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Optical Properties of Coal Combustion Byproducts for Particle-Size Analysis by Laser Diffraction

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A B S T R A C T

Laser diffraction analysis is commonly used for determining the particle-size distribution (PSD) of fly ash. However, there is currently no standard method for preparing samples and analyzing them. The Mie and Fraunhofer optical models are used to calculate the PSD of fly ash from laser diffraction data. The Mie theory is most applicable for particles smaller than 50 µm, and is therefore the most accurate model for the analysis of fly ash. However, the refractive index (RI) of fly ash is complex and not well known. This study presents the analysis of several supplementary cementitious materials (SCMs) such as coal combustion fly ash, gasification slag, or blast-furnace slag with the objective of providing optical properties for these materials. The optical constants that are most applicable to a given type of fly ash and slag are suggested.

A R T I C L E   I N F O

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1. Introduction

Several methods for determining the particle size distribution (PSD) of dry powders can be found in the literature, in particular, ISO 13320-1 (1999). This is an excellent reference for the theory and general operation of a laser particle-size analyzer. However, there still exists a need for a more specific reference of the necessary operational parameters when analyzing supplementary cementitious materials (SCMs) such as coal combustion fly ash, gasification slag, or blast-furnace slag. The optical constants that provide the most accurate and consistent PSD of fly ash and other SCMs are presented in this paper.

The complex refractive index (RI) is an important property influencing the extinction behavior of particles. The refractive index of a material comprises a real part and an imaginary part. The real part is the refractive index of the bulk material. The imaginary part relates to the absorption and is often referred to as the absorption index. Several articles on the subject of refractive index (Goodwin and Mitchner, 1989; Hackley et al., 2004; Liu and Swithenbank, 1993; Marakis et al., 2001) make note as to the uncertainty of what the imaginary part should be for fly ash. It is likely that there are no universal refractive and absorption indices for fly ash. However, these indices are required when analyzing fly ash using laser diffraction and the Mie theory. The Mie theory was chosen because as the new ISO standard states, although the Fraunhofer method can still be used for the measurement of particles greater than 50µm, Mie theory is recommended for those below 50µm and it is applicable across all particle sizes (Malvern Instruments, 2000). The magnitude of the effect of variation in the optical properties on the determination of the size distribution has been well illustrated, particularly by Hackley, et al. (2004). The goal of this study was to determine the appropriate complex refractive index values of SCMs, to improve the accuracy of particle-size analysis by laser diffraction.

2. Experimental Procedures

2.1. Chemical Analysis

The fly ash and slag samples were analyzed for major oxides by X-Ray Fluorescence. Table 1 lists the results of the chemical

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Table 1
Chemistry of the coal fly ash samples (as a weight percent)

Ash Class – Sample #	CaO	MgO	Na_2O	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2
F – 1	**1.26**	0.91	0.37	57.56	29.29	5.51	2.60	1.51
F – 2	**3.69**	0.72	0.51	45.60	18.24	18.72	2.13	0.99
F – 3	**5.04**	1.28	0.58	55.85	22.28	9.87	2.92	1.15
F – 4	**4.65**	1.96	0.74	50.84	25.20	9.15	3.69	1.00
F – 5	**10.51**	1.85	0.32	52.16	24.20	4.60	0.87	1.37
F – 6	**0.45**	1.02	0.33	56.35	27.88	4.74	2.70	1.50
F – 7	**6.90**	1.75	2.44	58.34	21.89	4.56	1.20	0.99
F – 8	**10.66**	2.32	2.07	53.84	22.45	4.90	0.67	1.12
F – 9	**1.83**	1.22	0.62	53.79	26.87	7.06	2.60	1.40
C – 1	**18.34**	4.44	1.44	42.78	22.27	6.51	1.22	1.38
C – 2	**24.89**	5.47	1.74	35.60	17.77	5.77	0.44	1.08
C – 3	**25.08**	4.22	1.37	34.32	18.75	4.97	0.48	1.17
C – 4	**29.04**	5.57	2.03	32.06	17.48	5.32	0.27	1.31
C – 5	**29.39**	4.53	1.97	30.45	17.06	4.08	0.32	1.11

