Identifying improved standardized tests for measuring cement particle size and surface area

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ABSTRACT

The Blaine fineness (Blaine) of a cement powder is a single parameter that is meant to characterize the specific surface area of a cement, and is assumed to be linked to physical and mechanical properties of the hydrated cement such as strength, setting time, and rheology. A single parameter cannot characterize the particle size distribution of a cement particle size distribution, upon which the hydration kinetics and solid properties depend. And as the cement industry continues to develop more sophisticated blended cements, it will be even more clearly seen that a single parameter fails to capture the true complexity of the cement. The laser diffraction (LD) measurement of the entire particle size distribution is currently being used by cement producers for quality control of their cements while still measuring the Blaine, which is based on surface area measurement. Despite its wide use by the cement industry, LD is not a standardized test. This project's goal is to examine various tests, such as laser diffraction and Blaine, which measure the particle size distribution and total surface area of cement powder, and then determine the most appropriate test based on correlation with macro-properties of the cement paste or mortar. In addition, the shape of the cement particles, for a partial particle size range, was determined using X-ray computed micro-tomography (X-Ray CT) and the relationship between X-ray CT, the Brunauer-Emmett-Teller surface area method (BET) (surface area), laser diffraction, and Blaine measurements was explored. The more fundamental and sophisticated experiments, nitrogen BET and X-ray CT, were used as "ground truth" to critically evaluate the laser particle size distribution and Blaine fineness measurements. The standardization of the laser diffraction test method is proposed.

INTRODUCTION

The Blaine fineness (standard test method ASTM C204, denoted "Blaine") of a cement powder is a single parameter that is meant to characterize the specific surface area and therefore the fineness of a cement, and is assumed to be linked to physical and mechanical properties, such as rheology, setting time, and strength of the fluid and hardened cement paste. However, a single parameter cannot characterize the particle size distribution of even an uniform composition cement. As the cement industry continues to develop more sophisticated blended cements, a single parameter will even more fail to capture a blended cement's true complexity. The laser diffraction measurement of the entire cement particle size distribution (PSD) is currently being used by most cement producers for quality control of their cements while still measuring the Blaine fineness. The laser diffraction test is less time consuming than the Blaine test and can be automated for efficient measurement. The information from laser diffraction particle size distribution (LD) measurement can also provide an estimate of powder surface area by assuming a specific geometry for the particles. Despite its extensive use by the cement industry, laser diffraction (LD) measurement of cement particle size distribution is not a standardized test. This project examines the results of the LD and Blaine tests, measuring the particle size distribution (laser diffraction only) and estimated total surface area (both tests) of various cement powders and then determine the most appropriate correlation of the results of both tests with some macro-properties, such as setting time and compressive strength, of cement paste and/or mortar made with those powders.

Since both the Blaine and laser diffraction tests assume that the cement particles are spheres, which is manifestly not the case, and thus only estimate the surface area, two more fundamental tests are carried out to aid in understanding the results of both tests. The surface area of the cement particles is measured using the nitrogen Brunauer-Emmett-Teller (BET) test, and the true 3-D shape of the particles is determined from X-ray computed micro-tomography (X-ray CT). The more sophisticated experiments, nitrogen BET and X-ray CT, will be used as "ground truth" to evaluate the LD-PSD and Blaine fineness measurements. Cement and Concrete Reference Laboratory (CCRL) cements are used in this project, taking advantage of the database of properties measured during the "CCRL - Proficiency Sample Program" (www.ccrl.us). Recommendations for how the LD test can be standardized and applied are provided.

TECHNIQUES USED

Fineness measurements

Overview

Cement is a reactive powder and thus one of its most important characteristics is its PSD, which in turn determines the total surface area. Since the Blaine measurement is related to a specific surface area (area per mass) and is referred to as a fineness measure, total specific surface area is often referred to as the fineness. The smaller the size of the particles, the larger is the specific surface area. There are several methods to measure or estimate the surface area. The most widely used method in the cement industry is the Blaine measurement (ASTM C204) [1]. A method that is not standardized but is widely used in the cement industry for quality control is the LD-PSD. Both of these tests assume that the particles are spherical. By comparison, methods such as nitrogen BET and X-Ray CT allow the measurement of the specific surface area at the scale of gas molecules (BET) and provide an assessment of the true shape of the particles (X-ray CT). In this section, all the tests will be described.

