Measuring Cement Particle Size and Surface Area by Laser Diffraction

DETAILS

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AUTHORS

Ferraris, Chiara; and Garboczi, Edward

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MEASURING CEMENT PARTICLE SIZE AND SURFACE AREA BY LASER DIFFRACTION

This digest summarizes key findings of NCHRP Project 20-07/Task 301, "Measuring Cement Particle Size and Surface Area by Laser Diffraction," conducted by the AASHTO Materials Reference Laboratory, Frederick, Maryland, in association with the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, under the direction of the principal investigator, Dr. Haleh Azari. This digest is based on the project final report authored by Drs. Chiara Ferraris and Edward Garboczi of the NIST.

CONTENTS

INTRODUCTION

The objectives of NCHRP Project 20-07/Task 301, "Measuring Cement Particle Size and Surface Area by Laser Diffraction," were to evaluate the practicality and effectiveness of the laser diffraction method to measure the particle size distribution and total surface area of cement powder compared with current methods in use by the state DOTs and to prepare a test method to measure particle size distribution and total surface area of cement powder by laser diffraction in AASHTO standard format.

The Blaine fineness (standard test method ASTM C204, denoted herein as "Blaine") of a cement powder is a single parameter that is meant to characterize the specific surface area and, therefore, the fineness of a cement and is assumed to be linked to physical and mechanical properties such as strength, setting time, and rheology or flow properties. However, a single parameter cannot characterize the particle size distribution of a cement; as the cement industry continues to develop more sophisticated blended cements, a single parameter will increasingly fail to capture a cement's true complexity.

A universally recognized standard method for characterizing the complete particle size distribution (PSD) of cement particles does not currently exist (*1*). The only standard test, ASTM C115 (*2*) (also known as the Wagner test), is really designed to measure the "fineness" of a cement powder; it is limited to a minimum particle size of 7.5 μm. Portland cement, however, has a significant portion of particles smaller than 7.5 μm, and these have a large impact on properties such as setting time and rheological parameters. As there is no standard procedure covering the whole range of cement PSD, the implementation of different measurement methods varies widely within the industry. Several test methods are available to measure the PSD of a powder (*3*).

The laser diffraction measurement of cement PSD is currently used by most cement producers for quality control of their cements, in association with the measurement of Blaine fineness. Therefore, the laser diffraction technique was selected in this project for evaluation as a proposed test method for cement PSD characterization. The laser diffraction test is less time consuming than the Blaine test and can be automated for efficient measurement. The

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information from laser diffraction particle size distribution (PSD-LD, called LD in this report) measurement can also provide an estimate of powder surface area by assuming a specific geometry for the particles. Despite its extensive use by the cement industry, laser diffraction (LD) measurement of cement particle size distribution is not a standard cement test. This report examines the results of the LD and Blaine tests by measuring the particle size distribution (LD only) and estimated total surface area (both tests) of various cement powders and then correlates the results of both tests with key macroscopic properties—such as setting time and compressive strength—of cement paste or mortar made with those powders.

Both the Blaine and LD tests assume that the cement particles are spheres, which is obviously not true, and, thus, these methods only estimate the surface area. Therefore, two more fundamental tests were performed to aid in understanding the results of both tests. The surface area of the cement particles was measured using the nitrogen Brunauer–Emmett–Teller (BET) test, and the true 3-D shape of the particles was determined from X-ray computed tomography (X-CT). These more sophisticated tests were used as "ground truth" to evaluate the LD-PSD and Blaine fineness measurements. Cement and Concrete Reference Laboratory cements were used in the project, taking advantage of the database of properties measured in the CCRL Proficiency Sample Program (www.ccrl.us). Proposals for standardizing and applying the LD test are provided in this report.

MATERIALS

The Cement and Concrete Reference Laboratory (CCRL) is sponsored by ASTM and administers the semi-annual Proficiency Sample Program (*4*). As part of the program, participant laboratories receive two samples of cement upon which they conduct standard tests and report the results back to CCRL for statistical analysis. With all the data collected, CCRL prepares a report that contains average values and standard deviations.

For this study, 32 cements from the CCRL database were selected, and the following properties were chosen to provide a statistical picture of the cements:

- Fineness by 45-µm sieve—ASTM C430;
- Fineness by air-permeability apparatus or Blaine—ASTM C204;
- Compressive strength of mortar cubes at 3 d, 7 d, and 28 d; and
- Initial and final setting time as measured by Vicat needle (ASTM C191).

These same properties were also collected for three cements (labeled in this report as non-CCRL) that were produced from one clinker, but ground to different fineness, by increasing the grinding time and not changing the cement chemistry. These cements were used in a previous study to determine relationships between fineness and macroscopic properties (*5*).

The other non-CCRL cements were two NIST Standard Reference Materials® (SRM)—that is, materials with well characterized chemical composition, physical properties, or both—used for fineness: SRM 114q and SRM 46h. SRM 46h was issued because SRM 114q was too fine to be useful when calibrating the 45-µm sieve to conduct the sieve residue test—too much material passed the 45-µm sieve, so not enough was left to analyze and give good statistics. The only certified value for SRM 46h is the 45-µm sieve residue; other values measured at NIST are provided for information only.

METHODOLOGY

Fineness Measurements

Overview

Cement is a reactive powder; thus, one of its most important characteristics is its PSD, which, in turn, determines its total surface area. Since the Blaine measurement is related to a specific surface area (area per mass of cement) and is referred to as a fineness measure, total specific surface area is often referred to as a fineness measure. The smaller the size of the particles, the larger their specific surface area. There are many methods used to measure or estimate the surface area of a powder, but the most widely used method in the cement industry is the Blaine measurement (ASTM C204) (*6*). The LD-PSD is not a standard test but it is widely used in the cement industry for quality control. Both the Blaine and LD-PSD tests assume that the cement particles are spherical. By comparison, methods such as nitrogen BET and X-CT allow for the measurement of the specific surface area at the scale of gas molecules (BET) and provide an assessment of the true shape of the particles (X-CT) at the micrometer length scale.

Fineness Standard Tests

Three standard tests are used to estimate fineness in the cement industry: Blaine in ASTM C 204 measures

specific surface area; Wagner in ASTM C115 reports an empirical measure of fineness; and sieve residue (45-µm sieve) in ASTM C430 (*7*) measures the mass fraction of particles retained on the 45-µm sieve. The Wagner test is also called the turbidimeter fineness test because it measures the turbidity of a cement suspension in kerosene (*8*). The Wagner test is seldom used today and is not discussed further in this report.

