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Physical and chemical characteristics of fly ash using automated scanning electron microscopy

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HIGHLIGHTS

- ASEM simultaneously measures size, shape, and chemistry of fly ash particles.
- ASEM showed consistent performance with repeat investigations.
- The bulk composition from ASEM and XRF analysis compared well.
- Particles of a certain chemistry are shared by both Class C and F ashes.

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ABSTRACT

Currently, bulk chemical analysis techniques are typically used to determine the composition of fly ash. While bulk analysis provides useful information, the bulk averaging process of a method removes the specificity of the data. Since the individual particles in the fly ash are participating in different reactions, the information about individual particles may be more useful for predicting the performance of fly ash within concrete. This paper presents a method to characterize fly ash on a particle-by-particle basis using automated scanning electron microscopy (ASEM). This technique can simultaneously measure the particle size and chemical composition. The data compares well with bulk powder measurements while also providing single particle information on thousands of samples. This paper also presented advanced characterization of fly ashes using this ASEM method, which cannot be observed from the bulk measurement of fly ash.

1. Introduction

Fly ash is a heterogeneous powder, which is the main residue of coal combustion. Fly ash particles tend to be spherical in shape, micrometers to millimeters in dimensions, and they can be highly reactive, depending on the chemistry of the individual particle. Such reactivity has caused its demand to grow steadily over past 30 years [1,2], especially as a low-cost binder in the concrete and construction industries [2–4]. In addition to the replacement of cement in concrete, fly ash has been used as an adsorbent for flue gas cleaning, treatment of wastewater, used as raw material for the synthesis of geopolymers, Portland cement, and zeolites, and as a backfill materials in mining [2,5,6].

Due to the increasing demand of fly ash and the distinct properties required in fly ash for its specific application, better understanding of the physical and chemical properties of the material is important. Fly ash characterization is typically done on their bulk chemistry and their performance in concrete [7–11]. Normally, the bulk chemical composition is determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD). However, it should be noted that fly ashes particles are assemblages produced by combustion, melting, and then solidification of mineral components within ground coal. During this process, each coal particle independently undergoes different physical and chemical changes while passing through the burning zone of the power plant. The composition of each individual particle of fly ash should be the results of the particular types of the coal and the physical and chemical process occurred in the power plant. Therefore, the bulk chemical analysis only provides an average description of these different particle assemblages. As a result, new alternative techniques have been pursued to investigate individual heterogeneous particles [9,12–15].

In particular, electron microscopy, including both scanning electron microscopy (SEM) [13,14] and transmission electron

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microscopy (TEM) [15] are promising tools for micro-characterization of individual fly ash particles. However, assessment of particles by SEM or TEM is limited by the performance of manual routines conducted by the users. Therefore, the results can be variable by the operator experience and is not practical to use routinely. To overcome this, alternative techniques have been developed that automate the usage of an SEM [12,16–30]. In this paper, this technique is referred to as automated scanning electron microscopy or ASEM. The ASEM method is powerful, as it can be used to simultaneously investigate the size, shape, and chemical composition of individual fly ash particles rapidly. Unfortunately, the ASEM approach for fly ash has not seen widespread usage. This can be attributed to little agreement in the past publications over sample preparation, analytical method, correction factors, and the number of particles to be investigated to produce a useful description of the sample [16–30]. Such differences in the ASEM techniques can result in a significant error in characterizing the chemical and physical properties of fly ash particles. Specifically, the comparison of the chemistry from electron techniques and bulk chemistry such as XRF from individual particles has been in error by as much as 50%. This poor agreement has been suggested to be caused by the geometry of the individual particles being quite different then the flat uniform plain assumed in most correction routines [31–33].

The focus of the first part of this paper is to synthesize the best practices, in a systematic approach, to be implemented in establishing a standard method for investigating fly ash using ASEM. The present paper provides: (i) a sample preparation technique, (ii) appropriate instrument settings, (iii) data correction techniques that uses a specialized atomic number, absorption, and fluorescence correction (ZAF) that takes into account the particle shape and size, and (iv) recommendations for the proper number of particles that provide the statistically reliable results for particle size distribution and bulk chemical composition. Advanced characterization of fly ashes using this ASEM methods are, then, presented, which cannot be observed from the bulk measurement of fly ash. The work presented will also show how this technique can be used for more detailed investigation of fly ash and other complex particles.

