ASTM INTERNATIONAL

Designation: C563 – 18

Standard Guide for
Approximation of Optimum SO$_3$ in Hydraulic Cement[1]

1. Scope*

1.1 This guide describes the determination of approximate optimum SO$_3$ for maximum performance as a result of substituting calcium sulfate for a portion of the cement.

1.2 This guide refers to the sulfur trioxide (SO$_3$) content of the cement only. Slag cements and occasionally other hydraulic cements can contain sulfide or other forms of sulfur. The determination of SO$_3$ content by rapid methods may include these other forms, and may therefore produce a significant error. If a significant error occurs, analyze the cement for SO$_3$ content using the reference test method of Test Methods C114 for sulfur trioxide.

1.3 Values stated as SI units are to be regarded as standard.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
C39/C39M Test Method for Compressive Strength of Cylindrical Concrete Specimens
C78/C78M Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading)
C109/C109M Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)

C114 Test Methods for Chemical Analysis of Hydraulic Cement
C150/C150M Specification for Portland Cement
C192/C192M Practice for Making and Curing Concrete Test Specimens in the Laboratory
C204 Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus
C305 Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency
C430 Test Method for Fineness of Hydraulic Cement by the 45-µm (No. 325) Sieve
C465 Specification for Processing Additions for Use in the Manufacture of Hydraulic Cements
C471M Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)
C595/C595M Specification for Blended Hydraulic Cements
C596 Test Method for Drying Shrinkage of Mortar Containing Hydraulic Cement
C1157/C1157M Performance Specification for Hydraulic Cement
C1437 Test Method for Flow of Hydraulic Cement Mortar
C1679 Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry
C1702 Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry

3. Significance and Use

3.1 The purpose of this guide is to estimate the SO$_3$ content for a hydraulic cement that gives maximum performance. The value obtained is one way to establish an appropriate level of sulfate in the manufacture of cements specified in Specifications C150/C150M, C595/C595M, and C1157/C1157M.

3.2 The SO$_3$ content of a cement giving maximum performance is different at different ages, with different performance criteria and with different materials such supplementary cementitious materials and chemical admixtures. A manufacturer can choose the performance criteriato determine optimum SO$_3$ content. This optimum SO$_3$ content may be a compromise between different ages and different performance criteria.

NOTE 1—Typically, the optimum SO$_3$ content is higher the later the age.

A Summary of Changes section appears at the end of this standard

3.3 This guide indicates optimum SO_3 content for cement, optionally in presence of supplementary cementitious materials and admixtures. Several alternate methods are allowed: compressive strength of concrete or mortar, heat of hydration of paste or mortar, and drying shrinkage of mortar.

3.4 It should not be assumed that the optimum SO_3 estimated in this guide is the same SO_3 content for optimum performance of a concrete prepared in the field using the same materials. The optimum SO_3 is influenced by parameters such as ambient and fresh concrete temperature, admixtures, and supplementary cementitious materials.

3.5 The guide is applicable to cements specified in Specifications C150/C150M, C595/C595M, and C1157/C1157M.

4. Apparatus

4.1 Use the apparatus as specified in Test Methods C109/C109M, C192/C192M, C596, or C1702.

5. Materials

5.1 *Calcium Sulfate*—Use calcium sulfate for addition to the cement that is either a high-grade natural gypsum having an SO_3 content of at least 46 %, or the calcium sulfate from the source used for the intended plant production. Grind the calcium sulfate to 100 % passing the 75-μm (No. 200) sieve, and at least 800 m^2/kg Blaine fineness (Test Method C204). If the SO_3 content of the calcium sulfate is unknown, analyze it in accordance with Test Methods C471M.

