## Measurement of Particle Size Distribution in Portland Cement Powder: Analysis of ASTM Round Robin Studies

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# Measurement of Particle Size Distribution in Portland Cement Powder: Analysis of ASTM Round Robin Studies

**ABSTRACT:** A distribution of particle sizes or particle size distribution (PSD) is a fundamental characteristic of cement powder. Accurate PSDs are required in computational efforts to model the hydration process and it is an important practical issue for the cement industry. Presently, the only available standard method for measuring the PSD of cement, namely ASTM C115, is limited in scope, with a lower size detection limit of 7.5  $\mu$ m. Since there are no standard procedures that adequately cover the broad particle size range associated with portland cement powder, the implementation of different measurement techniques varies widely within the industry. Two ASTM-sponsored round robin tests were performed to (1) ascertain the techniques and methods currently used in the cement industry and (2) develop and refine a standard method or methods. The results have been incorporated into a best practice method based on the technique of laser diffraction. The aim of the current paper is to summarize the findings based on the data generated during the round robins and to summarize the various approaches available to measure the PSD of cement. A summary of the statistical analysis of the test results is described.

KEYWORDS: cement, particle size distribution, PSD round robin, laser diffraction, reference material

#### Introduction

Accurate measurement of the particle size distribution (PSD) of a cement powder is both an important practical issue for the cement industry and a key limiting factor in on-going computational efforts to simulate the microstructure and predict the performance of cement-based materials (Bentz et al., 1999a, 1999b; Garboczi et al., 2003). Hence, the PSD is essential for the complete characterization of a cement powder and is closely linked to cement performance. Presently, the only relevant standard method is ASTM C115-96, a turbidimetric method for determining fineness (Standard Test Method for Fineness of Portland Cement by the Turbidimeter ASTM C115). This method is limited in scope, however, with a lower size detection limit of 7.5  $\mu$ m. Because there are no standard procedures that adequately cover the broad particle size range associated with portland cement powder, the implementation of different measurement techniques varies widely within the industry.

Cement is a problematic material with respect to the application of PSD methods. First, the size distribution itself is extremely broad, typically spanning two or three decades from the submicrometer range to 100  $\mu$ m. In general, sizing techniques work best over a limited size range. The optimum range for a particular technique varies according to a number of factors, including detector sensitivity, underlying principle of measurement, and assumptions

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inherent in the data analysis routine. Secondly, cement particles are highly agglomerated in the dry state, and therefore must be dispersed in order to differentiate between weakly bound agglomerates and primary units. Standard protocols for dispersing cement particles before analysis are nonexistent. The degree of dispersion achieved in dry aerosol methods will likely vary depending on particle size, the geometry of the dispersing device, the residence time in the sensing zone, and the applied shear force. Similarly, wet dispersion methods are subject to variations in surface chemistry of the powders, solids concentration, the nature of the medium, and the amount of mechanical energy expended to break up agglomerates. In addition, the most dispersive medium for cement, namely water, cannot be used due to the reactive nature of the solid phase. Dispersion introduces a potentially large source of variation at the sample preparation stage. Finally, cement particles are inhomogeneous in composition and often irregular (non-spherical) in morphology. Applicable commercial techniques are designed specifically for, or work best with, homogeneous spheres. Typically, an effective spherical particle diameter is reported. The degree to which irregularity affects the results will vary by technique, and is generally not well understood or properly accounted for in most methods (Bowen, 2002; Barth and Sun, 1985; Beddow and Meloy, 1980).

The issue of how to determine if a chosen method of analysis yields the *true* distribution must also be addressed. Within this context, defining a "true" PSD is an integral part of the method development and validation process. Currently, no material artifact (i.e., reference material) or universally accepted measurement method exists for cement powder PSD determination. Therefore, a PSD reference material for cement should be established, but also a standardized method for dispersing and analyzing test samples must be coupled to this reference.

To address these issues, two round robin tests, sponsored by ASTM Task Group C01.25.01, were conducted. The initial round

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robin involved 21 participants and was nonspecific with regards to methodology (i.e., participants used their in-house methods, and no protocols or parameters were specified). Four portland cements provided by the Cement and Concrete Reference Laboratory (CCRL) were included in the test: 131, 132, 135, and 136 (numbers were assigned by CCRL). The compositions and characteristics of these cements, measured as part of the CCRL proficiency program, are provided elsewhere (Ferraris et al., 2002a). The cement powder standard reference material (SRM) 114p was also included in this test. SRM 114p is routinely used to calibrate Blaine as well as other surface area measurements. The information requested from the participants included only the measurement technique and the cumulative PSD, so a detailed understanding of the various procedures used was not possible. The principal purpose of this initial round robin was to assess the overall variability in PSD measurements across the cement industry. A total of four techniques were reported by this group of participants: laser diffraction (LAS), electrical zone sensing (EZS), X-ray gravitational sedimentation (XRS), and scanning electron microscopy (SEM). Laser diffraction, using either wet or dry dispersion methods, was by far the most frequently reported technique. The high degree of variability in the data reported from the first round robin indicated the necessity for further research and testing.