Fineness standard tests

In the cement industry, there are three standard tests to measure the specific surface area: Blaine in ASTM C 204 [1], Wagner in ASTM C115 [2], and sieve residue (45 µm sieve) in ASTM C430 [3]. The Wagner test is also referred as the turbidimeter fineness test because it measures the turbidity of a cement suspension in kerosene [4]. This test is seldom used today, and thus will not be discussed further in this paper.

The Blaine measurement described in ASTM C 204 was adopted by ASTM in 1946. R.L. Blaine published the test in 1943 [5]. The principle of operation is that the permeability of a bed of fine particles is proportional to the fineness of the particles. Therefore, the test is a measurement of the flow rate of air through a bed of cement particles with vacuum on one side and atmospheric pressure on the other. Using an air permeability measurement of a powder to estimate surface area comes directly from the Kozeny-Carman approximate theory [6], which assumes a packing of monosize spherical particles. From the beginning, it was stated that this is a relative test as it depends on the shape of the particles, and the compaction level or porosity of the bed. For this reason, ASTM C 204 section 4.1 states that the calibration of the instrument needs to be done by using a Standard Reference Material, such as SRM 114 [7,8].

The sieve residue test (45 µm) is used to measure the residue or retained amount of cement on a calibrated sieve as an estimate of what fraction of the particles are greater than a certain size. The sieve was selected as having a 45 µm opening (No. 325[1]). Since a direct certification of sieve openings is impractical and expensive for production-scale work, sieves are calibrated by using a reference material, such as SRM 114. A sieve correction factor is calculated by measuring SRM 114 on the selected sieve and correcting the result with the certified value of the SRM 114.

In all these standard tests, there is a need for a standard reference material (SRM), which is a material that has been well characterized with regard to its chemical composition, physical properties, or both. At the National Institute of Standards and Technology (NIST), every SRM is provided with a certificate of analysis that gives the official characterization of the material's properties. SRM 114 is related to the fineness of cement, as measured by various standard methods and has been available since 1934. Different lots of SRM 114 are designated by a unique letter suffix appended to the SRM number. A certificate that gives the values obtained using ASTM C 204 (Blaine), C 115 (Wagner) and C 430 (45-µm residue) and also LD-PSD is included with each lot of the material.

Laser Diffraction method

The LD method involves the detection and analysis of the angular distribution of scattered light produced by a laser beam passing through a dilute dispersion of particles [9]. The total scattering or diffracted light pattern is mathematically inverted to give the particle size distribution of spheres that would give the equivalent scattering pattern. The surface area is calculated from the diameter distribution of the spherical particles. In general, the LD method

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

requires that the particles be dispersed, either in liquid (suspension) or in air (aerosol). The former is commonly referred to as the “wet” method (LD-W) while the latter is termed the “dry” method (LD-D). For cement, there is no difference between the two methods if there has been no initiation of hydration due to previous exposure to moist air, so that both methods adequately disperse the particles. As the cements used had been stored in the laboratory for some time and transported in simple plastic bags, in this report only data using the LD-W is used to ensure complete dispersion of the particles. The LD method is not only widely used in the cement industry [10], but is used for many different kinds of particles across many different industries [11]. SRM 114 is used in this case only to determine whether the instrument is functioning properly and if the dispersion method is adequate, not to calibrate the instrument as it is done for the Blaine test.

BET Surface Area

The BET technique is based on the adsorption of a monolayer of gas, in our case nitrogen, on the surface of particles. The total surface area of a powder can be calculated using the Langmuir theory and the BET generalization [12]. This approach is considered to be the most fundamental bulk measurement of surface area, since it can explore surface feature sizes down to the size of the nitrogen molecules. Generally, surface area is a length-scale dependent quantity, with the surface area increasing as finer and finer surface length scales are explored [13].

X-ray CT scan

The X-ray CT is used to provide particle shape determination, since cement particles are not spheres. Knowing the true shape of each type of cement particles will help in the comparison of different surface area measures. The X-ray CT measurements also measure the surface area at the voxel length scale at which the shape has been captured. A sub-set of the CCRL cements considered for LD-PSD and Blaine have been chosen for study using X-ray CT. After X-ray CT scanning, computer programs are used to analyze the particles in terms of their shape and other geometric factors [14,15].