NOTE 2—The calcium sulfate source can impact the optimum sulfate result due in part to differences in surface area and form of the calcium sulfate (for example, gypsum, calcium sulfate hemi-hydrate, or anhydrous calcium sulfate). Temperatures in cement finish mills during production can reach levels to partially or completely change the form of calcium sulfate in cement, while laboratory grinding of calcium sulfate may alter its reactivity through increased fineness and partial change of the form of the calcium sulfate. Different clinkers may react differently to the effect of sulfate forms. In particular, if the dissolution rate of sulfate during cement hydration is at any time lower than the sulfate consumption rate of the aluminates, the sulfate in solution may become temporarily depleted, resulting in elevated aluminate reactivity and significant reductions in alite reactivity. Elevated aluminate reactivity may lead to loss of workability and admixture performance as well as reduced rate of strength development and setting behavior that has a relatively low degree of repeatability and reproducibility. On the other hand, if the dissolution rate of sulfate before placing of concrete is higher than the sulfate consumption rate of the aluminates, precipitation of secondary gypsum may cause loss of workability and false set.

5.2 *Cement*—Make cements of different sulfate levels at a single production site. Make the cements so that the amount of calcium sulfate added, and the subsequent dilution effects, are the only difference in constituent materials.

5.2.1 Grind samples to a fineness within 13 m^2/kg of the other samples when tested in accordance with Test Method C204. Since calcium sulfate sources are typically softer than clinker, an adjustment of 10 m^2/kg for every 1 % calcium sulfate addition is permitted, as shown in Eq 1.

$$F_{A,X} = F_{M,X} - \frac{10 \cdot (SO_{3,X} - SO_{3,median})}{SO_{3,CS}/100} \qquad (1)$$

where:

$SO_{3,CS}$ = percentage of SO_3 in the calcium sulfate,

$SO_{3,median}$ = SO_3 percentage of the sample with the median SO_3 of the samples tested,
$SO_{3,X}$ = SO_3 percentage of cement sample X,
$F_{M,X}$ = measured fineness of cement sample X, and
$F_{A,X}$ = adjusted fineness of cement sample X.

NOTE 3—Differences in the mill conditions between samples of different sulfate levels should be minimized. For this reason samples are normally taken during the same production campaign. Strategies should be employed to minimize the differences in fineness of the clinker when taking samples, such as targeting a specific sieve size range and adjusting around that target within reasonable tolerances. Since calcium sulfate is softer, and thus easier to grind than clinker, increases in calcium sulfate content will elevate the fineness of the cement without a change in the grinding energy or the fineness of the clinker.

NOTE 4—As an example, consider the case of one cement sample with an SO_3 content of 2.7 % and a fineness of 380 m^2/kg, which is the sample with the median SO_3 content, and another sample with an SO_3 content of 3.7 % and a fineness of 405 m^2/kg. The second sample has a 1.0% higher SO_3 content, or 2.2 % more calcium sulfate addition, assuming the calcium sulfate was 45 % SO_3. The adjusted cement fineness of the second sample would be reduced by 22 m^2/kg (10 × 2.2) to 383 m^2/kg by using Eq 1 as shown in Eq 2. This value of 383 m^2/kg is within 13 m^2/kg of the fineness of 380 m^2/kg, and thus is acceptable for testing.

$$F_{A,X} = 405 - \frac{10 \cdot (3.7 - 2.7)}{\frac{45}{100}} = 383 \ m^2/kg \qquad (2)$$

5.2.2 Determine the percentage of the following analytes by Test Method C114 for each cement tested: silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sulfur trioxide (SO_3), loss on ignition, insoluble residue, sodium oxide (Na_2O), and potassium oxide (K_2O). Calculate the potential percentages of the following compounds for portland cements according to Specification C150/C150M: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. When applicable, report the amount of limestone and Specification C465 inorganic processing additions according to Specification C150/C150M. Determine the fineness of each cement tested according to Test Methods C204 and C430.

NOTE 5—The amount of material retained on the 45-μm sieve has been used as an indication of the clinker fineness. When high efficiency separators are used, the amount retained on a 20-μm sieve has also been used as an indicator of clinker fineness.

6. Procedure

6.1 *Sulfate Levels to Test*—Test at least five different sulfate levels.

