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CHEMICAL ANALYSIS OF CEMENTS

MAIN CONSTITUENTS OF PORTLAND CEMENT

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BRIEF HISTORY

The ISO Recommendation R 680, *Chemical analysis of cements – Main constituents of portland cement,* was drawn up by Technical Committee ISO/TC 74, *Hydraulic binders,* the Secretariat of which is held by the Institut Belge de Normalisation (IBN).

Work on this question by the Technical Committee began in 1958 and led, in 1963, to the adoption of a Draft ISO Recommendation.

In February 1965, this Draft ISO Recommendation (No. 773) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina	India	Poland
Australia	Ireland	Portugal
Austria	Israel	Romania
Belgium	Italy	Sweden
Czechoslovakia	Japan	Turkey
Denmark	Korea, Rep. of	U.A.R.
France	Netherlands	United Kingdom
Germany	New Zealand	U.S.S.R.
Hungary	Norway	Yugoslavia

One Member Body opposed the approval of the Draft :

U.S.A.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council which decided, in March 1968, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 680 March 1968

CHEMICAL ANALYSIS OF CEMENTS

MAIN CONSTITUENTS OF PORTLAND CEMENT

1. GENERAL INSTRUCTIONS

1.1 Reagents

All reagents should be of the analytical reagent grade.

1.2 Filter-paper

Filter-papers should be *ash-free*. Filter-papers with a close texture are called *slow*, filter-papers with a medium texture are called *medium* and filter-papers with an open texture are called *fast*.

1.3 Blank determinations

A blank determination is recommended in every case. If possible, it is best carried out with a substance of nearly the same composition as the sample to be analysed, but without the constituent to be determined; otherwise carry out all the described operations without introducing the sample.

2. DETERMINATION OF LOSS ON IGNITION

2.1 Procedure

Place 1 g of the sample in a weighed covered platinum crucible with a volume of 20 to 25 ml. Heat the crucible and its content to constant mass in a muffle furnace at a temperature of 925 ± 25 °C. The initial heating takes 15 ~~min~~, subsequent periods last 5 ~~min~~ minutes

2.2 Expression of results

Calculate the percentage loss on ignition to the nearest 0.1 %.

NOTE. – If heating is carried out at a different temperature this fact should be mentioned in the test report.

3. DETERMINATION OF INSOLUBLE RESIDUE

3.1 Procedure

To 1 g of sample add 10 ml of cold water and whilst vigorously stirring the mixture add 5 ml hydrochloric acid ($d = 1.19$).

If necessary, warm the solution gently and disperse the sample with the flattened end of a glass rod until decomposition of the cement appears to be quite complete.

Dilute the solution to 50 ml and digest for 15 ~~min~~ at a temperature just below boiling. Filter the residue on a medium filter-paper, wash six times with hot water. Transfer the filter-paper and its contents back to the reaction beaker. Add 100 ml of sodium hydroxide (10 g/1) and maintain the solution at a temperature just below boiling point for 15 min. In the presence of methyl red as indicator acidify the solution with hydrochloric acid, and add an excess amount equivalent to four or five drops of hydrochloric acid. Filter on a medium filter-paper and wash the residue twelve to fifteen times with a hot solution of ammonium nitrate (20 g/1). minutes

Ignite the residue in a weighed crucible at 900 to 1000 °C to constant mass.

3.2 Expression of results

Calculate the percentage of insoluble residue to the nearest 0.01 by multiplying the increase in mass in grammes per 100. If necessary, make a blank determination following the same procedure and using the same reagents, and correct the analytical results obtained accordingly. The resultant figure for the insoluble residue should be reported separately and should not in any case be deducted from the total silica.

4. DETERMINATION OF TOTAL SILICA (SiO_2) (MACZKOWSKI METHOD)

4.1 Principle

The soluble silicates are decomposed by hydrochloric acid in the presence of ammonium chloride which breaks down the gel of silica as it forms, thus allowing a rapid and quantitative precipitation of silicic acid by just heating for 30 min on a water-bath.

This is followed by filtration, ignition and weighing of the silica. Final determination of the proportion of silica is by volatilization of the latter in the form of silicon tetrafluoride in the presence of sulphuric acid.

4.2 Cause of errors

This shortened method of precipitation does not give correct results unless the procedure given below is strictly observed.

The residue from the purification by hydrofluoric acid should be heated to at least 1150 to 1200 °C otherwise traces of entrained total oxides R_2O_3 retain a measurable amount of sulphuric anhydride which can cause a significant error in the calculation of silica.

4.3 Procedure

Weigh accurately 1 g of the sample and 1 g of ammonium chloride. Mix the whole carefully in a 250 ml beaker and spread the material evenly over the bottom of the beaker.