Macro-Properties

The macroproperties considered here enable the characterization of the behavior of a paste or mortar prepared with the cement studied. The properties considered are compressive strength at 3 d, 14 d and 28 d, and the initial and final set times determined by the Vicat needle test (ASTM C191). The compressive strength and the set time were obtained from the reports prepared by CCRL [16].

MATERIALS USED

The Cement and Concrete Reference Laboratory (CCRL, www.ccrl.us) is sponsored by ASTM and administrates the Proficiency Sample Program bi-annually [16]. As part of the program, participant laboratories receive two samples of cement upon which they conduct standard tests and report the results back to CCRL for statistical analysis. With all the data collected, CCRL prepares a report that contains the average values and their standard deviations. For this study, 32 cements from the CCRL database were selected, and the following properties where chosen to provide a statistical picture of the cements:

- Fineness by 45-µm Sieve – ASTM C430
- Fineness by Air-Permeability Apparatus or Blaine – ASTM C204
- Compressive strength of mortar cubes at 3 d, 7 d and 28 d
- Initial and final set by Vicat needle (ASTM C191)

The same properties were also collected for three cements (labeled in this report Non-CCRL) that were produced from one clinker, but ground to different finenesses. These cements were used in a previous study to determine the relationship between fineness and macroproperties [17]. The other non-CCRL cements were the two SRMs used for fineness: SRM 114q and SRM46h. SRM 46h was issued because the SRM 114q was too fine to be useful when calibrating the 45 µm sieve to conduct the sieve residue test – too much material passed the 45 µm sieve so not enough was left to analyze and give good statistics. The only certified value for this SRM is the 45 µm sieve residue, but other values measured at NIST are provided for information only.

RESULTS AND DISCUSSION

The main goal of this study was to determine the best method to measure the fineness of cement in light of correlation to macroproperties. Therefore, the first step was to compare the various fineness methods and determine the correlation between test method results. Then we examined the shape of the particles to determine how the shape could influence the measurement of fineness. Finally, the impact of the fineness on macroproperties is discussed.

Fineness measurements comparison

In this paper, there were four methods used to determine fineness: BET, Blaine, sieve residue, and LD-PSD. The BET is the most direct and finest length-scale measurement of specific surface area as it makes no assumption about the shape of the particles. Figure 1 shows the relationship between the BET surface and the surface obtained either by Blaine or by LD-PSD. The following observations can be made: 1) the range of surface area measured with BET is the widest (686 m^2/kg to 2000 m^2/kg), emphasizing the differences between the cements; 2) the narrowest distribution is provided by the results of the Blaine method (349 m^2/kg to 545 m^2/kg).

The difference between the Blaine and the BET results is interesting since similar gases (pure nitrogen in the BET test and air, which is 80 % nitrogen, in the Blaine test) are being used to interrogate the surface area. Since it is known that the BET test measures a monolayer of nitrogen molecules covering the surface, the implication is that in the Blaine test, not all parts of the surface are interrogated. Since the air velocity goes to zero at the particle surface for non-turbulent air flow, there are probably many “dead zones” on the surface that the flowing air in the Blaine test does not see. This implies that the Blaine is not a true measure of the particle surface area, since these small regions, while not important for air flow, are probably important for reaction during hydration. So while BET showed clear differences between cement surface areas for these materials, the Blaine results were less sensitive. Therefore, there is no clear relationship between the surface area by Blaine and BET.

A clearer trend is observed with the three Non-CCRL cements that were ground from the same clinker. They were ground to have different Blaine values, so they show a clearer trend between BET and Blaine/LD. This could be also explained by the fact that these three cements had the same composition (one clinker and gypsum) and were prepared by the same ball mill. On the other hand, the CCRL cements do not have the same composition and were prepared by different manufacturers over several years. More data must be obtained to confirm the correlation between BET, LD and Blaine for cements with the same composition.