Table 2
Chemistry of the gasification and blast furnace slag samples (as a weight percent)

Slag Type – Sample #	CaO	MgO	Na_2O	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2
GS – 1	**3.71**	1.05	2.40	53.93	19.47	10.87	2.33	0.99
GS – 2	**2.04**	1.20	0.34	40.14	21.39	28.11	2.42	1.05
BFS – 3	**30.21**	3.71	0.49	50.71	12.84	1.35	0.33	0.43
BFS – 4	**36.96**	1.47	0.06	46.94	8.56	1.56	0.38	0.36
BFS – 5	**38.49**	9.70	0.25	36.62	10.35	1.01	0.42	0.44

analysis for fly ash. The elemental analysis of the slag samples is shown in Table 2.

2.2. Particle-Size Distribution

The analyzer was a Malvern Mastersizer 2000 operating a Hydro 2000G module. Particle size distribution was calculated from laser diffraction data using Mie theory, which is described in detail by (Hackley et al., 2004; Mishchenko et al., 2002; Malvern Instruments, 2000).

2.3. Sample preparation

The fly ash and slag samples were dried in a forced-air oven then the lumps were removed with a mortar and pestle. For some experiments, the fly ash was first ignited at 750°C to remove the carbon. Samples were pre-mixed in the liquid dispersant (e.g. water or propan-2-ol) and sonicated for one minute to completely disaggregate particle clusters (Figure 1). For Class F fly ash and slags, water was used as the dispersant, along with a water-reducing admixture and sodium citrate. The cementitious nature of Class C fly ash required the use of propan-2-ol as the dispersant, to prevent the fly ash from hydrating.

2.4. Refractive Index Determination

The refractive index (RI) of the ash and slag samples was measured using optical microscopy (Becke Line method) and laser diffraction. The accuracy of these methods has been documented

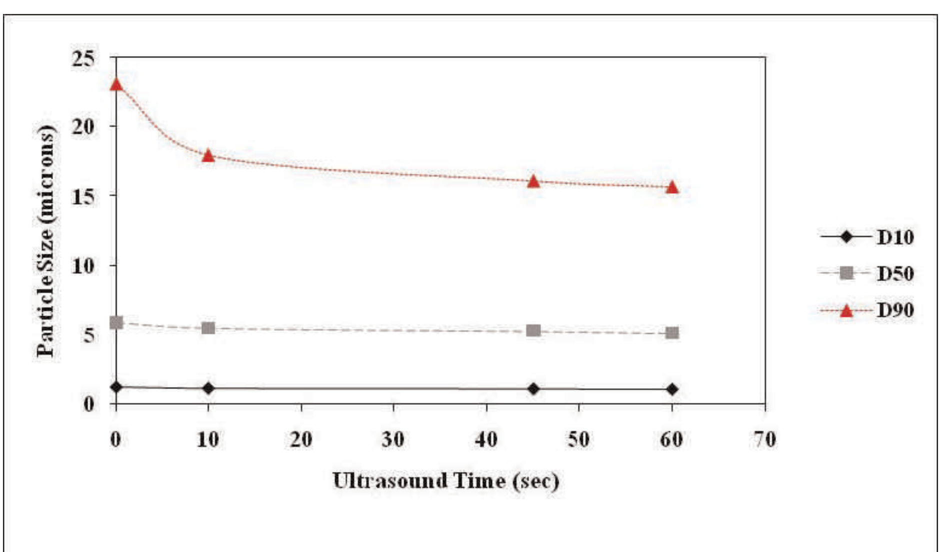

Fig. 1. Results of the Class F operational parameters tests. Each plotted line represents either the D_{10}, D_{50}, or D_{90} of the particle sizes.

