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Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase I

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National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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Abstract

Particle size distribution (PSD) is an essential property of cement. The only standard method to measure the PSD of cement, namely ASTM C115 [1] is limited in scope; this standard describes a method for determining “fineness” with a lower size detection limit of 7.5 µm. As there is no standard procedure covering the whole range of cement PSD, the implementation of different measurement methods varies widely within the industry. In general, the round-robin results summarized here have demonstrated the high variability between participants using instruments based on the same physical principles.

ASTM committee C01.25.01 sponsored a round-robin test to measure the PSD of cement. The aim of the current report is to analyze the data generated during those tests and to summarize the various approaches available to measure the PSD of cement. The analysis of the data is conducted in two parts. In the first part, an attempt is made to establish a reference distribution using a standard cement powder (SRM 114p). This is followed up by a comparison of the round-robin data in order to initiate discussion on developing a standard test method for cement PSD to be submitted for ASTM consideration. The report provides all raw data collected during the round robin tests, and the results of a statistical analysis of the collected data.

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Participants to the Round-Robin:

Ray Braun, Southdown Cement

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Mario Cesar Cabrera – Cabrera, CENAM

Bob Collins, Blue Circle

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TABLE OF CONTENT

TABLE OF FIGURES

TABLE OF TABLES

1 Introduction

Cement can be a problematic material in the application of particle size analysis. First, the size distribution itself is extremely broad, extending in most cases over two to three orders of magnitude, from about 100 µm down to below micrometer size. In general, sizing techniques work best over a limited size range. The optimum range of particle size analysis varies according to a number of factors, including detector sensitivity and the assumptions associated with the underlying principle of measurement. Second, cement particles are highly agglomerated in the dry state, and therefore must be properly dispersed in order to determine the "true" particle size distribution (PSD). Standard protocols for dispersing cement particles prior to analysis by wet methods are nonexistent, and the degree of dispersion achieved in dry dispersion (air) methods will likely vary depending on the method used, the geometry of the dispersing device, the residence time in the sensing zone and the applied shear force employed to separate physically agglomerated particles. This introduces a potentially large source of variation at the sample preparation stage. Third, cement particles are typically irregular in shape and inhomogeneous in composition. Most commercial methods (see Table 1) are designed specifically for, or work best with, homogeneous spheres. The degree to which irregularity affects the results vary with technique, and is generally not well understood or accounted for properly in many methods.

A universally recognized standard method for characterizing the complete PSD of cement particles does not currently exist [2]. The only standard test, ASTM C115 [1] (also known as the Wagner test), is really designed to measure the "fineness" of a cement powder and it is limited to a minimum particle size of 7.5 µm. As there is no standard procedure covering the whole range of cement PSD, the implementation of different measurement methods varies widely within the industry. Therefore, there is the necessity of having a method in which cement is used as a standard. Other potential sources of variability in sizing methods include adjustable instrument parameters or material property data required as inputs, and fundamental differences due to the nature of the technique itself. In the latter case, it must be acknowledged that different methods may "sense" a different aspect of the size distribution. For instance, a given method may be sensitive to either particle mass, particle number or projected surface area. As a result, for a polydisperse system, each method produces a distribution with a slightly different weighting. Thus the "mean" particle diameter values are expected to differ.

ASTM committee C01.25.01 sponsored a round-robin test to measure the PSD of cement. The scope of this report is to analyze the data generated during those tests and to summarize various methodologies available. The analysis of the data is conducted in two parts:

- Attempt to establish a reference distribution using a standard cement (SRM 114p)
- Discussion of the data obtained during round robin tests as an initial step toward development of a standard tests method for submission to ASTM.

Table 1: Particle size measurement methods commonly used in characterizing fine inorganic powders.

Method[1]	Abbrev.	Underlying Principle	Applicable Size Range[2] (µm)
LASER Diffraction [Fraunhofer Diffraction, Mie Scattering, LASER Light Scattering, Elastic Light Scattering] Dry method (-D) Wet method (-W)	LAS	electromagnetic wave interaction	0.1 - >100
Quasi-Elastic Light Scattering [Dynamic Light Scattering, Photon Correlation Spectroscopy, Optical Beating Spectroscopy] Heterodyne method Homodyne method	QELS	electromagnetic wave interaction	0.005-2
Small Angle Neutron Scattering Ultra-Small Angle Neutron Scattering	SANS USANS	wave interaction	0.001 - 10
Small Angle X-Ray Scattering Ultra-Small Angle X-Ray Scattering	SAXS USAXS	electromagnetic wave interaction	0.001 - 3
LASER Doppler Velocimetry [LASER Doppler Anemometry]	LDV	aerodynamics & electromagnetic scattering	0.5 - 10
Electrical Zone Sensing [Coulter Principle, Coulter Counter]	EZS	volume displacement	0.4 - >100
Differential Mobility Analysis	DMA	electrostatic classification	0.005 - 1
Scanning Electron Microscopy Field Emission SEM	SEM FE-SEM	imaging	0.02 - 10
Transmission Electron Spectroscopy	TEM	imaging	0.01 – 0.5
X-Ray Gravitational Sedimentation	XGS	sedimentation	0.5 - 100
Optical Centrifugal Sedimentation	OCS	sedimentation	0.01 - >5
X-Ray Centrifugal Sedimentation	XCS	sedimentation	0.01 - >5
Sedimentation Field Flow Fractionation	SdFFF	sedimentation classification	0.03 - >1
Sieving	-	size exclusion	2 - >100
Gas Adsorption Surface Area Analysis [Brunauer-Emmet-Teller]	BET	surface area	no limit
Acoustic Attenuation Spectroscopy [Ultrasonic Attenuation Spectroscopy, Ultrasonic Spectroscopy] Coupled phase theory Scattering theory Multiple scattering theory	AAS	acoustic wave interaction	0.025 - >100
Electroacoustic Spectroscopy [Electrokinetic Sonic Amplitude]	ESA	electroacoustic response	0.1 - 10

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[1] Terms in brackets represent other names by which the method is commonly known and/or closely related techniques that have been grouped together under a single general method. Indented terms represent specific variants, implementations or theoretical constructs used to analyze measurement results.

[2] Size ranges are approximate and provide the extreme limits attainable, given access to all commercially available adaptations of that method. Actual size ranges may vary significantly between instruments and may depend on the test material.

2 Description of methods used in the cement industry[1]

Based on participation in the round-robin testing, and a general knowledge of the industry, the most commonly used techniques for characterization of the particle size distribution (PSD) in cement are as follows:

1. LASER Diffraction
    a. with the specimen dispersed in liquid (suspension-based)
    b. with the specimen dispersed in air (aerosol-based)
2. Electrical Zone Sensing (Coulter Principle)
3. Sedimentation
4. Sieving
5. Scanning Electron Microscopy

In this section, we present a brief description of each method. We discuss the principles of operation, the range of application, the key parameters, and the requirements for sample preparation and their potential impact on the measurement results.

2.1 LASER Diffraction

The LASER diffraction (LAS) method involves the detection and analysis of the angular distribution of light produced by a LASER beam passing through a dilute dispersion of particles. Typically, a He-Ne LASER (λ=632.8 nm) in the 5 mW to 10 mW range is employed as the coherent light source, but more recently solid-state diode LASERs have come into use and provide a range of available wavelengths in the visible and UV spectrum. Since the focal volume of the beam senses many particles simultaneously, and thus provides an average value, it is referred to as an *ensemble* technique. With the exception of single particle optical scattering (SPOS), all scattering methods are ensemble techniques, and only ensemble methods will be considered here. There are a number of different diffraction and scattering phenomena that can be utilized for particle sizing. Likewise, there are a number of different ways to define and classify these methods, depending on the underlying principle or its application. We have chosen here to classify all time-averaged scattering and diffraction phenomena involving LASER optics, under the general heading of LASER diffraction; however, it should be noted that "LASER diffraction" is often used in a more narrow way to refer to techniques that utilize only low-angle scattering. See Table 1 for a list of equivalent or related methods.

Strictly speaking, one can differentiate between light waves that are *scattered*, *diffracted* or *absorbed* by the dispersed particles. The scattered light consists of reflected and refracted waves, and depends on the form, size, and composition of the particles. The diffracted light arises from edge phenomena, and is dependent only on the geometric shadow created by each particle in the ballistic light beam: diffraction is therefore independent of the composition of the particles. In the case of absorption, light waves are removed from the incident beam and converted to heat or

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[1] 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.

electrical energy by interaction with the particles; absorption depends on both size and composition.

The influence of composition is revealed through the complex refractive index, $m = n - ik$, where $i = \sqrt{-1}$. For nonabsorbing (i.e., transparent) particles, $k = 0$, where k, the imaginary component of the refractive index, is related to the absorption coefficient of the material. Both the real part of the refractive index, n, and the imaginary part, k, are wavelength-dependent. Scattering arises due to differences in the refractive index of the particle and the surrounding medium (or internal variations in heterogeneous particles). Therefore, in order to use a scattering model to calculate the PSD that produced a specific scattering pattern, one must first know the complex refractive index of both the particles and the medium (typically, the latter is selected such that $k = 0$). Values of n have been published for many bulk materials [3], but in the case of cement, n is routinely estimated based on a mass average of the refractive indices for the individual material components [4]. The imaginary refractive component is more difficult to determine and/or find in the published literature [5, 6], and this often represents a significant challenge to the use of scattering methods for fine particle size measurements [7].

The influence of absorption becomes more important as the particle size decreases, and is therefore more likely to impact the range below the micron of the cement PSD. As a general rule of thumb, the darker or more colored a specimen appears, the higher the imaginary component. For white powders, such as high-purity alumina, k=0. Cement, on the other hand, is generally gray to off-white in color, and therefore one can anticipate a finite, but relatively low value for the imaginary component ($k = 0.1$ is often reported for cement, although this value is unverified and will likely vary for different formulations).

Mie theory, which describes scattering by homogeneous spheres of arbitrary size, is the most rigorous scattering model available, and is used in many commercial instruments. For non-spherical particles like cement, Mie theory provides a volume-weighted equivalent spherical diameter. Mie theory has been applied with mixed success to the analysis of fine powders with diameters from several 100s of micrometers down to several tenths of micrometers. An accurate representation of the "true" size distribution by Mie scattering is dependent on a knowledge of the complex refractive index, and will be impacted by the degree of asymmetry present in the particles and the dispersion procedure used to prepare the test sample. The Mie approach does not work well for extremely fine particulates in the range below 100 nm, possibly because of increased sensitivity to changes in the refractive index that occur with these materials.

For very large particles (relative to the wavelength of light), the diffraction effect can be exploited without reference to Mie theory or the complex index of refraction. 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, again assuming spherical geometry. The range of validity for this 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 [8]. For somewhat more transparent particles, or particle with a moderate refraction contrast, the lower limit is increased to about 40 times the wavelength of light. For a He-Ne LASER, this corresponds to about 25 μm. The benefit of using Fraunhofer diffraction is that the interpretation is not dependent on the absorptive or refractive properties of the material. A totally absorbing black powder, a translucent glass powder, and a highly reflective white powder, having the same particle size and shape, will produce identical Fraunhofer patterns within the valid size range. On the other hand, inappropriate use of the Fraunhofer approximation outside of the valid range can lead to large systematic errors in the calculated PSD [4,9]. These errors are especially prevalent in the range below the micron size, where errors exceeding 100 % are possible. Partial transparency can lead to the appearance of "ghost" particles. These are virtual particles, generally in the range below the micron size, produced as an artifact of refractive dispersion of light within the transparent particles. The refracted light is registered at large scattering angles as anomalous diffraction, and is therefore interpreted by the Fraunhofer analysis as being produced by very small particles.

In general, the LAS method requires that the particles be in a dispersed state, either in liquid (suspension) or in air (aerosol). The former is commonly referred to as the "wet" method (LAS-W) while the latter is termed the "dry" method (LAS-D). In Fraunhofer diffraction, the pattern does not depend on the refractive index, so there is no theoretical difference between using a liquid or a gas as a dispersing medium. For Mie scattering, the higher refractive index contrast in air, compared with most liquids, may somewhat impact the scattering pattern, but should not alter the results in any way.

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 for example, or to break up aggregates using mechanical or ultrasonic energy. Thus, in general, a better state of dispersion can be achieved in an appropriately selected liquid medium. For silicates and most metal oxides, 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 well for large, non-colloidal-phase spheroids, where the interfacial contact area is small and the physical bonds holding the individual particles together are relatively weak. For the particles smaller than a micron and highly asymmetric, the higher surface-to-volume ratio results in more intimate and numerous contact points and, as a consequence, a greater driving force is needed to separate aggregated particles.

2.2 Electrical Zone Sensing (Coulter Principle)

The electrical zone sensing (EZS) technique is based on the Coulter principle. In this method, the powder is dispersed at a very low concentration in an electrolytic (i.e., conducting) solution, which is then drawn through a small orifice in an insulating wall on either side of which electrodes are placed. As each 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 this 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.

In order to relate the registered pulse amplitude to a specific particle size or volume, the instrument must be calibrated using particles having a narrow size distribution (i.e., monodisperse). Alternatively, the instrument can be calibrated using the test powder itself, if the entire size range of the powder is covered in the measurement. If particles are present that are too small to register a pulse, then the fraction of undetected particles can be determined by comparing calibration results from both methods.

Different size apertures can be used depending on the size range of interest; multiple orifices can be employed for powders having a very broad distribution of sizes, like cement. In the latter case, the orifice detection ranges should overlap. A range of orifice sizes are normally available, from 10 μm up to 2000 μm. The applicable range of particle sizes that can be measured using any given orifice is from about 2 % to 40 % of the orifice diameter [11]. Therefore, the maximum applicable size range is from 0.2 μm to 800 μm, although a lower limit of 0.6 μm is probably more realistic for normal operating conditions [10]. The lower detection limit arises due to electrical and thermal interference. For particles with a density similar to the liquid, there is no theoretical upper limit. For denser particles, the ability to keep the larger particles suspended is a limiting factor. The use of higher viscosity liquids can help in this case.

Coincident passage of two or more particles through the sensing zone is a potential source of error in EZS measurements. Coincidence can cause the instrument to count the combined pulse height of multiple small particles as a single large particle, thereby skewing the size distribution towards the high end. A pulse discrimination system can be adjusted to correct for this effect by rejecting distorted pulses. Another potential problem is particle asymmetry. Asymmetric (flaky) particles, commonly found in cement, rotate as they pass through the orifice. Since it is the volume swept out by the particle that is measured, this can also lead to oversizing. Porous particles (e.g., fly ash) are generally unsuitable for EZS measurements, because their effective densities are not known.

2.3 Scanning Electron Microscopy

In this method, a focused electron beam (5 kV to 50 kV) is scanned over the sample in parallel lines. The particles are fixed onto a planar substrate, and are normally coated with a thin conductive layer, often an amalgam of gold and palladium. The electrons interact with the sample, producing an array of secondary effects, such as back-scattering, that can be detected and converted into an image. The image can then be digitized and presented to an image analyzer, which uses complex algorithms to identify individual particles and record detailed information about their morphology. In this manner, size and shape can be accurately assessed, but only for a relatively small population of particles (a few hundred at best). By comparison, most ensemble techniques (e.g., LAS) sample thousands or tens of thousands of particles simultaneously. Scanning electron microscopy (SEM) is therefore a *particle counting* technique and produces a number-weighted size distribution. In actuality, SEM measures the projected surface area diameter or length.