Blaine ASTM C204. The Blaine measurement described in ASTM C204 was adopted by ASTM in 1946. R.L. Blaine published the test in 1943 (*9*). The principle of operation is that the permeability of a bed of fine particles is proportional to the fineness of the particles. Therefore, the test is a measurement of the flow rate of air through a bed of cement particles with vacuum on one side and atmospheric pressure on the other. The relationship between the air permeability of a powder and its surface area comes directly from the Kozeny–Carman approximate theory (*10*), which assumes a packing of mono-sized spherical particles. From the beginning, it was stated that this is a relative test as it depends on the shape of the particles and the compaction level or porosity of the bed. For this reason, ASTM C204 Section 4.1 states that the calibration of the instrument must be done by using a Standard Reference Material, such as SRM 114 (*11, 12*).

In brief, the test is performed by packing the powder in a cell of known volume and placing it on top of a U-tube manometer that contains a non-hygroscopic liquid of low viscosity and density—for example, dibutyl phthalate or a light grade of mineral oil. The cell is placed on the U-tube in such a way that a tight vacuum seal is created under the cement cell so that the liquid in the manometer is higher toward the cell. Then, the air is allowed to flow back only through the cement sample. The time for the liquid in the manometer to descend a set distance is measured. This time is used to calculate the fineness quantified by the surface area S of the cement, as measured by the Blaine and interpreted by Kozeny–Carman theory, defined using the following formula:

$$S = \frac{S_s\sqrt{T}}{\sqrt{T_s}}$$

where

S_s is the surface area of the reference material (i.e., SRM 114);

T_s is the time of flow using the reference material (i.e., SRM 114);

T is the time of flow of the material under test; and

S is the surface area of the material under test.

Therefore, the surface area of the material tested can be calculated from that of the reference material.

Sieve Residue ASTM C430. The sieve residue test (45-µm) is used to measure the residue or retained amount of cement on a calibrated sieve as an estimate of what fraction of the particles are greater than a certain size. A sieve with a 45-µm opening (No. 325[1]) was selected. Since a direct certification of sieve openings is impractical and expensive for production-scale work, sieves are calibrated by using a standard reference material such as SRM 114. A sieve correction factor is calculated by measuring SRM 114 or SRM 46h on the selected sieve and correcting the result for the cement with the certified value for SRM 114 or SRM 46h. The reason for the development of SRM 46h is that the SRM 114q was selected as a typical cement, but it proved too fine to allow the calculation of the correction factor. The mass fraction of the sieve residue of SRM 114 is only 0.79% ± 0.19%, while that of the SRM 46h residue is 7.43% ± 0.79%. The higher percentage of residue with SRM 46h allows operators that might have a sieve that is slightly larger than the 45µm to still have enough powder retained on their sieve to calculate the correction factor as described in ASTM C430.

Particle Size Distribution

Laser diffraction (LD) is the method most commonly used by the cement industry to quantify the PSD of a powder. The method is simple to perform and can be automated. Thus, this method was critically examined in this project to determine whether it should be proposed for adoption as a standard AASHTO test method.

The LD method involves the detection and analysis of the angular distribution of scattered light produced by a laser passing through a dilute dispersion of particles (*13*). The total scattering or diffracted light pattern is mathematically inverted, using Fraunhofer or Mie scattering theory, to yield the particle size distribution of spheres that would give the equivalent scattering pattern. The surface area is calculated from the diameter distribution of the spherical particles. In general, the LD method requires that the

[1]Sieve number follows the USA definition given in ASTM E11.

particles be dispersed either in liquid (suspension) or in air (aerosol). The former is commonly referred to as the "wet" method (LD-W), while the latter is termed the "dry" method (LD-D). For cement, there is no difference between the results from the two methods if there has been no initiation of hydration due to previous exposure to moist air. The cements used in this project had been stored in the laboratory for some time and transported in simple plastic bags, so only data from the LD-W method were used to ensure complete dispersion of the particles.

A key parameter that needs to be known to use the LD method is the complex refractive index, $m = n - ik$, where $i = \sqrt{-1}$. From the study done by Hackley et al. (*13*), the values of n and k for Portland cement may be set to 1.7 and 1.0, respectively. These values represent an average over the typical mineral composition of Portland cement. A sensitivity analysis of the influence of n and k on the PSD done by Hackley et al. (*13*) found that for Portland cement, the values selected for the SRM are representative. If the cement contains other products (such as limestone or other supplementary cementitious materials), reassessment of the parameters would be necessary. To the authors' knowledge, such a study has not yet been conducted.

The LD method is not only widely used in the cement industry (*14*) but is used for many different kinds of particles across many different industries (*15*). While SRM 114 or SRM 46h are used as calibration tools in the standard fineness methods, they are only used in the LD method for quality control to ensure that the LD equipment is operating properly.

BET Surface Area

In the BET technique, an adsorption isotherm is measured by plotting the volume of gas adsorbed versus the pressure, *P,* of the gas—in this case, nitrogen (*16*). Usually, the pressure is represented as P/P_0, where P_0 is the saturation pressure of the absorptive gas. The total surface area of a powder can be calculated using the Langmuir theory and the BET generalization. This technique is considered to provide the most fundamental bulk measurement of surface area since it can access surface features down to the size of the nitrogen molecules. Generally, surface area is a length-scale dependent quantity, with the surface area increasing as finer and finer surface length scales are included in the measurement (*17*).

The calculation of surface area is based on an extension of the Langmuir theory to a multimolecular layer adsorption. The main equation is as follows (*18*):

$$V_a = \frac{V_m C P}{\left(P_0 - P\right)\left[1 + \left(C - 1\right)\frac{P}{P_0}\right]}$$

where

V_a is the quantity of gas adsorbed at pressure P (measured value),
V_m is the quantity of gas adsorbed for the entire surface to be covered,
C is a constant,
P_0 the saturation pressure of the gas, and
P is the gas pressure of the measurement.

This equation can be rearranged to

$$\frac{P}{V_a\left(P_0 - P\right)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C}\left(\frac{P}{P_0}\right)$$

The plot of $Y = a + b\,(P/P_0)$ should be linear, where

$$Y = \frac{P}{V_a\left(P_0 - P\right)}$$

$$a = \frac{1}{V_m C}$$

$$b = \frac{C - 1}{V_m C}$$

Thus, the values of V_m and C can be obtained from the linear plot. From the value V_m, it is possible to calculate the surface area if the area occupied by a single adsorbate molecule is known. In this present project, the gas was nitrogen and the area for a single molecule was assumed to be 0.162 nm^2 (*18*). Most solids measured with this technique show a straight line in the range of P/P_0 values between 0.05 to 0.3. In this research, the linearity of the isotherm was checked before accepting the surface area calculation that is provided by the BET instrument.