Table 3
Refractive index values for the dispersants used in the obscuration tests. An Abbe refractometer model 2WAJ was used to measure the RI

Dispersant	Refractive Index
H_2O	1.330
H_2O + Na-Citrate + Gelenium	1.330
Propan-2-ol (IPA)	1.390
63% Lithium Hetropolytungstates (LST) (in LST-H_2O) soln	1.446
84% LST (in LST-H_2O) soln	1.486
100% LST	1.520
76% Cassia Leaf Oil in IPA	1.560
83% 1-MethylNapthalene (in Meth-IPA soln)	1.580
95% Cassia Leaf Oil in IPA	1.604

(Malvern Instruments, 2000; Nesse, 1991; Gilard and Dubrul, 1937). The Becke Line method, or immersion method, was used to measure the refractive indices of the fly ash and slag samples (Nesse, 1991). For fly ash, the measured RI should be considered as a mean value because of sample heterogeneity. Blast furnace slag was considerably more homogeneous.

As an independent method to verify the microscopy results, the laser diffraction analyzer was used to estimate the RI for a Class F fly ash using a procedure described by Malvern Instruments. This method uses a series of dispersants with different refractive indices while maintaining a constant mass of sample, to determine the obscuration for each dispersant. The minimum obscuration percentage reflects the matching of the dispersant RI to the fly ash RI (Malvern Instruments, 2009). The RI of the dispersants was measured with an Abbe refractometer (Table 3).

Table 4
Refractive index values for the fly ash samples as determined by the Becke line method

Ash Class – Sample #	Refractive Index	Range
F - 1	1.55	1.54 – 1.56
F - 2	1.55	1.53 – 1.57
F - 3	1.55	
F - 4	1.56	1.54 – 1.58
F - 5	1.56	1.55 – 1.57
F - 6	1.57	1.56 – 1.58
F - 7	1.57	
F - 8	1.58	1.56 – 1.60
F - 9	1.61	1.58 – 1.64
C - 1	1.60	1.56 – 1.64
C - 2	1.63	1.59 – 1.67
C - 3	1.65	1.60 – 1.70
C - 4	1.65	1.63 – 1.67
C - 5	1.65	1.64 – 1.66

3. Results and discussion

3.1. Microscopy

Figure 2 is an optical micrograph of a Class F fly ash suspended in immersion oil with a refractive index of 1.552. By examining the fly ash in a series of immersion oils of different RI, the correct oil would be selected in which approximately half the particles had a RI greater than the oil, and half had a lower RI than the oil. The RI of this oil represents the mean refractive index of the particles. The mean and deviation of the RI for each fly ash and slag sample is shown in Table 4 and Table 5.

