Application Note

Cement

AN159

Clay and lime were used for centuries in construction due to its ability to hold structures together. Cement replaced those materials in the last century because of its greater binding strength. Cement is a water-based binder used to join other building materials, like sand and aggregate together. It is used in the production of mortar and concrete during the construction process. Its binding properties is the reason cement is one of the most common construction materials today.

Introduction

Cement is made by heating limestone in a kiln to 1450°C with small quantities of other materials such as clay or sand. The resulting 'clinker,' dark grey nodular materials, is then ground with a small amount of gypsum into a powder to make Portland cement. The most common use for Portland cement is in the production of concrete. It's a composite material consisting of cement, aggregate (gravel and sand), and water.

As a general rule, reducing the particle size increases rate of hydration and strength. On the other hand, grinding cement to smaller sizes increases energy costs, creating a critical need for measurement and control of the final product size. Further details can be found in references [1-5].

Measurement Techniques

Historic techniques to determine the particle size and surface area of cement include sieving [6-7] and air permeability, or Blaine, tests [8]. Modern cement laboratories deploy laser diffraction to perform particle size analysis. Laser diffraction has the advantage of speed, ease of use, and reproducibility. Although it is possible to correlate laser diffraction results to sieve and Blaine values, the techniques are inherently different. Hence, the correlation typically falls apart if the sample type changes. Therefore, it is wiser to use directly-calculated volume distribution results from the instrument's software package.

NIST SRM 114Q STANDARD

Portland cement, NIST Standard Reference Material (SRM) 114q, is analyzed throughout this study because the material has been well characterized in its chemical composition, physical properties, and is readily available for commercial purchase. The cement industry uses the material as the standard for calibrating fineness-testing equipment in accordance to ASTM Standard Methods; the instrumentation industry uses the material for round-robin studies using laser diffraction technique. There is no better choice than 114q in this case.

Experimental

Accurate measurement of cement in laser diffraction particle size analyzers proceeds either as a dry powder dispersed in air, or as a suspension dispersed in alcohol (typically isopropanol). Method development for wet or dry cement measurements follows the basic guidelines described in HORIBA Application Notes [9,10].

Choosing the refractive index to use for cement requires thought, since cement consists of so many different chemical species. The chemistry of cement is complex, but the basic ingredients include tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite, and calcium sulfate (gypsum). The NIST SRM 114q certificate suggests using 1.70 and 1.0i, thus all results presented here incorporate those values.

Dry results for cement shown in this document were obtained with a HORIBA Partica LA-960 laser diffraction particle size analyzer. Owing to the hard, robust nature of the material, all measurements used the highest air pressure setting for the PowderJet Dry Feeder. The PowderJet maintains a constant mass flow rate through the measurement zone via the clever use of an automatic feedback loop - resulting in the control of the vibration rate based on light source transmittance readings.

The system settings used for the dry measurements are presented below:

PowderJet	Small nozzle, max pressure
Iteration Number	15 (default)
Refractive Index	1.70-1.0i in 1.000 (air)

The wet results presented here were collected on both the LA-960 and LA-350 laser diffraction particle size analyzers. The LA-960 has a broader dynamic range (0.01-5000 µm) compared to the LA-350 (0.1-1000 µm). Both systems are suitable for this application, since most cement samples including the samples analyzed below contain little to no powder below 0.1 µm.

All measurements were made in isopropanol (IPA). Monitoring the optical background is important when using IPA as thermal fluctuations may cause additional scattering, leading to inconsistent results. When encountering this phenomenon, recirculating the IPA to obtain a stable background is typically required.

The system settings used for the wet LA-960 and LA-350 measurements are presented below:

Iteration Number	15
Refractive Index	1.70-1.0i in 1.390 (IPA)
Ultrasound	60 seconds @ level 7 (full power)
Circulation Speed	6
Measurement Time	5000 acquisitions/second

Results

The results from three measurements of NIST SRM 114q cement measured on the LA-960 dry PowderJet are shown below in Figure1 and Table1. Note the excellent reproducibility of the results, with the coefficient of variation well below those suggested in ISO 13320-1 [11].