X-Ray Computed Tomography (X-CT)

X-CT was used to provide particle shape information since cement particles are not spheres. The apparent spherical diameter depends on the shape of the particle, so knowing the shape statistics of the various cement powders enables a more informed comparison between different surface area measurements. The X-CT also measures the surface area at the voxel[2] length scale at which the shape has been

[2] A volumetric pixel.

captured. A sub-set of the CCRL cements considered for LD-PSD and Blaine were chosen for X-CT study. After X-CT scanning, particle shape and other geometric factors were computed (*19, 20*).

Standard Reference Materials

All the standard tests previously discussed require the use of an SRM. NIST provides every SRM with a certificate of analysis, which gives the official characterization of the material's properties. SRM 114 is a reference material for the fineness of cement, as measured by various standard methods, and has been available since 1934. Different lots of SRM 114 are designated by a unique letter suffix appended to the SRM number. The current lot is SRM 114q. A certificate that gives the values obtained using ASTM C204 (Blaine), C115 (Wagner), C430 (45-µm residue), and LD-PSD is included with each lot of the material. As previously described, SRM 46h was developed for exclusive use with ASTM C430 (45-µm residue) because SRM 114q has too small of a residue on a 45-µm sieve to be useful to industry.

The values attributed to SRM 114q were developed from round-robin testing by the CCRL proficiency laboratories for all the certified values except the ASTM C430 (45-µm residue), which was measured only at NIST. The sieve residue values for SRM 46h were also developed from measurements done only at NIST.

The round-robin testing for the Blaine measurement of SRM 114q also required the Blaine measurement for SRM 114p, which was used as a reference. This opens the possibility of error propagation from one Blaine certified value to the following lot of SRM 114, starting from the first use of SRM 114 for Blaine certification.

Macroproperties

Macroproperties of paste or mortar prepared with each of the studied cements were measured to characterize their behavior. The properties considered were mortar compressive strength (ASTM C109) at 3 d, 14 d, and 28 d, and the initial and final times by Vicat needle (ASTM C191). The compressive strength and the time were obtained from the reports prepared by CCRL (*4*).

RESULTS AND DISCUSSION

Fineness Measurements Comparison

Four methods were used to determine fineness: BET, Blaine, sieve residue, and LD-PSD. BET is the most fundamental measurement of specific surface area because it makes no assumption about the shape of the particles. Figure 1 shows the weak relationship between the BET surface area and the surface area obtained either by Blaine or by LD-PSD. The following observations can be made:

- The range of surface area measured with BET is the widest (686 m^2/kg to 2000 m^2/kg), emphasizing the differences among the cements; and
- The narrowest distribution is provided by the Blaine method (349 m^2/kg to 545 m^2/kg).

The difference between the Blaine and the BET results is interesting since similar gases (pure nitrogen

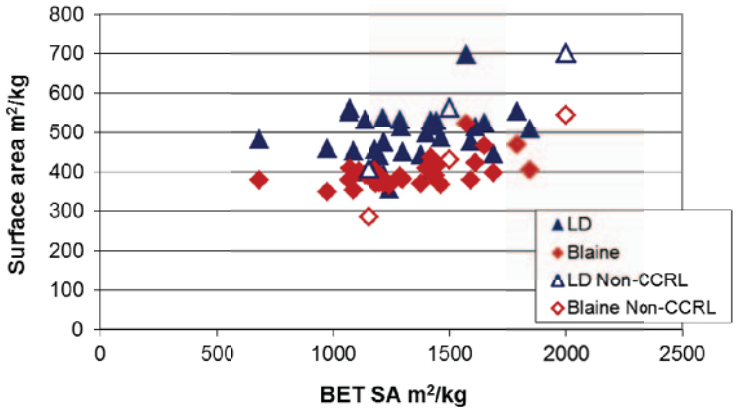

Figure 1 Blaine and LD-PSD surface area versus BET surface area. The standard deviation for the Blaine was ± 11m^2/kg, for the LD was 5%, and for BET was 10%.

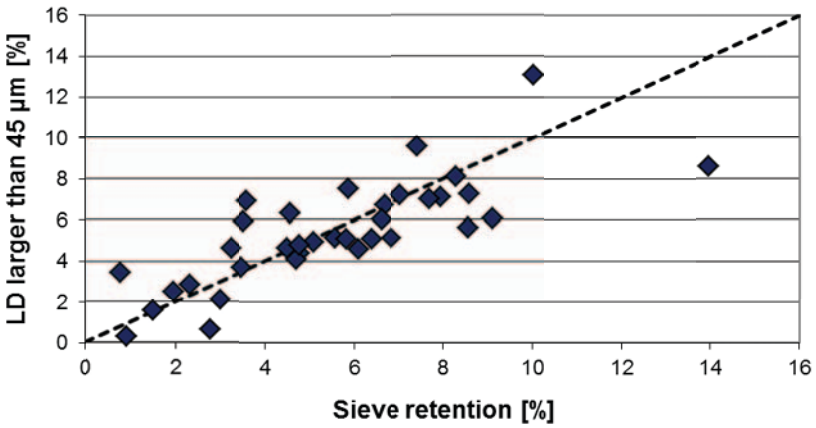

Figure 2 Relationship between the percentage of particles larger than 45 µm by LD and by the sieve method (ASTM C430). The dashed line is the line of equality (slope = 1). The standard deviation for the LD was 5% and for sieve retention was 10%.

in the BET test and air, which is 80% nitrogen, in the Blaine test) are being used to interrogate the surface area. Since it is known that the BET surface area is determined by the monolayer coverage of the surface by nitrogen molecules, the implication is that not all parts of the surface are interrogated in the Blaine test. Since the air velocity goes to zero at the particle surface for non-turbulent air flow, there are perhaps many "dead zones" on the surface that the flowing air in the Blaine test does not see. This suggests that the Blaine test is not an accurate measure of the particle surface area since these small regions, while not important for air flow, are likely important for reaction during cement hydration. So while BET showed clear differences between cement surface areas for these materials, the Blaine results were less sensitive. Therefore, there is no clear relationship between the surface area by the Blaine and BET methods.

A clearer trend is observed with the three non-CCRL cements that had the same composition and were ground from the same clinker by the same ball mill for research purposes. Since they were intentionally ground to have different Blaine values, they show a clearer trend between BET and the Blaine and LD results. On the other hand, the CCRL cements do not have the same composition and were prepared by different manufacturers over several years.

The last technique is the 45-µm sieve test. As this method only measures the percentage of material retained on a sieve and not a specific surface area, there is no correlation with the various surface area results. But from the LD distribution curve of PSD, the percentage of particles larger than 45 µm could be calculated. As shown in Figure 2, there is some scatter, but the data points are closely grouped around the line of equality (slope = 1), indicating that the LD results could perhaps substitute for the 45-µm sieve results.