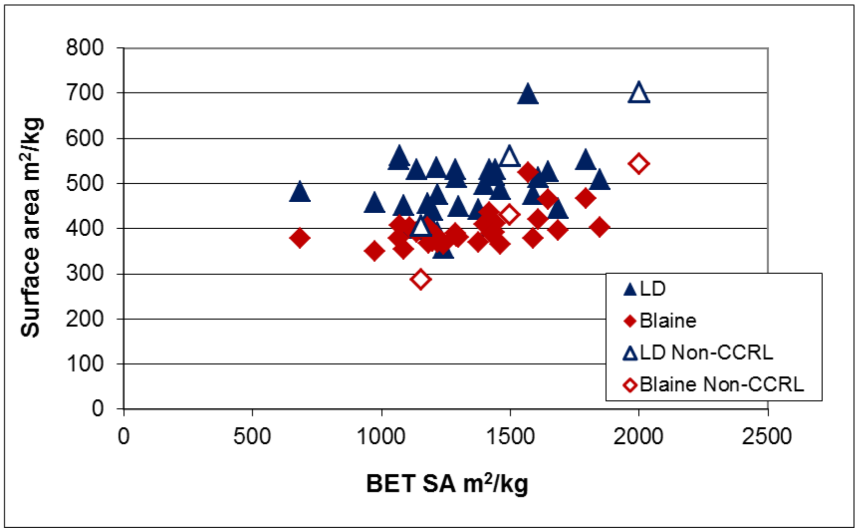

Figure 1: Blaine and LD-PSD surface area vs. BET surface area.

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

So far, it has been established that both the Blaine and the LD provide a surface area that is weakly correlated with the BET, the most direct and fundamental method. So, in an ideal world, the BET should be adopted as the measurement of the surface area, but it is an expensive device that requires at least half a day to measure one cement sample. So the Blaine and the LD tests are more practical surface area measurement methods for cement industry production. Figure 3 shows the correlation between the Blaine and the surface area measured by LD. There is significant scatter of the data points for the CCRL cements, but in all cases the value of the surface area by LD is larger than the Blaine result. For the Non-CCRL cements, a linear relationship between LD and Blaine was observed having a value of R^2 = 0.98. The CCRL cements were not included in the correlation because the data points were too narrowly dispersed, i.e., the cements had similar values of Blaine or LD specific surface areas.

In summary, it could be stated that BET is the most direct method for specific surface area measurement. On the other hand, BET is also too expensive a test, in terms of both cost and time to perform a measurement, to be adopted by industry. Although neither LD nor Blaine

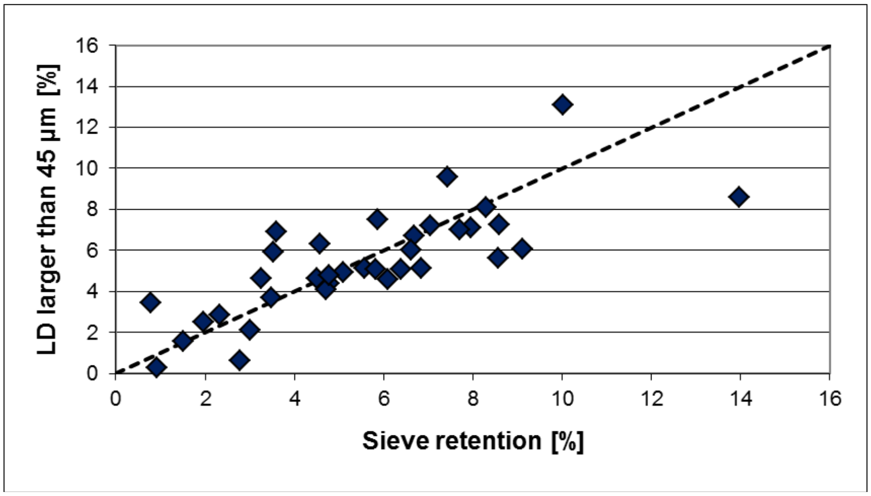

Figure 2: Relationship between the percentage of particles larger than 45 um by LD and by the sieve method (ASTM C430). The dashed line is the line of equality (slope = 1).