Limitations and errors in the SEM method generally arise from two sources: sample preparation and image distortions or irregularities. Probably the single largest source of error is sample preparation. In order for the analyzer to avoid confusing single particles that are touching (coincident) with larger particles or agglomerates, the primary particles must be well dispersed in a monolayer on the substrate surface, and must be clearly separated from each other. Specimens formed by drying of a dilute suspension onto a SEM support often contain agglomerates that form during the drying process. Specimens formed from a dry powder always exhibit agglomerative artifacts, and are not suitable for size assessment. In addition, the particles in the test specimen must be homogeneously distributed over the measurement field, so that the analysis accurately reflects the true distribution. Segregation of particles during sample preparation can lead to heterogeneous deposition, which can cause large systematic errors. An additional source of uncertainty comes from the poor statistical sampling that results from the relatively low number of particles counted by SEM analysis, compared with ensemble methods like LAS or other single particle counting techniques like EZS.

A practical resolution of 15 nm to 20 nm can be expected for SEM, establishing a lower limit for accurate particle size analysis of about 0.2 µm in secondary electron mode. An order of magnitude improvement can be obtained using the newer field emission SEM (FESEM), which has a practical resolution of about 1 nm. The FESEM uses lower electron voltages and generally does not require a conductive coating. The upper limit for imaging techniques like SEM is statistically-limited, since fewer large particles will be present in the same imaging field, and thus as the particle size increases it will require a prohibitively large number of separate specimens to obtain a statistically acceptable number of particles. This counting issue will be especially important at the upper size range for cement, where particles approach 100 µm in diameter. The image analyzer can be calibrated using a standardized graticule.

The primary benefit of SEM analysis is that it provides highly detailed information about not only particle size, but also particle shape, surface texture and chemical composition, and at resolutions not approachable by other techniques. Transmission electron microscopy (TEM), which measures the transmitted electron beam after it passes through the sample, is applicable for particle sizing in the extreme lower size limit, below 0.2 µm, although much of the three dimensional information is lost in this case. Drawbacks of using electron microscopy as a routine sizing method are time, high cost and the high level of operator expertise and training necessary.

2.4 Sedimentation

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 (i.e., free falling). For low Reynolds numbers (i.e., laminar flow conditions), the terminal velocity depends on the density contrast between the particle and medium, the viscosity, and the particle size.

Applications of sedimentation can be grouped into cumulative and incremental techniques [11]. In the cumulative method, the rate at which the particles settle is determined, typically by weighing the mass of settled particles at a certain depth over time. In the incremental method, the change in concentration or density of the material with time is measured at known depths, typically using optical or X-ray sensing. Because of the faster analysis time and better suitability for automation, incremental methods have found greater commercial application. In particular, the X-ray sedimentation (XGS) method is well established in several industries. In XGS, the absorption of a thin horizontally collimated X-ray beam is determined at a known depth and time, and referenced to the absorption of the pure solvent. The absorption caused by the presence of the particles at a specified depth at a given time is proportional to the concentration (by mass) of particles at that depth having a diameter smaller than d_S, where d_S is the calculated Stokes diameter. By measuring the particle density at different depths and times, a cumulative mass-averaged distribution is generated.

Stokes' Law is valid only if the Reynolds number (*Re*) does not exceed about 0.25 (in order for the error in the Stokes' diameter not to exceed about 3 %) [12]. Since *Re* is a function of particle size, this permits calculation of a well-defined upper size limit for sedimentation methods. Portland cement is commonly assigned a density of 3.2 g/cm^3. This value does not consider that different particles will have different density values depending on their composition, it simply applies a single mean density value for the powder. It also does not consider that variations in cement formulations will undoubtedly impact the average density. For purposes of estimating the upper limit, we will use a value of 3.2 g/cm^3. The largest (spherical) particle diameter that can be sized accurately using XGS is therefore about 95 µm in isopropyl alcohol at 25 °C. Particles larger than this value will settle more slowly than the velocity predicted by Stokes' Law. The upper size limit can be increased by using a suspending fluid with a higher viscosity. Irregularly shaped particles should settle according to their equivalent spherical volume at very low *Re* values. At higher *Re* values, the drag force is greater for asymmetric particles compared to spherical particles of an equivalent volume, and so the settling rate will decrease relative to Stokes' Law. For fine particles, 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 isopropyl alcohol. Convection currents in the settling suspension may further limit the lower size range. Although instrument manufacturers frequently claim a lower limit of 0.2 µm, XGS results for particles smaller than a micrometer must be viewed with a critical eye.

The only parameters required for XGS are the density of the solid and liquid phases, and the viscosity of the pure liquid. Particle concentrations required for XGS analysis depend on the X-ray absorption properties of the solid, but for ceramics are typically around 1 % to 3 % in terms of volume fraction. The correct sample concentration will reduce the X-ray beam intensity by roughly 20 % to 30 % [13]. The particles must remain stable against agglomeration during settling. An unstable suspension will exhibit a distribution skewed toward larger sizes. Dispersing agents, coupled with pH adjustment, are commonly utilized to increase stability in aqueous systems.

Gravitational sedimentation has limited practical value for particles under a few micrometers in diameter due to the prohibitively long settling times. It is not uncommon for a single size distribution analysis to require six hours or more, depending on the finest size fraction present. By replacing the gravity field with a centrifugal field, smaller particle sizes can be analyzed in much shorter periods of time. The underlying principles for centrifugal sedimentation are largely the same as in the gravitational case, but the calculations and measurement geometry are more complex because the particle velocity increases with distance from the center of rotation. Since most commercial instruments based on the centrifugal method are designed principally for the analysis of very fine particulates, the upper size range tends to be rather low (typically between 2 µm and 10 µm). On the low size end, the analysis range can extend down to about 0.01 µm, depending on the speed of the centrifuge and the sensitivity of the detection system. Centrifugal systems use either light or X-ray detection to determine particle concentration as a function of distance.

2.5 Sieving

Sieving is a simple and widely used method of classifying powders according to their physical size alone, independent of other physical or chemical properties, by using a series of woven wire or punch plate sieves arranged in decreasing order of aperture size [14]. The sieve method covers a wide particle size range, from roughly 37 µm to 125 mm using woven wire sieves [15]. Micromesh sieves extend the lower size range to about 5 µm, but as the aperture decreases in size, the time required to sieve an equivalent mass of powder increases. Sieves are identified according to their ASTM mesh size, where a 400 mesh sieve corresponds to a minimum square aperture of 37 µm. A variety of sieve aperture ranges are available. Sieving can be performed either dry or wet, with manual or machine agitation, and for a set time or until a sufficiently low and constant powder flow rate is observed through the sieves. Key variables that influence sieving results include particle shape, presence of very fine particles, initial sieve loading, time and method of agitation, and cohesiveness of the powder (in dry sieving only). Repeatability can be high, although reproducibility is often poor due to the many variables that provide sources for user error [11].

Because of size limitations at the lower end, sieving, by itself, is not a suitable method for characterizing the complete PSD of cement powders. In conjunction with other methods, however, it can serve as a means for pre-classification of powders. Overall, sieving is better suited for analyzing the large size fraction contained in cement powders, i.e., larger than 50 µm.

3 Analysis of data from the Round-robin

ASTM committee C01.25.01 sponsored a round-robin test to measure the PSD of cement. The participants were asked to use the PSD technique that they routinely use. The data requested from the participants included only the measurement method and the cumulative PSD. No detailed description of the procedure was required. Twenty-one organizations participated and the first four methods described in Section 2 were used. The identity of participant organizations remains confidential, therefore a letter is used to distinguish between participants.

Four portland cements provided by the Cement and Concrete Reference Laboratory (CCRL) to all participants were included in the tests: 131, 132, 135 and 136 (the numbers were assigned by CCRL). The characteristics of these cements, as measured in the CCRL proficiency program, are given in Appendix A. The standard cement, SRM 114p, was also used to establish a reference PSD for cement.

Appendix B summarizes in a tabular format all PSD data received from the participants of the round-robin. In the remainder of this section, the data is analyzed first to establish the reference distribution using SRM 114p and then to provide a detailed examination of the data with results for the four portland cements arranged according to measurement method. Unfortunately, in some cases (e.g., SEM, sieving), only a single set of results is available to represent each method. Therefore, it is not possible to analyze reproducibility between laboratories in those cases. Later in this report (Section 4), we provide a direct comparison of methods.

3.1 Reference distribution using SRM 114p

The round-robin results for SRM 114p were analyzed separately from the other cements with the objective of producing a reference material that instrument operators could use to "calibrate" their systems or at least validate their methodology. In other words, the reference distribution of SRM 114p could be used to check that the PSD results obtained by a particular instrument fall within a defined margin of error, or it could be used to offset the measured values by a size-range-dependent factor in order to bring them within the acceptable margin of error. To achieve this goal, two approaches were considered:

1. Establish a single calibration curve that represents an average distribution for all methods inclusive.
2. Establish a single calibration curve for each method, e.g., LAS-W or EZS.

Both approaches have advantages and disadvantages. In the first case (Approach 1), the calibration curve would be less precise (greater margin of error) due to variations in the precision of different methods being averaged. On the other hand, the first approach is simpler and more convenient because everyone would use the same calibration curve. In the second case (Approach 2), the distribution could be more precise, because variations resulting from differences in measurement principle or precision would be eliminated. As a disadvantage, several calibration curves would have to be established: one for each method.

From the data in Appendix B, there were 15 participants using the LASER diffraction method with the specimen dispersed in a liquid (LAS-W), while no more than two participants used any other method. Thus, following Approach 2 leads to the determination only of the calibration curve for LAS-W. Obviously, all 21 sets could be used if Approach 1 is followed.

Another key issue is to eliminate outliers from the calculation of the reference distribution curve. A criteria for determining outliers was needed. By examining the data in Appendix B for SRM 114p, it is clear that some sets of data are so different from the others that they can be considered as outliers (Figure 1). It is obvious that sets R and L should not be considered. To determine the outliers from the rest of the data, a more sophisticated method called bootstrapping was used. A description of this method and its use is presented in Appendix C. Full discussion of how to select the outliers and determine the mean distribution will be discussed in Sections 3.1.1 and 3.1.2.

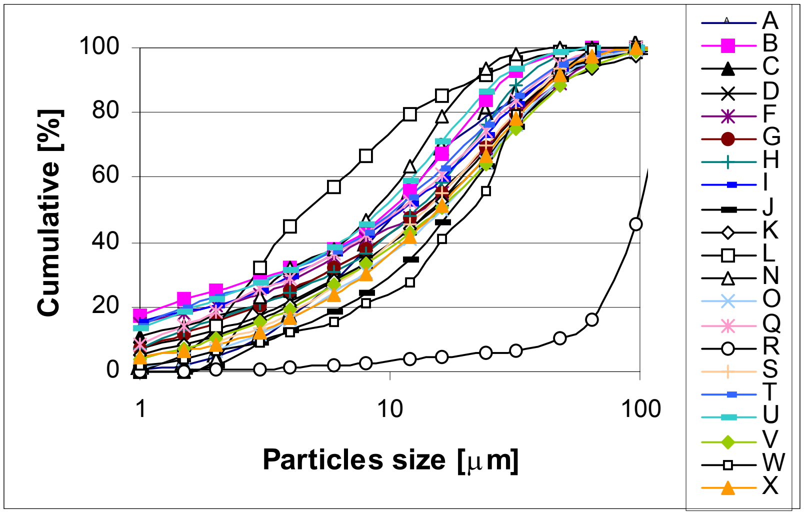

Figure 1: All data from SRM 114p.

3.1.1 Determination of reference distribution using Approach 1: all methods

Table 2 shows the results obtained from all SRM 114p data without sets R and L. It also shows the mean and the two-sided 95 % confidence limits as calculated using the bootstrap method (detailed on this method in Appendix C). The next step is to determine any outliers. The bootstrap method does not give the criterion needed to determine the outlier. Therefore, we arbitrarily selected the following criterion: if an organization's set of data contained more than four data points that are more than 5 % absolute value outside the confidence limits of all data sets, then it is considered an outlier. The absolute value 5 % is defined as the difference between the measured value and the confidence limits, high or low.

Table 2: Data from all methods except sets L and R. The results from the Bootstrap calculation are also shown. Data that lie outside the 95 % confidence limits are shown in bold, and data that are greater than 5 % outside the 95 % confidence limits are indicated as gray cells.

Size	Data from all devices																			Bootstrap results		
[μm]	A	B	C	D	F	G	H	I	J	K	N	O	Q	S	T	U	V	W	X	Mean	Low	High
1	**0.5**	**17.2**	**10.7**	6.9	**15.1**	6.8	7.1	**15.7**		**5.2**	**0.0**	**1.3**	8.3		**14.4**	**13.6**	**3.9**	**2.2**	**4.5**	7.9	5.4	10.51
1.5	**2.0**	**22.2**	**14.3**	10.3	**18.2**	11.7	12.6	**18.3**	**0.1**	8.3	**0.1**	**3.6**	**14.2**		**19.9**	**18.6**	7.4	**3.9**	**6.4**	10.7	7.2	14.06
2	**4.4**	**25.2**	**17.0**	12.9	**20.6**	15.2	16.1	**20.7**	**2.2**	11.1	**3.9**	**6.3**	**18.5**	**9.0**	**23.3**	**22.4**	10.2	**6.7**	**8.3**	13.4	10.1	16.58
3	**10.3**	**29.1**	21.4	17.6	**23.7**	20.5	20.8	**25.2**	**8.8**	16.2	**23.0**	**11.5**	**25.6**	**13.6**	**27.8**	**27.4**	**15.1**	**8.8**	**12.3**	18.9	16.2	21.75
4	**16.5**	**32.1**	25.2	21.5	**27.6**	24.8	24.4	**29.3**	**12.9**	20.6	**32.0**	**16.3**	**29.1**	**18.1**	**31.2**	**31.2**	**19.5**	**12.3**	**16.4**	23.2	20.5	26.17
6	27.6	**37.7**	31.9	28.2	**35.0**	31.8	30.6	**36.3**	**18.9**	28.0	**38.1**	**24.2**	**36.2**	**26.1**	**37.2**	**38.5**	*27.0*	**15.4**	**23.9**	30.2	27.4	32.98
8	38.2	**43.4**	37.5	34.0	**40.8**	37.6	36.5	**42.1**	**24.1**	34.1	**46.7**	**30.5**	**42.3**	**33.1**	**43.1**	**45.4**	**33.1**	**21.3**	**30.4**	36.6	33.2	39.41
12	**54.8**	**55.6**	47.3	44.1	47.6	47.3	48.0	**51.7**	**34.7**	44.1	**63.4**	**41.0**	**52.4**	45.2	**53.8**	**59.2**	**42.8**	**27.4**	**41.5**	47.5	43.7	51.21
16	**68.2**	**67.2**	55.6	**53.0**	55.3	55.4	58.6	59.9	**45.8**	**52.5**	**78.7**	**50.0**	60.8	55.2	**62.7**	**71.1**	**50.9**	**41.1**	**51.0**	57.4	53.8	61.37
24	**78.8**	**84.1**	69.0	68.7	69.1	69.2	*76.6*	73.2	**63.5**	**66.1**	**93.8**	**65.0**	74.3	70.0	76.1	**86.4**	**64.3**	**56.0**	**66.6**	72.1	68.5	76.26
32	84.1	**92.8**	**79.3**	78.9	**79.4**	79.8	**88.4**	82.9	**75.9**	**76.2**	**98.0**	**76.6**	83.9	80.3	85.2	**93.8**	**74.9**	**79.7**	**78.3**	82.6	79.9	85.63
48	92.7	**98.6**	**91.4**	91.8	**89.0**	92.5	**97.8**	93.7	**90.2**	**88.2**	**99.8**	**90.3**	*94.7*	93.6	*94.7*	**98.7**	**88.3**	**91.4**	91.7	93.1	91.6	94.62
64	**96.3**	**99.9**	**96.3**	96.7	**95.4**	97.8	**99.6**	98.0	**95.5**	**93.7**	**100.0**	**96.3**	**98.7**	97.6	98.0	**99.7**	**94.5**	**99.2**	97.3	97.4	96.6	98.18
96	99.4	**100.0**	**98.9**	99.2	99.2	99.6	**100.0**	**100.0**	**98.5**	**97.4**	**100.0**	99.4	**100.0**	99.3	99.7	**100.0**	**98.7**	**100.0**	**100.0**	99.4	99.11	99.72
128	**99.9**	**100.0**	99.5	99.7	99.5	99.8	**100.0**	**100.0**	99.3	**98.1**	**100.0**	99.6	**100.0**	99.8	**100.0**	**100.0**	99.7	**100.0**	**100.0**	99.73	99.49	99.89

In Table 2, all data points that are outside the confidence limits are in bold and data points of more than absolute value 5% outside the confidence limits are in gray cells. So, if any column contains more than 4 data in a gray cell, than that data set is an outlier. Using this criterion, the sets A, B, J, N, T, U and W were considered outliers.