6.1.1 SO_3 contents are to be at least 0.20 % different unless more than five different SO_3 contents are being tested. The maximum and minimum SO_3 content of the blended samples must differ by at least 2.0 % SO_3 content.

NOTE 6—The same mixture design and materials shall be used when comparing different SO_3 contents. Use one or more of the following test methods to evaluate the performance:

6.1.1.1 When adding calcium sulfate it is considered as part of the mass of cement for proportioning.

6.1.1.2 Use the following equation to calculate the total SO_3 in the blended sample of cement and calcium sulfate:

$$SO_{3\text{-}Total} = \frac{M_{calcium\ sulfate}}{M_{calcium\ sulfate} + M_{cemennt}} \times SO_{3\text{-}calcium\ sulfate}$$

$$+ \frac{M_{cement}}{M_{calcium\ sulfate} + M_{cement}} \times SO_{3\text{-}cement} \qquad (3)$$

where:

$M_{calcium\ sulfate}$ = the mass of the calcium sulfate,
M_{cement} = the mass of the cement,
$SO_{3\text{-}cement\ sulfate}$ = the percent by mass of SO_3 in the calcium sulfate, and
$SO_{3\text{-}cement}$ = the percent by mass of the SO_3 in the cement.

Note 7—More sulfate levels may be tested to help improve the precision of the interpretation of the results. Extremely high and low sulfate levels can give results that deviate from the typical peak behavior which may need to be treated as outliers when using a mathematical fitting procedure.

6.2 The same mixture design and materials shall be used when comparing different SO_3 contents. Use one or more of the following test methods to evaluate the performance:

6.2.1 *Mortar compressive strength*—Determine mortar compressive strength at each sulfate level at the age of 24 ± ¼ h, 3 days ± 1 h, or 7 days ± 3 h in accordance with Test Method C109/C109M except as follows:

6.2.1.1 When mixing in accordance with the "Procedure for Mixing Mortars" section of Practice C305, add the calcium sulfate to the water, unless the calcium sulfate addition has been previously ground and mixed with the cement; then start the mixer and mix at slow speed (140 ± 5 rpm) for 15 s; then stop the mixer and add the cement to the water; then start the mixer and mix at slow speed (140 ± 5 rpm) for 30 s.

6.2.1.2 Use the amount of mixing water to produce a flow of 110 ± 5 for one of the mixtures using 25 drops of the table as determined in the section on Procedures in Test Method C1437. Use that same amount of water (constant w/cm) for each mixture with different sulfate levels.

Note 8—The mixture with the median sulfate level or lowest sulfate level is often used to determine the water content.

6.2.2 *Heat of hydration*—Determine heat of hydration at each sulfate level at the desired ages in accordance with Test Method C1702 except as follows:

6.2.2.1 If making calcium sulfate powder additions to an industrially produced cement sample, add the cement and calcium sulfate powder directly into the calorimetry sample vial and dry mix the solids inside the calorimetry sample vial to ensure that the calcium sulfate is blended with the cement prior to water addition. If using industrially-produced cement samples with the calcium sulfate additions already interground, follow the procedure for Test Method C1702 Method A or B except as follows. Alternatively, produce a mortar as described 6.2.1.

6.2.2.2 Additions of other materials typically used in concrete, such as supplementary cementitious materials and chemical admixtures, can be used, provided that the content of supplementary cementitious materials, chemical admixtures, or both are kept the same for each different mixture.

6.2.2.3 When testing with mortars use the same sand content for each different mixture.

6.2.2.4 Testing at temperatures besides 23°C is allowed. Use the same temperature for each different mixture.

Note 9—Experience shows that mixing cement paste externally and transferring a subset of paste or mortar to the sample vial generates higher variability because of increased variability of the masses of cement and calcium sulfate transferred from the external mixing vial to the sample vial. If using cement paste with additions of calcium sulfate powder not already interground in the cement, it is recommended to weigh and mix all materials inside the sample vial without removing any material from the sample vial after mixing.

