

Particle size distribution by LASER diffraction spectrometry: application to cementitious powders

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ABSTRACT

Particle size distribution (PSD) measurements are now routinely employed to characterize cement powders. A variety of techniques are available for this purpose. However, at present, an industry standard does not exist for PSD analysis, nor do uniform methods exist for sample preparation. Two international round-robin tests sponsored by ASTM committee C01.25.01 revealed high variability in reported PSDs, even among participants using similar instruments. The round-robin studies also identified LASER diffraction spectrometry (LDS) as the most common technique used by the cement community for routine determination of PSD. Therefore, studies were conducted to identify and examine the factors that significantly influence the determination of the PSD in cement powder by LDS. Potentially, the most significant influence on variability of PSD measurement is the state of dispersion of the powder prior to analysis by LDS; dispersion efficiency will depend on factors such as solids concentration, choice of dispersion medium, and the application of chemical and/or mechanical de-agglomeration methods. Another potentially significant source of error originates from the conversion of the measured optical spectrum to a PSD, a process that requires input of optical constants (real and imaginary components of the refractive index) of the solid phase which in cement is a multi-phase particle. The current work was undertaken with the objective of improving the precision, and therefore the degree of confidence, associated with the LDS technique in its application to cement characterization, and to assess the overall measurement precision of LDS under controlled conditions. We report relevant experimental data gathered in the course of these studies, and briefly summarize each set of results pertaining to a specific influence or parameter. Cement is composed of particles of finely interground clinker and gypsum. Knowledge of the separate PSD of the two components is critical for the prediction of cement properties. A novel technique to extract the PSD of gypsum from the total cement PSD by matching optical constants will be presented.

KEYWORDS: cement, gypsum, laser diffraction, particle size distribution

I. INTRODUCTION

Portland cement is a man-made material and one of the main binding agents for the aggregate in concrete. In 2004, the world production was about $2.1 \cdot 10^9$ t, an increase of 7 % from 2003 [1]. To produce cement, limestone and clay are crushed and fired at about 1400 °C in a rotating kiln. The firing produces roughly spherical particles of up to 20 mm in size, called clinker. The clinker is then finely ground, with addition of about 5 % by mass of gypsum, to form cement. Due to this production process and the raw materials used, the cement is an angular [2], multiphase powder. Cement reacts exothermically with water to form solid products of hydration. These products grow to eventually form a three-dimensional load-bearing network. The surface area of the cement powder partially governs its rate of reaction with water. Therefore, it is paramount in the characterization of a cement powder to know its specific surface area.

The standard reference material (SRM[®]) for fineness of cement, SRM[®] 114, has been provided by NIST since 1934 and is an integral part of the calibration material routinely used in the cement industry to qualify cements. Different lots of SRM 114 are designated by a unique letter suffix to the SRM[®] number, e.g., 114a, 114b, , 114q. The current lot, SRM[®] 114q, was issued in 2005. To establish the values a round-robin was organized [3] involving the laboratories that are part of the proficiency program from the Cement and Concrete Reference Laboratory (CCRL)¹.

Two international round-robin tests [4, 5, 6, 7] sponsored by ASTM committee C01.25.01 revealed high variability in reported PSDs, even among participants using similar instruments. The round-robin survey also identified LASER diffraction spectrometry (LDS) as the most common technique (90 % of round-robin participants) for the measurement of PSD used by the cement industry. Quite a few parameters affect the results, such as: complex refractive index, the dispersion procedure, the dispersion medium, the theory used to calculate the PSD from the diffraction angles, and the shape of the particles. The real component, n , of the refractive index of each major phase in portland cement is shown in Table 1. Each particle of cement may be composed of more than one phase shown in Table 1. Therefore, cement does not possess a single value of n , although a homogenized value can be estimated by a volume-weighted average [8] of the value of n of each phase. The estimate most often used for Portland cement is $n \approx 1.70$. The imaginary component, k , of the refractive index is more difficult to determine and/or find in the published literature [9, 10]. This often represents a significant challenge to the use of light scattering methods for fine particle size measurements [11]. Cement is generally gray to off-white in color, and therefore one can anticipate a finite, but relatively low value for k . In the literature, a value of $k = 0.1$ is often reported for cement [5].