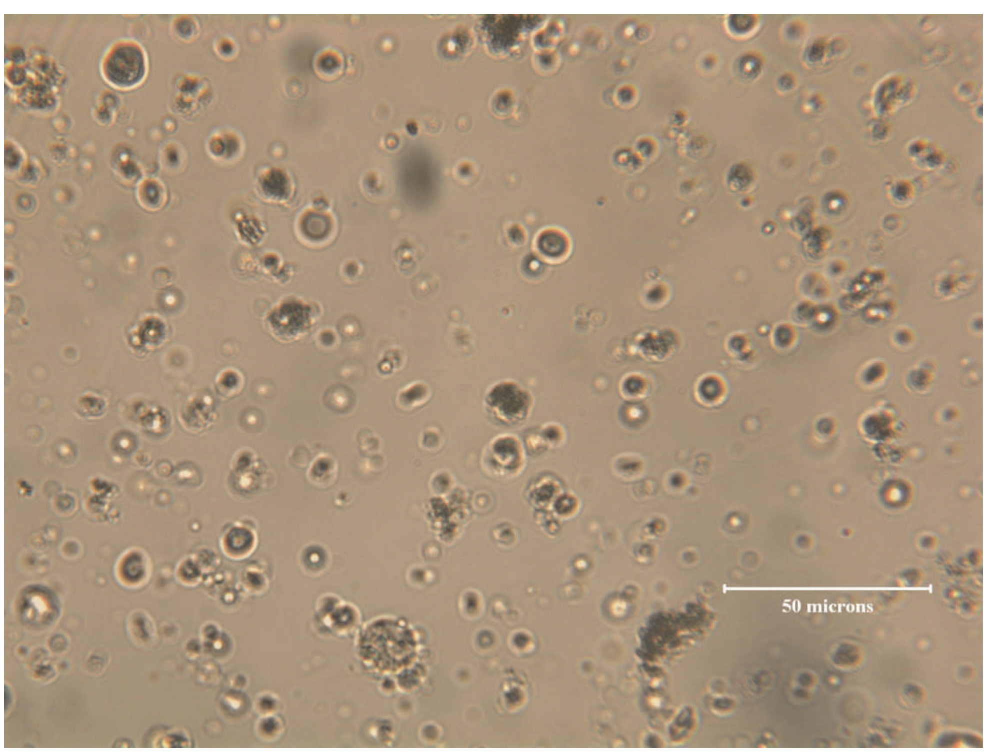

Fig. 2. Petrographic image of Class F fly ash particles. Particles in this view are generally less than 20 microns in diameter. Magnification is 50x. The light band around the fly ash particles is the interference band, or Becke Line.

Table 5
Refractive index values for the slag samples. GS – Gasification slag; BFS – Blast-furnace slag

Slag Type – Sample #	Refractive Index	Range
GS – 1	1.55	1.54 – 1.56
GS – 2	1.62	1.61 – 1.63
BFS – 3	1.61	1.60 – 1.62
BFS – 4	1.62	1.61 – 1.63
BFS – 5	1.65	1.63 – 1.67

3.2. Particle-Size Analyzer

Figure 3 shows the obscuration curve for a Class F fly ash. The data indicated a minimum obscuration at 1.56 RI, which was consistent with the microscopy data for this sample. The result of the PSA test is supported by the findings of Watt and Thorne (1965) from their research on the properties of fly ashes.

3.3. Calculation of the Refractive Index

3.3.1. Fly Ash and Slag

The RI for the fly ash and slag samples was calculated based on the weight percent of each major oxide that comprises the sample, using the equation and constants of Gilard and Dubrul (1937) for glass. Because fly ash and slag are primarily made-up of amorphous glassy material, the formula was applied to these materials and produced a refractive index trend similar to that obtained using the Becke Line method. As seen in Figure 4, a linear relationship existed between the concentration of CaO in the fly ash, or for the blast furnace slag, and the calculated refractive index; The refractive index generally increased with increasing CaO content. This trend was consistent with the microscopy data (Figure 4) although the exact RI values differ, in part, because of the presence of crystalline ferrite spinel, other crystalline material such as quartz and mullite, and the heterogeneous composition of the amorphous glassy material. Unlike the blast furnace slag, the gasification slag samples had a low CaO concentration, a high Fe_2O_3 content, and a high refractive index. Therefore, they did not exhibit the same relationship with CaO content that was observed for fly ash and blast furnace slag.

3.4. Absorption Index

The absorption values were determined by comparing the known concentration of the fly ash sample in solution to the concentration determined by the analyzer (Rawle, 2006). The volume concentration was determined based on the mass of material used and the specific gravity in a constant volume of dispersant. The absorption index entered into the analyzer software was then varied until the calculated concentration approached the known concentration (Rawle, 2006). For a Class F ash, an absorption value of 1.0 was found to provide the most accurate concentration (using a RI=1.56); whereas, for a Class C ash an absorption value of 0.1 was selected (using a RI=1.65). Cyr and Tagnit-Hamou (2001) report a refractive index value for fly ash of 1.73. This RI value is similar to that of Portland cement (1.73), C_3S (1.71-1.72), and C_2S (1.72-1.74). However, no chemical data for the fly ash was provided. The high RI value reported in the paper may be caused by a high CaO and/or Fe_2O_3 content.