The second round robin expanded to 41 participants and included both specified and nonspecified measurement methodologies. Two portland cements provided by CCRL were included in the tests: 143 and 144. The characteristics of these cements, as measured in the CCRL proficiency program, are given elsewhere [Ferraris et al., 2002b]. SRM 114p was again included, with the specific intent of establishing a consensus reference PSD. Establishing a true analytical PSD for SRM 114p was considered to be neither practical nor fundamentally sound, given our present limited understanding of cement particle dispersion and the limitations of available analytic methods. In the second test, only three techniques were reported (LAS, EZS, and SEM), with 93% of participants using LAS. The issue of how to best disperse cement powder for PSD analysis was addressed by conducting additional studies at the National Institute of Standards and Technology (NIST), which were then incorporated into the design of the second round robin.

The purpose of this paper is then to summarize findings based on the data generated during the round robins and to summarize the various approaches available to measure the PSD of portland cement. A summary of the statistical analysis of the test results is described. The analysis of reported data is conducted in two parts. In the first part, an attempt is made to establish a consensus reference PSD based on SRM 114p. This is followed by an examination of the parameters and methodology used by the participants in order to initiate discussion on developing a standard test method for cement PSD to be submitted for ASTM consideration. The complete set of raw data collected during the round robin tests, and the accompanying statistical analyses, are available in two separate reports (Ferraris et al., 2002a, 2002b).

#### **Description of Techniques**<sup>4</sup>

Although a wide variety of techniques are available for the determination of PSD in powders, only a relative few appear to be

<sup>4</sup> Commercial equipment, instruments, and materials mentioned in this report are identified to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

used currently within the cement industry. The choice of technique is probably based on both capability (relative to the material properties of cement) and speed and convenience of analysis. Based on the results of the two ASTM round robin studies, the currently utilized measurement techniques are: laser diffraction, electrical zone sensing (Coulter principle), sedimentation (X-ray sensing), scanning electron microscopy (imaging).

Sieving, though known to be used by the cement industry in the past, was not reported as a technique of choice by any of the round robin participants. The technique most often reported was laser diffraction. In fact, only a handful of participants reported using techniques other than laser diffraction (less than 10%). In this section, we provide a synopsis for each technique as it relates to cement analysis. Greater detail is provided for laser diffraction, since it is the most widely used method for cement powder sizing.

#### Laser Diffraction (LAS)

In the LAS technique, the angular distribution of light scattered from a dilute particle dispersion is measured. To be precise, light can be scattered, diffracted, or absorbed by the dispersed particles (Bohren et al., 1983). Scattered light consists of reflected and refracted waves and depends on the form, size, and composition of the particles. Diffracted light arises from edge phenomena and is dependent only on the geometric shadow created by each particle: diffraction is independent of the composition of the particles. Absorption occurs when light is converted to heat or electrical energy by interaction with the particles, and is influenced by both size and composition. The so-called laser diffraction technique incorporates all three of these effects, but is generally limited to the more forward scattering angles. The key material parameter for LAS is the complex refractive index, m = n - ik, where n is the real component and k is the imaginary (absorptive) component. Scattering arises due to differences in the refractive index of the particle and the surrounding medium (and internal variations in the case of heterogeneous particles). Values of n have been published for many bulk materials (see for example Handbook of Optical Constants of Solids, 1985, 1991), but in the case of cement, n is routinely estimated based on a mass average of the refractive indices for the individual material components (Cyr et al., 2000). Absorption becomes important primarily in the fine fraction, especially below 1 µm. Cement is generally gray to off-white in color, and therefore a finite, but relatively low value for the imaginary component is expected. The value k = 0.1 is often reported for cement, although the origin of this value is unclear and its appropriateness for general use has not been established.

There are two principal methods of data analysis for LAS: Mie and Fraunhofer. Mie theory describes scattering by homogeneous spheres of arbitrary size and is the most rigorous optical scattering model available. For non-spherical particles, Mie provides a volume-weighted equivalent spherical diameter. Mie theory has been applied with mixed success to the analysis of powders with diameters from several hundreds of micrometers down to about 100 nm. An accurate representation of the "true" size distribution by Mie scattering is dependent on the input of an accurate value for the complex refractive index. For particles much larger than the wavelength of light, the Fraunhofer method can be used without knowledge of the refractive index, because it is based on the diffraction effect only. The range of validity for Fraunhofer is limited at the fine end to diameters a few times greater than the wavelength of light, denoted by  $\lambda$ , for particles that are opaque or have a large refractive index contrast with the medium (ISO 13320-1:1999(E)). For more transparent particles, or particles with a moderate refraction contrast, the lower limit is raised to about  $40 \times \lambda$ . For  $\lambda = 633$  nm (red light), this corresponds to about  $25 \,\mu$ m. The benefit of using Fraunhofer diffraction is that the interpretation is not dependent on the absorptive or refractive properties of the material. On the other hand, use of the Fraunhofer approximation beyond the valid range can lead to large systematic errors in the calculated PSD (ISO 13320-1:1999(E)).

The LAS method requires that the particles be in a dispersed state, either in liquid (suspension) or in air (aerosol). The former is presently referred to as the "wet" method (LAS-W) whereas the latter is termed the "dry" method (LAS-D). Differences between LAS-D and LAS-W methods arise primarily from the different ways in which the particles are dispersed in each case.