The next step is to recalculate mean distribution of SRM 114p and its 95 % confidence limits without the outliers. The reason of this recalculation is to have a better-defined distribution. This was done again using the bootstrap method and the results are shown in Table 3. Figure 2 shows the data with the bootstrap mean and 95 % confidence limits, after the outliers were eliminated. It is clear that the distribution obtained is narrower than shown in Figure 1. The data in Table 3 could be used to correct the data obtained by all methods as shown in Appendix D-1.

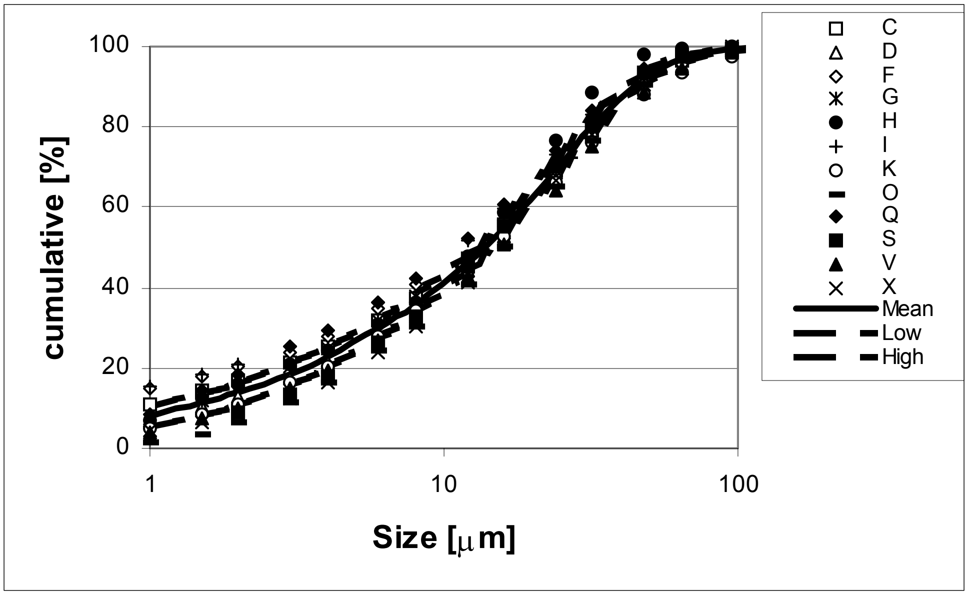

Figure 2: Data with the Bootstrap mean after the outliers are eliminated.

Table 3: Bootstrap mean and 95 % confidence limits calculated without the outliers.

Size [μm]	1	1.5	2	3	4	6	8	12	16	24	32	48	64	96	128
Mean	7.8	11.4	13.8	18.6	22.8	29.9	36.0	46.1	54.8	69.4	79.9	91.9	96.8	99.3	99.6
Low	5.5	8.7	11.1	16.0	20.2	27.5	33.7	44.2	53.0	67.4	78.0	90.5	95.9	98.8	99.3
High	10.4	14.1	16.4	21.2	25.3	32.1	38.3	48.1	56.6	71.6	82.2	93.5	97.8	99.7	99.9

Therefore, the methodology that uses the mean curve to correct the data measured by various instruments would be:

- Calculate the correction factor for each size, defined as the ratio between the measured value and the mean value as shown in Table 3. It should be noted that in this round-robin test the particle sizes shown in Table 3 were arbitrarily pre-selected.
- Multiply all measured data by this correction factor.

This procedure was applied to the four cements used in this study using all the data sets available with the exception of sets R and L because they were clear outliers. Appendix D-1 shows graphs of all data.

This method could then be used to correct data obtained with any method and could be considered as a calibration of the instrument. Unfortunately, it is not that simple. If the results obtained would have being considered outliers, (i.e., sets of data that are more than 5 % absolute value outside the confidence limits obtained with the Bootstrap method), the correction is not enough. This can be seen in Figure 3A where sets W, J or N are still clearly outside the confidence limits. On the other hand if the data set is within the confidence limits, the correction factor will reduce the spread of the data (Figure 3B). Therefore, the reference SRM 114p could be used in two ways:

- To check that the measurements are within acceptable range of the reference. This will allow the operator to determine if experimental errors or malfunctioning of the instrument should be considered
- To calibrate the instrument by correcting the results obtained using the reference cement

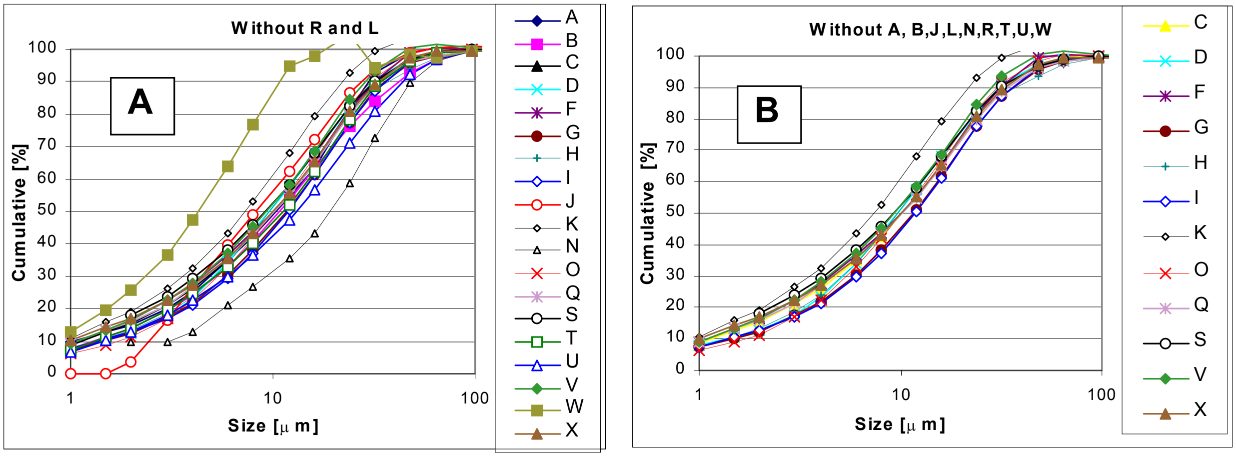

Figure 3: Example of correction obtained using the correction factor. The cement used was CCRL 131. (A) only the outliers R and L were not plotted; (B) the outliers identified by the bootstrap method are not included

3.1.2 Determination of the reference distribution for LASER wet only (Approach 2)

If the same procedure is followed but this time using only the data obtained by Laser wet (LAS-W), new Bootstrap mean and 95 % confidence limits can be calculated (Table 5). Using the same criteria as in Approach 1 (Section 3.1.1) the outliers are the set B, J, N and U. The outliers are the same as in the first case with the exception of set T. It is not quite clear why set T is an outlier in this case. The Bootstrap mean can then be calculated without using the outliers and this is shown in Table 4. These data could be used to calculate the correction factor as shown above (Section 3.1.1). The resulting size distributions are shown in Appendix D-2.

Table 4: Bootstrap data for the LAS-W without the outliers (B, J, N , U)

Size [µm]	1	1.5	2	3	4	6	8	12	16	24	32	48	64	96	128
Mean	8.7	12.6	15.5	20.2	24.2	32.2	37.2	47.2	55.9	70.3	80.8	92.4	97.0	99.4	99.7
Low	6.3	9.4	12.2	17.1	21.5	28.6	34.7	44.6	53.8	68.1	78.9	90.8	96.1	98.9	99.3
High	11.3	15.4	18.3	23.1	27.0	33.7	39.8	49.7	58.4	72.7	83.2	94.0	97.9	99.8	99.9

3.1.3 Summary

Two approaches to determine the reference distribution for cement were examined. In Approach 1 all data available with no consideration of the measurement method were used. On Approach 2 only the data generated with the LAS-W method were used. In both cases, a mean distribution was generated. Figure 4 shows the two distributions generated. It can be noticed that the two curves are not very different, but somewhat higher values are calculated, especially in the fines, when only the LAS-W data are used.

In the second step, the cements were corrected using a correction factor. The correction factor is the ratio between the measured data and the reference distribution. The results of this correction are shown in Appendix D-1 and D-2.

The calculated mean distribution curve could be used as a reference to calibrate any instrument to be used for measuring the PSD of cement. Eventually, this method for generating the reference distribution could be standardized and be attached to the specifications of the SRM 114p or any other future SRM cement.

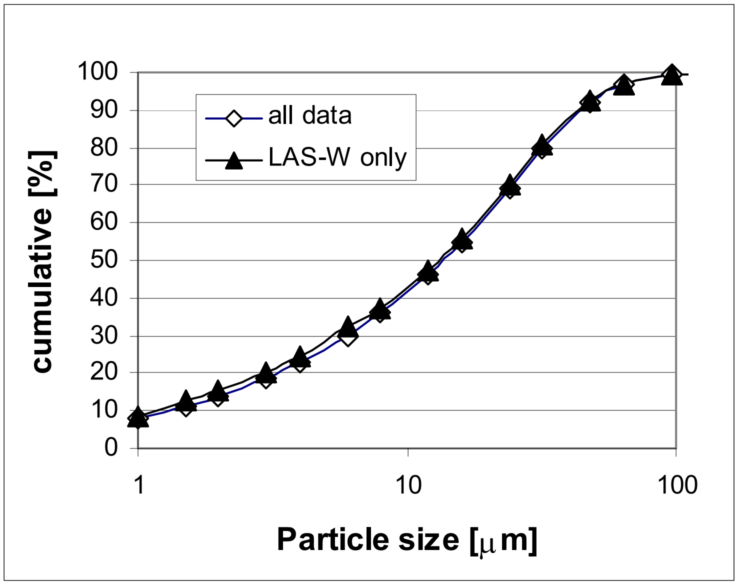

Figure 4: Comparison between the distribution calculated from all the data and the one calculated from only the LAS-W data.

Table 5: Data from LAS-W without the sets L and R. The results from the Bootstrap calculation is also shown. In bold the data that are outside the 95 % confidence limits and in the gray area the data that are more than 5 % outside the 95 % confidence limits.

Size	Data from LASER Wet															Bootstrap results		
[μm]	B	C	D	F	G	H	I	J	K	N	O	Q	T	U	X	Mean	Low	High
1	**17.2**	10.7	6.9	**15.1**	6.8	7.1	15.7	**-**	**5.2**	**0.0**	**1.3**	8.3	**14.4**	**13.6**	**4.5**	8.9	6.4	12.1
1.5	**22.2**	14.3	10.3	**18.2**	11.7	12.6	18.3	**0.10**	**8.3**	**0.05**	**3.6**	14.2	**19.9**	**18.6**	**6.4**	11.8	8.5	15.2
2	**25.2**	17.0	12.9	**20.6**	15.2	16.1	20.7	**2.2**	**11.1**	**3.9**	**6.3**	**18.5**	**23.3**	**22.4**	**8.3**	14.9	10.9	17.9
3	**29.1**	21.4	17.6	**23.7**	20.5	20.8	25.2	**8.8**	**16.2**	23.0	**11.5**	**25.6**	**27.8**	**27.4**	**12.3**	20.8	17.2	23.5
4	**32.1**	25.2	21.5	**27.6**	24.8	24.4	29.3	**2.9**	**20.6**	**32.0**	**16.3**	**29.1**	**31.2**	**31.2**	**16.4**	24.9	21.1	27.6
6	**37.7**	31.9	**28.2**	**35.0**	31.8	30.6	36.3	**18.9**	**28.0**	**38.1**	**24.2**	**36.2**	**37.2**	**38.5**	**23.9**	31.7	29.0	34.4
8	**43.4**	37.5	**34.0**	**40.8**	37.6	36.5	42.1	**24.1**	**34.1**	**46.7**	**30.5**	**42.3**	**43.1**	**45.4**	**30.4**	37.8	34.7	40.8
12	**55.6**	47.3	**44.1**	47.6	47.3	48.0	51.7	**34.7**	**44.1**	**63.4**	**41.0**	52.4	**53.8**	**59.2**	**41.5**	48.7	45.2	52.5
16	**67.2**	55.6	**53.0**	**55.3**	**55.4**	58.6	59.9	**45.9**	**52.5**	**78.7**	**50.0**	60.8	62.7	**71.1**	**51.0**	58.4	55.0	63.1
24	**84.1**	**69.0**	**68.7**	**69.1**	**69.2**	76.6	73.2	**63.5**	**66.1**	**93.8**	**65.0**	74.3	76.1	**86.4**	**66.6**	73.5	69.7	78.9
32	**92.8**	**79.3**	**78.9**	**79.4**	79.8	**88.4**	82.9	**75.9**	**76.2**	**98.0**	**76.6**	83.9	85.2	**93.8**	**78.3**	83.3	80.1	87.2
48	**98.6**	**91.4**	**91.8**	**89.0**	92.5	**97.8**	93.7	**90.2**	**88.2**	**99.8**	**90.3**	94.7	94.7	**98.7**	**91.7**	93.5	91.9	95.6
64	**99.9**	**96.3**	96.7	**95.4**	97.8	**99.6**	98.0	**95.5**	**93.7**	**100.0**	**96.3**	**98.7**	98.0	**99.7**	97.3	97.5	96.6	98.5
96	**100.0**	98.9	99.2	99.2	99.6	**100.0**	100.0	**98.5**	**97.4**	**100.0**	99.4	**100.0**	99.7	**100.0**	**100.0**	99.5	98.9	99.7
128	**100.0**	99.5	99.7	99.5	99.8	**100.0**	100.0	99.34	**98.1**	**100.0**	99.6	**100.0**	100.0	**100.0**	**100.0**	99.7	99.3	99.9

3.2 Analysis of the data by method

3.2.1 LASER Diffraction with the specimen dispersed in a liquid (LAS-W)

The plot of all data using the LAS-W technique is shown in Appendix E. Clearly, there is significant, although not large, scatter in this data. As shown in Table 6 (columns labeled "all data"), this scatter is reflected in the calculated median (50 % of mass less than) diameters. As discussed on Section 3.1.2, the sets B, J, N, and U were found to be outliers and it was shown that the correction factors are not enough to correct them. Therefore, the median was recalculated without these sets. Table 6 shows how the median diameters and their standard deviations change with the elimination of the outliers. The standard deviation is reduced but not for all cements. For instance CCRL 131 median size did not change. By looking at the graphs in Appendix E, it is clear that different outliers could be picked if instead of cement 114p another of the other cements was taken as the reference. As no details are known from these measurements, it is hard at this time to determine why.