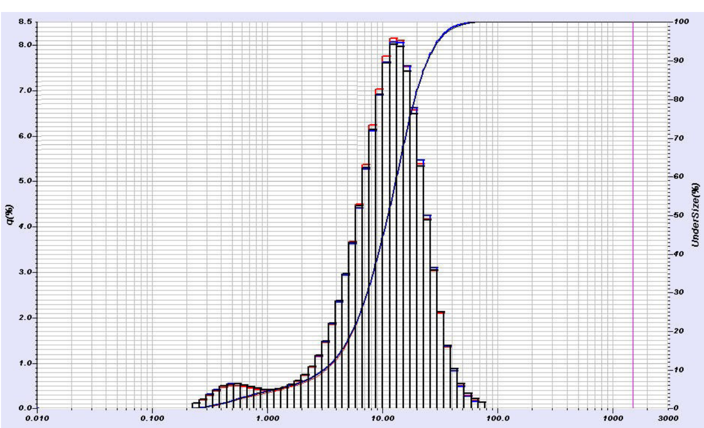

Figure 1. Three replicates of Portland cement was measured dry with the LA-960. The results have proven to be well below the coefficient of variation suggested by the ISO 13320-1 (11).

File Name	Dv10	Dv50	Dv90
LA-960 Dry Cement_1	3.256	11.152	24.586
LA-960 Dry Cement_2	3.116	11.183	24.671
LA-960 Dry Cement_3	3.112	11.128	24.92
Average	3.161	11.154	24.726
Std. Dev.	0.082	0.027	0.173
CV(%)	2.589	0.245	0.701
ISO13320-1	5%	3%	5%

The same material measured wet in IPA in the LA-960 appear below in Figure 2 and Table 2. These results, again, exhibit excellent reproducibility and meet ISO 13320-1 guidelines.

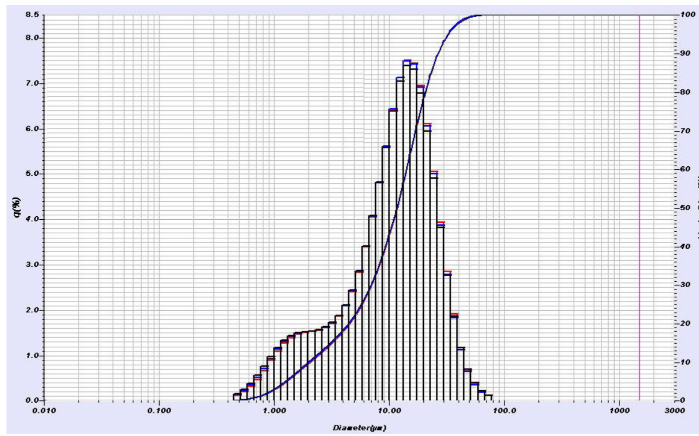

Figure 2. Three replicates of Portland cement was measured wet in IPA with the LA-960. Again, note these results exhibit excellent repeatability and meet ISO13320-1 guidelines.

File Name	Dv10	Dv50	Dv90
LA-960 Dry Cement_1	2.122	11.81	27.047
LA-960 Dry Cement_2	2.058	11.696	26.743
LA-960 Dry Cement_3	1.999	11.614	27.001
Average	2.06	11.707	26.93
Std. Dev.	0.062	0.098	0.164
CV(%)	2.996	0.838	0.607
ISO13320-1	5%	3%	5%

Once again, NIST SRM 114q is analyzed with the LA-350 0 Laser Diffraction Particle Size Distribution Analyzer. The LA-350 measures suspensions, and is well suited for routine QC measurements where a smaller, more portable, and economically-priced solution is beneficial.

