



# Standard Test Method for Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure<sup>1</sup>

This standard is issued under the fixed designation C 1356; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers a systematic procedure for measuring the percentage volume of the phases in portland cement clinker by microscopy.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.3 The values stated in SI units are to be regarded as the standard.

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 150 Specification for Portland Cement<sup>2</sup>

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials<sup>3</sup>

D 75 Practice for Sampling Aggregates<sup>4</sup>

D 3665 Practice for Random Sampling of Construction Materials<sup>4</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *clinker phase, n*—a physically and chemically distinct optically identifiable portion of the clinker sample, including both principal phases (alite, belite, aluminate, and ferrite), minor phases (for example, free lime, periclase, and alkali sulfates), and voids.

3.1.1.1 *Discussion*—Voids, though not a phase in the sense of being a crystalline compound, are a distinct, identifiable portion of a clinker microstructure.

3.1.2 *voids, n*—isolated or interconnected open areas in the clinker, also called pores.

### 3.2 Principal Clinker Phases:<sup>5</sup>

3.2.1 *alite, n*—crystalline tricalcium silicate ( $C_3S$ ), modified in composition and crystal structure by incorporation of foreign

ions; the crystals are pseudo-hexagonal with well-defined faces, though less regular shapes commonly occur.

3.2.2 *aluminate, n*—tricalcium aluminate ( $C_3A$ ) modified in composition and crystal structure by incorporation of a substantial proportion of foreign ions; aluminate forms cubic crystals when relatively pure, and forms identifiable elongated crystals commonly called "alkali aluminate" when in solid solution with significant amounts of potassium or sodium, or both.

3.2.3 *belite, n*—crystalline dicalcium silicate ( $C_2S$ ), modified in composition and crystal structure by incorporation of foreign ions; belite usually occurs as rounded crystals marked by striations formed by cross sections of lamellae, and may occur as single crystals or in clusters.

3.2.4 *ferrite, n*—a solid solution of approximate composition tetracalcium aluminoferrite ( $C_4AF$ ) modified in composition by variation in the Al/Fe ratio and by substantial incorporation of foreign ions; ferrite is characterized by high reflectivity in polished sections and is normally the only strongly colored compound among the principal clinker phases.

3.2.4.1 *Discussion*—Aluminate and ferrite form most of the interstitial material between the silicate crystals and, under certain conditions of cooling, may not be easily identifiable or resolved by ordinary light microscopy.

### 3.3 Minor Clinker Phases:

3.3.1 *alkali sulfates, n*—sodium sulfate, potassium sulfate, and double sulfates such as calcium langbeinite ( $K_2SO_4 \cdot 2CaSO_4$ ).

3.3.2 *free lime, n*—calcium oxide (C) found mostly as round crystals.

3.3.3 *periclase, n*—crystalline form of free magnesium oxide (M), that has not been taken up in solid solution with other phases.

## 4. Summary of Test Method

4.1 The test method consists of the preparation and microscopical examination of a specimen produced by encapsulating clinker in a mounting medium and sectioning the specimen so as to expose the interior of particles for visual examination. Polishing the section surface and treating it with etchants to highlight specific phases complete the preparation. During microscopical examination phases are identified and their proportions determined by a point-count procedure. In this

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 04.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 04.03.

<sup>5</sup> C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>,  $\bar{S}$  = SO<sub>3</sub>, M = MgO, N = Na<sub>2</sub>O, and K = K<sub>2</sub>O in cement chemistry notation.

procedure, the specimen is moved in uniform increments on a microscope stage, and phases falling under the cross hairs of the eyepiece are identified and counted (1-5).

## 5. Significance and Use

5.1 This test method provides a relatively simple and reliable microscopical means of measuring the phase abundance of portland cement clinker (Note 1). Microscopical point counting provides a direct measure of the clinker phase composition in contrast to the calculated Bogue phase composition (Note 2).

