1, 2, 3 and 4 and substitute the following.

'1. } *Text deleted.*'
2. }
3. }
4. }

Foreword (as amended by Amendment No. 1). Delete the penultimate paragraph and substitute the following.

'The methods for determination of alkalis by flame photometry and for chloride are now published in BS EN 196-21. As further parts of EN 196 'Methods of testing cement' are implemented as British Standards, corresponding test methods that conflict with them will be deleted from BS 4550 by amendment, in accordance with the CEN regulations.'

Clause 16. Determination of Na₂O and K₂O by flame photometry (as amended by Amendment No. 1). Delete the existing clause entirely and substitute the following.

'16. DETERMINATION OF Na₂O AND K₂O BY FLAME PHOTOMETRY
***Text deleted.*'**

Clause 17. Chloride (method recommended for UK internal purposes) (as amended by Amendment No. 3). Delete the existing clause entirely and substitute the following.

'17. CHLORIDE
***Text deleted.*'**

METHODS OF TESTING CEMENT

Part 2. Chemical Tests

BS 4550 : Part 2 : 1970

Incorporating amendments issued May 1983 (AMD 4260)
and September 1983 (AMD 4373)

BRITISH STANDARDS INSTITUTION

Incorporated by Royal Charter

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THIS BRITISH STANDARD, having been approved by the Cement, Lime and Gypsum Products Industry Standards Committee, was published under the authority of the Executive Board on 19th February, 1970.

SBN: 580 05746 1

The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 9,000, fully indexed and with a note of the contents of each, will be found in the BSI Catalogue which may be purchased from BSI Sales Department. The Catalogue may be consulted in many public libraries and similar institutions.

This standard makes reference to the following British Standards:

- BS 12. Portland cement (ordinary and rapid-hardening).
- BS 146. Portland-blastfurnace cement.
- BS 410. Test sieves.
- BS 915. High alumina cement.
- BS 1370. Low heat Portland cement.
- BS 1752. Laboratory sintered or fritted filters.
- BS 4027. Sulphate-resisting Portland cement.
- BS 4246. Low heat Portland-blastfurnace cement.
- BS 4248. Supersulphated cement.
- BS 4402. Specification for safety requirements for laboratory centrifuges.
- BS 5252. Framework for colour co-ordination for building purposes
- DD 80. Laboratory fume cupboards.

*As amended
May, 1983*

*As amended
Sept., 1983*

*As amended
May, 1983*

British Standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

*As amended
May, 1983*

The following BSI references relate to the work on this standard:
Committee reference CAB/1 Draft for comment 67/26698

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6. Total calcium oxide	ISO Method 14 UK Method 15
7. Alumina	ISO Method 17 UK Method 17
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*As added
May, 1983*

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CO-OPERATING ORGANIZATIONS

The Cement, Lime and Gypsum Products Industry Standards Committee under whose supervision these recommendations were prepared consists of representatives from the following Government departments and scientific and industrial organizations:

- *Association of Consulting Engineers
- British Granite and Whinstone Federation
- *British Precast Concrete Federation
- British Railways Board
- *British Ready Mixed Concrete Association
- *British Slag Federation
- *British Steel Industry
- *Cement and Concrete Association
- *Cement Makers' Federation
- Chalk Quarrying Association
- *Chemical Industries Association
- *Concrete Society Ltd.
- *Federation of Civil Engineering Contractors
- *Greater London Council
- Gypsum Plasterboard Development Association
- *Institution of Civil Engineers
- *Institution of Municipal Engineers
- *Institution of Structural Engineers
- Institution of Water Engineers
- Limestone Federation
- *London Transport Board
- Ministry of Housing and Local Government
- *Ministry of Public Building and Works
- *Ministry of Public Building and Works—Building Research Station
- Ministry of Transport
- *National Federation of Building Trades Employers
- *Royal Institute of British Architects
- *Royal Institution of Chartered Surveyors
- Sand and Gravel Association of Great Britain
- *Society of Chemical Industry
- Welwyn Hall Research Association

The Government departments and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committees entrusted with the preparation of these recommendations:

British Transport Docks Board
Crown Agents for Oversea Governments and Administrations
Ministry of Transport—Road Research Laboratory
Overseas Geological Surveys
Royal Institute of Chemistry

BRITISH STANDARD METHODS OF TESTING CEMENT

Part 2. Chemical Tests

FOREWORD

This British Standard has been prepared under the authority of the Cement, Lime and Gypsum Products Industry Standards Committee. It collects together and revises the chemical test methods described in appendices to the following British Standards:

- BS 12 : 1958, ' Portland cement (ordinary and rapid-hardening) '.
- BS 146 : 1958, ' Portland-blastfurnace cement '.
- BS 1370 : 1958, ' Low heat Portland cement '.
- BS 4027 : 1966, ' Sulphate-resisting Portland cement '.
- BS 4246 : 1968, ' Low heat Portland-blastfurnace cement '.
- BS 4248 : 1968, ' Supersulphated cement '.