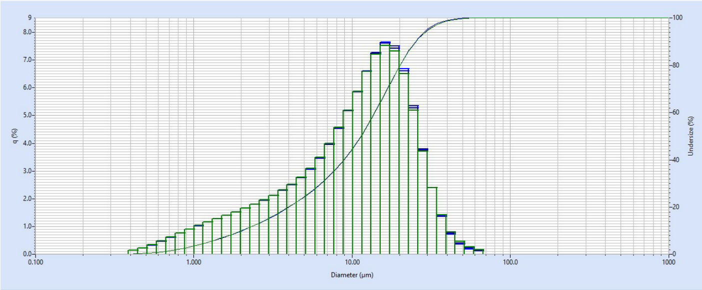

Figure 3. **Portland cement was measured wet in IPA with the LA-350. The results display excellent repeatability and good agreement with NIST SRM 114q reference PSD. This verified the efficacy of the LA-350 and the procedure used.**

File Name	Dv10	Dv50	Dv90
LA-350 Cement_1	2.047	11.447	25.246
LA-350 Cement_2	2.038	11.429	25.405
LA-350 Cement_3	2.033	11.355	25.486
Average	2.039	11.410	25.379
Std. Dev.	0.007	0.049	0.122
CV(%)	0.348	0.427	0.481
ISO13320-1	5%	3%	5%

Lastly, for validation purpose, analysis of NIST SRM 114q on the LA-960 shows the instrument's response compared to the NIST documentation. Figure 4 (below) displays the LA-960 result along with the certified 114q values, and the lower and upper limits of accepted results. As seen, the LA-960 results fall well within the accepted range.

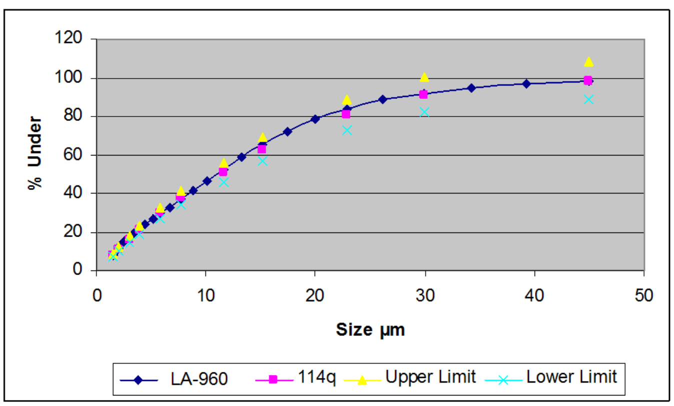

Figure 4. Dry LA-960 results are plotted against certified NIST SRM 114q values. The LA-960 results fall well within the lower and upper limits of the accepted values.

Conclusions

The laser diffraction technique is a mature and preferred method for particle size analysis. While both wet and dry dispersion offer excellent analysis result, measuring cement in dry allows the sample to remain in its original state, and eliminate the need to use IPA/dispersant. Both the LA-960 and LA-350 successfully meet the needs for research and routine quality control through the provision of speed, ease of use, repeatability, reproducibility, and reliability.

References

1. Frigioine G, Marra S., Relationship between particle size distribution and compressive strength in Portland cement, Cem Concr Res 6 (1976) 113-128

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3. Pommersheim J, Effect of particle size distribution on hydration kinetics. Materials Research Society Symposium Proceedings, 85, Mat Res Soc, Pittsburgh, 1987, pp. 301-306.

4. Wakasugi S, Sakai K, Shimobayashi S, and Watanabe H, Properties of concrete using belite-based cement with different fineness. in: O.E. Gjorv (Ed.), Concrete Under Severe Conditions 2, E & FN Spon, London, 1998, pp. 2161-2169.

5. Bentz D, Garboczi E, Haecker C, and Jensen O, Cement and Concrete Research, Vol. 29 (10), 1663-1671, 1999

6. ASTM C430-9C430-96 Standard Test Method for Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve.

7. ASTM C786-96 Standard Test Method for Fineness of Hydraulic Cement and Raw Materials by the 300-μm (No. 50), 150-μm (No. 100), and 75-μm (No. 200) Sieves by Wet Methods.

8. ASTM C204-07 Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus.

9. AN151 Wet Method Development, HORIBA Scientific Particle Analysis Application Note

10. AN154 Dry Method Development, HORIBA Scientific Particle Analysis Application Note

11. ISO13320-1 Particle Size Analysis – Laser Diffraction Methods, Part 1: General Principles.