Table 6: Average median diameter from LAS-W method.

Cement	All data		no B J N U	
	Median Diameter [μm]	Standard Deviation [μm]	Median Diameter [μm]	Standard Deviation [μm]
114P	12.9	2.6	13.3	1.8
131	10.3	2.4	10.2	2.4
132	8.0	2.4	7.3	1.1
135	12.2	1.7	12.1	1.4
136	12.9	2.0	12.7	1.6

3.2.2 LASER diffraction with the specimen dispersed in air (LAS-D)

The plot of the measurements is shown in Appendix E. As we have only two PSDs to consider, and no indication of the methods used to disperse the material for analysis, it is not possible to determine the specific reasons for the observed variations. It is also impossible to determine the outlier, other than by comparing with the other methods distribution. In that case the set L is an outlier. Table 7 shows the median for the two sets with the standard deviation and the median for the set V (the set supposedly correct). The median values of V are higher than the ones of the average of sets L and V.

Table 7: Average median diameter from LAS-D method.

Cement	Median Diameter [μm]	Standard Deviation [μm]	Median diameter only V [μm]
114P	10.2	7.5	15.6
131	7.4	4.7	10.7
132	6.0	2.5	7.8
135	8.9	6.9	13.8
136	10.8	7.6	16.2

3.2.3 Electrical Zone Sensing (EZS)

The plot of the measurements is shown in Appendix E. As we have only two PSDs to average, and no indication of the methods used to disperse the material for analysis, it is not possible to determine the specific reasons for the observed variations. It is also impossible to determine the outlier, other than by comparing with the other methods distribution. In that case the set R is an outlier. Table 8 shows the median for the two sets with the standard deviation and the median for the set W (the set supposedly correct). The median values of W are lower than the average of the R and W. On the other hand, the set W was also considered an outlier when SRM 114p was analyzed (see Section 3.1.1). As we have no other data, there is no possibility of determining a better value for this method.

Table 8: Average median diameter from EZS method.

Cement	Median Diameter [μm]	Standard Deviation [μm]	Median diameter only W [μm]
114P	59.9	55.4	20.8
131	14.7	7.2	9.6
132	45.0	53.9	6.8
135	48.2	57.1	7.8
136	50.0	54.2	11.7

3.2.4 SEM and Sedimentation (SED)

The other two measurements methods, SEM and Sedimentation (SED), did not have replicates. Therefore, we cannot perform a similar analysis as done with the other three methods examined here. Nevertheless, Table 9 shows the median diameters calculated for the two methods.

Table 9: Median diameters by SEM and Sedimentation

Cement	Median Diameter [μm]	
	SEM	Sed.
114P	10.8	13.9
131	9.0	10.1
132	10.1	7.7
135	10.8	12.2
136	10.4	13.1

3.2.5 Summary

The following findings are observed:

- The measurement by LAS-W exhibited some scatter, but elimination of outliers reduced the scatter considerably.
- The measurements by LAS-D or by EZS show a very large scatter. Because of the small data set size (2 PSDs per measurement method), it is not possible to determine the source of this scatter nor to determine which, if either, of the PSDs is an outlier, unless the data are compared to all the other sets.

The possible reasons that could explain some of the scatter observed in the data from all these tests are:

- The parameters used to determine the distribution from the measurement assume certain values for material properties, such as the index of refraction of the cement and of the medium or the density of the particles. Since these parameters are not standardized, and were not reported by the participants, different laboratories may have used different or incorrect values.
- The experimental conditions, such as the dispersion medium, the preparation of the specimen (dispersion method), as well as the instrument used to measure the PSD, may have varied between laboratories.

These observations point to the difficulties in determining the correct method and value for a cement PSD. In future round-robin testing, care should be taken to ensure that the same sample preparation method is used for each technique and that the parameter values used by the operators are also the same or determined using the same method. We recommend that the ASTM committee address the issue of determining the correct experimental set-up and sample preparation protocol for each measurement method.

4 Comparison of the various methods used

To compare all the particle size distributions measured with the various sets, an average distribution could be calculated for each measurement method. The recommended procedure to calculate this representative curve should be to use the Bootstrap method to calculate the mean and the two sided 95 % confidence limits, given the data for each measurement method. But as only the LAS-W has enough data to justify such a procedure, the average median diameters will be used as a comparison. Also, the calculation of median values from only two sets and in some cases one set should be used with caution. In an ideal situation, all the median diameters should be identical regardless of the method used. It is clear that is not the case in Figure 5.

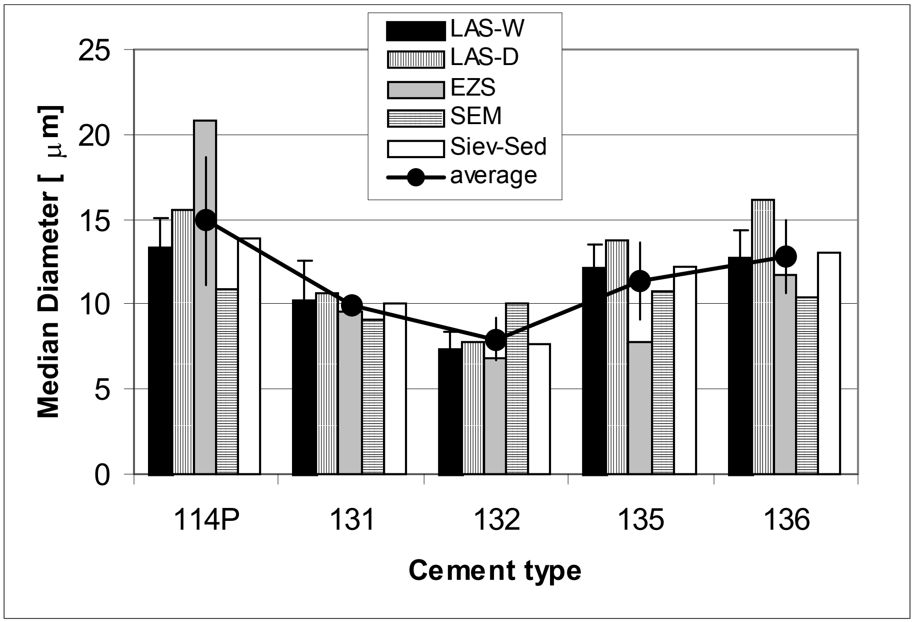

Figure 5: Bar graph of the median diameters for all the methods.

The following observations can be made:

- If only the LAS-D data from set V is considered, then the data corresponds very closely with the LAS-W method. As this similarity between the two methods is based on only one data set for LAS-D, more testing is needed to verify this similarity.
- The EZS does not compare with the other methods. However, it should be kept in mind that the only value that we considered was set W, which was considered an outlier for SRM 114p. The other set available was R, which was also considered an outlier for SRM 114p.
- Depending on the cement used, the SEM method median value is either higher or lower than the average value. Only once for cement CCRL 131, the SEM value is similar to the others. But again this is the result from only one set, therefore, there is not enough evidence for indication of variability. It should be also noted that the SEM seems to "see" fewer small particles and more larger one, as shown by the graphs in Appendix E. This is probably due to agglomeration of the small particles.

- The sedimentation method seems to follow the average of all methods. It should be noted that measurements below 3 µm in size were reported. As we do not have more details, it is impossible if this is a limitation due to the method or the reporting.

These are very preliminary findings because of the limited sample size (i.e., number of data) for most of the measurement methods and the lack of knowledge about the parameters used to interpret the measurements.

5 Conclusions

From this round-robin test, the most frequently used PSD measurement technique by the industry is LASER diffraction with dispersion of cement in a liquid. The SEM method, as applied in the current test, is relatively new and was used by only one participant in the round robin. Similarly, the sedimentation method was used by only one participant and it did not report data below 3 µm; it should be determined if this represents the complete PSD or if it is a reporting issue. There were two sets using EZS, but both were determined to be outliers based on measurements of the reference material SRM 114p. Because the scope of the ASTM committee is to determine the best method or methods to measure PSD of cement, the methods to be standardized should be carefully selected. In other words, the committee should concentrate its initial efforts on the most widely used and most promising measurement methods (e.g., wider range of size and better reproducibility).

In this first round-robin test, there was not enough information collected to be able to definitively determine the reference distribution using SRM 114p or to determine the best methods to measure the cement PSD. Therefore, the following recommendations should be considered in organizing the next round-robin:

- Reduce the number of cements (2-3 maximum)
- Provide with each sample a standard report form, in which the participant is asked to provide detailed information on procedures and parameters used during the tests.
- A draft protocol could be prepared for each method and the operator could be asked to measure the specimens using first this draft method and then their usual method at least for SRM 114p. This will allow the determination of whether the scatter is due solely to the protocol used or also could be attributed to the instrument used.
- Have several replicate measurements using the same method, instrument and cement

It is the belief of the authors that an ASTM standard should include a standard procedure for each method that is specialized for cement. It would certainly help if a reference distribution for a cement such as SRM 114p could be determined. This will help the operator determine if the PSD measured is within an acceptable error margin.

In conclusion, before a standard test can be proposed, further research needs to be conducted to determine the correct methodology for any of the tests discussed in this report.

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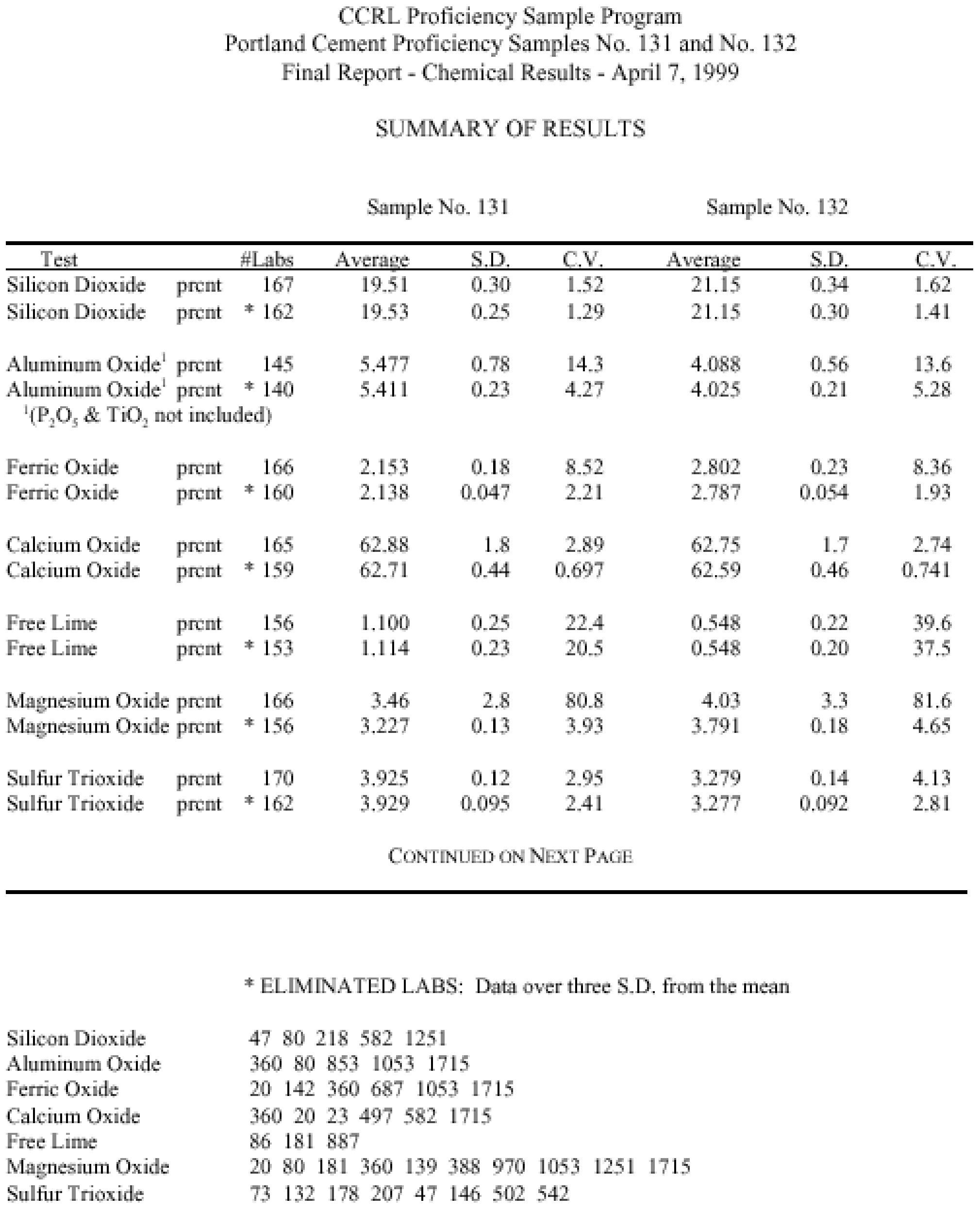
APPENDICES

TABLE OF CONTENT

Appendix A: Cement characteristics



CCRL Proficiency Sample Program
Portland Cement Proficiency Samples No. 131 and No. 132
Final Report - Chemical Results - April 7, 1999