Publication of BS 'Methods of testing cement ' will enable these standards to be revised by deletion of the relevant appendices, thus avoiding repetition in the expanding range of cement standards and ensuring that if changes are made in any of the test methods the standards do not get out of step. As part of this process it will be necessary for the committees concerned to examine the standards for the various types of cements and decide which methods of test are appropriate in each instance so that the necessary cross references may be given in the individual specifications.

Furthermore, the opportunity has been taken of including certain test methods which have been undergoing consideration by the International Organization for Standardization's Technical Committee, ISO/TC 74—Hydraulic Binders, and most of which have now become ISO Recommendations. These have been reproduced in the standard as the BS reference methods for international trade. They have been edited in order to bring them into conformity with current practice as to the contents of British Standards. In so doing the wording has not been altered any more than was felt to be necessary: a technical change which would lead to a more accurate or reliable result has been regarded as permissible, but not a change such that a different result (entailing a consequential alteration in specification limits) would have been required. Where a departure in technical detail has been made from an ISO method, attention has been drawn to it in a footnote but without assigning a reason. Where the ISO method is the only one given, a recommendation is implied that this should be adopted for trade within the United Kingdom. Where a second method is given

this is recommended for the purposes of UK internal trade. It should however be appreciated that whilst the main purpose of the standard is to provide cross references for the benefit of cement specifications, it is also intended as a complete British Standard for methods of testing cement and some of the tests might never need to be referred to in the British Standards for cements.

These methods are intended primarily for use in the accurate analysis of cements covered by BS 12*, BS 1370† and BS 4027‡. Modifications may be necessary in the case of some cements, such as those covered by BS 146§, BS 915||, BS 4246¶ and BS 4248**, which have an essentially different composition (e.g. the tests for determination of loss-on-ignition given in Section 13 are unsuitable for use with slag cements, including supersulphated cement). The accuracy obtainable by an analyst of moderate experience should be sufficient for all purposes other than those of specialized research.

An analytical tree is introduced in this standard as a guide to the method by which analyses may be carried out. It should also prove useful to those who wish to do only a partial analysis. The aliquot parts as shown are considered to be sufficient to produce results of the precision required for the chemical analysis.

For the calculation of the lime-saturation factor or potential Bogue components of the cementitious material it is necessary to exclude the unreacted silica, alumina or other oxide derived from firebrick or from shale or other impurities added with the gypsum. The standard specifications for Portland cement, in order to maintain cement quality, limit the amount of such adventitious material by the test for insoluble residue. If this insoluble residue is separately analysed (see 3.2), the analysis can be subtracted item by item from that of the total material to give the appropriate figures for the reactive constituents.

Particularly in view of the position taken by ISO on this matter it has been thought best to adopt this course of separate analysis of the insoluble residue rather than to attempt to determine insoluble residue and silica plus insoluble residue by procedures which would, without hydrofluoric acid treatment, permit obtaining soluble silica by difference. The ammonium-chloride-acid attack adopted for silica separation is so powerful that it may render some non-cementitious material soluble and its use to determine silica plus insoluble residue might therefore lead to some error.

The constituent subject to the greatest analytical errors in the past has been Al_2O_3 , since it was determined by the difference $R_2O_3 - Fe_2O_3$, whereas

* BS 12, 'Portland cement (ordinary and rapid-hardening)'.

† BS 1370, 'Low heat Portland cement'.

‡ BS 4027, 'Sulphate-resisting Portland cement'.

§ BS 146, 'Portland-blastfurnace cement'.

|| BS 915, 'High alumina cement'.

¶ BS 4246, 'Low heat Portland-blastfurnace cement'.

** BS 4248, 'Supersulphated cement'.

in fact the R_2O_3 (ammonia precipitate) contained TiO_2 , P_2O_5 , SiO_2 and sometimes Mn_2O_3 in appreciable quantities. The direct method now proposed gives the so-called naked alumina, which may well be as much as 0.6 % lower than the $R_2O_3 - Fe_2O_3$ formerly reported.