Note 10—Blending of two industrially produced cement samples as described in 5.2, produced within the same day with a low and a high SO_3 content to obtain a series of sub samples with varying SO_3 contents, is known to give good results, provided that the clinker fineness and the clinker reactivity are similar. Alternatively, the addition of calcium sulfate powder to a single industrial cement sample allows for testing the effect of different sulfate forms and may yield a less variable approximate optimum sulfate level as the sulfate level is the only parameter that varies in the test.

6.2.2.5 Any thermal power measured prior to the minimum at point (B) observed prior to the onset of the main hydration peak (C), Fig. 1, shall be excluded from the calculated heat of hydration.

Note 11—Experience shows that optimum SO_3 estimated at a given age using isothermal conduction calorimetry with cement paste is similar to the optimum SO_3 estimated using compressive strength of mortar in Standard Guide C1679. The early heat measurements before the minimum B, Fig. 1, are typically subject to high levels of variability and influenced by relatively small differences in calorimeter and material temperatures, and are therefore excluded.

6.2.2.6 *Composition of Test Mixture*—Adjust the mass of solids and water as needed to obtain a suitable mix size, with the optional addition of sand and other materials typically used in concrete. Ensure that the total masses of cement and cement plus calcium sulfate differ by no more than 5 % within a given test series. Weigh or determine volumetrically a fixed and sufficient amount of water to completely wet and easily mix each individual mixture.

6.2.2.7 Use the same mixing method for all samples to be compared.

Note 12—Several paste mixing methods are known to give suitable results, including: Internal mixing using a disposable impeller left inside the sample vial after mixing; external mixing using a disposable spoon left inside the sample vial after mixing; external mixing using vibration or ultrasound contacting the outside of the sample vial, external mechanical mixing of paste or mortar which is then added to the sample vial. However, better reproducibility can be achieved when the mixing is done within the calorimeter sample vial, as error due to different sampling from a separate mixing bowl to sample vial is avoided, and mixing temperature conditions are easier to control within the sample vial.

6.2.2.8 *Test Duration*—Continue collecting calorimetry data for the period over which sulfate optimization is desired to be achieved.

Note 13—Generally optimum SO_3 levels are found to be higher when the degree of cement hydration is higher. Accordingly it is useful to perform this test for several days so that the change in optimum with a cement from a particular clinker source and sulfate source and form can be better understood.

6.2.2.9 Calculate the heat of hydration normalized per gram of cement (any calcium sulfate addition is considered as part of the cement) as described in the section on Calculation in Test Method C1702 with the following exceptions:
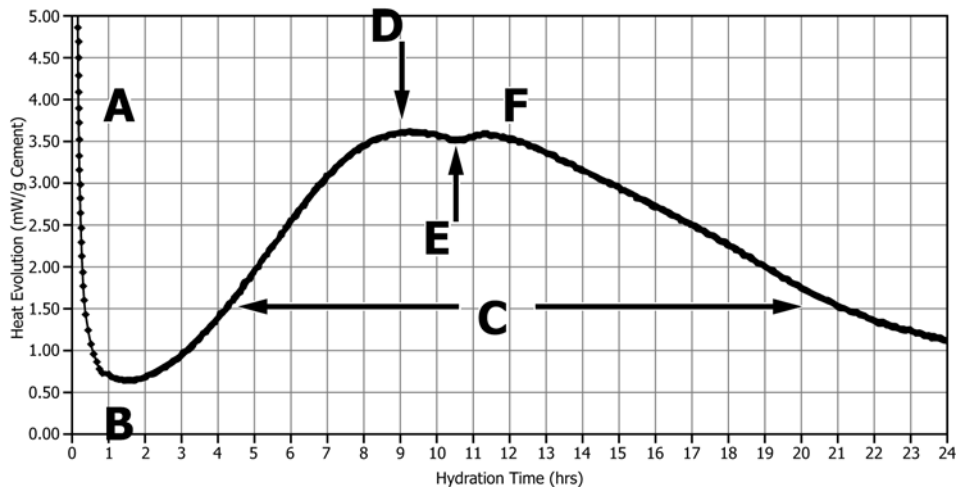
FIG. 1 (A) initial thermal power by dissolution of cement and initial cement hydration; (B) dormant period associated with very low thermal power indicating slow and well-controlled hydration; (C) main hydration peak associated mainly with hydration reactions contributing to setting and early strength development, with maximum at (D); and (E) sulfate depletion point, followed by (F) accelerated calcium aluminate activity. In this example the approximate time of onset of the main hydration peak is 1 h 45 min.