In liquid, it is possible to modify solution conditions by changing pH or adding chemical dispersing agents, and one can disrupt aggregates using mechanical or ultrasonic energy. Thus, for the very fine fraction, a better state of dispersion can be achieved in an appropriately selected liquid medium. Generally, water is an excellent dispersing medium. However, due to the reactive nature of cement in water, alcohols, such as isopropanol, methanol, and ethanol, are commonly used in its place.

In the LAS-D method, a stream of compressed air (or a vacuum) is used to both disperse the particles and to transport them to the sensing zone. This method of dispersion works best for the coarse size fraction, where the interparticle contacts are weak. For particles smaller than a micrometer, or highly asymmetric particles, air dispersion is generally not appropriate for sizing.

#### Electrical Zone Sensing (EZS)

Electrical Zone Sensing is based on the Coulter principle. The powder is dispersed at a highly dilute concentration in a conducting liquid, which is then drawn through a small orifice in an insulating wall on either side of which are placed electrodes. As a particle enters the orifice, or sensing zone, the volume of solution displaced by the particle causes a transient change in the measured electrical impedance across the opening. The amplitude of the impedance pulse is proportional to the particle's volume. By accumulating pulses over time, a PSD is constructed. EZS is a particle counting method capable of producing a number-weighted or mass-weighted distribution of particle sizes and requires calibration. Different size orifices are used to capture broad PSDs. The applicable particle size range is from about 0.2-800 µm, although a lower limit of 0.6 µm is probably more realistic for normal operating conditions (Allen, 1990; ISO 13319:2000(E)). Errors can arise from coincident passage of multiple particles through the orifice and from high asperity particles, both of which skew the PSD towards larger sizes. A pulse discrimination system can be used to correct for the coincidence effect by rejecting distorted pulses. Porous particles (e.g., fly ash) are generally unsuitable for EZS measurements because their effective densities are not known. The dispersion procedure and solids concentration are critical parameters for accuracy in EZS measurements.

#### Sedimentation (XRS)

The change in concentration or density of a moderately dilute (1–6% mass fraction) suspension with time is measured at known depths, using optical or X-ray sensing. X-ray gravitational sedimen-

tation (XRS) is well established in several industries. Sedimentation methods are based on the application of Stokes' Law, which describes the terminal velocity for an isolated sphere settling in a viscous fluid under the influence of a gravitational field. Stokes' Law is valid only if the Reynolds number (Re) does not exceed about 0.25 (ISO 13317-1:2001). Using a density value of  $3.2 \text{ g/cm}^3$  for portland cement, the largest (equivalent spherical) diameter that can be sized accurately with XRS is about 95 µm in isopropanol (IPA) at 25 °C. Particles larger than this will settle much more slowly than predicted by Stokes' Law. The upper size limit can be increased by using a higher viscosity fluid. Irregularly shaped particles should settle according to their equivalent spherical volume at low Re values. For fines, the effect of Brownian motion exerts a significant influence on settling at diameters below about 1 µm in water and about 0.7 µm in IPA. Convection currents in the settling suspension may further limit the lower size range. Parameters required for XRS are solid and liquid phase density, and liquid phase viscosity. The particles must remain stable against agglomeration during settling or the measured PSD will be skewed toward larger sizes.

#### Scanning Electron Microscopy (SEM)

The SEM is an analytical tool that uses a focused beam of electrons to form magnified images. Under ideal conditions, the SEM is capable of producing images with a feature resolution at the nanometer level. In addition to image capabilities, a properly equipped SEM can provide information on the elemental composition of microscopic features. Information on the image and elemental characteristics of a sample are obtained through the interaction of the electron beam with the sample material, which produces various effects that can be monitored with suitable detectors. The resulting signals, which include secondary and backscattered electrons along with characteristic photoelectron X-rays, can be collected in synchronization with the position of the electron beam to provide detailed spatial and compositional information. A computer controlled SEM (CCSEM) can provide simultaneous measurement of individual particle size, shape (aspect ratio), and elemental composition by combining an SEM, an X-ray analyzer (EDS), and a digital scan generator under computer control [Schwoeble et al., 1988]. Use of the computer to control the analysis permits relatively large numbers of individual particles to be analyzed (e.g., 1000 s). Elemental composition, though an important benefit for research purposes, was not part of the round robin tests. Errors typically arise because of poor counting statistics for large particles, an inability to differentiate between primary particles and agglomerates, 3-D/2-D effects, and/or artifacts created during sample preparation.

#### **Data Analysis Methodology**

In both round robins, the results for SRM 114p were analyzed separately from the other cements with the objective of producing a reference curve that instrument operators could use to "calibrate" their systems or to validate their methodology. In other words, the reference distribution of SRM 114p could potentially be used to check that the PSD obtained by a particular instrument falls within a defined margin of error, or it could be used to offset measured values by a size-range-dependent factor to bring them within the acceptable margin of error. The more significant errors associated with the measured PSD curves coming from different laboratories and users are most likely due to systematic differences that result because devices differ in systematic ways on nuisance factors. To

determine the reference distribution for SRM 114p, two approaches were considered:

- Approach 1: Establish a single calibration curve that represents an average distribution for all techniques inclusive (i.e., all-inclusive approach);
- Approach 2: Establish a calibration curve for each technique (i.e., technique-specific approach)

Both approaches have advantages and disadvantages. In the first approach (all-inclusive), the calibration curve would be less precise (greater margin of error) as a result of cumulative variations in the precision of different methods. On the other hand, the first approach is simple and convenient, because every customer would use the same calibration curve. In the second approach (technique-specific), the calibration should be more precise, because variations resulting from differences in measurement principle or precision would be eliminated. As a disadvantage, several calibration curves would need to be established independently, one curve for each method, and this would require a statistically relevant pool of round robin participants for each technique. The best possible approach, of course, would be to establish a calibration curve based on an independent determination of the "true" PSD, using a method that can be validated theoretically and/or experimentally; such a method does not currently exist for cement.