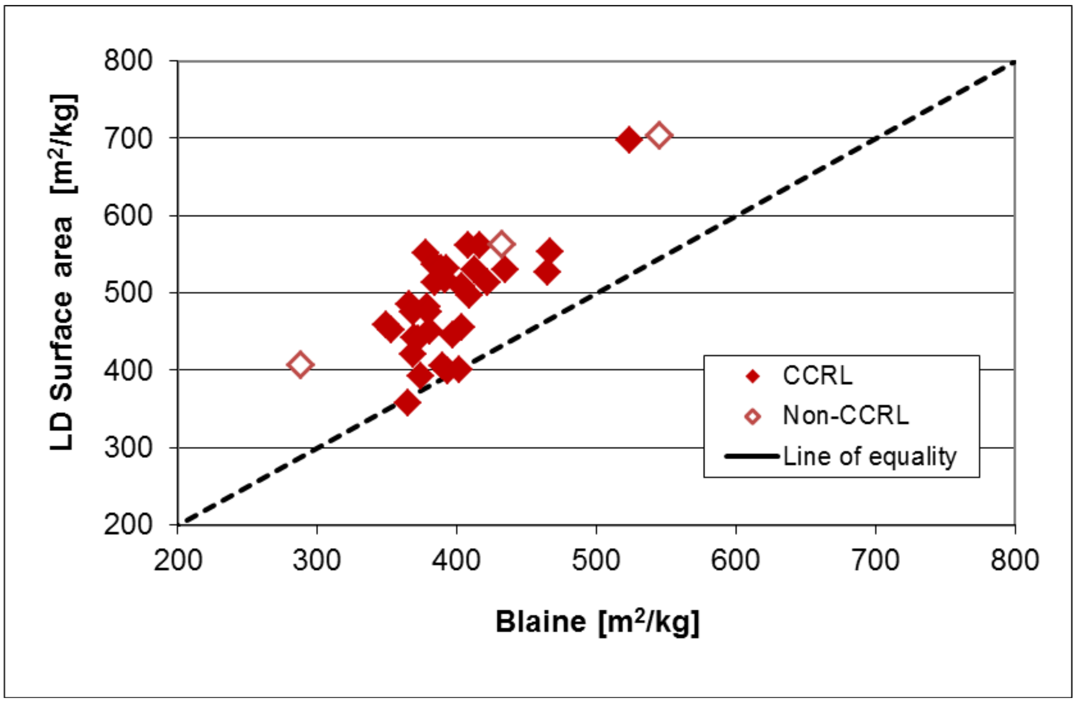

Figure 3: Relationship between Blaine and LD surface area. The dashed line is the line of equality (slope = 1).

provides a perfect measurement of cement surface area, LD also provides an excellent measurement of the particle size distribution and the correct 45 µm sieve residue, which are not provided by the Blaine measurement. The instrument is more expensive than the Blaine apparatus but the measurement takes less than 30 min and can be automated, thus saving labor cost vs. the Blaine measurement. It also does not require calibration using a reference material such as SRM 114q. The SRM is useful for the LD test only to verify that the device being used is operating as expected.

Fineness and the shape of the particles

The X-ray CT is being used to provide particle shape determination, since cement particles are not really spheres. Knowing the true particle shape for each kind of cement will help in the comparison of different surface area measures. The X-ray CT measurements also give a measure of surface area for each particle measured. A sub-set of the CCRL cements considered for LD-PSD and Blaine have been chosen to be examined with X-ray CT, along with the three Non-CCRL cements listed in Table 1. Samples were made, consisting of cement particles dispersed in low viscosity-epoxy and contained in 3 mm diameter plastic tubes [18]. After X-ray CT scanning, computer programs were used to analyze the particles found in terms of shape and other geometric factors [17]. The number of particles computationally extracted from the samples for each cement type ranged from about 20,000 to 450,000. For the cement with the highest particle number, a total particle volume of about 1.2 mm^3 was examined. Using a spherical harmonic function expansion for each particle [17], different particle geometry parameters were computed for each particle, including their *volume equivalent spherical diameter* (VESD), which is the diameter of the (imaginary) sphere with the same volume as a given particle, and length (L), width (W), and thickness (T) of a particle, as defined in ASTM D4791 [19]. If the particles were truly spherical, then VESD = L = W = T.

Table 1: Properties of Non-CCRL cements [17]

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

Using VESD as a rough measure of particle "size," the cement particles processed had VESD ranges of about 10 µm to 100 µm. The particles smaller than this size were not able to be imaged by the X-ray CT apparatus available at NIST, so that a complete PSD and specific surface area could not be computed to directly compare with the other techniques.