For both the blast furnace slag and the gasification slag an absorption value of 1.0 produced the most accurate results (using a RI=1.62). Table 6 and Table 7 show the range of absorption values obtained for several of the ash and slag samples. The variation in absorption values between the two classes of ash may be attributed to the surface roughness of the particles, as described in ISO 13320-1 (1999), or due to the presence of irregularly shaped particles.

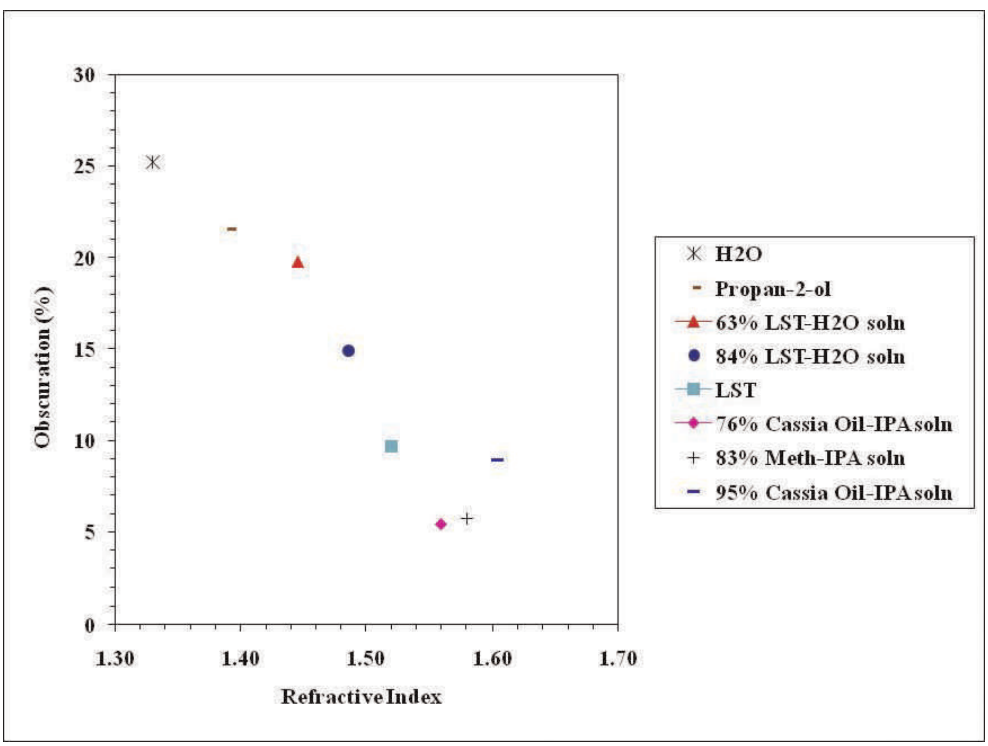

Fig. 3. Obscuration test results from the PSA for the Class F fly ash samples. The lowest point in the curve represents the RI of the fly ash.