So far, the results established that both the Blaine and the LD provide a surface area value that is weakly correlated with that measured with the BET, the most fundamental method. In an ideal world, the BET should be considered for routine measurement of the surface area as it provides the fundamental surface area without assumption of particle shape, but it is an expensive device that requires at least half a day to measure one cement. So the Blaine and the LD tests are more practical surface area measurement methods for cement industry production.

Figure 3 shows the correlation between the Blaine and the surface area measured by LD. There is

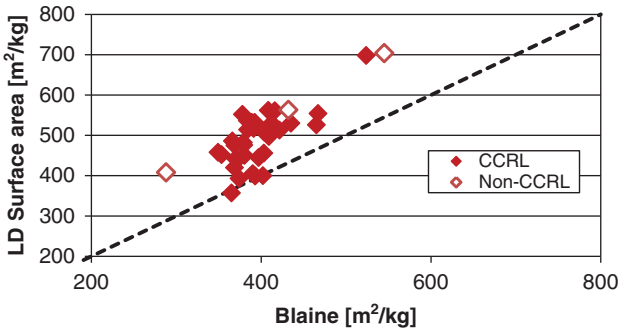

Figure 3 Relationship between Blaine and LD surface area. The dashed line is the line of equality (slope = 1). The uncertainty is contained in the symbol.

significant scatter of the data for the CCRL cements, but in all cases the value of the surface area by LD is larger than the Blaine result. For the non-CCRL cements, a linear relationship between LD and Blaine was observed, with a value of $R^2 = 0.98$. The CCRL cements were not included in the correlation because their data were too narrowly dispersed—that is, the cements had similar values of Blaine or LD specific surface areas.

In summary, BET is the most reliable method for specific surface area measurement, but the time required to make a measurement is impractically long for the cement industry. Although neither LD nor Blaine provides fundamental measurement of cement surface area, LD also provides an efficient measurement of particle size distribution and is correctly correlated with the 45-µm sieve residue, neither advantage being shared by the Blaine measurement. The LD measurement takes less than 30 minutes and can be automated. It also does not require calibration using a reference material such as SRM 114q. In the SRM 114q certificate, the SRM is used for an LD measurement only to verify that the device is operating as expected.

Fineness and Particle Shape

X-CT is used to determine particle shape since cement particles are not really spheres. More detailed description of particle shape distribution for each kind of cement aids in the comparison of different surface area measures. Different particles, having equal volume but different shapes, will give a different apparent spherical diameter and different apparent specific surface area in LD measurements (*20, 21*). The shape statistics can be determined for the various cements used, and their impact, if any, on the measured particle size distribution or apparent specific surface area assessed. X-CT measurements also give a measure of surface area for each particle measured.

A sub-set of the CCRL cements considered for LD-PSD and Blaine were examined with X-CT, along with the three cements listed in Table 1. Samples were made of cement particles dispersed in low viscosity-epoxy and contained in 3-mm-diameter plastic tubes (*21*). After X-CT scanning, computer programs were used to analyze the particles found in terms of shape and other geometric factors (*11*). Between 20,000 and 45,000 particles were extracted computationally from the samples for each cement type. For the cement with the highest particle number, a total particle volume of about 1.2 mm^3 was examined. Using a spherical harmonic function expansion for each particle (*11*), different particle geometry parameters were computed, including their volume equivalent spherical diameter (VESD)—which is the diameter of the (imaginary) sphere with the same volume as a given particle—and L, W, and T—the length, width, and thickness of a particle as defined in ASTM D4791 (*22*). If the particles were truly spherical, then VESD = L = W = T. Using VESD as a rough measure of particle "size," the cement particles processed fell in a VESD range of about 10 µm to 100 µm. The X-CT apparatus available at NIST could not image particles smaller than about 10 µm, so a complete PSD and specific surface area could not be computed to directly compare with the other techniques.

Figure 4 is an image of a typical particle from the cement in the second line of Table 1, taken directly from the X-CT measurement and spherical harmonic expansion. In this case, the non-sphericity is quite marked.

The following ratios of the particle geometry parameters serve as shape parameters (aspect ratios): L/W, W/T, and L/VESD. Again, for spheres these ratios are unity. Figure 5 shows how the values of L/W are distributed for CCRL Cement 163, in terms of the volume fraction of the particles having a certain

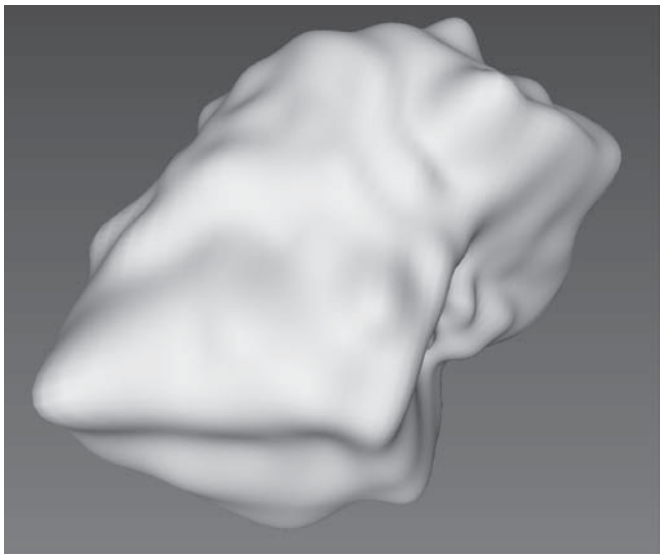

Figure 4 A typical particle from the cement in the second line of Table 1, as imaged by X-ray CT and reconstructed using spherical harmonics. At a VESD value of 81 µm, this is one of the largest particles in this cement type.

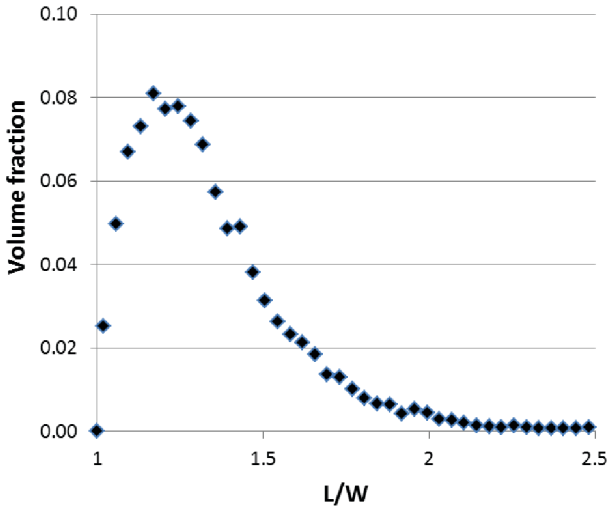

Figure 5 The distribution of the L/W aspect ratio for CCRL Cement 163, in terms of volume fraction (the same as mass fraction in this case), as computed from X-CT measurements and spherical harmonic expansions.

value of L/W. We see that there is a range of values for L/W for the CCRL 163 particles, with almost all of the particles having a value of L/W of less than 2.5 and most of them having a value around the peak value at about L/W = 1.25. To create Figure 5, the symbols correspond to each bin in L/W used. The ordinate in Figure 5 is exact. The uncertainty in determining the value of L, W, and T for each particle is estimated to be about 2%, based on past comparisons to direct measurements on larger particles (23), so that the uncertainty in the aspect ratios are about 3%.