In the second round robin (used as the basis for development of a reference curve), 39 participants (93% of all participants) used the LAS technique. Of these, 26 (62% of all participants) dispersed their powders in a liquid (LAS-W) and 13 (31%) used a dry powder method (LAS-D). On the other hand, there was only one participant that reported using SEM and two who reported using EZS. Therefore, using the technique-specific approach (Approach 2), a statistically relevant calibration curve could only be determined for LAS-W and LAS-D. Obviously, all 42 sets could be used if the all-inclusive method (Approach 1) was followed, but the resulting curve would be heavily weighted by the relatively large number of LAS results. Therefore, it was determined that an all-inclusive calibration curve was not appropriate for this database and the development of a reference PSD curve was limited to the LAS technique.

To determine the curve that best represents the consensus PSD for LAS, outliers must first be identified and excluded from calculation of the reference curve. The method that was adopted here is based on calculation of the mean and the two-sided 95% confidence limits using the bootstrap method. The bootstrap method replaces difficult (or even impossible analytical) solutions to statistical problems with raw computing power (details on the bootstrap method are provided in Appendix C of ref. [Ferraris et al., 2002a]). The bootstrap method does not explicitly provide the criteria needed to determine outliers. Therefore, we selected the following criteria for elimination of outliers: if more than 27% of points (i.e., four data points) in a single round robin data set (i.e., a curve provided by one round robin participant) exceed by more than 5% the confidence limits determined by analysis of all data sets in the grouping (i.e., curves provided by all participants), then this individual data set is identified as an outlier. The tolerance value of 5% is based on the absolute difference between the measured value and the closest confidence limit value. Once the outliers are determined, the mean and 95% confidence limits are recalculated excluding the outliers. The resulting mean curve is then defined as the consensus reference curve representing SRM 114p. No judgment was made on how the data were generated in the LAS, i.e., what parameters were used such as refractive indices, dispersion methodology, etc. Discussion of these parameters will be given below.

#### Determination of the Reference PSD for Laser Diffraction

For LAS measurements, both wet and dry, two sets of results were collected:

- Participant's in-house method (PM): the participants were requested to use the method that they normally use and to describe it in detail.
- Specified method (SM): all participants were requested to use a set of parameters specified by NIST (Appendix D of ref. [Ferraris et al. 2002b]).

We have examined the two sets of data separately and then in combination, after first excluding the outliers. As a result of this process, three mean bootstrap curves with 95% confidence limits are provided for both LAS-W and LAS-D. The issue is then to decide which mean curve or curves is most appropriate as a reference for SRM 114p using the LAS technique. Note that high and low intervals are not symmetric about the mean. These limits can be asymmetric around the sample mean. This is caused by a slight skewness of the generated bootstrapped sampling distribution of the mean.

All individual data sets used in this analysis are reported elsewhere [Ferraris et al., 2002b]. Six outliers were found for LAS-W out of 25 participants, and two outliers were determined for LAS-D out of 13 participants. The bootstrap results are given in Table 1 for LAS-W and Table 2 for LAS-D. A graphical comparison of the three distributions is provided in Fig. 1 for LAS-W and Fig. 2 for LAS-D. As shown in these figures, the differences between the three PSDs are not very large. Because the combined distribution represents a larger statistical pool, it could be argued that the combined PSD should be used as a single consensus reference curve.

#### Correction Procedure for Unknown PSDs

The purpose of a reference PSD based on an easily accessible reference material is twofold: to verify the efficacy of the instrument or method being used, and to correct measurement results by applying a set of correction factors. A procedure in which the mean PSD curve is used to correct measured data obtained using various instruments would work in the following manner: 1) Calculate the correction factor for each size, defined as the ratio between the measured value and the mean value as shown in Table 1 for LAS-W and Table 2 for LAS-D; 2) Multiply measured size data for unknown samples by this correction factor.

This procedure was applied to all available data sets for CCRL 143 and 144, which were provided to the participants of the second round robin study. Figure 3 shows some selected results from this analysis. The complete results are provided in a separate publication [Ferraris et al., 2002b]. It was initially expected by the ASTM committee that a single method and reference PSD could be used to correct all measurements; however, in practice this proved problematic. If the target measurement results themselves (not the calibration curve) contain outliers, (i.e., data points that are more than 5% outside the confidence limits obtained with the bootstrap method), the correction is not sufficient to bring the entire curve within the confidence limits of the calibration curve