SUMMARY OF RESULTS

			Sample No. 131			Sample No. 132		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
Silicon Dioxide	prcnt	167	19.51	0.30	1.52	21.15	0.34	1.62
Silicon Dioxide	prcnt	* 162	19.53	0.25	1.29	21.15	0.30	1.41
Aluminum Oxide[1]	prcnt	145	5.477	0.78	14.3	4.088	0.56	13.6
Aluminum Oxide[1]	prcnt	* 140	5.411	0.23	4.27	4.025	0.21	5.28
[1](P_2O_5 & TiO_2 not included)								
Ferric Oxide	prcnt	166	2.153	0.18	8.52	2.802	0.23	8.36
Ferric Oxide	prcnt	* 160	2.138	0.047	2.21	2.787	0.054	1.93
Calcium Oxide	prcnt	165	62.88	1.8	2.89	62.75	1.7	2.74
Calcium Oxide	prcnt	* 159	62.71	0.44	0.697	62.59	0.46	0.741
Free Lime	prcnt	156	1.100	0.25	22.4	0.548	0.22	39.6
Free Lime	prcnt	* 153	1.114	0.23	20.5	0.548	0.20	37.5
Magnesium Oxide	prcnt	166	3.46	2.8	80.8	4.03	3.3	81.6
Magnesium Oxide	prcnt	* 156	3.227	0.13	3.93	3.791	0.18	4.65
Sulfur Trioxide	prcnt	170	3.925	0.12	2.95	3.279	0.14	4.13
Sulfur Trioxide	prcnt	* 162	3.929	0.095	2.41	3.277	0.092	2.81

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* ELIMINATED LABS: Data over three S.D. from the mean

Silicon Dioxide	47 80 218 582 1251
Aluminum Oxide	360 80 853 1053 1715
Ferric Oxide	20 142 360 687 1053 1715
Calcium Oxide	360 20 23 497 582 1715
Free Lime	86 181 887
Magnesium Oxide	20 80 181 360 139 388 970 1053 1251 1715
Sulfur Trioxide	73 132 178 207 47 146 502 542

CCRL Proficiency Sample Program
Portland Cement Proficiency Samples No. 131 and No. 132
Final Report - Chemical Results - April 7, 1999

SUMMARY OF RESULTS

Test		#Labs	Sample No. 131 Average	S.D.	C.V.	Sample No. 132 Average	S.D.	C.V.
Loss on Ignition	prcnt	196	1.280	0.16	12.9	1.183	0.18	15.0
Loss on Ignition	prcnt	* 184	1.273	0.072	5.62	1.156	0.075	6.50
Insoluble Residue	prcnt	183	0.221	0.14	61.5	0.239	0.16	67.6
Insoluble Residue	prcnt	* 171	0.200	0.078	39.2	0.208	0.088	42.6
Sodium Oxide	prcnt	140	0.305	0.078	25.5	0.107	0.060	55.6
Sodium Oxide	prcnt	* 131	0.308	0.039	12.7	0.097	0.029	30.0
Potassium Oxide	prcnt	144	0.995	0.045	4.51	0.697	0.047	6.70
Potassium Oxide	prcnt	* 138	0.996	0.036	3.67	0.696	0.027	3.93
Phosphorus Pent	prcnt	68	0.199	0.060	30.3	0.162	0.047	29.0
Phosphorus Pent	prcnt	* 62	0.194	0.027	14.0	0.154	0.020	13.4
Titanium Dioxide	prcnt	80	0.216	0.052	24.1	0.261	0.060	22.8
Titanium Dioxide	prcnt	* 74	0.218	0.015	7.08	0.263	0.021	7.93

* ELIMINATED LABS: Data over three S.D. from the mean

Loss on Ignition	134 181 787 970 86 98 166 167 218 360 497 996
Insoluble Residue	90 146 159 413 582 19 93 497 853 887 996 1768
Sodium Oxide	388 497 611 8 142 996 1190 1251 1379
Potassium Oxide	23 181 360 388 493 1251
Phosphorus Pentoxide	360 107 146 996 1644 1676
Titanium Dioxide	360 107 440 911 996 1644

CCRL PROFICIENCY SAMPLE PROGRAM
Portland Cement Proficiency Samples No. 131 and No. 132
Final Report - Physical Results - April 7, 1999

SUMMARY OF RESULTS

			Sample No. 131			Sample No. 132		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
N.C. Water	prcnt	227	30.29	1.0	3.48	30.10	1.3	4.31
N.C. Water	prcnt	* 219	30.29	0.63	2.07	30.02	0.83	2.75
Vicat TS Initial	min	218	127.2	17.9	14.0	133.4	24.3	18.2
Vicat TS Initial	min	* 211	126.8	14.0	11.0	133.5	19.5	14.6
Vicat TS Final	min	217	237.4	39.7	16.7	248.7	37.4	15.0
Vicat TS Final	min	* 212	234.5	34.2	14.6	245.9	33.1	13.4
Gillmore TS Initial	min	178	165.7	27.9	16.9	176.4	28.5	16.2
Gillmore TS Initial	min	* 174	165.9	26.0	15.6	176.8	25.8	14.6
Gillmore TS Final	min	177	274.2	43.0	15.7	282.5	41.1	14.6
Gillmore TS Final	min	* 173	274.0	38.0	13.8	282.2	37.2	13.2
False Set	prcnt	188	75.0	10.3	13.8	54.2	25.4	46.8
False Set	prcnt	* 187	75.2	9.9	13.1	54.5	25.1	46.1
Autoclave Expan	prcnt	215	0.233	0.095	40.9	0.092	0.054	59.0
Autoclave Expan	prcnt	* 208	0.243	0.067	27.7	0.098	0.037	37.7
Air Content	prcnt	216	8.48	1.7	19.9	7.92	1.8	23.2
Air Content	prcnt	* 207	8.39	1.0	12.0	7.81	1.0	12.9
AC Mix Water	prcnt	212	69.75	8.5	12.1	70.03	9.5	13.6
AC Mix Water	prcnt	* 200	71.04	2.5	3.53	71.58	2.7	3.74
AC Flow	prcnt	212	88.3	8.6	9.69	87.2	8.5	9.75
AC Flow	prcnt	* 203	87.4	3.3	3.74	86.3	3.6	4.16

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* ELIMINATED LABS: Data over three S.D. from the mean

N.C. Water	37 73 96 242 687 691 1053 1435
Vicat TS Initial	25 31 33 49 126 515 917
Vicat TS Final	41 208 219 255 1174
Gillmore TS Initial	106 431 691 917
Gillmore TS Final	41 146 917 1435
False Set	1174
Autoclave Expansion	22 33 44 49 96 696 1190
Air Content	265 694 828 48 173 888 917 1379 1676
AC Mix Water	35 265 375 828 248 887 993 48 127 565 899 1435
Air Content Flow	84 73 166 248 611 687 887 993 996

CCRL PROFICIENCY SAMPLE PROGRAM
Portland Cement Proficiency Samples No. 131 and No. 132
Final Report - Physical Results - April 7, 1999

SUMMARY OF RESULTS

			Sample No. 131			Sample No. 132		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
Comp Str 3-day	psi	229	4872.4	344.5	7.07	4925.4	355.7	7.22
Comp Str 3-day	psi	* 227	4881.9	330.5	6.77	4936.2	337.6	6.84
Comp Str 7-day	psi	227	5561.7	371.1	6.67	5687.6	395.0	6.94
Comp Str 28-day	psi	172	6425.7	493.4	7.68	7081.4	542.3	7.66
Comp Str 28-day	psi	* 170	6447.6	450.6	6.99	7101.8	510.5	7.19
CS Flow	prcnt	189	99.2	12.6	12.8	94.1	13.1	13.9
CS Flow	prcnt	* 185	99.6	10.8	10.8	94.5	10.8	11.4
Fineness AP	sqcm/g	215	4945.7	331.6	6.70	5703.7	368.5	6.46
Fineness AP	sqcm/g	* 202	4966.2	225.1	4.53	5758.8	273.0	4.74
Fineness WT	sqcm/g	41	2467.6	153.3	6.21	2891.0	365.8	12.65
Passing 325 Sieve	prcnt	205	97.953	3.53	3.603	99.038	0.34	0.346
Passing 325 Sieve	prcnt	* 194	98.232	0.36	0.366	99.076	0.19	0.189

* ELIMINATED LABS: Data over three S.D. from the mean

Compressive Str 3-day	5 208
Compressive Str 28-day	1 25
CS Flow	52 98 265 493
Fineness Air Perm	41 43 64 94 912 5 123 207 231 257 694 970 1768
Passing No. 325 Sieve	101 222 515 611 684 787 106 166 242 619 828

CCRL Proficiency Sample Program
Portland Cement Proficiency Samples No. 135 and No. 136
Final Report - Chemical Results - March 24, 2000

SUMMARY OF RESULTS

			Sample No. 135			Sample No. 136		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
Silicon Dioxide	prcnt	146	21.440	0.32	1.49	20.842	0.34	1.63
Silicon Dioxide	prcnt	* 141	21.449	0.21	0.988	20.858	0.28	1.322
Aluminum Oxide[1]	prcnt	128	4.442	0.26	5.94	5.307	0.37	6.97
Aluminum Oxide[1]	prcnt	* 123	4.454	0.16	3.65	5.336	0.24	4.41
[1](P_2O_5 & TiO_2 not included)								
Ferric Oxide	prcnt	145	3.062	0.13	4.31	3.565	0.15	4.33
Ferric Oxide	prcnt	* 138	3.068	0.061	1.98	3.575	0.073	2.04
Calcium Oxide	prcnt	144	63.812	0.44	0.688	63.900	0.40	0.623
Calcium Oxide	prcnt	* 140	63.805	0.36	0.564	63.909	0.36	0.567
Free Lime	prcnt	145	0.644	0.20	31.4	0.587	0.22	37.3
Free Lime	prcnt	* 142	0.638	0.18	27.9	0.583	0.20	34.9
Magnesium Oxide	prcnt	143	2.426	0.22	8.96	1.539	0.25	16.03
Magnesium Oxide	prcnt	* 136	2.417	0.118	4.90	1.511	0.099	6.52
Sulfur Trioxide	prcnt	149	2.457	0.136	5.53	2.369	0.087	3.67
Sulfur Trioxide	prcnt	* 143	2.460	0.075	3.04	2.364	0.074	3.15

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: Data over three S.D. from the mean

Silicon Dioxide	19 36 156 178 582
Aluminum Oxide	5 206 582 881 1053
Ferric Oxide	4 80 121 162 582 1025 1053
Calcium Oxide	34 80 139 175
Free Lime	35 105 502
Magnesium Oxide	36 80 582 5 305 1053 1251
Sulfur Trioxide	80 162 36 206 252 1190

CCRL Proficiency Sample Program
Portland Cement Proficiency Samples No. 135 and No. 136
Final Report - Chemical Results - March 24, 2000

SUMMARY OF RESULTS

			Sample No. 135			Sample No. 136		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
Loss on Ignition	prcnt	179	0.810	0.10	12.6	1.632	0.21	12.8
Loss on Ignition	prcnt	* 162	0.809	0.066	8.11	1.659	0.061	3.68
Insoluble Residue	prcnt	165	0.192	0.23	122.2	0.278	0.19	69.8
Insoluble Residue	prcnt	* 158	0.156	0.073	46.8	0.252	0.067	26.7
Sodium Oxide	prcnt	123	0.197	0.038	19.6	0.114	0.032	28.4
Sodium Oxide	prcnt	* 115	0.199	0.023	11.8	0.113	0.022	19.2
Potassium Oxide	prcnt	125	0.829	0.045	5.40	0.224	0.026	11.83
Potassium Oxide	prcnt	* 119	0.834	0.022	2.59	0.226	0.014	6.27
Phosphorus Pent	prcnt	67	0.106	0.021	19.9	0.210	0.025	12.0
Phosphorus Pent	prcnt	* 60	0.106	0.013	11.99	0.209	0.017	8.20
Titanium Dioxide	prcnt	75	0.207	0.038	18.2	0.303	0.055	18.1
Titanium Dioxide	prcnt	* 68	0.215	0.016	7.39	0.319	0.018	5.64

: Data over three S.D. from the mean

Loss on Ignition	34 90 92 137 203 178 504 611 996 1053 1054 8 64 95 158 252 1174
Insoluble Residue	93 870 178 493 886 1053 1251
Sodium Oxide	494 996 1053 5 56 177 582 1916
Potassium Oxide	206 40 124 582 996 1053
Phosphorus Pentoxide	176 502 18 126 982 1190 1676
Titanium Dioxide	177 996 46 142 438 582 1676

CCRL PROFICIENCY SAMPLE PROGRAM
Portland Cement Proficiency Samples No. 135 and No. 136
Final Report - Physical Results - March 24, 2000

SUMMARY OF RESULTS

			Sample No. 135			Sample No. 136		
Test		#Labs	Average	S.D.	C.V.	Average	S.D.	C.V.
N.C. Water	prcnt	220	24.81	2.4	9.85	23.64	2.3	9.81
N.C. Water	prcnt	* 212	24.90	0.34	1.36	23.69	0.40	1.71
Vicat TS Initial	min	211	168	18.5	11.0	168	24.5	14.6
Vicat TS Initial	min	* 204	168	15.9	9.49	166	20.8	12.53
Vicat TS Final	min	209	279	40.6	14.5	292	46.2	15.8
Vicat TS Final	min	* 208	278	39.4	14.2	292	46.3	15.8
Gillmore TS Initial	min	172	197	27.3	13.8	202	34.6	17.1
Gillmore TS Initial	min	* 169	196	24.1	12.3	200	32.0	16.0
Gillmore TS Final	min	172	304	41.9	13.8	321	48.0	15.0
Gillmore TS Final	min	* 166	302	35.9	11.9	321	42.1	13.1
False Set	prcnt	184	65.8	12.8	19.5	75.0	8.7	11.7
False Set	prcnt	* 182	66.3	12.1	18.3	75.1	8.5	11.4
Autoclave Expan	prcnt	205	0.022	0.055	244	0.011	0.058	538
Autoclave Expan	prcnt	* 196	0.021	0.012	58.7	0.006	0.011	182.6
Air Content	prcnt	202	8.84	1.7	19.3	7.34	1.9	25.6
Air Content	prcnt	* 198	8.77	1.0	12.0	7.25	1.3	17.5
AC Mix Water	prcnt	203	68.37	5.6	8.16	67.92	5.7	8.37
AC Mix Water	prcnt	* 198	68.78	2.4	3.56	68.37	2.7	3.98
AC Flow	prcnt	202	87.1	3.4	3.91	87.6	3.4	3.87
AC Flow	prcnt	* 201	87.0	3.3	3.82	87.6	3.4	3.87

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: Data over three S.D. from the mean

N.C. Water	10 52 12 48 125 134 853 1251
Vicat TS Initial	12 48 49 207 246 375 497
Vicat TS Final	246
Gilmr TS Initial	408 431 1621
Gilmr TS Final	221 246 289 408 438 1435
False Set	289 687
Autoclave Expan	25 222 779 96 99 458 504 1251
Air Content	11 34 828 1054
Ac Mix Water	26 23 78 173 819
AC Flow	736

CCRL PROFICIENCY SAMPLE PROGRAM
Portland Cement Proficiency Samples No. 135 and No. 136
Final Report - Physical Results - March 24, 2000