The values of these parameters, averaged over all the particles of a given cement, serve as a simple way to compare the shape of the cement particles against each other and against the spherical assumption. For the cements considered—CCRL 115, 116, 133, 135, 146, 140, 141, 152, 161, 162, 163, and the three cements in Table 1—the average value of L/W ranged from 1.32 to 1.43 among the 14 cements, with a standard deviation for each cement, reflecting the distribution functions like that shown in Figure 5, of about 0.27. The shape parameter W/T ranged from 1.32 to 1.49, with a standard deviation for each cement of about 0.32. For the L/VESD parameter, the range was 1.45 to 1.61, with a standard deviation for each cement of about 0.20. The standard deviations in this case are only calculated for the purpose of giving an idea of the width of the distributions, and their near equality for each aspect ratio among cements implies that their aspect ratio distributions are similar to the CCRL 163 distribution shown in Figure 4. Based on these values, these cement particles are not approximately spherical, an observation that must be keep that in mind when interpreting the Blaine and LD measurements for specific surface area and particle size since both measurements assume spherical particles. However, the similarity in shape among the different cements implies, encouragingly, that particle shape has a negligible effect on the difference in surface area or PSD among different cements.

The ratio of the surface area of each particle, as measured by X-CT, to the surface area of the volume-equivalent sphere can also be computed. This ratio, averaged over all particles, is about 1.2 for each cement. This suggests that the LD results should be increased by a factor of about 20% to get a better estimate of the surface area. Also, it seems, at least as judged by these three shape parameters and surface area ratios, that all these cements have particles of similar shapes. However, if the detailed mineralogy of the individual cement types was known (actual clinker minerals, not just oxide abundances as given in the CCRL reports and mill sheets), some correlation of shape and mineralogy probably could be made (*12*).

Fineness and Macroscopic Properties

The values of compressive strength measured at 3 d, 7 d, and 28 d were collected from the CCRL database. Unfortunately, due to the type of cement

Table 1 Properties of non-CCRL cements.

Surface area			LD data				Setting time		Strength
LD m^2/kg	Blaine m^2/kg	BET m^2/kg	% by vol. > 45 μm	d_{10}, μm	d_{50}, μm	d_{90}, μm	Initial min	Final min	28D MPa (psi)
408	288	1152.2	12.89	1.85	17.8	49.9	226	298	52.6 (7936)
563	432	1497.9	2.83	1.25	11.2	39.9	130	191	66.2 (9604)
704	545	1998.3	0.00	0.98	6.8	17.4	115	160	86.8 (12593)

used, the values were all very similar and the range of values was not much larger than the calculated measurement uncertainty:

- 3 d—25.2 MPa ± 3.6 MPa (3660 psi ± 528 psi). The average uncertainty as determined by CCRL is 1.7 MPa (252 psi).
- 7 d—32.2 MPa ± 3.1 MPa (4677 psi ± 444 psi). The average uncertainty as determined by CCRL is 2.1 MPa (309 psi).
- 28 d—41.4 MPa ± 3.9 MPa (6007 psi ± 529 psi). The average uncertainty as determined by CCRL is 2.7 MPa (396 psi).

Therefore, it is difficult to establish correlations between surface area, LD-PSD, and compressive strength using the CCRL cements. However, when the properties of three of the non-CCRL cements (no strength data is available for the SRMs) were examined, clear correlations between strength at 28 days, the initial and final Vicat setting times, and fineness were clearly seen, as has been noted previously (*5*).

Comparison between the LD and BET surface areas of non-CCRL cements in Table 1 shows that the BET surface areas are almost 3 times larger. This suggests that the <1 nm nitrogen molecules can reach places on the particle surface that the laser light, of wavelength 450 nm, cannot penetrate. Or, stated in another way, the LD is not able to measure particle size smaller than 0.4 µm, thus the potentially large surface of such sized particles is not taken into account in the LD surface area. This could indeed be the case for any fine surface texture.

Proposed Fineness Standard

The foregoing discussion supports the conclusion that the most comprehensive, yet practical, test providing both surface area and sieve residue is the LD measurement of the cement PSD. Currently, there is no standard for measuring PSD by LD in the United States although a general ISO standard exists that is not specific to cements. Thus, a standard test method is proposed in Appendix A for consideration by AASHTO. The method could be used to measure particles from 0.4 µm to 2000 µm, largely covering the range of a typical cement PSD. It is also clear that the specifications now used to qualify cement fineness, such as ASTM C150, will need to be revised—for example, by the addition of clarifying text stating what the surface area range should be for each cement type.

A summary of the proposed LD test method in Appendix A is as follows. For an LD-W determination, a sample of cement powder is dispersed in isopropyl alcohol (IPA) and recirculated through the path of the laser beam. In a LD-D determination, a dried sample of cement powder can be pushed under air pressure or pulled under vacuum so that it flows through the beam. The particles pass through the beam and scatter light. Photodetector arrays collect the scattered light, which is then converted to electrical signals and analyzed by a computer. The signals are converted to a PSD using an optical model based on Fraunhofer diffraction or Mie scattering. Scattering information is analyzed assuming spherical particles. Calculated particle sizes are therefore presented as equivalent spherical diameters.

Typically the specimen is manually introduced in the LD device (less than 1 g for the LD-W and about 5 g to 10 g for the LD-D). The rest of the process is automated and depends on the manufacturer's specific device design. SRM 114q may be used to establish the best standard operating procedure as the results obtained should match the curve provided by the SRM certificate. Other details of the method are in the proposed standard (see Appendix A).

The following key parameters should be reported:

- The 10%, 50%, and 90% diameters (d_{10}, d_{50}, and d_{90} respectively), which are the volume fraction with measured diameters less than these values. These values can be used to calculate the span $(d_{90} - d_{10})/d_{50}$, which is a measure of the width of the PSD.
- The cumulative (volume% versus diameter) PSD.
- The calculated specific surface area in m^2/kg based on a user-provided specific gravity for the cement powder. This functionality is built into most LD devices.