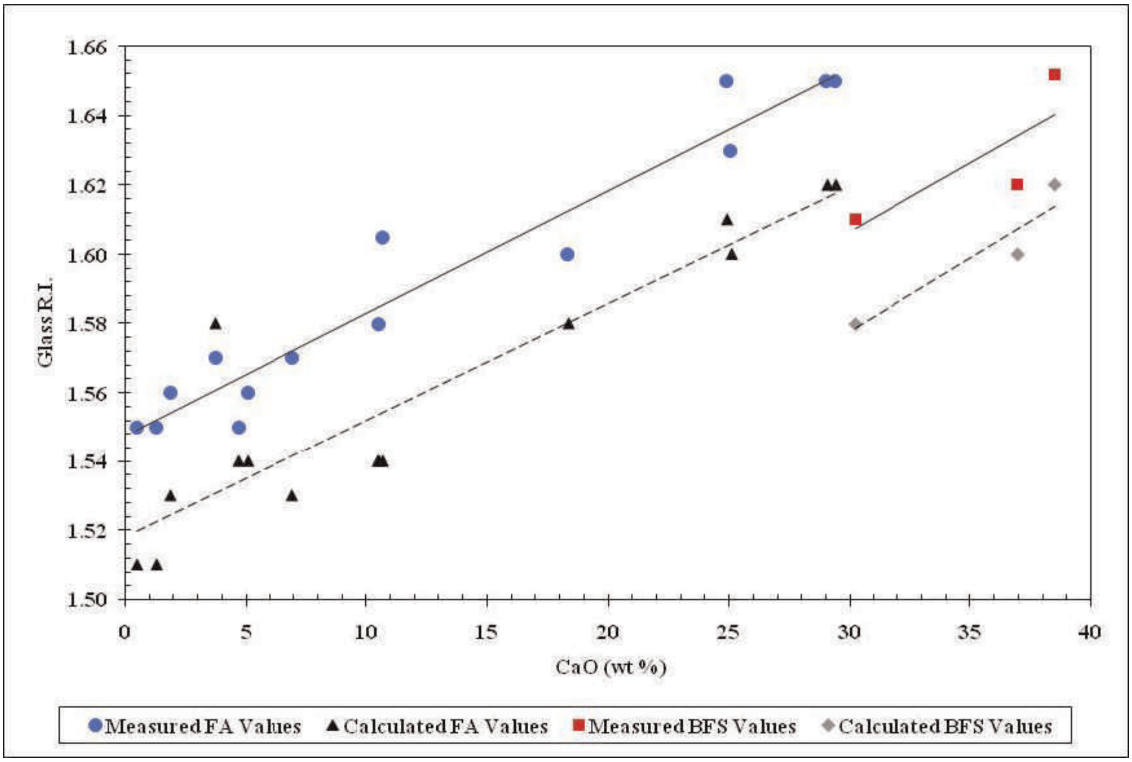

Fig. 4. Chart illustrating the measured RI data compared to the calculated values based on the Gilard-Dubrul formula. FA = Fly Ash; BFS = Blast-furnace Slag

Table 6
Range of concentrations produced by varying the absorption value; and the corresponding weighted residual percentages for fly ash

Ash Class - Sample #	Measured Concentration (Vol. %)			
	Abs = 1.0	Abs = 0.1	Abs = 0.01	Known Vol. %
F – 2	**0.0066**	0.0084	0.0109	**0.0060**
F – 3	**0.0052**	0.0070	0.0090	**0.0060**
F – 4	**0.0050**	0.0076	0.0087	**0.0060**
F – 9	**0.0050**	0.0067	0.0077	**0.0057**
C – 1	0.0038	**0.0053**	0.0071	**0.0057**
C – 2	0.0034	**0.0054**	0.0065	**0.0055**
C – 5	0.0034	**0.0054**	0.0062	**0.0055**

Table 7
Range of concentration produced by varying the absorption value; and the corresponding weighted residual percentages for slag

Slag Sample	Measured Concentration (Vol. %)			
	Abs = 1.0	Abs = 0.1	Abs = 0.01	Known Vol. %
GS – 1	**0.0049**	0.0073	0.0082	**0.0058**
GS – 2	**0.0062**	0.0084	0.0100	**0.0058**
BFS – 3	0.0047	**0.0068**	0.0081	**0.0059**
BFS – 4	**0.0053**	0.0076	0.0092	**0.0058**
BFS – 5	**0.0060**	0.0082	0.0101	**0.0058**

4. Summary and conclusions

Based on the foregoing, it is apparent that fly ash does not have a universal refractive index or absorption value. However, by following several different methods to determine the real and imaginary parts of the complex refractive index, two sets of values for fly ash, and one value for slag, were determined to improve the accuracy of particle-size analysis by laser diffraction. The results indicated that the RI of fly ash and blast furnace slag can be estimated if the CaO content is known. Gasifier slag did not follow the same trend, probably because of its high iron content. Based on the experiments completed in this study, fly ash with less than 10% (by weight) of CaO had an apparent absorption value of 1.0, whereas fly ash and blast furnace slag with greater than 10% CaO had an absorption value of 0.1.

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