NOTE 1—This test method utilizes a reflected light microscope. Related methods such as transmitted light microscopy, scanning electron microscopy, and automated imaging techniques may also be used for clinker analysis but are not presently included in this test method.

NOTE 2—This test method allows direct determination of the proportion of each individual phase in portland-cement clinker. This test method is intended to provide an alternative to the indirect estimation of phase proportion using the equations in Specification C 150 (footnote C in Table number 1 and footnote B in Table number 2).

5.2 This test method assumes the operator is qualified to operate a reflected light microscope and the required accessories, is able to correctly prepare polished sections and use necessary etchants, and is able to correctly identify the constituent phases.

5.3 This test method may be used as part of a quality control program in cement manufacturing as well as a troubleshooting tool. Microscopic characterization of clinker phases may also aid in correlating cement properties and cement performance in concrete, to the extent that properties and performance are a function of phase composition.

## 6. Apparatus

6.1 Reflected light microscope.

6.2 Mechanical stage with stepping increments ranging from 0.05 to 2.0 mm (to enable analysis of clinkers of different average crystal sizes) and vernier scales graduated in both X and Y directions.

6.3 Microscope objectives of magnification 5×, 10×, 20×, and 40× or other magnifications suitable for the task.

NOTE 3—The use of reflected light with oil immersion is optional. It is highly recommended for study of finely crystalline aluminates and ferrites which typically form the ground mass in which the silicates occur. Reflected light objective lenses with magnification up to 100× designed for use in oil-immersion are required.

6.4 Assorted eyepieces (5×, 10×, 20×) which when combined with the objectives described in 6.3 will provide magnifications up to 800×.

6.5 Eyepiece reticles (graticulae) with a linear grid pattern containing 9, 16, or 25 intersections.

6.6 Eyepiece micrometer for measuring dimensions of the object under investigation and calibrated for each magnification.

6.7 Stage micrometer for the calibration of the eyepiece micrometer.

6.8 Light source that provides uniform and consistent illumination of the field and light of constant intensity.

6.9 Counting (tallying) device capable of recording up to ten categories of data.

6.10 Crushing device capable of reducing sample particle size to between 1 and 4 mm.

6.11 Riffle sample splitter to reduce sample from initial volume to approximately 100 g.

6.12 Wire cloth sieves with openings suitable for sieving the entire clinker sample to broadly define the model size class, and sieves with 1-mm and 4-mm square openings to concentrate particles of recommended size for specimen preparation.

6.13 Vacuum impregnation device to force epoxy into clinker voids. (Vacuum bell jar or desiccator connected to a vacuum pump.)

6.14 Curing oven, hot plate, slide warmer, or ultraviolet light may be used to accelerate the epoxy hardening.

6.15 Thin, diamond-rimmed wafering saw for sectioning the encapsulated clinker.

6.16 Glass grinding (lapping) plates (300 mm × 300 mm × 5 mm) required only if the mechanical system is not equipped to handle the final grinding with alumina powder.

6.17 Ultrasonic cleaning device (optional) to clean the sample prior to, between, and after polishing steps.

## 7. Reagents and Materials

7.1 Consumable grinding (lapping) and polishing supplies. After the encapsulated specimen has been cut with the saw, all or most of the following grinding and polishing steps are required: 120-, 320-, and 600-grit silicon carbide grinding papers or equivalent and 5 μm, 0.3 μm, and 0.05 μm alumina polishing powders or their equivalent. Diamond grinding discs, silicon carbide paper, or polishing cloths and alumina polishing powder may be used. Various types of polishing cloths may be used to produce a nearly flat clinker surface or a relief surface to aid in identification of periclase (1).<sup>6</sup>

7.2 Sample cups (with volumes ranging from 10 to 20 mL) to contain epoxy-clinker mix during hardening.

7.3 Epoxy resin and hardener for encapsulation of the clinker. Low viscosity resin will facilitate penetration into clinker voids. When hardened it should have an abrasive resistance close to that of the clinker to minimize relief during polishing. It should be resistant to substances used for washing and etching.