The inter-laboratory study performed to certify SRM 114q provides the precision statement for both within-laboratory precision and multi-laboratory precision (*12*). The LD uncertainty was determined to establish the values for the SRM 114q. It was found (see SRM 114q certificate) that the simultaneous 95% expanded uncertainties for the difference between a typical laboratory and the certified value of SRM 114q in percent varies depending on the particle size between 1.2% to 7.6% for a single laboratory. It is higher between laboratories—up to 20%. For the Blaine according to the ASTM C204 test

method, the within-laboratory uncertainty is 3.4% and the between-laboratory uncertainty is 6%. Thus, the LD between-laboratory uncertainty is higher than that for the Blaine test, but within-laboratory uncertainties are similar. It should be kept in mind that since no standard test is available for the LD, each laboratory might use a somewhat different LD methodology to measure the PSD. If a LD standard test method becomes available, the uncertainty between laboratories would be expected to decrease.

SUMMARY AND CONCLUSIONS

This project evaluated the practicality and effectiveness of the laser diffraction method to measure the PSD and total surface area of cement powder compared with current methods in use by the state DOTs. It was found that LD provides PSD, specific surface area, and a good approximation of the 45-µm sieve residue. More than 30 cements were analyzed to compare fineness measured by Blaine, LD, 45-µm sieve residue, and BET. The BET provides the most fundamental surface area measurement, is not based on the assumption that the particles are spherical, and is able to better sample the fine surface texture of the particles. The correlations between BET and the other test methods were poor. Although nitrogen BET is the most accurate test, it takes too long to perform for practical industry use. The LD-PSD test gives good correlation with the 45-µm sieve residue test and measures a wider range of values for the surface area than the Blaine, better distinguishing particle size differences between cements. X-CT results showed that particle shape was not a factor in these comparisons. Thus, this study proposes the AASHTO standardization of the LD-PSD method for cement powders. The development of the SRM 114q provides statistically valid information on the uncertainty of the Blaine versus the LD-PSD.

The particles in cement powders are not spherical, which must be kept in mind when interpreting the Blaine and LD measurements for specific surface area and particle size because both measurements assume spherical particles. The cements studied here seem to have similar shapes, as least as measured by the three shape parameters and the surface area parameter considered. This is perhaps not so surprising, considering the ball-mill grinding process that likely produced all these cements. This finding validated specific surface area comparisons between the cements in this study based solely on particle size differences, not particle shape differences. Any future comparisons should also include particle shape.

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APPENDIX A

Standard Method of Test for

Particle Size Analysis of Hydraulic Cement and Related Materials by Light Scattering

AASHTO Designation:
ASTM Designation: N/A

American Association of State Highway and Transportation Officials
444 North Capitol Street N.W., Suite 249
Washington, D.C. 20001

Standard Method of Test for

Particle Size Analysis of Hydraulic Cement and Related Materials by Light Scattering

AASHTO Designation:
ASTM Designation: N/A

Chapter 1 SCOPE

This test method covers the determination of the particle size distribution of hydraulic cement and related compounds by means of the laser diffraction technique, reported as volume percent of particulate materials[3]. This test method applies to analyses with both non-aqueous dispersions and in gaseous dispersion. This test method is applicable to the measurement of particulate materials in the size range of 0.4 µm to 2000 µm.

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

***This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use*.**

Chapter 2 REFERENCED DOCUMENTS

***AASHTO Standards*:**

- None

***ASTM Standard*:**

- B 822 Test Method for Particle Size Distribution of Metal Powders and Related Compounds by Light Scattering
- C 219 Terminology Relating to Hydraulic Cement
- C 115 Test Method for Fineness of Portland Cement by the Turbidimeter4
- C 430 Standard Test Method for Fineness of Hydraulic Cement by the 45-µm (No. 325) Sieve
- C 204 Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus

[3] This test method is a modification of Test Method B 822 so that it can be used for hydraulic cement.

ISO Standard:

N ISO 13320-1 (E), Particle Size Analysis — Laser Diffraction Methods — Part 1: General Principles.

ISO 14887:2000, Sample Preparation — Dispersing Procedures for Powders in Liquids

Non Standard document:

- Ferraris, C.F, Hackley V.A., Avilés A.I., Buchanan C.E., "Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase I" NISTIR 6883, Nat. Inst. of Stds. And Tech., May 2002. (http://ciks.cbt.nist.gov/~garbocz/nist6883/nistir6883.htm).

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Chapter 3 TERMINOLOGY

***Definitions*:**

3.1.1 **laser diffraction** ***—a method for determining the particle size distribution based on the detection and analysis of the angular distribution of scattered light, produced by a laser, passing through a dilute dispersion of particles.***

3.1.2 **background** ***— extraneous scattering of light by elements other than the particles to be measured; includes scattering by contamination in the measurement path.***

3.1.3 **Mie theory** ***— the electromagnetic theory that describes the scattering of light by spherical particles.***

3.1.4 **Fraunhofer diffraction** ***— the optical theory that describes the low-angle scattering of light by particles that are large compared with the wavelength of the incident light.***

3.1.5 **multiple scattering** — ***The rescattering of light by a particle in the path of light scattered by another particle. This typically occurs in dispersions with high particle concentrations.***

3.1.6 **wet method** — ***The particles are dispersed in isopropyl alcohol, then recirculated through the path of the light beam.***

3.1.7 **dry method** — ***The particles are dispersed in air, then passed through the path of the light beam.***

3.1.8 **d10, d50, and d90** –***particle size values corresponding to a cumulative distribution at 10%, 50%, and 90% respectively.***

3.1.9 **span** – ***The width of the differential particle size distribution, calculated using the following formula:***

$$span = \frac{(d_{90} - d_{10})}{d_{50}} \qquad (1)$$

Chapter 4 SUMMARY OF METHOD

The method consists in dispersing the cement particles in a medium (wet or dry) and passing through a laser beam. The wet method involves a sample of cement powder dispersed in isopropyl alcohol (IPA) and recirculated through the path of the light beam. A dry sample can be pushed under air pressure or pulled under vacuum so that it flows through the light beam. The particles will scatter the light. Photo-detector arrays collect the scattered light, which is then converted to electrical signals and analyzed by a computer. The signals are converted to a particle size distribution (PSD) using an optical model based on Fraunhofer diffraction or Mie scattering. Scattering information is analyzed assuming spherical particles. Calculated particle sizes are therefore presented as equivalent spherical diameters. Additional information pertaining to the general principles of PSD analysis by light scattering can be found in ISO Standard 13320 or in the publications by Ferraris et al (see section 13).