The LDS method will not be described here, as it is a well-known technique used for many materials. Instead, the implication of the technique for cement will be discussed. The LDS 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 (LDS-W) while the latter is termed the “dry” method (LDS-D). Here, only the LDS-W will be considered. The current work was undertaken with the objective of

¹ For more information on CCR see <http://www.ccril.us/>

improving the precision, and therefore the degree of confidence, associated with the LDS technique in its application to cement characterization, and to assess the overall measurement precision of LDS under controlled conditions. A summary of the influence of each parameter on the results for cement will be presented.

Table 1: Typical composition and refractive index values (real) for constituent phases in a typical portland cement powder. Phases present in smaller quantities are not included.

mineral phase	Percentage by mass fraction [12]	refractive index, [§] n
Ca_3SiO_5	54	1.72
Ca_2SiO_4	22	1.73
$\text{Ca}_3\text{Al}_2\text{O}_6$	6	1.71
$\text{Ca}_4\text{Al}_x\text{Fe}_{4-x}\text{O}_{10}$	9	2.03
$\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ Gypsum	3	1.53

[§] mean value from reported range in Ref. 13

For predictive microstructural modeling of the hydration of cement, it is important to know the PSD of each of its two main components: clinker and gypsum. Because these two components have different hardnesses and are interground during the production of cement, the overall PSD measured on a cement powder may not accurately represent that of either of the individual components. To complicate matters, the gypsum and clinker components are difficult to separate either physically or chemically once they have been ground in a mill.

To estimate the PSD of each of the two components in cement without resorting to physical separation or chemical extraction, we have developed an *in situ* technique that uses optical matching within the LDS instrument. The technique is based on the principle that particles in suspension will not scatter light if their complex refractive index is matched to that of the surrounding fluid. Table 1 indicates that gypsum has a significantly lower value of n (1.56) than do any of the clinker materials. Therefore, an LDS-W measurement using a suspending liquid A with $n \approx 1.56$ should probe only the clinker components, while a measurement using a low-index liquid B should probe both the clinker and gypsum particles. The PSD of gypsum, $f_g(x)$, can in principle be inferred from these two measurements according to

$$f_g(x) = f_B(x) - (1 - \phi_g)f_A(x) \quad (1)$$

where $f_A(x)$ and $f_B(x)$ are the normalized PSDs measured using liquids A and B, respectively, ϕ_g is the volume fraction of gypsum in the cement and x is the particle size.

III. RESULTS AND DISCUSSION

A study was conducted [14] to investigate the influence of various parameters on the PSD measurement of cement. A study of the repeatability and precision of the PSD measurements is described in Ref. [14]. It was found that the coefficient of variation (CV) of replicate sequential runs within a subsample was about 1%. The sample to sample variation with a CV ranging from 5% for d_{10} to 16% for d_{90} .

The first parameter identified [14] is the medium in which the particles are dispersed. This study included a series of alcohols, namely: methyl, ethyl, isopropyl

(IPA), and n-butyl (see Table 2). Because water reacts rapidly with cement, it cannot be considered a suitable dispersing medium unless an effective hydration retarder is incorporated. Since the effectiveness of such agents varies depending on the cement composition, it is not considered to be a generally viable approach.

It was observed that the reproducibility of the PSD measurements increased with the viscosity of the medium. The explanation for this behavior is tied to the sample preparation procedure: the specimen to be tested was first dispersed in the medium external to the measuring device and then transferred dropwise using a pipette to the measurement reservoir containing additional pure medium until the required optical density was achieved. The low viscosity medium did not permit a consistent transfer without some loss of material due to sedimentation and segregation, while the high viscosity medium maintained the dispersed state of the powder and led to more consistent transfer. Therefore, it seems that the common industrial selection of IPA as a dispersing medium for cementitious material is justified, since its viscosity is the second highest of the liquids studied.

Table 2. Physical and optical parameters for suspending media at 20 °C.[†]

medium	refractive index, <i>n</i>	density (g/cm ³)	viscosity (mPa s)
methyl alcohol	1.329	0.7914	0.60
ethyl alcohol	1.361	0.7893	1.20
isopropyl alcohol	1.378	0.7855	2.31
n-butyl alcohol	1.399	0.8098	2.95

[†] From Ref. 15, or calculated from relationships provided therein.

The most common method to disperse the cement in the medium is to apply ultrasonic energy. The duration of the treatment needs to be selected to ensure that the measured PSD is reached a final distribution that is not changing. It was found that using a high-intensity submersible ultrasonic horn increased the dispersion of the suspensions. The optimum duration of this treatment was found to be about 1 min, since for duration longer than 1 min, no significant changes in the PSD were observed.