Cover the beaker with a watch glass and add slowly, using a graduated pipette, 10 ml concentrated hydrochloric acid (d = 1.19) down the side of the beaker. When the reaction has subsided, stir the mixture with a glass rod to break down any lumps which may have formed.

Place the beaker together with its cover on a water-bath for 30 min. The temperature should not exceed 100 °C.

During this time stir the contents of the beaker frequently with the glass rod to prevent the formation of lumps.

Dilute the syrupy residue at the bottom of the beaker with about 50 ml of hot distilled water and pour on to a fast filter-paper of 11 cm diameter. Thoroughly wash the precipitate twice with hot 5 % hydrochloric acid and then with hot distilled water until the washings are free from chloride (tested by means of silver nitrate).

Place the precipitate with its filter-paper in a weighed platinum crucible, cover the crucible with its lid and heat gently to smoke off the filter-paper without it flaming, so that entrainment of silica does not take place. Finally, ignite at 1150 to 1200 °C in an electric furnace for 45 min. Cool in a desiccator to ambient temperature (about 15 min) and weigh.

This gives the total silica, contaminated with impurities, mainly the oxides (Al_2O_3, Fe_2O_3 etc.).

4.4 Purification of the silica

Moisten the contents of the crucible with a few drops of water and on to this pour 5 ml of pure concentrated hydrofluoric acid and three or four drops of concentrated sulphuric acid. Evaporate the contents of the crucible on a sand bath or any other convenient evaporator, ignite for 5 min at a temperature of 1150 to 1200 °C, cool in a desiccator and weigh. This gives the traces of oxides retained by the silica; subtract this mass from the original mass to give the pure silica; multiply the result by 100 and calculate to the nearest 0.1 %.

NOTES

1. In order to prevent the fluosilicic acid vapours from spreading, it is advisable to cover the sand bath with a lead funnel connected by a lead pipe to a water pump to draw off the fumes.
2. The residue from the silica should be brought into solution for the accurate determination of titanium dioxide (see ISO Recommendation R 681, *Chemical analysis of cements Minor constituents of Portland Cement*).
3. If an error of 0.1 % is of importance, the completeness of separation can be checked by colorimetry on an aliquot part of the filtrate from the precipitate of silica.
4. The figure for the insoluble residue should not in any case be deducted from the total silica.

5. DETERMINATION OF TOTAL OXIDES (R_2O_3)
(aluminium-, iron-, titanium-, vanadium-, chromium oxide and phosphoric anhydride)

5.1 Principle

Precipitation of the combined hydroxides using ammonia in the presence of ammonium salts and weighing the sum of the oxides after ignition.

5.2 Particular points

(a) Presence of ammonium salts.

These salts allow a more controlled neutralization and flocculate the colloid. They also reduce the absorption of other elements and prevent the precipitation of hydroxides of magnesium and calcium by the formation of complex salts. They prevent the entrainment of sodium chloride and sulphuric anhydride.

(b) Presence of Ti^{4+}, PO_4^{3-}; V^{5+} and Cr^{3+}.

These ions precipitate at the same time as aluminium hydroxide and if they are found to be present in appreciable quantity it is advised that a separate determination of these should be made in order to obtain their value for the estimation of aluminium oxide by difference (see Section 9).

(c) The presence of carbon dioxide in the ammonia solution.

This carbonation causes the entrainment of a certain quantity of lime.

5.3 Procedure

Add about 5 ml of bromine water to the filtrate from the silica separation (double this volume in the presence of high concentrations of manganese); 3 % hydrogen peroxide solution can also be used as a means of oxidation instead of bromine water. Evaporate until all free bromine has been driven off, and to a volume of 150 ml. Then add two or three drops of methyl red solution and 1 g of ammonium nitrate and precipitate the hydroxides by the addition drop by drop of ammonia (1 + 9) free of carbonic acid until the solution is coloured yellow. Stir vigorously during the precipitation. Then cover the beaker with a watch glass and allow the precipitate to settle for a few minutes. Decant the solution on to a medium filter-paper of 11 cm diameter, which has been thoroughly rinsed with a dilute solution of ammonium nitrate,* add to the precipitate a hot solution of ammonium nitrate,* pour the whole on to the filter-paper and wash the precipitate with the same solution.

Then proceed with a second precipitation. For this carefully take the filter-paper with its precipitate from the funnel, place in the beaker used for the precipitation and redissolve in hot (1 + 1) hydrochloric acid; mix to disintegrate the filter-paper and carry out a second precipitation using diluted ammonia (1 + 9) in the presence of methyl red. Filter on a medium filter-paper and wash the hydroxides with a dilute solution of ammonium nitrate * The filter-paper with its precipitate is placed in the platinum crucible containing the residue from the evaporation of the fluosilicic acid. After having smoked off the filter-paper, ignite the precipitate at a minimum temperature of 1100 °C for 30 min, allow to cool in a desiccator and weigh; this gives the total oxides. Verify that the mass remains constant.