- ITBEET Bootshap data jot End th (after excitating outliers). Size rejets to equivalent spherical particle atamet	TABLE 1-	-Bootstrap data for	LAS-W (after excl	luding outliers). Siz	e refers to equivalent	t spherical particle diameter
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Size [µm]	PM Only			SM Only			PM + SM		
	Mean	Low	High	Mean	Low	High	Mean	Low	High
1	5.0	3.5	6.3	6.0	3.9	8.3	5.4	4.2	6.7
1.5	7.9	6.4	9.5	9.5	7.2	12.1	8.7	7.2	10.0
2	11.1	9.6	12.5	13.7	11.6	15.9	12.2	10.9	13.5
3	16.3	14.8	17.8	19.0	16.7	21.3	17.5	16.2	19.0
4	20.5	19.0	22.1	23.4	21.1	25.7	21.8	20.4	23.2
6	27.9	26.5	29.4	30.7	28.3	33.3	29.1	27.7	30.6
8	34.1	32.8	35.5	37.3	34.9	39.7	35.5	34.1	37.0
12	45.8	43.9	47.8	49.0	45.7	52.1	47.2	45.4	49.1
16	54.7	52.7	56.6	58.0	55.0	61.2	56.2	54.2	57.9
24	69.7	68.0	71.6	72.5	69.8	75.1	71.0	69.5	72.6
32	80.4	78.8	82.1	83.4	81.3	85.3	81.7	80.3	83.1
48	92.6	91.5	93.7	94.3	93.0	95.5	93.4	92.5	94.2
64	97.1	96.4	97.9	98.3	97.5	98.9	97.6	97.1	98.1
96	99.4	99.0	99.7	99.7	99.5	99.9	99.6	99.3	99.8
128	99.9	99.7	100.0	100.0	99.9	100.0	99.9	99.8	100.0

TABLE 2—Bootstrap data for LAS-D for PM (after excluding outliers). Size refers to equivalent spherical particle diameter.

	PM Only			SM Only			PM + SM		
Size [µm]	Mean	Low	High	Mean	Low	High	Mean	Low	High
1	5.0	2.7	7.3	4.4	2.6	6.2	4.7	3.3	6.1
1.5	7.9	4.5	10.9	6.7	3.9	9.2	7.3	5.4	9.5
2	12.3	10.2	14.5	11.9	10.3	13.3	12.1	10.6	13.4
3	18.1	15.5	20.6	17.2	15.4	19.3	17.7	16.1	19.3
4	23.0	20.2	26.0	21.5	19.3	23.6	22.3	20.3	24.2
6	30.9	27.6	34.4	28.7	26.0	30.8	29.9	27.8	32.0
8	37.1	33.9	40.5	34.7	32.1	36.7	35.9	33.9	38.1
12	47.3	44.0	50.7	45.3	43.2	47.3	46.4	44.4	48.4
16	55.3	52.2	58.4	53.7	52.0	55.4	54.6	52.8	56.7
24	68.9	65.9	71.6	67.9	66.7	69.3	68.4	66.9	70.1
32	78.8	76.4	81.2	78.6	77.6	79.7	78.7	77.3	80.2
48	90.7	88.7	92.6	91.5	90.4	92.7	91.1	89.9	92.2
64	95.9	94.2	97.5	96.7	95.9	97.7	96.3	95.3	97.3
96	98.7	97.5	99.7	99.5	99.2	99.8	99.1	98.3	99.6
128	99.1	97.9	99.9	99.9	99.8	100.0	99.5	98.8	100.0





FIG. 1—Graphical comparison of the Bootstrap mean curves obtained in Table 1 (LAS-W). For clarity, the confidence intervals are not shown here, but can be found in Table 1.

FIG. 2—Graphical comparison of the Bootstrap mean curves obtained in Table 2 (LAS-D). For clarity, the confidence intervals are not shown here, but can be found in Table 2.

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FIG. 3—Corrections of selected data for cement CCRL 143. A) Data as measured; B) Data corrected. In the legend, 450, 611, and V6 represent coded data sets from participants in the round-robin. Also shown in these graphs are the 95% limits.

(Fig. 3). On the other hand, if the data set lies completely within the confidence limits defined by the reference curve, the correction factor will reduce the overall spread of the data. Therefore, the reference curves for SRM 114p could be used in two ways: 1) As part of a validation method, to check that measurements are within the confidence limit range of the reference. This will allow the operator to determine if sample preparation problems or possibly a malfunctioning instrument should be considered; 2) As a calibration curve to correct data from unknown samples, after the method has first been validated as mentioned above. This correction should be used carefully, since the corrected PSD could remain outside the acceptable range.

#### Measurement Methodology

The scope of this study was also to compare the test sample preparation and measurement parameters used within the cement industry for a given technique. To facilitate this comparison, participants were asked to provide specific detailed information about their in-house methods. This information was kept confidential, such that no specific technique, method or set of results could be identified with a particular organization. In this section, we will examine the methods used and determine if it is possible to develop a "best practice" that could eventually be presented to ASTM for approval as part of a standard test method. Only the information submitted for laser diffraction will be examined here, as we do not have statistical representation for other methods.

#### Laser Diffraction with the Specimen Dispersed in a Liquid (LAS-W)

Participant-provided information concerning in-house methodology was divided into two areas: sample preparation and analysis. It is important to examine the responses with two goals in mind: 1) can a consensus procedure or procedures be established, and 2) can we identify parameters that significantly impact results?

### Summary of Industry Practice for Sample Preparation

In the area of sample preparation, the following key information was requested where appropriate: dispersion medium, solids concentration, dispersion procedure, surfactant (if used), and type and duration of ultrasonic treatment (if used).