SUMMARY OF RESULTS

Test		#Labs	Sample No. 135 Average	Sample No. 135 S.D.	Sample No. 135 C.V.	Sample No. 136 Average	Sample No. 136 S.D.	Sample No. 136 C.V.
Comp Str 3-day	psi	222	3688	272.9	7.40	3306	266.6	8.06
Comp Str 3-day	psi	* 217	3702	247.4	6.68	3325	237.2	7.13
Comp Str 7-day	psi	221	4599	314.2	6.83	4565	333.4	7.30
Comp Str 28-day	psi	170	5898	401.6	6.81	6033	382.1	6.33
Comp Str 28-day	psi	* 167	5885	358.8	6.10	6030	359.9	5.97
CS Flow	prcnt	183	147.5	415.9	282	151.0	422.3	280
CS Flow	prcnt	* 173	118.4	8.2	6.97	121.6	9.6	7.88
Fineness AP	sqcm/g	216	3932	117.8	3.00	3896	143.9	3.69
Fineness AP	sqcm/g	* 201	3928	79.0	2.01	3903	78.5	2.01
Fineness WT	sqcm/g	38	2042	389.5	19.1	1995	374.6	18.8
Fineness WT	sqcm/g	* 36	2122	129.6	6.11	2073	112.5	5.43
45μm Sieve	prcnt	201	95.161	1.00	1.05	91.440	0.98	1.07
45μm Sieve	prcnt	* 196	95.218	0.70	0.736	91.419	0.77	0.845

: Data over three S.D. from the mean

Comp Str 3-day	12 13 413 819 853
Comp Str 28-day	25 557 904
CS Flow	25 52 146 154 43 134 309 441 828 1644
Fineness AP	20 23 31 52 64 15 22 24 49 112 159 698 181 360 828
Fineness WT	175 441
45μm Sieve	18 178 221 828 1483

Appendix B: PSD data as received

114P

Lab	A	B	C	D	F	G	H	I	J	K	L	N	O	Q	R	S	T	U	V	W	X
[µm]	SEM	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-D	LAS-W	LAS-W	LAS-W	EZS	Sedim.	LAS-W	LAS-W	LAS-D	EZS	LAS-W
1	0.5	17.2	10.7	6.9	15.1	6.8	7.1	15.7	0.0	5.2	0.2	0.0	1.3	8.3	0.1		14.4	13.6	3.9	2.2	4.5
1.5	2.0	22.2	14.3	10.3	18.2	11.7	12.6	18.3	0.1	8.3	4.9	0.0	3.6	14.2	0.2		19.9	18.6	7.4	3.9	6.4
2	4.4	25.2	17.0	12.9	20.6	15.2	16.1	20.7	2.2	11.1	13.9	3.9	6.3	18.5	0.5	9.0	23.3	22.4	10.2	6.7	8.3
3	10.3	29.1	21.4	17.6	23.7	20.5	20.8	25.2	8.9	16.2	32.2	23.0	11.5	25.6	0.8	13.6	27.8	27.4	15.1	8.8	12.3
4	16.5	32.1	25.2	21.5	27.6	24.8	24.4	29.3	12.9	20.6	44.6	32.0	16.3	29.1	1.1	18.1	31.2	31.2	19.5	12.3	16.4
6	27.6	37.7	31.9	28.2	35.0	31.8	30.6	36.3	18.9	28.0	56.9	38.1	24.2	36.2	1.7	26.1	37.2	38.5	27.0	15.4	23.9
8	38.2	43.4	37.5	34.0	40.8	37.6	36.5	42.1	24.1	34.1	66.6	46.7	30.5	42.3	2.4	33.1	43.1	45.4	33.1	21.3	30.4
12	54.8	55.6	47.3	44.1	47.6	47.3	48.0	51.7	34.7	44.1	79.7	63.4	41.0	52.4	3.7	45.2	53.8	59.2	42.8	27.4	41.5
16	68.2	67.2	55.6	53.0	55.3	55.4	58.6	59.9	45.9	52.5	85.4	78.7	50.0	60.8	4.8	55.2	62.7	71.1	50.9	41.1	51.0
24	78.8	84.1	69.0	68.7	69.1	69.2	76.6	73.2	63.5	66.1	91.8	93.8	65.0	74.3	5.9	70.0	76.1	86.4	64.3	56.0	66.6
32	84.1	92.8	79.3	78.9	79.4	79.8	88.4	82.9	75.9	76.2	95.6	98.0	76.6	83.9	6.6	80.3	85.2	93.8	74.9	79.7	78.3
48	92.7	98.6	91.4	91.8	89.0	92.5	97.8	93.7	90.2	88.2	98.6	99.8	90.3	94.7	10.3	93.6	94.7	98.7	88.3	91.4	91.7
64	96.3	99.9	96.3	96.7	95.4	97.8	99.6	98.0	95.6	93.7	99.4	100.0	96.3	98.7	15.7	97.6	98.0	99.7	94.5	99.2	97.3
96	99.4	100.0	98.9	99.2	99.2	99.6	100.0	100.0	98.5	97.4	100.0	100.0	99.4	100.0	45.5	99.3	99.7	100.0	98.7	100.0	100.0
128	99.9	100.0	99.5	99.7	99.5	99.8	100.0	100.0	99.3	98.1	100.0	100.0	99.6	100.0	91.9	99.8	100.0	100.0	99.7	100.0	100.0

131

Lab [μm]	A SEM	B LAS-W	C LAS-W	D LAS-W	F LAS-W	G LAS-W	H LAS-W	I LAS-W	J LAS-W	K LAS-W	L LAS-D	N LAS-W	O LAS-W	Q LAS-W	R EZS	S Sedim.	T LAS-W	U LAS-W	V LAS-D	W EZS	X LAS-W
1	0.6	17.1	11.8	7.1	17.7	6.2	6.8	15.2	0.0	7.1	0.0	0.0	1.0	9.8	0.4		13.6	11.5	4.5	3.6	5.9
1.5	2.3	22.4	16.1	9.7	21.6	10.6	11.8	17.2	0.0	11.6	3.2	0.6	2.9	16.8	1.2		19.6	16.7	8.6	6.8	8.1
2	4.8	25.8	19.3	11.8	24.9	13.8	15.4	19.0	0.6	15.6	12.7	2.7	5.2	21.8	2.5	11.7	23.7	20.9	12.1	12.4	10.3
3	11.2	30.6	24.4	16.7	28.8	19.1	20.8	23.1	7.9	23.0	34.4	12.2	10.5	29.2	4.7	17.4	29.3	26.5	18.3	17.2	14.9
4	18.5	34.4	28.9	22.1	33.5	23.8	25.6	27.4	15.3	29.5	49.5	18.1	16.2	34.5	6.8	23.2	33.7	30.8	24.0	25.6	19.6
6	32.1	41.4	37.2	32.4	42.7	32.5	34.8	35.8	25.2	40.7	63.2	27.0	26.6	43.1	12.1	33.4	41.1	38.5	33.7	32.9	28.5
8	44.6	49.0	44.4	41.3	49.5	40.0	43.9	43.6	32.8	50.1	72.9	35.0	35.5	50.5	18.8	42.2	48.2	46.1	41.7	45.6	36.5
12	65.2	64.6	56.7	55.2	56.7	52.3	60.6	56.5	46.9	65.1	86.2	49.1	49.9	62.5	34.2	57.1	60.9	61.1	54.2	56.4	50.1
16	79.0	77.6	66.1	66.0	66.0	62.2	74.1	66.9	60.4	75.8	91.2	61.9	61.1	72.0	44.8	68.7	71.3	73.6	63.9	73.3	61.0
24	92.4	92.2	79.9	81.1	80.9	77.3	90.5	81.8	79.4	88.6	95.7	79.2	77.6	85.6	55.9	83.0	86.2	88.4	78.4	84.4	77.5
32	97.4	97.4	88.9	89.7	89.7	87.3	97.0	90.6	89.4	94.9	98.4	89.0	87.5	93.5	61.4	90.9	94.4	94.8	87.7	94.3	87.7
48	100.0	99.7	96.7	96.9	96.1	96.4	99.8	98.0	97.1	99.4	99.9	97.4	96.8	99.2	68.5	98.6	99.3	98.8	96.6	97.8	97.1
64	100.0	100.0	98.8	98.9	99.1	99.1	100.0	100.0	99.1	100.0	100.0	99.3	99.9	100.0	76.9	99.6	100.0	99.7	99.2	99.9	99.8
96	100.0	100.0	99.8	99.7	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	100.0	100.0	100.0
128	100.0	100.0	99.7	99.9	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

132

Lab [µm]	A SEM	B LAS-W	C LAS-W	D LAS-W	F LAS-W	G LAS-W	H LAS-W	I LAS-W	J LAS-W	K LAS-W	L LAS-D	N LAS-W	O LAS-W	Q LAS-W	R EZS	S Sedim.	T LAS-W	U LAS-W	V LAS-D	W EZS	X LAS-W
1	0.6	21.5	14.1	10.1	19.3	8.2	9.3	19.0	0.0	7.9	1.1	0.0	1.4	12.3	0.3		17.0	13.3	6.1	5.0	6.3
1.5	2.2	27.9	19.2	15.0	24.2	14.3	16.5	22.2	0.0	12.8	8.0	0.1	4.6	20.8	0.9		24.8	19.3	11.6	9.4	9.6
2	4.6	31.8	23.2	18.8	28.1	19.0	21.6	25.2	0.9	17.1	17.6	2.4	8.3	26.8	1.6	15.0	29.9	23.9	15.9	17.1	13.0
3	10.3	37.0	29.6	25.4	32.7	26.5	28.9	31.2	14.3	24.6	35.8	13.0	16.0	35.2	2.6	22.0	36.3	29.9	23.4	23.5	19.5
4	16.5	41.2	35.2	31.0	38.1	32.8	34.7	36.9	23.8	31.2	48.3	18.0	23.2	41.2	3.5	29.0	41.2	34.2	30.0	34.3	25.5
6	28.2	49.7	44.7	40.6	48.1	43.2	45.4	46.9	33.8	42.4	62.5	23.9	35.6	51.0	5.6	41.3	50.1	42.6	41.5	43.4	36.2
8	39.2	59.2	52.8	49.2	56.3	51.7	55.8	55.6	42.1	52.2	73.6	29.2	45.9	59.3	8.3	51.8	58.6	51.2	51.1	58.9	45.5
12	60.3	76.6	67.0	64.8	66.1	65.3	74.4	69.9	60.1	68.0	87.5	40.0	62.2	72.7	13.7	69.9	75.1	69.1	66.2	71.9	61.1
16	77.2	88.0	78.2	77.5	76.8	76.2	87.0	80.5	78.0	79.2	93.6	51.3	74.6	82.9	18.0	83.4	87.3	83.0	77.3	88.7	73.2
24	93.8	97.0	91.8	91.7	91.0	90.9	97.4	92.7	94.7	91.7	98.5	67.9	89.4	94.5	22.3	93.9	97.7	95.4	90.3	95.2	88.7
32	96.9	99.2	96.9	96.9	96.8	97.0	99.6	97.6	98.5	97.1	99.8	79.7	95.9	98.2	23.7	97.6	99.7	98.7	96.0	98.0	95.7
48	98.5	99.9	98.9	99.5	99.5	99.4	100.0	100.0	100.0	99.8	100.0	94.7	99.6	99.8	27.2	99.4	100.0	99.9	99.2	99.1	99.8
64	99.4	100.0	99.4	99.9	100.0	99.8	100.0	100.0	100.0	100.0	100.0	99.0	100.0	100.0	31.4	99.7	100.0	100.0	99.4	100.0	100.0
96	100.1	100.0	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	62.6	99.8	100.0	100.0	99.4	100.0	100.0
128	100.1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.7	100.0	100.0

135

Lab	A	B	C	D	F	G	H	I	J	K	L	N	O	Q	R	S	T	U	V	W	X
[μm]	SEM	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-D	LAS-W	LAS-W	LAS-W	EZS	Sedim.	LAS-W	LAS-W	LAS-D	EZS	LAS-W
1	0.3	15.3	11.4	6.8	15.3	6.0	6.6	14.3	0.0	5.4	0.0	0.0	0.7	8.1	0.1		11.9	10.1	3.8	3.3	4.0
1.5	1.3	20.2	15.6	9.3	18.9	10.4	12.0	15.9	0.0	8.8	2.7	0.0	2.3	14.1	0.4		17.4	14.8	7.3	6.5	4.7
2	3.0	23.6	18.7	11.4	21.8	13.8	15.8	17.6	0.7	11.8	12.2	1.7	4.5	18.5	0.9	10.0	21.2	18.7	10.4	12.6	5.5
3	8.0	28.2	23.7	16.2	25.4	19.4	21.5	21.5	7.8	17.4	34.5	12.3	9.8	25.1	1.7	15.0	26.5	24.1	15.8	18.4	7.8
4	14.2	31.6	28.1	21.1	29.6	24.3	26.1	25.7	14.3	22.2	50.0	19.1	15.4	29.8	2.4	20.0	30.5	28.1	20.7	28.7	11.2
6	26.6	37.4	35.4	29.8	37.2	32.6	33.8	33.7	22.2	30.2	63.0	27.4	25.3	37.2	4.1	28.8	37.0	35.1	28.8	37.3	19.6
8	37.3	43.2	41.6	36.9	43.1	39.3	40.7	40.7	28.0	36.9	71.8	33.8	33.3	43.6	6.2	36.4	43.1	41.8	35.4	51.1	27.9
12	55.6	55.3	52.0	48.0	50.1	49.6	53.2	52.0	39.1	47.9	83.8	45.6	45.6	54.2	10.3	49.5	54.1	55.3	46.0	62.0	42.1
16	69.0	66.6	60.5	57.1	58.0	57.9	64.1	61.1	50.6	57.0	88.0	57.2	55.3	63.1	13.5	60.0	63.5	67.2	54.8	77.6	53.0
24	85.7	81.7	73.9	71.7	71.9	71.6	81.5	75.4	68.7	71.6	92.3	74.6	70.6	77.1	17.2	74.9	78.2	83.3	69.3	87.2	69.4
32	95.4	91.2	83.8	82.1	81.9	82.0	91.9	85.3	81.1	82.2	95.3	87.0	81.7	86.9	18.7	84.7	88.0	91.8	80.2	95.5	80.6
48	99.7	98.1	94.6	93.5	90.8	93.9	98.9	95.6	93.9	94.2	97.9	98.7	93.9	96.7	23.2	96.7	97.2	98.1	92.6	98.3	93.1
64	100.1	99.7	98.2	97.5	96.4	98.5	99.9	99.1	98.0	98.6	99.1	100.0	98.5	99.5	26.2	99.2	99.5	99.5	97.4	99.9	97.9
96	100.1	100.0	99.5	99.3	99.2	99.8	100.0	100.0	99.9	100.0	100.0	100.0	100.0	100.0	57.2	99.8	100.0	100.0	99.9	100.0	99.9
128	100.1	100.0	99.7	99.7	99.2	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Lab	A	B	C	D	F	G	H	I	J	K	L	N	O	Q	R	S	T	U	V	W	X
[μm]	SEM	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-W	LAS-D	LAS-W	LAS-W	LAS-W	EZS	Sedim.	LAS-W	LAS-W	LAS-D	EZS	LAS-W
											136										
1	0.3	14.4	9.9	6.3	14.9	5.6	5.7	13.8	0.0	4.8	0.2	0.0	0.6	7.9	0.2		11.3	10.0	3.4	3.7	4.7
1.5	1.4	19.2	13.8	9.6	18.4	9.8	10.6	15.9	0.0	7.8	4.4	0.2	2.3	13.6	0.5		17.0	14.7	6.4	7.0	6.9
2	3.4	22.4	16.7	12.2	21.2	13.1	14.3	18.0	0.8	10.5	12.7	3.7	4.5	17.6	1.0	9.0	21.0	18.3	9.0	12.5	9.2
3	8.8	26.8	21.4	16.9	24.7	18.5	19.7	22.4	7.4	15.4	29.8	14.5	9.7	23.6	1.8	14.0	26.4	23.3	13.5	17.1	14.2
4	14.8	30.0	25.3	20.9	28.9	23.4	24.1	26.6	13.2	19.8	41.7	19.6	14.8	28.0	2.6	19.0	30.5	27.0	17.8	24.7	19.3
6	26.3	35.7	32.3	27.8	36.5	31.8	31.7	34.4	20.7	27.3	54.0	26.0	23.8	35.2	4.4	27.7	37.4	34.0	25.2	31.0	28.4
8	36.7	41.4	38.4	33.7	42.5	38.6	38.4	41.0	26.2	33.7	63.7	31.4	31.0	41.5	6.6	35.0	43.9	40.5	31.3	41.7	35.8
12	58.5	53.1	48.7	44.0	49.6	49.0	50.2	51.6	37.0	44.1	77.0	42.4	42.6	52.0	10.8	47.4	55.7	53.3	41.4	50.8	47.2
16	70.8	64.2	56.6	53.1	57.5	57.2	60.6	60.1	47.9	52.6	83.1	53.5	52.2	60.7	14.2	57.2	65.8	64.5	49.7	65.8	56.2
24	90.5	80.9	69.2	67.9	71.1	70.5	77.4	73.4	65.0	66.1	89.8	69.7	67.9	74.3	17.5	71.3	81.3	80.2	63.2	77.3	70.7
32	96.7	90.4	78.8	78.5	80.9	80.5	88.3	82.9	76.7	76.2	94.0	80.8	79.7	83.9	19.3	80.7	90.9	89.3	73.8	91.1	81.5
48	100.0	97.6	90.3	91.0	89.8	92.2	97.4	93.6	90.3	88.8	98.0	94.7	92.7	94.8	24.4	94.1	98.2	97.1	87.4	96.7	93.7
64	100.0	99.5	95.5	96.1	95.9	97.5	99.5	98.0	95.5	94.9	99.3	99.0	97.7	98.8	27.3	98.3	99.7	99.3	93.9	99.9	98.4
96	100.0	100.0	98.7	98.9	99.7	99.9	100.0	100.0	98.7	99.2	100.0	100.0	99.7	100.0	57.2	99.6	100.0	100.0	98.7	100.0	100.0
128	100.0	100.0	99.3	99.6	100.0	100.0	100.0	100.0	99.5	99.9	100.0	100.0	99.9	100.0	100.0	99.9	100.0	100.0	99.8	100.0	100.0