The result obtained is multiplied by 100 and calculated to the nearest 0.1 %.

* A solution of ammonium nitrate (20 g/l) made just alkaline to methyl red with ammonia.

6. DETERMINATION OF TOTAL LIME (CaO)

6.1 Procedure

Evaporate the filtrate from the hydroxides to a volume of about 300 ml and make it just acid with hydrochloric acid. Add 2 g oxalic acid dihydrate, bring to the boil and neutralize, while still boiling, with diluted ammonia (1 + 4) until the solution is coloured yellow (pH 4 to 5). Then allow the precipitate to settle for about 15 min keeping the solution hot. Filter on a medium ash-free filter paper and wash with a solution of ammonium oxalate (1 g/l) which should be as cold as possible.

Carefully remove the filter-paper with its precipitate from the funnel and place in the beaker in which the first precipitation was carried out. Dissolve in 50 ml (1 + 4) hydrochloric acid. After digestion dilute to 200 ml and add a few drops of methyl red and 20 ml of ammonium oxalate solution (50 g/l) or 1 g oxalic acid dihydrate. Heat close to boiling point and precipitate the calcium oxalate at around 70 to 80 °C by neutralizing the solution, while stirring carefully with dilute ammonia (1 + 4) added drop by drop until the appearance of the yellow colour of the indicator. Allow to stand for 1 to 2 hours, filter with a medium filter-paper and wash with the ammonium oxalate solution (1 g/l). Burn off the filter-paper with its precipitate in a weighed platinum crucible and ignite for 20 min at a minimum of 1100 °C, to obtain a more stable calcium oxide. Cool in a desiccator preferably containing granules of lime calcined at a lower temperature (900 °C) and freshly dehydrated silica gel or magnesium perchlorate (calcium chloride is unsuitable). The weighing of a single crucible placed in a desiccator 20 cm in diameter is possible after 5 min. Re-ignite until the mass is constant.

The result obtained is multiplied by 100 and calculated to the nearest 0.1 %.

7. DETERMINATION OF MAGNESIA (MgO)

7.1 Principle

In an ammoniacal solution and in the presence of ammonium salts magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) precipitates quantitatively. Precipitation is obtained from acid medium by addition of ammonium hydroxide. An excess of ammonium salts prevents the precipitation of magnesium hydroxide and diminishes the solubility of the precipitate. The magnesium ammonium phosphate is ignited to convert it to magnesium pyrophosphate in which form it is weighed.

7.2 Causes of errors

Precipitation is incomplete in the presence of a large amount of oxalate ions, due to the formation of complexes. It is necessary that the concentration of ammonium oxalate be less than 1 g per 100 ml. If this is not the case, evaporate the filtrate from the calcium to dryness and treat with 40 ml nitric acid (d = 1.42) boiling until the nitrous vapours are finally expelled. Then dilute (200 to 400 ml) and proceed as described below.

If potassium is present in considerable quantity, it is absorbed by the precipitate.

In order to prevent reduction of the pyrophosphate, it is recommended to burn off the filter-paper separately as indicated in the procedure below.

7.3 Procedure

Combine the filtrates resulting from the lime separation, slowly acidify with dilute hydrochloric acid and evaporate to a volume of about 400 ml. To the hot solution add 20 ml of saturated diammonium hydrogen phosphate solution and about 50 ml of concentrated ammonia (d = 0.910).

At the same time cool the solution under a stream of cold water down to ambient temperature and mix the solution, using a stirrer, for 20 to 30 min. Allow to settle for another 30 min and filter on a medium filter-paper. Wash the precipitate thoroughly with cold water containing 2.5 % ammonia.

Burn off the filter-paper separately in a porcelain crucible, with the addition of one or two drops of concentrated nitric acid, add the precipitate and ignite at 1000 °C for 20 min. Weigh. The result obtained is the mass of magnesium pyrophosphate ($Mg_2P_2O_7$). The transformation factor for MgO is 36.23. The result is calculated to the nearest 0.1 %.

NOTE. – The separation of the filter-paper from the precipitate is only carried out if the amount of magnesia is large. Otherwise (as is usual for cements) burn off the filter-paper directly in a platinum crucible and heat gently in an oxidizing atmosphere to eliminate all traces of carbon and ignite at 1100 °C to constant mass. The complete combustion of the filter-paper can be helped by finishing the washing of the precipitate with 20 ml of a (1+ 3) ammoniacal solution containing about 2 g/l of ammonium nitrate.