The method for determination of alkalis by flame photometry, originally recommended for UK internal purposes, has been amended to correct erroneously high results revealed in practice and confirmed by collaborative tests. The sodium reading was found to be too high because insufficient aluminium was added to the sample solution to suppress all the calcium radiation. The potassium reading was too high because the aluminium added to the calibration solutions, which do not contain calcium, depressed the potassium radiation whereas the aluminium added to the sample solution, which does contain calcium, did not depress the potassium radiation. These errors have been corrected by adding calcium to the calibration solutions and increasing the aluminium added to both the calibration and sample solutions.

*As added
May 1983*

A test for the determination of propylene glycol by gas liquid chromatography has been included. This material may be added to cement clinker as a grinding aid to reduce the energy required and traces may remain in the ground cement.

METHODS OF TEST

1. GENERAL

1.1 SCOPE

Part 2 of this British Standard gives methods for the chemical testing of cement.

1.2 INTRODUCTION

1.2.1 Preparation at the laboratory of a sample for chemical analysis. Mix the 7 kg sample and remove about 100 g for chemical analysis, replacing the remainder in its original container for physical tests.

Remove the 100 g sample by repeated riffing, or by use of a rotating sampler, or by spreading the material in a thin layer and taking about 50 evenly spaced spoonfuls.

Separate the cement into coarse and fine fractions by passing the sample through a 150 microns (No. 100 mesh) BS 410* test sieve. Remove with a magnet any iron from the material retained on the sieve and then grind the remainder so that it passes the 150 microns sieve.

Transfer the sample to a clean, dry 200 ml bottle with an airtight closure and thoroughly mix the sample by tumbling, rolling and shaking for at least 2 min.

1.2.2 Balance and weights. The analytical balance used should normally be of a damped type, with projection reading of decimal places beyond the first or second, to permit rapid weighing. If a rider-type balance is used, particular care shall be taken to minimize errors due to long exposure of the material weighed. The balance should be precise within 0.1 mg.

* BS 410, 'Test sieves', Part 1, 'Fine and medium test sieves (woven wire)'.

The weights used, whether separate or built into the balance, shall be consistent among themselves and when compared with one external weight (e.g. 10 g) taken as standard, none shall differ from its nominal weight by more than 0.2 mg. It is desirable, though not essential, that the external weight shall be one certified by the National Physical Laboratory, or be compared with an N.P.L. certified weight by substitution. Differences greater than 0.05 mg are to be determined so that appropriate corrections can be made whenever necessary.

The full-scale deflection of a projection reading balance shall be checked by placing an accurately known external weight of the appropriate value (e.g. 0.1 g) on the pan: the mean of three of four deflections should be correct within the limit of readability. The external weight may be N.P.L. certified, or may be compared with the corresponding weight used in the balance.

NOTE. The sensitivity, and thus the reading for full-scale weight, of many balances varies with atmospheric temperature, etc. When atmospheric conditions are not nearly constant, sensitivity should be checked frequently. In such conditions it is better to apply any necessary corrections rather than adjust sensitivity repeatedly. This is so particularly if more than one person is using the same balance.

1.2.3 Colorimetry. Where colorimetric methods are specified it is in all cases necessary to make a scale of standard colorimetric solutions. These should contain known quantities of the constituent being determined, treated in the prescribed manner.

It is possible to obtain an approximate determination by visual comparison of the prepared sample solution with these standards.

A more precise determination can be made using either a spectrophotometer which employs a prism or a grating-monochromator to select a wavelength band of about 1 nm (= 1 millimicron), or an absorptiometer which employs an optical filter of the ordinary or the interference type, allowing the passage of a band of 5 nm to 20 nm. The narrower the wavelength-band the more accurately does the additivity law apply to the optical densities measured.

In this case use the series of standard colorimetric solutions to construct the working curve relating optical density to concentration of constituent.

1.2.4 Reagent. Throughout this Part of the standard it is assumed, unless otherwise stated, that all reagents used are of analytical reagent quality.

Unless otherwise stated the following reagents are concentrated and have these densities:

Hydrochloric acid	($d = 1.18$)
Hydrofluoric acid	($d = 1.13$, or '40 %')
Nitric acid	($d = 1.42$)
Perchloric acid	($d = 1.70$)
Phosphoric acid	($d = 1.75$)
Sulphuric acid	($d = 1.84$)
Ammonium hydroxide solution	($d = 0.880$)

1.2.5 Water. Wherever the word 'water' appears in this part of the standard, use distilled or de-ionized water.

1.2.6 Blank determinations. Carry out a relevant blank determination for all analytical determinations.

1.2.7 Results. The result of each determination is calculated as a percentage to the nearest 0.01 %, without implication that this accuracy is reached in every determination.

2. A SCHEME FOR THE ANALYSIS OF PORTLAND CEMENTS RECOMMENDED FOR UK INTERNAL PURPOSES