The dependence on the optical model (i.e., Mie vs. Fraunhofer), and more specifically the refractive indices values used, are a potentially significant source of uncertainty. To examine their effect, a systematic variation [14] was performed using the same measured diffraction data (determined in IPA) analyzed with the Mie optical model: A) *k* was fixed at 0, 0.01, 0.1 and the *n* was varied for each *k* from 1.4 to 2.7; B) *n* was fixed at 1.4 to 2.7 (seven values selected in the interval) and *k* was then varied from 0 to 1. It was found that the influence of either parameter can be large, as shown by the examples in Fig. 1 and Fig. 2, especially in the sub-micrometer range. The effect on the calculation of the large size fraction is less sensitive to the refractive index, as would be expected. The Fraunhofer model, which does not depend on refractive index, is shown for comparison. From Fig. 1, it appears the value of *k* primarily influences the appearance of the fine fraction, while application of Fraunhofer results in a large volume of small particles (less than 1 μm). Particles below about 1 μm in diameter are not observed for a value of *k* below 0.05, while the PSD becomes largely insensitive to the value of *k* at a level of 0.05 or higher. Clearly, the choice of *k* will have a measurable impact on the

apparent presence of fines in the powder. Figure 2 demonstrates that the real component of the complex refractive index has an even stronger impact on the calculated PSD. It is evident that even a variation from 1.6 to 1.7 dramatically affects the fine fraction of the PSD. Interestingly, the Fraunhofer model yields a PSD that is almost identical to Mie with $n = 1.6$ and $k = 0.1$.

To test the technique for estimating the PSD of gypsum from that of a cement powder, pure gypsum powder was added to a finely ground clinker to produce a blend with a gypsum volume fraction of 0.24. The PSD of both gypsum and clinker were measured separately using IPA as the suspending medium. In addition, the PSD of the cement blend was measured both in IPA and in benzyl alcohol (BA), for which at 25 °C $n = 1.38$ and 1.54 , respectively. Figure 3 shows the PSD measured using IPA for the pure gypsum powder, and also compares the PSD measured using BA for the mixture and the pure clinker. The gypsum powder is coarser than the clinker. More importantly, the PSD measured for the clinker in BA and for the mixture in BA are quite similar in contrast to the gypsum PSD. The similarity of the latter two measurements indicates that measurements in BA are probing predominantly the clinker particles. Fig. 4 compares the PSD of the cement mixture measured using IPA and using BA. The curve shown for the BA measurement has been scaled by a constant factor of 0.76 to better indicate the relative solid volumes being sampled by the two measurements. According to Eq. (1), the difference between these two curves—the solid black curve in Fig. 4—should be an estimate of the PSD of the gypsum component in the mix. A comparison of Fig. 3 and Fig. 4 indicate that, indeed, the estimated PSD for gypsum is reasonably close to the gypsum PSD measured in IPA. The mode of the estimated gypsum distribution agrees quite well with the measured mode in Fig. 3. The estimated distribution has a small peak at diameters less than 1 μm , which is consistent with the fact that the measured gypsum PSD in Fig. 3 has nonzero values in this size range. The major difference between the estimated and the measured gypsum PSDs is in the range from 1 μm to 5 μm , in which the estimated PSD is zero. This discrepancy is caused, not by a shortcoming in the optical matching concept, but by a difference in the state of dispersion of the *clinker* particles in the two liquids. Figure 5 shows the PSD of the pure clinker powder measured using IPA and BA. In IPA, the clinker distribution has a minor peak at about 2 μm . In BA, this peak is much less pronounced, while at the same time the volume fraction of sub-micrometer particles has increased relative to that measured in IPA. Therefore, the smaller clinker particles are better dispersed in IPA than in BA. Obviously, the accuracy of the optical matching approach depends on the ability to measure the majority phase consistently in both liquids. To the extent that the clinker PSD measurement is different in the two liquids, the subtraction operation will be inaccurate.

It is well known that the van der Waals attraction between particles in suspension is influenced by the contrast in dielectric permittivity between the particle and the liquid. Refractive index is directly related to the high-frequency dielectric permittivity tensor [16], so it is reasonable to expect that the tendency for agglomeration is different in liquids with different refractive indices. Therefore, the most sensible way to ensure a uniform state of dispersion of the clinker particles in different liquids is to stabilize the particles with a suitable deflocculant in each case. Unfortunately, polymer admixtures that can stabilize cement have been developed almost exclusively for aqueous suspensions in which the strong polar nature of water is key to their effectiveness.