The ratios of the "size" quantities serve as shape parameters (aspect ratios): L/W, W/T, and L/VESD. Again, for spheres these ratios would all be unity. Figure 4 shows how the values of L/W are distributed for CCRL cement 163, in terms of the volume fraction of the particles having a certain value of L/W. We see that there is a range of values for L/W for the CCRL 163 particles, with almost all of the particles having a value of L/W of less than 2.5. To create Figure 4, the symbols correspond to each bin in L/W used. The y-axis in Fig. 4 is exact. The uncertainty in determining the value of L, W, and T for each particle is estimated to be about 2 %, so that the uncertainty in the aspect ratios are about 5 %.

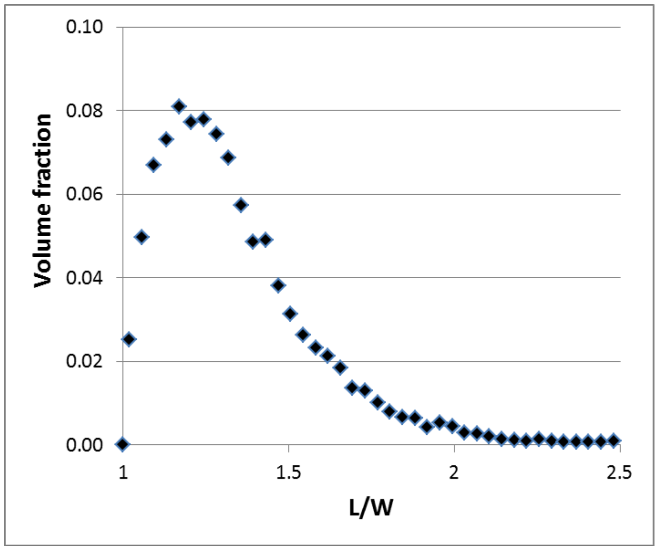

Figure 4: The distribution of the L/W aspect ratio for CCRL cement 163, in terms of volume fraction (the same as mass fraction in this case), as computed from X-ray CT measurements and spherical harmonic expansions.

The values of these parameters, averaged over all the particles of a given cement, serve as a simple way to compare the shape of the cement particles against each other and against the spherical assumption. For the cements considered, CCRL 115, 116, 133, 135, 146, 140, 141, 152, 161, 162, 163, and the three cements in Table 1, it was found that the average value of L/W ranged from 1.32 to 1.43 among the 14 cements, with a standard deviation for each cement, reflecting the distribution functions like that shown in Figure 4, of about 0.27. For the W/T parameter, the range was from 1.32 to 1.49, with a standard deviation for each cement of about 0.32. For the L/VESD parameter, the range was 1.45 to 1.61, with a standard deviation for each cement of about 0.20. The standard deviations in this case are only calculated for the purpose of giving an idea of the width of the distributions, and their near equality for each aspect ratio among cements implies that their aspect ratio distributions are similar to the CCRL 163 distribution shown in Fig. 4. Based on these values, these cements do not exhibit the properties of spherical particles, and one must keep that in mind when interpreting the Blaine and LD measurements for specific surface area and particle size, since both measurements assume spherical particles. One can also compute the ratio of the surface area of each particle, as measured by X-ray CT, to the surface area of the volume-equivalent sphere. This ratio, averaged over all particles, is about 1.2 for each cement. One might guess, then, that the LD results should be increased by a factor of about 20 % to get a better value for the surface area. However, a blended cement made with fly ash might not need the full 20 % correction, since fly ash particles tend to be more spherical than cement particles. Also, it seems, at least as judged by these three shape parameters and surface area ratios, that all these cements have particles of similar shapes. However, if we knew the detailed mineralogy of the individual cement types (actual clinker minerals, not just oxide abundances as given in the CCRL reports and mill sheets), some correlation of shape and mineralogy probably could be made (see reference [18]). Figure 5 shows an image of a typical particle from the cement in the second line of Table 1, taken directly from the X-ray CT measurement and spherical harmonic expansion. In this case, the non-sphericity is quite marked.