Each of these items should be clearly defined if a standard test is proposed to ASTM. Only a summary will be given here as the details are described in reference [Ferraris et al., 2002b].

Most LAS-W participants used alcohol as a dispersion medium: 54% used isopropanol (IPA), 31% used ethanol and 8% used methanol (percentage were rounded). However, the use of alcohol was not universal. Two participants (8%) used an aqueous medium, despite the obvious problem with hydration.

The second issue concerns the concentration of cement in the measuring cell, and the dispersion and/or dilution method used to achieve that concentration. This information is paramount because it can affect the ability to fully disperse the cement, and could lead to a user bias or increased variability in the measurements. Furthermore, solids concentration is a key parameter for any light scattering technique, due to the effects of multiple scattering when concentrations are too high and minimum signal requirements when they are low.

The majority of round robin participants prepared their cement powder suspensions in a single step (i.e., they analyzed the samples as prepared, without further dilution). In some cases, a known amount of cement was added, while in other cases the addition amount was varied to achieve a certain optical obscuration level in the cell. The optimum percentage obscuration range is predetermined by the measurement device requirements. As a result, the concentration used in the round robin varied widely and was reported explicitly by only 12 of 26 participants who used liquid dispersion. It could be concluded from these results that the most common practice is to adjust concentration in situ (i.e., with the suspending liquid in the measurement cell) based on obscuration levels. It might be difficult, therefore, to prescribe a fixed-solids concentration in a standard test method, since different instruments may require different obscuration levels. An alternative approach would be to specify the solids content for a stock concentrate, allowing some control over sample preparation, but the stock would then be diluted in situ (using the chosen suspending medium) to obtain the optimal obscuration level for a particular instrument.

Another factor influencing dispersion relates to the use of ultrasonication to break up agglomerated particles, a common practice in many industries. Round robin results show that 69% of LAS-W



FIG. 4—Correlation of reported ultrasonic treatment duration and the dispersion of the smaller size fraction represented here by  $D_{10}$ .

users employed ultrasonic treatment of cement dispersions before measurement. Of these, 63% used in-line ultrasonication provided by the instrument, while the remainder used an externally applied ultrasonic device prior to sample introduction to the measuring cell. One participant reported using both external and in-line ultrasonication, in series. The power and the duration of the ultrasonication should be compared to determine the best procedure for an ASTM standard. Unfortunately, the power cannot be explicitly compared because values are not always reported in fundamental units (i.e., Watts versus a relative % scale) nor is output power always clearly defined with respect to the device geometry and sample volume. Furthermore, the sound frequency is rarely known or reported. On the other hand, the duration of treatment was reported by all participants using ultrasonics, and it ranged from 10-300 s, with a median value of 60 s. A comparison of reported ultrasonic treatment durations and the measured  $D_{10}$  values<sup>5</sup> is given in Fig. 4. There is no clear dependence of the fine fraction size on duration, nor is there any apparent correlation between duration and the occurrence of outliers. Further studies to determine the impact of ultrasonic treatment duration on dispersion of cement in alcoholic media were performed at NIST (Hackley et al., 2004). In these studies, an external ultrasonic immersion device was employed. Suspensions were prepared at a solids volume fraction of 5% in IPA. Results, summarized in Fig. 5, indicate that after an initial treatment duration of 60 s at an output power of 90 W, further treatment provided no additional dispersive benefit. From the resulting PSDs, it is clear that the initial treatment improved dispersion of the finer fraction (below 20 µm), while having no appreciable impact on the coarse fraction.

#### Summary of the Analysis Methods

The three specifications requested from the participants with respect to the analysis step were: duration of the measurement, model used to fit scattering results (Mie or Fraunhofer), and, if Mie, complex refractive index used (real and imaginary) for both cement and medium.

The reported measurement duration varied from 4–120 s. This is a wide range that seems to depend primarily on the commercial



FIG. 5—Cumulative PSD of cement powder (CCRL 135) in IPA as a function of ultrasonic treatment duration.

device used. Nevertheless, the majority of measurements were of 60 s duration or less, and this is clearly one reason that LAS has become so prevalent within the cement industry. However, no clear correlation was observed between measurement time and PSD results, and presumably this is because each instrument determines the length of measurement necessary to reach some internally set signal-to-noise ratio.

As stated in the introduction, of the two optical models for interpreting angle-dependent scattering by particles, Fraunhofer and Mie, only the second one requires the refractive indices to be specified. According to ISO 13320-1, the Fraunhofer model works well for particle sizes  $>50 \mu m$ . For particle sizes  $<50 \mu m$ , the Mie model is preferred if a reasonable estimate of the refractive indices are available. In the intermediate range from about 1 µm to 50 µm, the appropriateness of the choice of optical model will depend on whether the relative refractive indices (ratio of particle to medium) are high or low, and thus the decision is more complicated. In the submicrometer range, the Fraunhofer model is not applicable. The availability of different optical models on a particular commercial instrument may also be a limiting factor for some users. It was found that 80% of the participants used either Fraunhofer, Mie, or both. It is surprising that as many as 16% of the participants seem unaware of which optical model they are using to analyze their data.