Chapter 5 SIGNIFICANCE AND USE

Accurate measurement of the PSD of cement powder is a beneficial tool for process monitoring in the cement industry. In addition, the PSD is a key factor in on-going computational efforts to simulate microstructure development and predict the performance of cement-based materials.

The only other relevant standard method is Test Method C 115, a sedimentation method. Designed primarily to determine fineness of cement in terms of surface area per unit mass, this sedimentation method also provides a non-mandatory procedure to determine the PSD down to a particle size of 7.5 µm. This lower limit is not acceptable for proper description of the PSD of hydraulic cement.

The Blaine procedure for fineness of cement, given in Test Method C 204, does not provide the PSD, but provides the specific surface area based on the air permeability of a compacted specimen of cement.

The fineness of cement is also measured using Test Method C 430. This method is limited to the measurement of the percentage of particles less than 45 µm, and therefore does not provide the full PSD.

The laser diffraction method is capable of measuring powders with a size distribution ranging from 0.4 µm to 2000 µm, covering the full size range in hydraulic cement. The interpretation of the measurements is related to the type of light scattering model used, either Fraunhofer or Mie. The limitation of this test method is that it is not a direct measurement of particle size. In order to calculate the PSD, some assumptions must be made: (1) the particles are spherical; (2) the refractive indices of the particles and of the medium are known (needed for the Mie model only). Also, to correctly measure the particles, the powder must be dispersed so that individual particles, and not agglomerates of particles, will scatter light independently.

5.1.1 ***Diffracted light is concentrated in the forward direction, forming the so-called Fraunhofer diffraction rings. The intensity and distribution of diffracted light around the central beam can be related to particle size, assuming a circular cross-section geometry for the diffracting entities. The range of validity for this test method is limited on the low end to particle diameters a few times greater than the wavelength of the incident light for particles that are opaque or have a large refractive index contrast with the medium. In Fraunhofer diffraction, the pattern does not depend on the refractive index, so in theory there is no difference between using a liquid or a gas as a dispersing medium.***

5.1.2 ***For non-spherical particles like cement, Mie theory provides a volume-weighted equivalent spherical diameter. An accurate representation of the "true" size distribution by Mie scattering depends on knowledge of the complex refractive index, and will be affected by the degree of particle non-sphericity and the***

dispersion procedure used to prepare the test specimen. For Mie scattering, the higher refractive index contrast in air, compared with most liquids, may somewhat affect the scattering pattern, but should not alter the PSD results significantly.

5.1.3 *It is important to recognize that the results obtained by this test method may disagree with the results obtained from other methods for particle size determination using different physical principles. The results are influenced strongly by the physical principles employed by each method of particle size analysis. The results of any indirect particle sizing method should not be regarded as absolute when comparing with results obtained by other methods.*

5.1.4 *A key aspect of the procedure is to ensure dispersion of the cement particles. To verify the adequacy of the procedure that is used, the PSD of a sample of SRM 114 is measured, and the resulting PSD is compared with the reference PSD. Lack of agreement means that the procedure for dispersing the cement sample needs to be modified or that the instrument is not functioning properly*

Chapter 6 INTERFERENCES

Air bubbles entrained in the circulating fluid will scatter light and be reported as particles. Circulating fluids may require degassing, and shall be bubble-free upon visual inspection. The presence of air bubbles can also be detected by the presence of two peaks in the particle size distribution, with the second peak being at about 1500 μm or higher.

In most devices using a fluid, there is the option of dispersing the particles by applying an ultrasound vibration to the suspension. This method is highly effective in dispersing the particles, but it could also increase the temperature of the medium. Therefore, after satisfactory dispersion is achieved, the suspension should be allowed to regain an equilibrium temperature. Typically a wait of about 10-15 min is enough.

Contaminants, such as particles or foreign substances dispersed in IPA, scatter light, and thus are reported as part of the PSD.

The presence of oil, water, or foreign substances in air will cause clogging or agglomeration in dry dispersal that will bias the particle size results. The air supplied shall be free of such substances.

Agglomeration or settling of particles during analysis will cause erroneous results. Dispersions shall be prepared in accordance with the instrument manufacturer's instructions, and a stable dispersion shall be maintained throughout the analysis. A sufficient flow rate for wet

dispersions shall be maintained during the analysis in order to prevent settling of large particles.

A low concentration of particles in the dispersion may result in poor data repeatability. A high concentration of particles in the dispersion may cause excessive light attenuation and multiple scattering, resulting in an erroneous PSD. Follow the instrument manufacturer's instructions in determining the correct light attenuation level.

Chapter 7 APPARATUS

Particle Size Analyzer **—based on Fraunhofer diffraction or Mie scattering, or a combination of both models. Use care to ensure that the analyzer system or its subsystems are appropriate for the size range of hydraulic cement or related compounds.**

Liquid or air sample handling system **— to transport the dispersed test specimen across the light beam.**

IPA **— isopropyl alcohol, reagent grade, to be used with the wet method.**

Fine Sand **— as recommended by the manufacturer to clean the instrument after a measurement using the dry method.**

SRM 114[4] **— current reference cement available from NIST. A letter indicating the lot numbers follows the number 114. This material is provided with a certificate including a reference PSD. This reference PSD is obtained by statistical analysis of test results from an ASTM sponsored round-robins, for SRM 114P and from NIST sponsored round-robins for subsequent reference materials.**

Chapter 8 SAMPLING

Obtain a representative specimen of hydraulic cement. The amount needed for the wet method is less than 1 g and for the dry method is about 3 g to 4 g. The exact amount depends on the loading method adopted.

Note 1– The operator needs to ensure that fines are not lost. It is suggested that samples should be homogenized in closed vessels, and settled layers should be gently recombined before extracting the final samples.

[4] SRM 114 can be obtained from NIST. To order go to the URL: www.nist.gov and select "Standard Reference Materials" under the heading "Products and Services."

For the wet method, disperse the specimen either in the device or external to the device. Follow the manufacturer's recommendations to determine the most appropriate method. For the dry method, load the specimen directly on the device feeder.

Chapter 9 CALIBRATION AND STANDARDIZATION

Verify proper operation of the instrument using Test Method E 1458 or the manufacturer's calibration procedure.