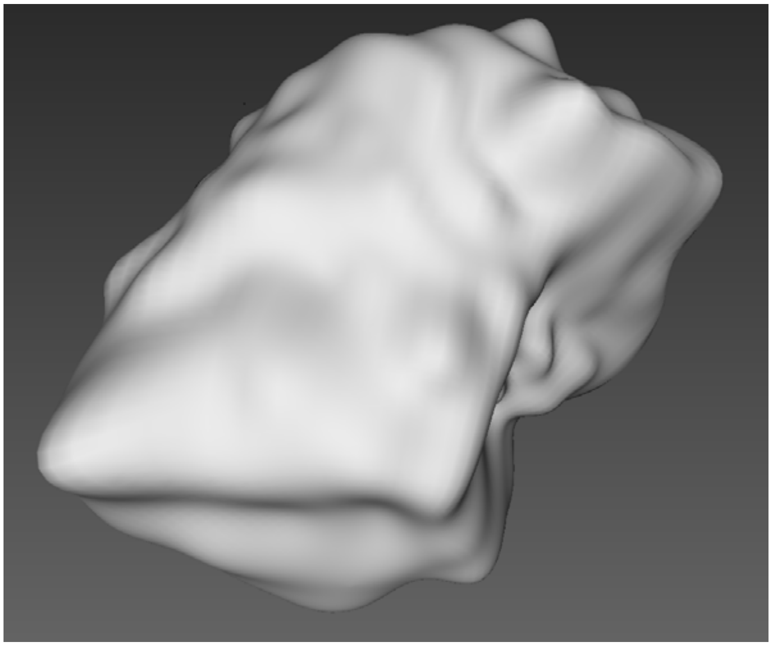

Figure 5: A typical particle from the cement in the second line of Table 1, as imaged by X-ray CT and reconstructed using spherical harmonics. At a VESD value of 81 µm, this is one of the largest particles in this cement type.

Fineness and macroproperties

The compressive strength measured at 3 d, 7 d and 28 d were collected from the CCRL database. Unfortunately, due to the type of cement used, the values of compressive strength were all very similar and the range of values was almost contained within the measurement uncertainty:

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

Therefore, it would be difficult to establish correlations between surface area, LD-PSD, and compressive strength using the CCRL cements. However, when the properties of three of the Non-CCRL cements (no strength data were collected for the SRMs) were examined, clear correlations between strength at 28 days, initial and final set and the fineness were clearly seen, as have been noted previously [17].

PROPOSED LASER DIFFRACTION STANDARD

From the discussion in this paper, it is clear that the most comprehensive test, providing both surface area and sieve residue, is the measurement by LD of the cement PSD. As of today, there is no standard for measuring PSD by LD in the US. There is a general ISO standard and ASTM standards that are not specific to cements. Thus, a standard test method is proposed that would be presented to AASHTO for adoption. The method could be used to measure particles from 0.4 µm to 2000 µm largely covering the range of a typical cement PSD.

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

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

Some key parameters should be reported:

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

The inter-laboratory study performed to certify SRM 114q provides the precision statement for both within-laboratory precision and multi-laboratory precision [8].

CONCLUSION

The most practical and comprehensive method of cement specific surface area is the laser diffraction (LD) test, and it also provides the particle size distribution (PSD), the specific surface area, and a good approximation of the 45 µm sieve residue. Over 30 cements were analyzed to compare fineness measured by Blaine, LD, 45 µm sieve residue and BET. The BET provides the most fundamental and direct surface area measurement, not based on the assumption that the particles are spherical. Correlation between BET and the other tests methods was not found to be excellent. This is not surprising, as cement particles are not spherical. Although in an ideal world nitrogen BET should be selected as the standard test, the method is slow to execute and is expensive in terms of time and labor. On the other hand, the LD-PSD provides a good correlation with 45 µm sieve residue and results in a wider range of values for the surface area than the Blaine, thus better distinguishing cements that perform differently. Thus, this study proposes the standardization of the LD-PSD method for cement powders. During an inter-laboratory study [10] it was determined that about 93% of the laboratories accredited by CCRL use LD for PSD. The test has been proposed to AASHTO for standardization.

The particles in cement powders are not spherical, and one must keep that in mind when interpreting the Blaine and LD measurements for specific surface area and particle size, since both measurements assume spherical particles. The cements studied here seem to have similar shapes, as least as measured by the three shape parameters and the surface area parameter considered. This is perhaps not so surprising, considering the ball-mill grinding process that likely produced all these cements.

It was found to be difficult to establish correlations between surface area, LD-PSD, and compressive strength using the CCRL cements, since the compressive strengths were tightly clustered and almost fell within the measurement uncertainty. However, when the properties of three of the Non-CCRL cements (no strength data were collected for the SRMs) were examined, clear correlations between strength at 28 days, initial and final set and the fineness were clearly seen.

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