The choice of complex refractive index is critical if the Mie optical model is used to interpret the data and produce the PSD of the cement. For the cement phase, the value of the real component of the index reported by round robin participants varies from 1.23 to 1.88. But if we exclude the single value at 1.23, the minimum value is then 1.6 and the range is significantly narrowed. The median value is 1.73, if 1.23 is excluded. Most participants (64%) used 0.1 for the imaginary (absorption) component of the refractive index of cement, a value that is widely reported by instrument manufacturers and in the literature. Other values reported were 0.01 (by 27% of the participants) and 1.5 by a single participant.

<sup>&</sup>lt;sup>5</sup> Particle diameter below which 10% of the mass of the PSD is found. Represents a characteristic particle size for the finest fraction.



FIG. 6—Calculated cumulative PSD for cement powder (CCRL 135) dispersed in IPA as a function of the imaginary component (Im) of the complex refractive index, with the real component fixed at 1.7.

A consensus value for the real and complex indices would yield 1.73 and 0.1, respectively. It should be noted that the data set produced using the refractive index value of 1.5, far from the mean, nevertheless was not determined to be an outlier in the subsequent statistical analysis. Sources for the refractive index values reported by the participants were not requested and were not shown. Because these values can vary with powder composition, it is an interesting observation that each participant apparently selects a single set of values and applies them to all cements regardless of composition. If some consideration was given to the compositional variations during the selection process, it was not possible to determine this from the round robin study.

The influence of variations in the real and imaginary components on the cement PSD calculated using the Mie optical model was examined at NIST. The imaginary refractive component primarily impacted the fine fraction of the PSD, as indicated in Fig. 6 for CCRL 135 cement in IPA. When the real component was fixed at 1.7 (i.e., close to the consensus value derived from the round robin results) and the imaginary component was allowed to vary, only sizes below 10 µm were significantly impacted. These results demonstrate that ignoring absorption or using a value for the imaginary component that is too small, leads to an underestimation of the fine fraction, particularly sizes below 2 µm. The impact of the imaginary component also depends on the value of the real component. For highly refractive materials, having a real component above 1.7, the effect of absorption on the PSD quickly becomes negligible. The effect of varying the real component, with the imaginary component fixed at 0.1 (i.e., the consensus round robin value) is shown in Fig. 7. For values of 1.7 and higher, only the fine fraction is significantly impacted by changes in the real component, and the effect is relatively small. However, for values below 1.7, the



FIG. 7—Calculated cumulative PSD for cement powder (CCRL 135) dispersed in IPA as a function of the real component (Re) of the complex refractive index, with the imaginary component fixed at 0.1.

entire PSD changes drastically with relatively small changes in the real component. The behavior is similar for smaller fixed values of the imaginary component, where we find that the critical value for the real component (i.e., the value at which further increases have minimal impact on the calculated PSD) decreases with decreasing imaginary component. In other words, the more refractive materials (high real component) are less subject to absorptive effects, and the less transparent materials (high imaginary component) can exhibit strong refractive index effects if the real component is below a critical value.

A standardized test method would have to account for the possibility that either the Fraunhofer or the Mie model might not be available to every user. An ASTM standard should also recommend refractive indices to be used for certain types of cement, or, alternatively, a method for estimating these values based on the known composition of the powder. Further studies to establish the influence of the model choice and model parameters were conducted at NIST (Hackley et al., 2004).

#### Laser Diffraction with the Specimen Dispersed in Air (LAS-D)

The sample preparation issue is greatly simplified in the case of LAS-D, since powders are introduced to the measurement device in dry form with dispersion provided internally by the instrument. Aerosol dispersion methods for commercial LAS-D instruments are based on the use of either compressed air or an applied vacuum. In addition, each instrument company incorporates its own proprietary sample delivery and dispersion system, which might include, for instance, use of vibration or other mechanical devices. There were 13 participants who used LAS-D: 85% of these used systems based on compressed air, one used a vacuum based system, and

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FIG. 8—Relationship between  $D_{10}$  and the reported pressure used during LAS-D measurements.

one used a system incorporating both compressed air and vacuum, presumably in series. One should keep in mind that this information was reported by the participant, and is not necessarily an accurate and complete assessment of the instrument's actual specifications or capabilities. The duration of the measurements, another potentially significant measurement parameter, varied from 4–130 s. The median value was 15 s. So, on average LAS-D appears to be somewhat faster than the corresponding LAS-W measurement.

The pressure used during the measurement when compressed air was employed varied from 1–4 bar. As shown in Fig. 8, there is no clear correlation between the diameter of the finer fraction of the particles, represented by  $D_{10}$ , and the reported air pressure. This lack of correlation may be due to the high level of scatter from other effects, including user and instrument bias, or these pressure levels may be above the minimum level necessary to fully disperse the material to the extent possible in a dry powder.

Like LAS-W, LAS-D requires the use of an appropriate optical model and, where appropriate, the selection of refractive index values. The majority of round robin participants reported using the Fraunhofer model ( $\approx$ 45%), 31% reported using Mie, 8% used both, and 15% were classified as "other." The category "other" includes those not reporting a specific model or providing information that could not be clearly identified with either Fraunhofer or Mie. The variation in the refractive index reported by LAS-D users is relatively small. This is not surprising, as most used the Fraunhofer model, which does not require knowledge of the optical constants.