Hydraulic cement SRM 114 is intended to be used as a reference material. The use of SRM 114 will not permit direct calibration of the instrument, i.e., an instrument correction factor should not be calculated. The scope of the SRM 114 is to provide the means to the operator to develop an appropriate procedure for measuring PSD by optimizing the parameters of the instrument. To use SRM 114, conduct a test using a method as described in section 11. To use these uncertainties to assess agreement with other laboratories, the user should compute the absolute difference in cumulative volume fraction between his or her results and the certified values for SRM 114q for each particle size. These differences should then be compared to the appropriate expanded uncertainties in Columns 3 or 4 of Table 5 in Appendix A of the SRM 114q certificate to determine conformance. If the observed absolute difference between the user's results and the certified values for SRM 114q is always less than the corresponding expanded uncertainty, then the user can conclude that his or her results are in agreement with other laboratories with a confidence level of approximately 95%. If one or more of the observed absolute differences is larger than the corresponding expanded uncertainty, on the other hand, this is evidence that the user's results are not in agreement with the results of other laboratories and that changes to the measurement procedures are needed.

Note 2 –For more details on this methodology see Ferraris, C.F., Avilés, A.I., Guthrie, W., Peltz, M., Haupt, R., MacDonald B., Certification of SRM 114q; Phase II (Particle Size Distribution), NIST SP260-166 (2006).

Chapter 10 PROCEDURE

Install the desired sample delivery system and select the applicable instrument range, as indicated by the manufacturer's instructions.

Allow the instrument to warm up for at least 20 min.

If necessary, establish the correct optical alignment according to the requirements of the manufacturer.

Note 3 – It is advisable that optical alignment be checked upon startup, whenever the sample delivery system is changed and frequently.

Measure the background in the mode in which the analysis will be conducted. Ensure that the carrier (air or IPA) is flowing through the light path while measuring background. Background values shall not exceed the specifications of the manufacturer. If the background values exceed the manufacturer's specifications, perform the necessary procedures as specified by the manufacturer to bring the background values within acceptable limits.

Extract a test portion from the cement sample. Refer to the manufacturer's recommendation to ensure that the quantity of test material is acceptable to achieve optimum light scattering conditions. A wide range of sample sizes is acceptable, depending on the median particle size (d50), particle density (mass/volume), refractive indexes and sample delivery system. Select the appropriate run time for the test portion. This procedure is very specific to the equipment and material and is generally gauged by the run-to-run repeatability and by the use of SRM 114 (see Section 10).

Select the appropriate refractive indices. Recommended refractive indices of cement are real 1.7, imaginary 0.1; recommended refractive index for IPA: real 1.378, imaginary 0.

Select the desired data output parameters, according to the manufacturer's requirements. Usually, the PSD reported is the cumulative distribution. To simplify data interpretation, the following particle sizes are to be used: 0.5, 1, 1.5, 2, 3, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, and 128 µm. Other sizes can be reported without affecting the quality of the results.

Transfer the test portion directly to the sample delivery system. For the wet method, allow recirculation for at least 20 s prior to beginning measurement. For the dry method, engage

the sample switch to allow the sample to begin flow past the light source before starting measurement.

Select the appropriate measurement parameters. For the wet method, parameters such as ultrasonication intensity and time, flow rate, and measurement duration are to be selected. For dry method, parameters such as intensity of vibration applied to the sample feeder, air pressure or vacuum level are to be selected. Refer to the instrument manual for further specifications.

Perform the sample analysis according to the manufacturer's instructions.

Collect at least three sets of PSDs and calculate the average value for each particle size on the same test portion of the wet method and on three different test portions for the dry method.

For the wet method, drain and fill the sample dispersion system in preparation for the next sample analysis. Drain and rinse as necessary, to achieve background values within the acceptable operating limits, as specified by the manufacturer.

For the dry method, brush or vacuum to remove all particles throughout the sample system. Purge with air or use fine sand to remove particles remaining in the sample system, as described in the manufacturer's instructions.

Follow the manufacturer's instructions to determine the frequency and the procedure for cleaning the lenses.

Chapter 11 REPORT

Practice E 1617 specifies three levels of detail for reporting PSD data. It is up to the supplier and user of the data to agree on the level of reporting required. As a minimum, report the following information.

11.1.1 The instrument name and model number used and the range selected

11.1.2 The method of dispersing the test portion, i.e., wet or dry

11.1.3 The instrument measurement run time

11.1.4 The parameters selected under 11.10

11.1.5 The number of replicates that were used to calculate the average

11.1.6 ***The 10%, 50%, and 90% diameters (d10, d50, and d90, respectively). These values can be used to calculate the span***

11.1.7 ***The cumulative (volume% versus diameter) PSD. This could be provided in electronic form as well.***

Chapter 12 PRECISION AND BIAS

Precision **—The analysis of the interlaboratory round-robin, sponsored by NIST for the development of the next SRM 114 presented here, was used to develop the precision values.**

Within-Laboratory Precision **— The standard deviation of PSD determinations within a laboratory for a given material, are given in the second column of Table 1. The standard deviations for the different particle sizes, indexed by the cumulative volume fractions observed for this material, are given in the first column of Table 1. Criteria for comparing two PSD values for a particular particle size within a laboratory, the expanded uncertainty of the difference of two cumulative volume fractions, is given in the third column of Table 1. This value gives the acceptable range of two measurements that is likely to be caused by random variation.**

Multilaboratory Precision **— Between laboratory uncertainties are given in the last two columns of Table 1. The standard uncertainties were obtained by taking the standard deviation of the mean PSD values for each laboratory at each particle size.**

Bias **– This test method has no determinable bias as the values obtained can only be defined in terms of this test method.**

Table 1— Standard uncertainties and expanded uncertainties for the difference of two cumulative volume fractions within and between laboratories

Cumulative Volume Fraction (CVF),%	Standard Uncertainty of CVF's Obtained from a Typical Lab[a],%	Expanded Uncertainty for the Difference of Two CVF's Obtained from a Typical Lab[a],%	Standard Uncertainty of CVF's Obtained from Different Labs,%	Expanded Uncertainty for the Difference of Two CVF's Obtained from Different Labs,%
5.075	0.175	0.496	2.511	7.103
8.033	0.281	0.794	3.233	9.144
11.195	0.342	0.969	3.889	10.999
16.286	0.450	1.274	4.526	12.801
21.005	0.530	1.500	5.138	14.532
29.636	0.565	1.598	5.948	16.823
37.573	0.600	1.696	6.191	17.509
51.045	0.603	1.706	6.352	17.967
62.795	0.552	1.561	6.385	18.058
80.823	0.501	1.417	4.982	14.092
91.150	0.384	1.085	3.453	9.766
98.359	0.217	0.614	1.326	3.750
99.695	0.049	0.139	0.565	1.597
99.886	0.003	0.009	0.458	1.295
99.895	0.000	0.000	0.460	1.300

a. Different laboratories have significantly different within-lab standard deviations, so some labs will find that smaller differences are statistically significant while others will find that larger differences are not significant.

APPENDIXES

(Nonmandatory Information)

TRB

Transportation Research Board
500 Fifth Street, NW
Washington, DC 20001

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