7.4 Isopropyl alcohol (2-propanol) for washing the specimen and for use in the ultrasonic cleaner. Propylene glycol is suitable as a lubricant for the saw blade.

7.5 Immersion oil with an index of refraction of 1.51 if reflected light immersion-oil technique is used.

7.6 Etching material to highlight different phases for counting. (See Appendix X3.)

## 8. Sampling

8.1 Take samples of portland-cement clinker in accordance with the applicable provisions of Practices D 75 and D 3665 so as to be representative of the quantity of material with which testing is concerned (see Appendix X1).

8.2 Sieve the initial sample to obtain clinker particles representing approximately 70 % of the clinker particle size

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

distribution, centered about the mode. This particle size interval represents a size range of approximately two standard deviations, one on each side of the mode, and is herein defined as the “bulk mode” ( $M_b$ ), the combined material between the extremes of the particle size distribution. State the sieve sizes used. If either extreme of the particle size distribution is to be studied, the selected portion shall be identified as non-modal, and the percentages retained or passing standard sieves shall be stated. The recommended size fraction for microscopical analysis is 2 to 4 mm. Therefore, that portion of the initial clinker sample representing the bulk mode shall be crushed, sieved, and riffled to provide approximately 100 g. Whole clinkers may be encapsulated to study the phase distribution within clinker nodules.

## 9. Preparation of Sample Specimen

9.1 Polished sections shall be polished to a fineness such that grinding pits and scratches have been eliminated (see Appendix X1).

9.2 Etching of the clinker surface may be used to facilitate identification of clinker phases (1); additional information may be found in the Appendix X1.

## 10. Counting Procedure

10.1 Choose the microscope magnification such that adjacent reticle grid points do not fall on the same crystal, except for a few unusually large crystals. Magnification from 200× to 500× will accommodate most clinkers. Reticles with multiple grid points are recommended. Single crosshair reticles are not suitable.

10.2 Choose the stepping interval such that an entirely different field of view is observed after each step.

10.3 Attach a mechanical stage to the microscope. The mechanical stage may be an electrically driven specimen carriage connected to an automatic electronic counter or a simple hand-operated carriage and counter. Place a small amount of soft modeling clay on a standard, petrographic glass slide (27 mm × 46 mm) and level the sample thereon. Either use a commercial leveling device or use a small spirit level to adjust the mount while pressing it firmly into the clay. A tissue paper between the polished section and the leveling device or spirit level prevents surface scratches. Place the glass slide with attached clay and leveled mount on the mechanical stage. Check the accuracy of leveling by observing the focus at several points on the polished surface. Move to a starting point (the initial field of view from which data will be taken) at the edge of the mount and record the position in the X-Y coordinate system, using the graduated scales on the mechanical stage.

10.4 Use a tally sheet or a counting device to record the phases as required. The observer should not keep a mental tally of any data because of possible bias. Identify and record each phase under the grid intersections. In some cases, the aluminates and ferrite quantities may be combined and labeled “matrix”. Move the mechanical stage a distance of one stepping interval in the chosen X or Y direction to bring another field into view. The phases under the grid points are identified, counted, and the mechanical stage advanced one stepping interval to an adjacent field of view. This procedure is continued until a range

of 3000-4000 points are recorded.

At the clinker periphery, some of the reticle points may fall on the encapsulating epoxy that surrounds the clinker particle. Count only points within the clinker, and disregard the reticle points over epoxy at the clinker periphery. Thus, the clinker void space (porosity), if determined in the point count, does not include cavities on the surface of the clinker particle. As one steps over irrelevant areas (such as epoxy exterior to the clinker or severally damaged portions of the polished surface that obscure the phase identification) the count is temporarily suspended until a suitable clinker surface again falls under the reticle grid points. Artifacts (for example, blot marks, residual liquids) on the section surface are not to be counted. If the identity of the phase is obscured by the area formed by the grid intersection, one should consistently use a specified corner of the intersection where the phase can be clearly observed.