Relatively little is known about how to ensure dispersion of cement in nonpolar liquids like those used here. Further investigation is required to identify suitable deflocculants for these systems, but if one can be found, then the results presented here indicate that optical matching has the potential to be an excellent approach for deconvoluting the PSDs of clinker and gypsum in cement powders.

IV. CONCLUSIONS

The use of LASER diffraction for powder size analysis of cementitious materials has become widespread in the industry, but variations in sample preparation methods, suspending medium and the choice of optical parameters to analyze the raw data can significantly impact the PSD results and precision. Greater consideration of these factors is necessary to establish limits and recommended practices. This study has examined the impact of several key factors in the application of LASER diffraction. In particular, the choice of refractive index values is deemed critical. Sensitivity of the method to the optical constants of the powder and dispersing medium presents challenges to accurate measurements on cement, particularly in the sub-micrometer size regime. But this sensitivity also can be exploited to help deconvolute the size distributions of different components within a multicomponent powder. For example, the size distribution of gypsum particles in a cement powder can be estimated reasonably well from the difference of the measured distributions of the cement in isopropyl alcohol and benzyl alcohol. In addition, this same optical matching method should be applicable to any other multicomponent powder for which there is significant contrast in the refractive index between two or more components. However, differences in the dispersability of each component in the different media must also be considered in developing such a method.

The cement industry needs a standard methodology to measure the PSD of cement. This research showed the possibilities and the limitation of this technique. These difficulties are compounded by the fact that each LASER diffraction device will impart different dispersion energy to the suspension leading to various levels of de-agglomeration. NIST is approaching the problem by providing the industry with a reference material, SRM 114, which could be used to correlate measurements obtained with different instruments. Also, NIST is working with ASTM to develop a methodology to measure the PSD by LASER diffraction of cement.

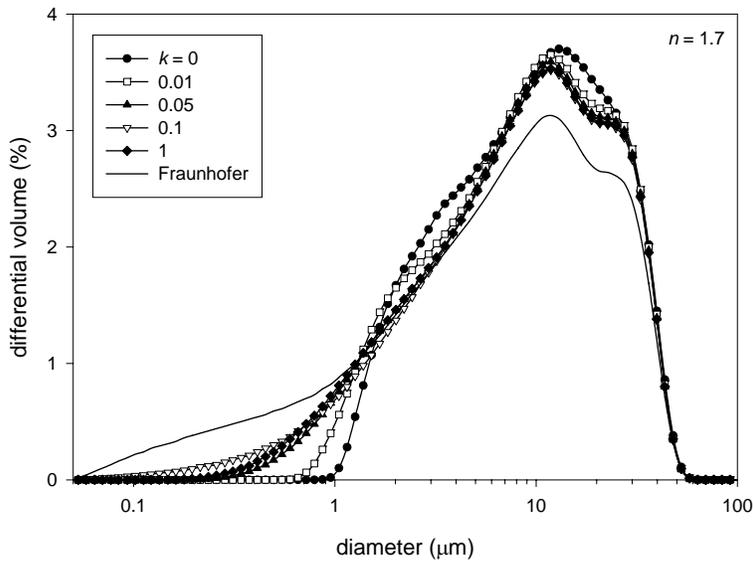


Figure 1. Sensitivity of calculated PSD to variation in imaginary component of complex refractive index for $n = 1.7$. Diffraction spectrum of CCRL 135 analyzed using Mie optical model.

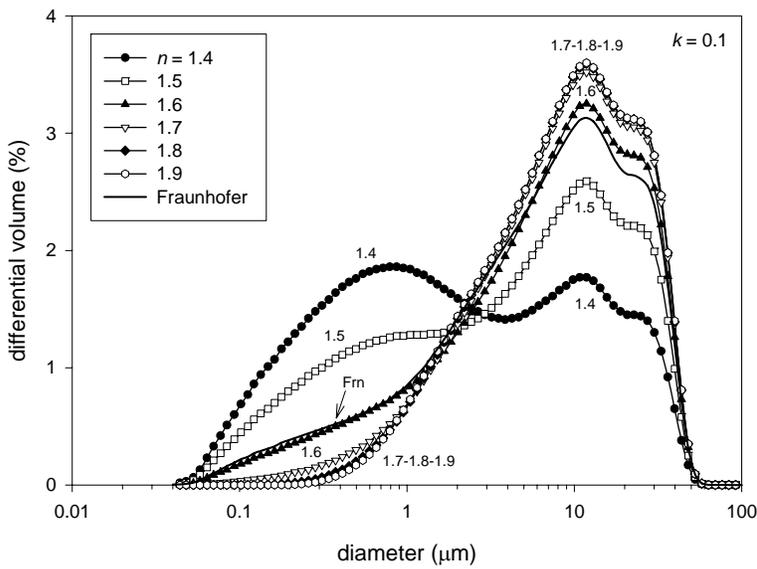


Figure 2. Sensitivity of calculated PSD to variation in real component of complex refractive index for $k = 0.1$. Diffraction spectrum of CCRL 135 analyzed using Mie optical model.