2. Materials

Twelve fly ashes were investigated for this work. Eight of the fly ashes were Class C and four were Class F based on ASTM C618 [34]. The bulk oxide compositions for all fly ashes were analyzed using XRF analysis with the provisions of ASTM D4326 [35] and the results are shown in Table 1. The sum of the elemental oxides do not exactly equal to 100% but are close. This slight difference is the result of the unreported elements, variations in the calibration procedure, and the assumptions made in the data analysis.

3. Method

3.1. Overview of ASEM

As briefly mentioned in the Introduction, the ASEM technique uses an SEM equipped with an image analysis based operating system and a silicon drift detector based energy dispersive X-ray spectrometer (EDS). The primary advantage is that the physical and chemical information of individual particles are simultaneously measured. Therefore, the ASEM technique provides detailed quantitative information about both the elements of individual particles and their morphological information. In addition, the ASEM technique with the current instrument and settings can investigate about 500 particles per hour. The ability of analyzing particles can be improved with improvements in detector design, stage mechanical systems, and optimization of scan parameters.

In this study, the analysis of fly ash was performed using SEM–EDS. An overview of the ASEM technique is illustrated in Fig. 1. The technique starts in a defined region of interest (ROI) as shown in Fig. 1(b). This ROI is then partitioned into the equal size squares referred to "fields" [Fig. 1(c)]. Each field is inspected by the electron beam to find fly ash particles using the back scattered electron (BSE) imaging. When a particle is found, it is screened according to the elemental and morphological criteria selected by the user. Any particle which does not satisfy the requirements is discarded. If the particle meets the criteria, the chemical and physical data of the particle is collected [Fig. 1(d)]. The elemental concentrations of individual particles were then calculated using the ZAF correction. The first part of this paper focuses on developing a systematic procedure to investigate fly ash particles using this technique.

It should be noted that many of the settings listed in this paper are intended to remove bias from the sampling. It can be said that bulk methods such as XRF and XRD do not significantly suffer from bias because the material analyzed is comprised of millions of particles. This method, comparatively, relies on the random sampling of a much smaller number of hundreds or thousands of particles. Therefore, settings that bias the sample collection or analysis must be addressed. This means that greater care must be taken in the sample prep and analysis then is typically required for bulk XRF or XRD.

3.2. Sample preparation

The size of fly ash particles typically varies within a range from 1 μm to 150 μm and most of particles are less than 75 μm (No. 200 sieve) [2–4,10]. Larger particles were removed by first sieving the fly ash with the No. 200 sieve. These larger particles provide challenges for the image analysis techniques since they may span several fields. In addition, including large particles could skew the results of the bulk analysis because one single large particle would have the same volume of thousands of smaller particles.

Next, the particles are uniformly dispersed on a substrate for analysis. This was achieved by using 15–18 mg of sieved fly ash that was added to 50 ml of solvent containing an equal proportion of acetone and isopropyl alcohol in a polypropylene conical vial. The fly ash to solvent ratio is kept very low to reduce particle agglomeration and this low ratio help the SEM identifying particles automatically. With too much fly ash, the automated routines will often fail to identify single particles, instead passing the electron beam over agglomerations and biasing the results. Although image analysis techniques can help remove these from the final data sets, it is best to prepare samples in the best manner possible to minimize agglomerations.

The solvents were chosen to limit the leaching of ions from the fly ash. Since the compositional analysis is of paramount importance to the methodology, non-polar and fast drying solvents were chosen.

Once the requisite sample of fly ash was placed in the mixture, it was capped, sealed, and then sonicated for 30 min using an ultrasonic cleaner. This sonication of the fly ash suspension dispersed the particles, broke up the agglomerated particles, and held them in suspension. Two or three drops of the suspension was, then, placed using a pipette onto a double-faced adhesive carbon substrate which was applied on an aluminum gun shot residue (GSR) mount. The solution evaporated leaving behind the fly ash particles on the substrate. All prepared sample stubs were stored in the vacuum desiccator until testing. It should be noted that rapid drying is also important, since high surface tension solutions can move particles across a substrate and agglomerate them. The acetone–alcohol mixture has low surface tension and extremely high vapor pressure, resulting in a rapid drying process that deposits the particles in a uniform film.