When the edge of the mount is reached at the end of a line of traverse, the mount is translated one stepping interval perpendicular to that line and counting continues in the opposite direction, or the mount is repositioned to a point at the original starting boundary to keep the same direction of travel. As one progresses along the lines of traverse the data are accumulated until 3000–4000 points ( $N$ ) are recorded.

## 11. Calculation of Results

11.1 Calculate the volume fraction of each phase in the sample by dividing the number of points counted for that phase by the total number of points counted. This number multiplied by 100 yields the phase content in volume per cent.

11.2 The number of points to be counted is to be between 3000 and 4000 (2). The absolute error at the 96 % confidence interval has been shown to be:

$$\delta = 2.0235 \sqrt{\frac{P(100 - P)}{N}} \quad (1)$$

where:

$\delta$  = absolute measuring error in percentage for a given constituent,

$P$  = phase percentage, and

$N$  = total number of points counted.

Therefore for any error percentage deemed acceptable and expected value of  $P$ , the required number of points,  $N$ , can be calculated:

$$N = \left(\frac{2.0235}{\delta}\right)^2 \times (100 - P)P \quad (2)$$

If an estimate of  $P$  is not available, the above equation takes on a maximum when  $P = 50$ . Using this value will provide a conservative estimate for the number of points required.

11.3 To express phase abundance in terms of mass fraction, multiply phase volume fractions by their respective mass density (see Table 1) and normalize the totals to 100 %.

## 12. Reporting Results

12.1 The report of the point count results to microscopically determine the phase percentages in portland cement clinker should include the following information:

12.1.1 Identify the source of the samples, including sampling location and type of sample.

**TABLE 1 Mass Densities in g/cm<sup>3</sup> for Clinker Phases (7)**

Phase	Density
alite	3.18
belite	3.31
aluminat	3.03
ferrite	3.73
free lime	3.35
periclase	3.58
alkali sulfate	2.66

12.1.2 State how the sample was treated. If the sample was sieved, give the sieve designation size for the final sample. Indicate the type of each etchant used and etch time.

12.1.3 State the number of data points and percentages of each determined phase.

### 13. Precision and Bias

13.1 *Within-Laboratory Precision*—Single operator values of the one-sigma limit in percent (1S %), defined in accordance with Practice C 670 determined for volume fraction determi-

nation by point count analysis (see Note 4) have been found to be 0.71 % (1S) (6). Therefore, results of two properly conducted tests by the same operator on the same material should not differ by more than 2.58 % (D2S) from the average of the two results.<sup>7</sup>

NOTE 4—These levels of precision are based on data from the NIST RM Clinker certificate data. A bias statement is not available as these data are used to establish the phase abundance compositions of the RM clinkers.

13.2 A multi-laboratory round robin is planned to generate data for use in a precision and bias statement in accordance with Practice C 670.

### 14. Keywords

14.1 alite; aluminat; belite; ferrite; periclase; portland-cement clinker; reflected light microscopy

<sup>7</sup> Data pertaining to this precision statement are on file at ASTM Headquarters as report RR:C01-1005.

## APPENDICES

### (Nonmandatory Information)

#### X1. SAMPLING

X1.1 The task of obtaining a representative clinker sample for microscopical examination from the stream of material leaving the kiln presents special problems, and the solution depends greatly on local conditions. When sampling from a conveyor belt, an entire cross section of the material should be taken. When the sample is collected from material in free fall, for example at the end of the conveyor belt or at the discharge of a bucket elevator, all the particles falling during the sampling operation shall be included, and sampling devices and containers shall be of sufficient volume to contain the resulting amount. One litre is recommended for the initial clinker sample.

X1.2 If continuous sampling of a clinker flow is impractical, samples representing more extended periods of operation shall be composites of two or more grab samples obtained according to X1.1. The period of time covered and the frequency of sampling will depend on local conditions and the purpose of the test, but the procedure for obtaining each individual grab sample shall be identical.