(1) Plot the thermal power per gram of cement as a function of time. Determine the time at which the minimum B, Fig. 1, occurs for each sample

(2) Remove all such data points before the minimum B, Fig. 1, at the time of onset of the main hydration peak before calculating the heat of hydration normalized per gram cement.

NOTE 14—It is important to use the same time for the minimum for all the samples to be compared, rather than adjusting the time for slight variations between samples. If the range of times of observed minima for the samples tested exceed 20 min, reliability of the test is suspect.

6.2.2.10 Report the mixture proportions used, including type and amount of calcium sulfate used, mixing regime employed, and the test temperature in the calorimeter.

6.2.3 *Concrete Strength*—Prepare all material according to Practice C192/C192M except as follows:

6.2.3.1 Add the calcium sulfate to the water, unless the calcium sulfate addition has been previously ground and mixed with the cement.

6.2.3.2 When applicable, determine compressive strength according to Test Method C39/C39M. When applicable, determine flexural strength according to Test Method C78/C78M.

6.2.3.3 Testing at concrete and curing temperatures other than specified is allowed. Use the same material temperature (all mixtures within 10°C range) and the same curing temperature (all curing temperatures within 4°C range) for each of the different mixtures

6.2.4 *Drying Shrinkage of Mortar*—Prepare all material according to Practice C596 except as follows:

6.2.4.1 When mixing in accordance with the section on Procedure for Mixing Mortars of Practice C305, add the calcium sulfate to the water, unless the calcium sulfate addition has been previously ground and mixed with the cement; then start the mixer and mix at slow speed (140 ± 5 rpm) for 15 s; then stop the mixer and add the cement to the water; then start the mixer and mix at slow speed (140 ± 5 rpm) for 30 s.

6.2.4.2 Instead of using the amount of mixing water sufficient to produce a flow of 110 ± 5, use the amount of mixing water to produce a flow of 110 ± 5 for one of the mixtures using 25 drops of the table as determined in the section on Procedures in Test Method C1437. Use that same amount of water (constant w/cm) for each mixture with different sulfate levels.

NOTE 15—The mixture with the median sulfate level or lowest sulfate level is often used to determine the water content.

7. Interpretation of Results

7.1 Approximate the SO_3 content which gives the maximum performance by one of the following methods:

NOTE 16—See the appendix for an example of how this interpretation is done for each method described below. Depending on which method is chosen the results may differ.

7.1.1 *Visual Fit*—Plot the performance level versus SO_3 content and interpolate the sulfate level at the peak.

7.1.2 *Least Squares Parabolic Fit.*

7.1.2.1 Determine the equation of a least squares fit according to follow equation:

$$\text{Performance Level} = a(SO_3)^2 + b\,SO_3 + c$$

where a, b, and c are fitting coefficients.

NOTE 17—Spreadsheet and graphing programs have the capability to calculate the least squares parabolic fit.

7.1.2.2 Approximate the optimum SO_3 by calculating vertex of the parabolic least squares fit from the following equation:

$$\text{Optimum } SO_3 \text{ approximation} = -b/(2\,a)$$

where a and b are coefficients of the parabolic least squares fit.

7.1.3 *Asymmetric Fit*—In cases where the performance level versus SO_3 is skewed to the right or left of the peak a fit using an asymmetric distribution function may provide a better fit than parabolic fit.