In LAS-D, since the dispersing medium is air, the refractive index is needed only for the particle phase. All participants who reported a complex refractive index used 0.1 for the imaginary component. Most of the reported values for the real component were close to 1.7. One participant reported a value of 1.0, which is clearly too low for cement powder. Based on the typical composition of portland cement and the known refractive index values for the individual components ([Cyr et al., 2000]) a value near 1.7 seems appropriate. Again, a procedure for selecting or estimating the refractive index should be established as part of a LAS-based standard.

#### Conclusions

This report had two principal goals related to cement powder sizing, and therefore there should be two sets of recommendations,



FIG. 9—Graphical comparison between the distributions calculated for only the LAS-W (Table 1) or LAS-D data (Table 2). For clarity, the confidence intervals are not shown here, but can be found in the corresponding tables.

one relating to the prospect of establishing a reference material for PSD measurements, and one related to the development of a standard method for cement PSD measurements. Because the great majority of participants reported using a LAS-based technique, only LAS will be discussed in the context of reference materials and standards.

#### Reference Material

As SRM 114p is widely used in the cement industry for calibration of the Blaine measurement, it is an appropriate choice to be used as a reference material for PSD determination. Various PSDs were obtained by statistically analyzing the data obtained from round robin participants. From this study, two curves were developed, one for LAS-W and one for LAS-D. As shown in Fig. 9, the two curves do not differ significantly. Therefore, it could be argued that only one curve should be provided as reference. Nevertheless, the authors suggest that at this point the two curves should be provided. Further knowledge on this issue will be gained when the next generation of SRM 114 is developed by NIST.

The mean PSD curves obtained from the round robin tests have been added to the certificate for SRM 114p as informational data (i.e., not certified). The supplies of SRM 114p available at NIST cover industry needs until about summer 2004. Therefore, NIST initiated (2003) the procedure for securing and characterizing the next SRM 114 material. The certificate for the new SRM 114 will also include a reference PSD based on the LAS technique. A statistically meaningful reference PSD for techniques other than LAS was not possible, due to the low number of corresponding data sets obtained from the most recent round robin study.

#### Standard Method

Because the round robin results suggest that a large majority within the cement industry (over 90% of participants) use some form of LAS, it would seem logical to focus initial efforts on the development of a standard method (or best practice) for cement powder sizing based on this technique.

To establish such a standard, the procedures used by industry to measure PSD were examined by analyzing the information that was provided by the round robin participants. Although there is a wide range of methods used to prepare and analyze test samples, some trends could be identified. Additional experiments at NIST were used to examine the impact of key parameters related to the use of LAS techniques (ultrasonication and the index of refraction have been previously discussed). A combination of industry practice and supplemental experiments could be used as the basis for a draft standard method.

LAS-W is subject to the greatest amount of variation due to sample preparation. In LAS-W, the following parameters could be established based on the results of these studies: suspending medium-IPA; solids concentration-fixed stock suspension; obscuration level-modulated at dilution.

Based on measurements performed at NIST using several common alcohols (data not shown), IPA appears to be the best choice. Although the measured PSD varied very little between methanol, ethanol, and isopropanol in these experiments, the latter medium offers a viscosity advantage that could reduce variability arising from the sedimentation of large particles during sampling or measurement. For example, at 20 °C the viscosity of IPA ( $\eta = 2.41$ ) is roughly twice that of ethanol (1.20) and nearly four times higher than methanol (0.597). A number of surface-active agents were also tested to determine if an improvement in dispersion could be achieved in alcoholic media. No consistent or clear advantage could be observed for the addition of common commercial surfactants.

In regards to solids concentration, this parameter could be controlled in two ways. First, the solids content in the test suspension could be fixed, and therefore a single solids loading would apply to all cement formulations, users, and instruments. Second the optimal obscuration value as registered by the instrument would determine the final solids concentration after dilution from a stock concentrate. In the first case, the sample would be introduced to the instrument as prepared. In the second case, a concentrated stock suspension would be prepared at a fixed solids loading by all users and followed up by obscuration-based dilution into the pure suspending liquid preloaded into the instrument circulation system. The former method offers complete control over the sample preparation procedure, which is a large potential source of error, but optimal measurement concentrations may vary between cement formulations and instruments. The latter method offers less control over sample preparation, but is more flexible, broadly applicable, and may be a good compromise (prescriptive versus performance based methodology).

On the other hand, a better understanding of the influence of the following parameters on the results should be investigated further: 1) Refractive index used in Mie model and 2) Duration and intensity of ultrasonication.

Because there were fewer parameters to select for the LAS-D method, the standardization should be less complicated. The use of compressed air versus vacuum for powder dispersion is a factor determined by the manufacturer and not the user, and thus cannot be standardized. The pressure used in compressed air systems can be varied somewhat, but the possible influence of this factor on the measured PSD of cement requires further study. As the size of the finest fraction of particles cannot be accurately determined using Fraunhofer ([ISO 13320-1:1999(E)]), and the refractive indices of cement are not accurately known for cement, the authors suggest that both models be included in a standard or that a lower size limit be set for reporting PSDs. Further research to determine appropriate refractive index values for cement, in the case of Mie analysis, should be conducted or a consensus complex refractive index should be set.

Therefore, there is a strong argument for ASTM committee C01.25.01 and NIST to make an investment in time and effort to develop a standard test method to measure the PSD of cement powder using LAS (both wet and dry). From this report, several parameters could already be narrowed or fixed. A small task group could conceivably help define the next set of specifications to be recommended for a future round robin as part of the standards development process.

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