X1.3 Material judged atypical for the period, the process, or the equipment under study (kiln dust, kiln coating, etc.) may be removed prior to microscopical examination, but the removal of such material should be noted.

#### X2. SAMPLE IMPREGNATION AND POLISHING

X2.1 Label a sample cup with the sample identification (a tag may also be embedded in the epoxy) and coat the interior with a mold release agent. Place 10 to 20 g of the clinker sample in the cup and add low-viscosity epoxy resin previously mixed with the hardener. Place the sample cup under the vacuum jar and operate the vacuum pump to obtain adequate penetration of the resin. Break the vacuum several times to permit atmospheric pressure to force the epoxy into the material.

X2.3 Remove the specimen from the cup and, if necessary, label with a diamond engraver or indelible pen.

X2.4 Cut the encapsulation with the diamond-rimmed wafering saw to expose the clinker particle cross sections. Preparation liquids retained in clinker voids may interfere with etching and staining; therefore, a second application of vacuum impregnated epoxy on the polished surface may be necessary. A cyanoacrylate resin, smeared over the polished surface, may be used. The encapsulation is then reground and polished.

X2.2 Cure the epoxy as recommended by the manufacturer in an oven at a temperature not higher than 70°C. Some epoxies will harden rapidly at room temperature or under ultraviolet light.

X2.5 Grind the exposed surface by lapping with each of the selected grinding media (see 7.1), beginning with the coarsest, for 2 to 4 min each. Use propylene glycol, isopropanol, or other liquids as lubricants during grinding. After each step, wash the

surface with a forceful spray of isopropyl alcohol. Do not use water in cutting, grinding, polishing, or cleaning the encapsulated clinkers.

X2.6 Polish the surface with each of the chosen polishing media, beginning with the coarsest, for 2 to 4 min. Wash the surface after each polishing step with a forceful isopropyl

alcohol spray. Clean the specimen ultrasonically after the last wash, using isopropyl alcohol as the cleaning fluid. Rinse again with the alcohol spray. Dry the surface with a forced warm air current. Blotting is not recommended because of the production of blot marks.

### X3. ETCHES AND STAINS

X3.1 Certain liquids or vapors applied to the polished surface will produce a preferential phase coloration. One versatile liquid is nital (1 mL nitric acid in 99 mL isopropyl alcohol). Other commonly used stains and etchants are hydrofluoric acid vapor, potassium hydroxide, distilled water, aqueous ammonium chloride, dimethyl ammonium citrate, and others. Details of various etches and stains, immersion times, and techniques are given in Ref (1). The choice of etchant, etch time, and temperature of etchant can affect results. Therefore, these choices should be consistent for all specimens prepared for point counting.

NOTE X3.1—**Precaution:** Appropriate safety precautions must be observed when preparing and using stains and etchants. Review all Material Safety Data Sheets and always use suitable personal protective equipment including eye protection, apron, and gloves.

X3.2 For aluminate and free-lime coloration, the application of distilled water at 40°C for 5 s with the specimen at room

temperature, or 0.1 molar KOH for 20 to 30 s is recommended. The polished surface can also be placed on a water-saturated, clean, low-nap polishing cloth for 2 to 3 s and then quickly washed with a forceful isopropyl alcohol spray. This technique produces a structure etch on the silicates. The polishing cloth may be attached to a rotating wheel or may be stationary on a glass plate.

X3.3 For a clear differentiation of the silicates, alite and belite, a 6- to 8-s immersion in nital is recommended, quickly followed by an alcohol spray wash. One may choose to carry out a high magnification point count (550× or more) on the water-stained matrix, followed by a relatively low-magnification point count (approximately 300×) of the silicates on a nital-etched surface.

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- (7) ICDD/JCPDS Powder Diffraction File, International Centre for Diffraction Data, Newton Square, PA.

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