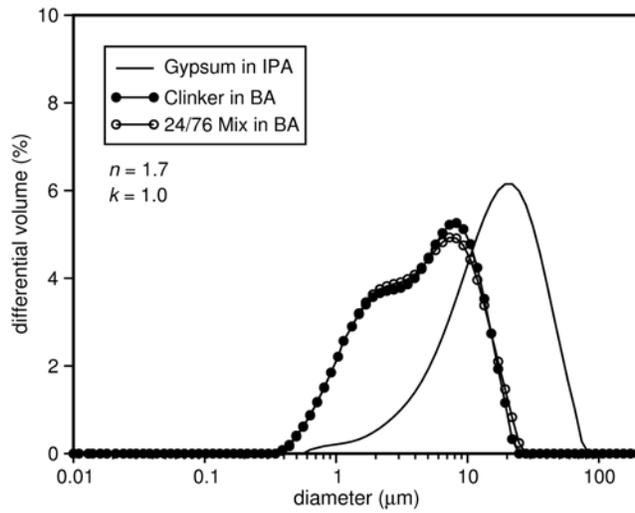


Figure 3. LSD-W measurements of the PSD of gypsum powder in IPA, of finely ground clinker in BA (filled circles) and of a clinker/gypsum powder mixture in BA (open circles).

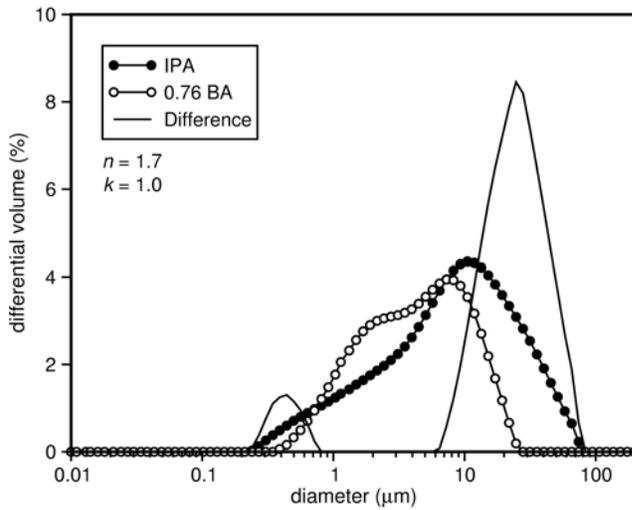


Figure 4. PSD measured for a gypsum/clinker cement mixture with a clinker volume fraction of 0.76. Measurement in IPA (solid circles), scaled measurement in BA (open circles), and the difference of the two (solid line) which is an estimate of the PSD of gypsum.

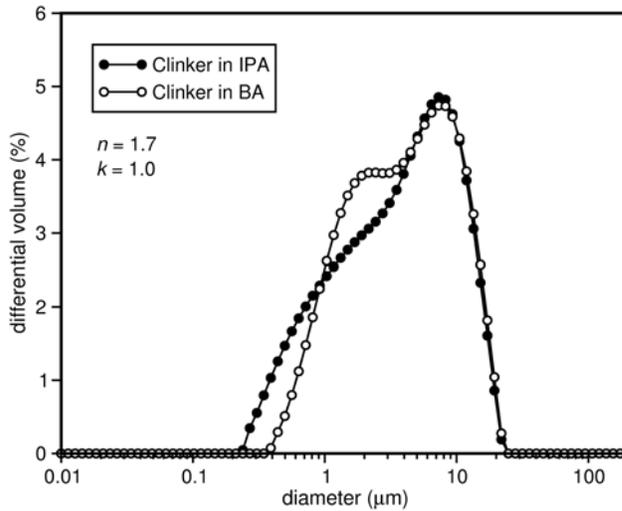


Figure 5. Measurement of clinker PSD in IPA (solid circles) and in BA (open circles).

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