Appendix C: The Bootstrap Method

Suppose a random sample $\mathbf{x} = (x_1, x_2, \ldots x_n)$ from an unknown probability distribution F has been observed and we wish to estimate a parameter of interest $\theta = t(F)$ on the basis of **x**. For this purpose, we calculate an estimate $\hat{\theta} = s(\mathbf{x})$ from **x**. How accurate is $\hat{\theta}$? The bootstrap[1] was introduced in 1979 as a computer-based method for estimating the standard error of $\hat{\theta}$.

The bootstrap is a data-based simulation method for statistical inference. It allows scientists to explore data and draw valid statistical inferences without worrying about mathematical formulas and derivations. The bootstrap parameter estimate is available no matter how mathematically complicated the estimator $\hat{\theta} = s(\mathbf{x})$ may be. In its non-parametric form, the bootstrap provides standard errors and confidence intervals without the usual normal-theory assumptions.

The bootstrap method draws repeated samples (with replacement) from the observed sample itself to generate the sampling distribution of a statistic (a data set of size n has 2^{n-1} nonempty subsets).

Bootstrapping of a statistic $\hat{\theta} = s(\mathbf{x})$ consists of the following steps:

1. B samples are drawn with replacement from the original data set **x**, with each sample the same size as the original data set. Call these bootstrap samples $\mathbf{x}^{*1}, \mathbf{x}^{*2}, \ldots \mathbf{x}^{*B}$.
2. The statistic of interest $\hat{\theta}$ is computed for each bootstrap sample, that is $\hat{\theta}(b) = s(\mathbf{x}^{*b})$ for $b = 1,2,\ldots B$. The mean, standard deviation, and percentiles of these B values form the basis for the bootstrap approach to inference.

Implementation of these steps in a computer language is not difficult. A necessary ingredient for any bootstrap program is a high quality uniform number generator. It is important to keep in mind that the bootstrap (and associate methods) are not tools that are used in isolation but rather are applied to other statistical techniques. For this reason, they are most effectively used in an integrated environment for data analysis. In such an environment, a bootstrap procedure has the ability to call other procedures with different sets of inputs (data) and then collect them together and analyze the results. The S, S-PLUS[2], Gauss, and Matlab packages are examples of integrated environment. In this report, we use the S-PLUS function *summary.bootstrap()*. For each data-column, 1000 samples of the data (with replacement) or replicates were generated and the mean of these samples was calculated. The 2.5th and 97.5th empirical percentiles for the replicates of the parameter estimate (sample mean) are the lower and upper bounds of the data set, respectively.

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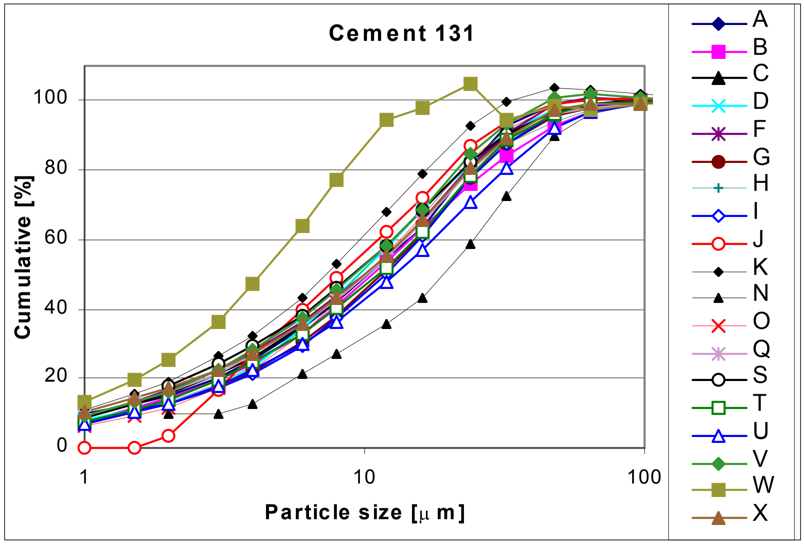
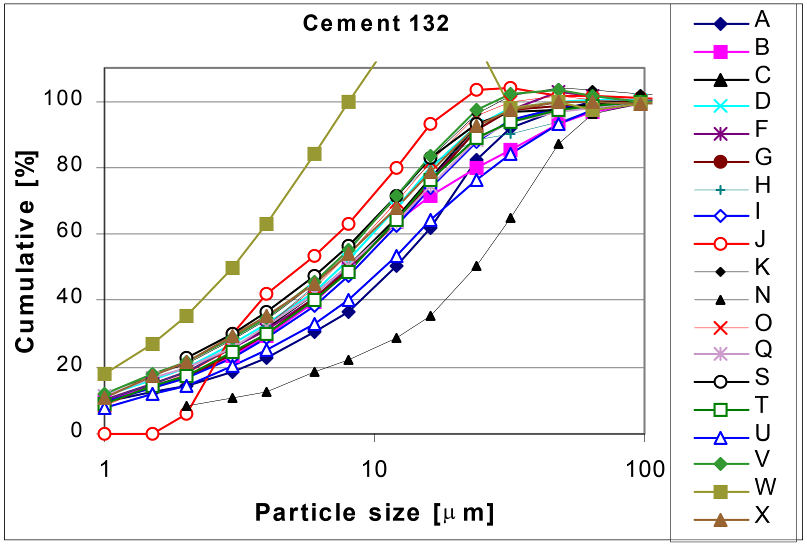
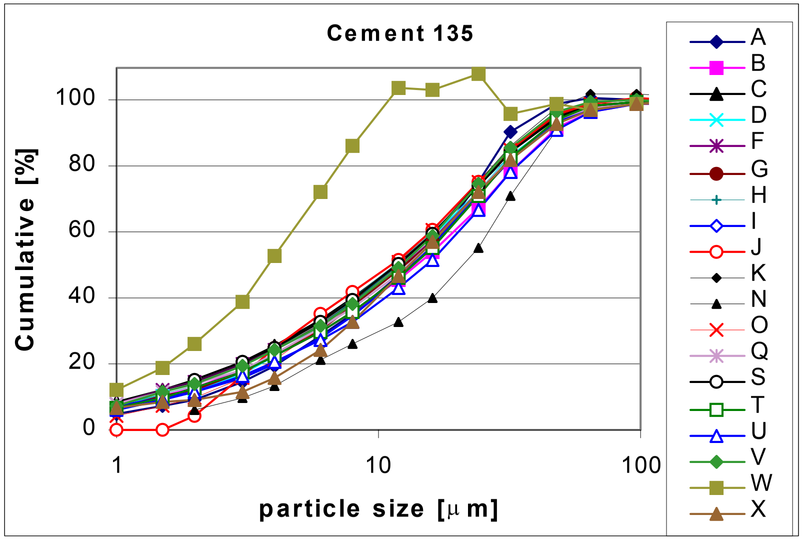
[1] The use of the term bootstrap derives from the phrase *to pull oneself up by one's bootstrap*. It is not the same as the term "bootstrap" used in computer science meaning to "boot" a computer from a set of core instructions, though the derivation is similar.

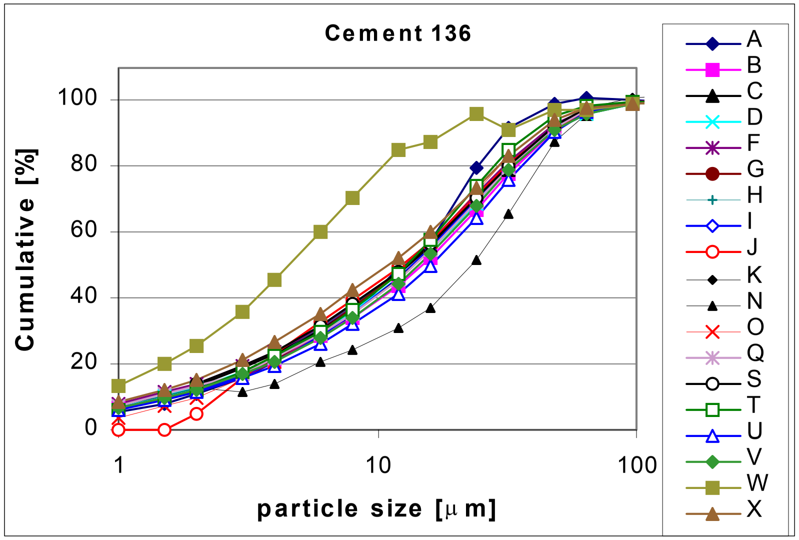
[2] Commercial equipment, instruments, and materials mentioned in this report are identified to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment identified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

APPENDIX D-1: Particle size distribution using all data corrected by the bootstrap method.

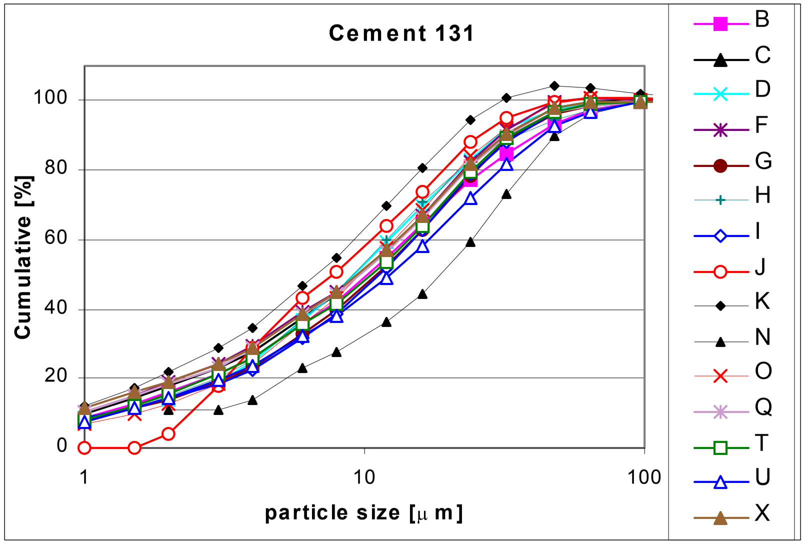


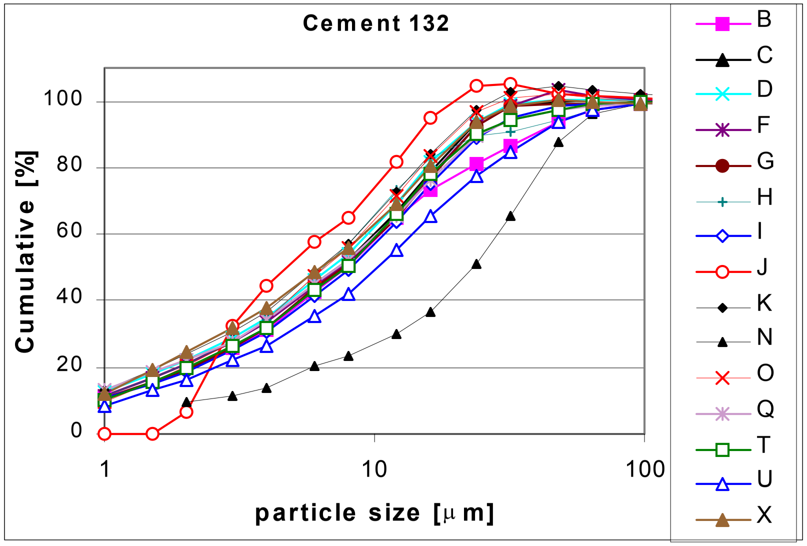


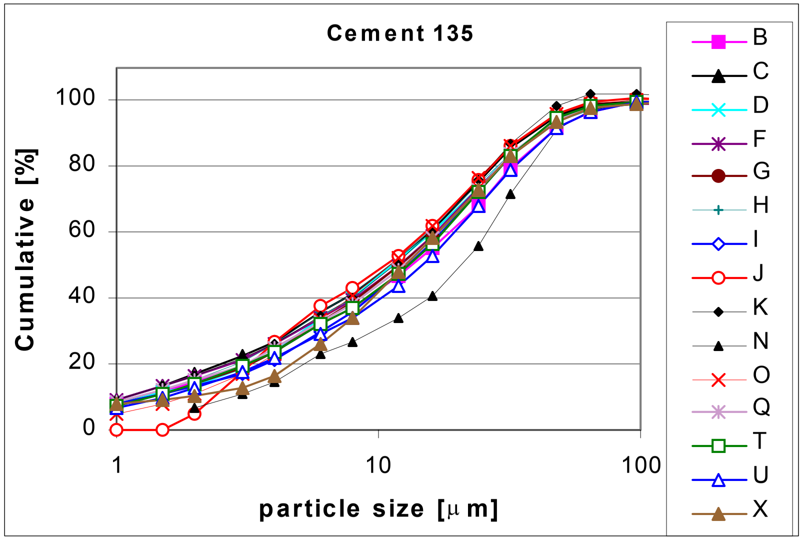


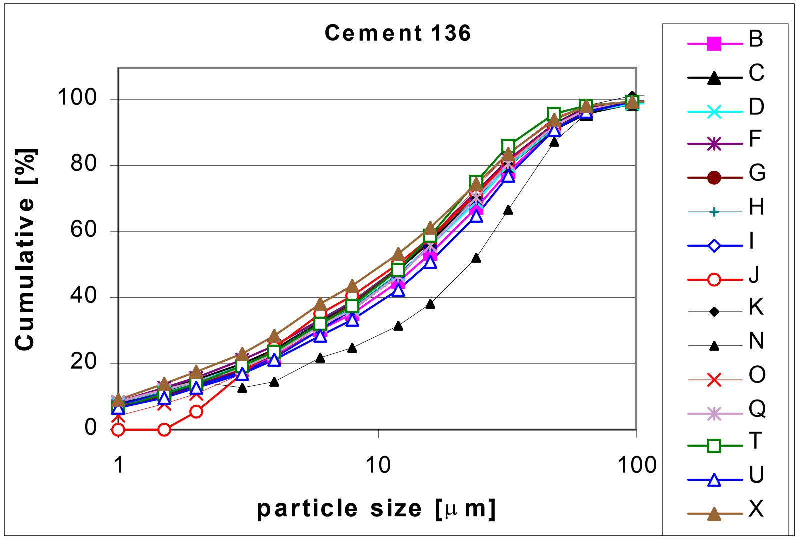


APPENDIX D-2: Particle size distribution using only data from Laser wet corrected by the bootstrap method.



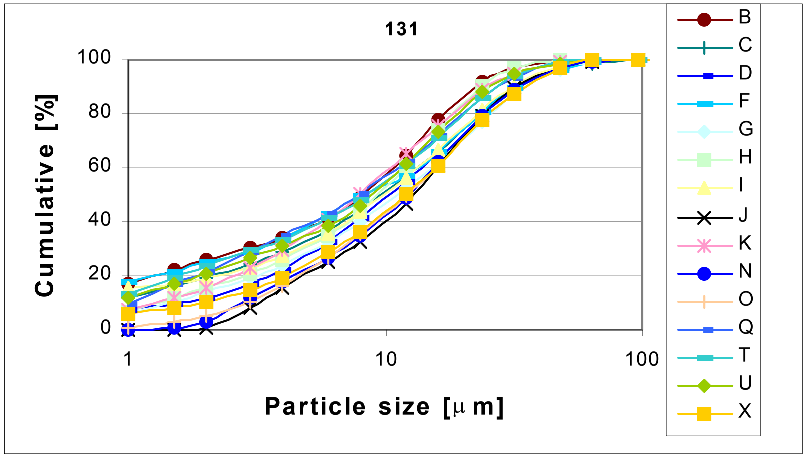


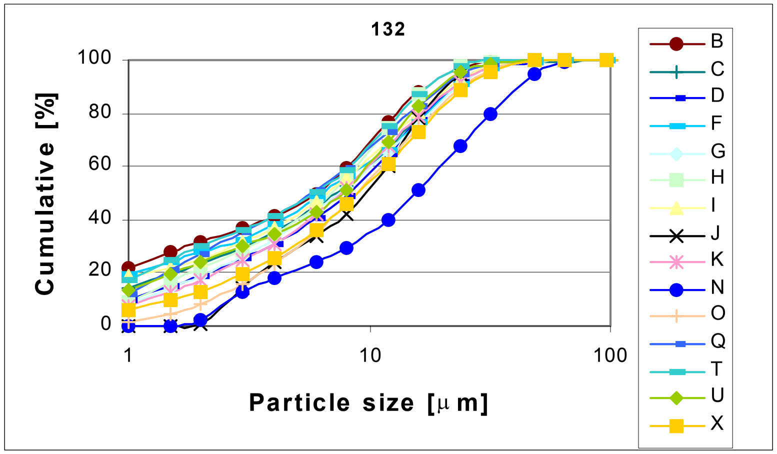


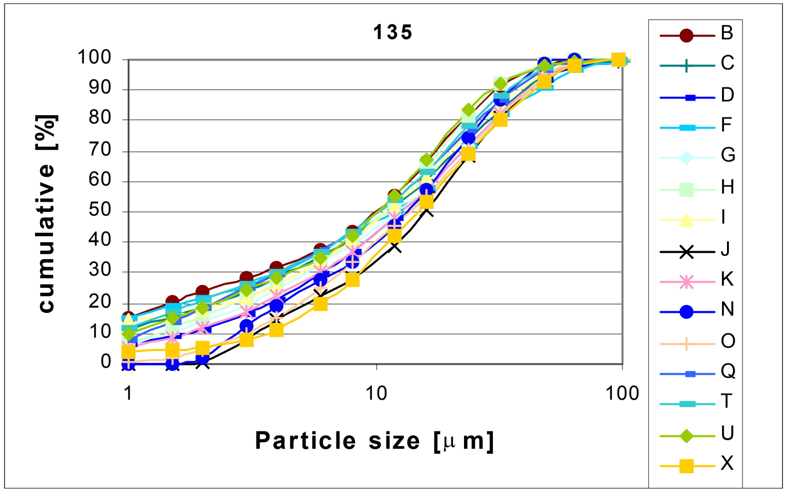


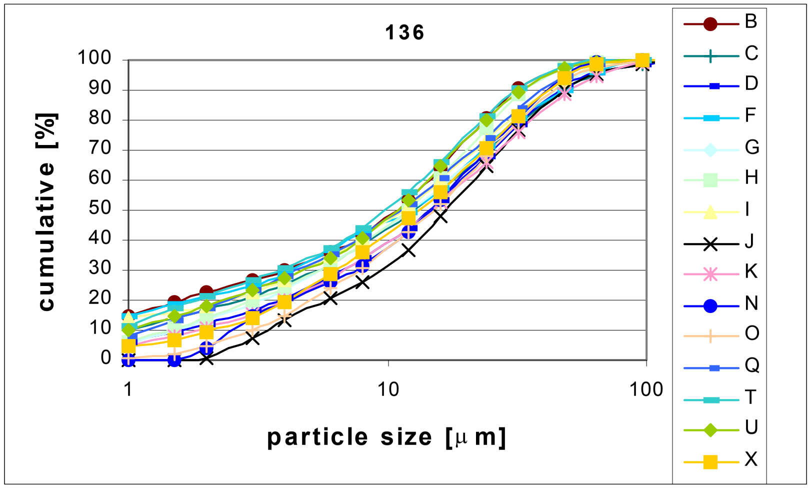
Appendix E: Graph for each method

All distributions from the various participants and for each cement as measured with LAS-W

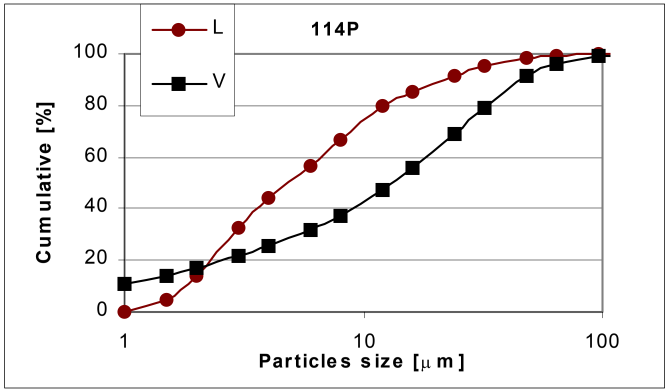


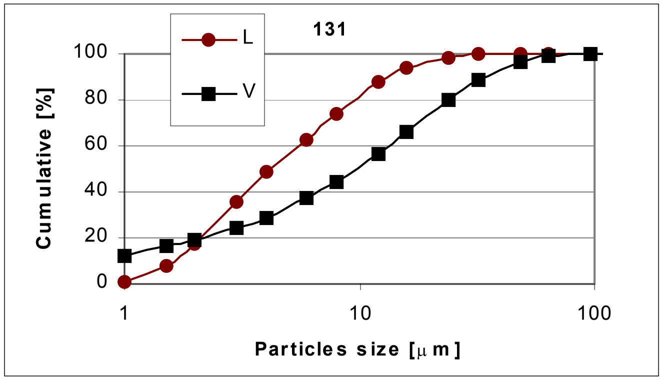


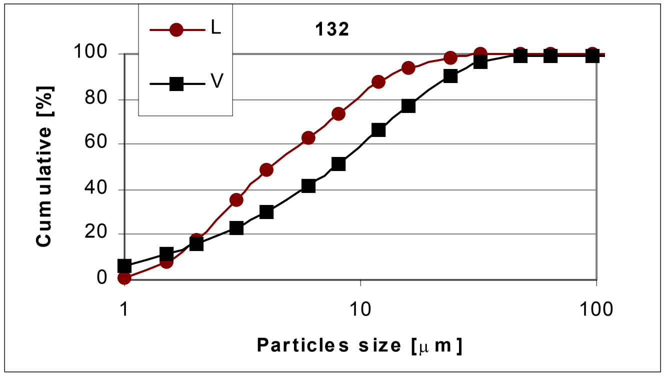


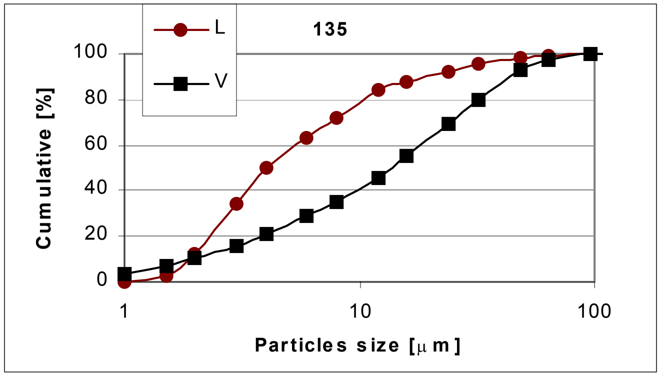


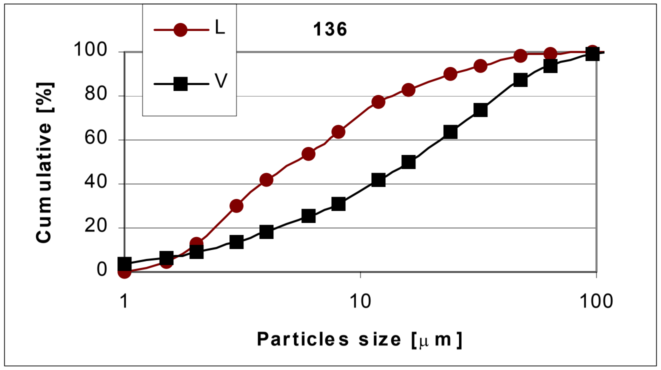
All distributions from the various participants and for each cement as measured with LAS-D



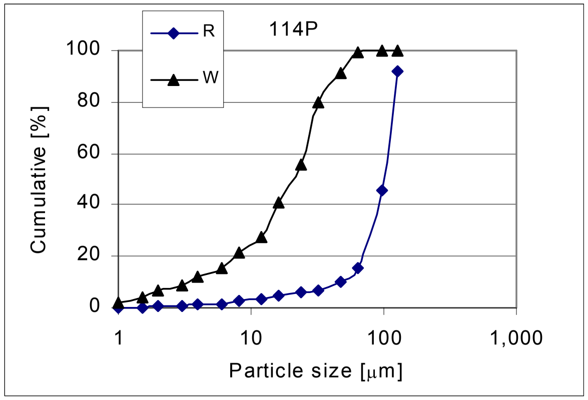


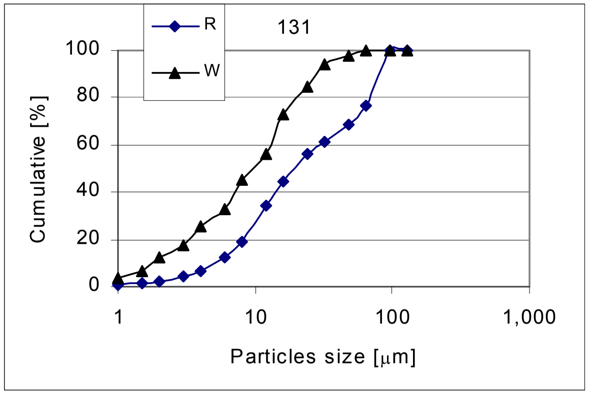


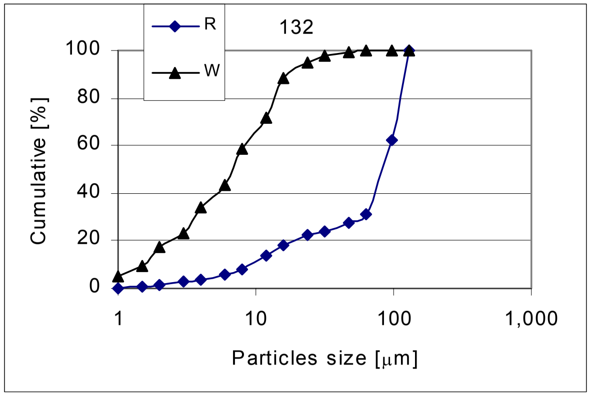


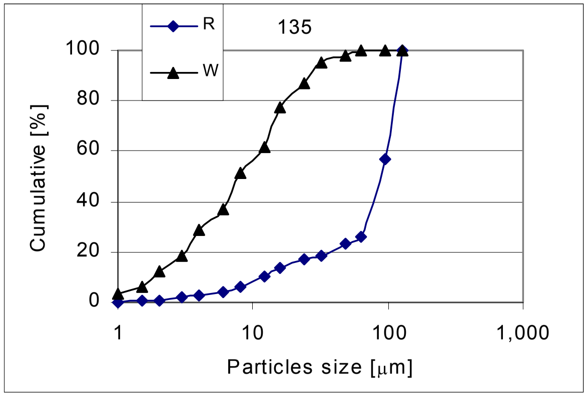


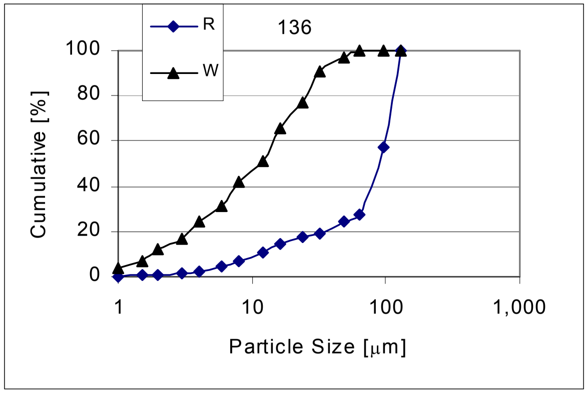
All distributions from the various participants and for each cement as measured with EZS method











All distributions for each cement as measured with SEM and Sedimentation