# A Performance-based Fly Ash Classification System Using Glassy Particle Chemical Composition Data

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ABSTRACT

The current ASTM C-618 standard for fly ash classification uses an index based on a limited set of elements determined by XRF. This approach treats the fly ash as if it were a homogeneous material of uniform composition. However, detailed analysis of thousands of individual fly ash glass particles by Automated SEM (ASEM) shows that the chemical composition can vary widely from one particle to another. The XRF data represent an average over all these diverse compositions including inert crystalline phases like quartz. Consequently, an index computed from the XRF data may not be a reliable predictor of fly ash performance. On the other hand, the chemical compositions of the individual glassy particles are not completely randomly distributed, but rather cluster around certain values that reflect the chemical compositions of the precursor clay minerals. These clusters could be the basis of a more accurate statistical description of the chemical composition of the fly ash in terms of the weighted compositional center of each of the clusters. Moreover, the clusters can be used to define the chemical compositions of a set of calcium aluminate silicate glasses. Each of these glasses has a characteristic reactivity that can be determined experimentally.

Thus a fly ash classification system could be developed based on a set of standard fly ash glass compositions that would predict the reactivity of the fly ash and hence its performance as a supplementary cementitious material.

## I. INTRODUCTION

The motivation for this research is the need for an improved classification system for fly ashes[1-3]. The ASTM specification C-618 defines just two classes based on bulk chemical composition in terms of the sum $Al_2O_3+SiO_2+Fe_2O_3$ with the criteria that Class C ashes 50-70% and Class F > 70%[4]. However, these classes are not directly related to pozzolanic activity, which depends upon mineralogy of the individual particles, rather than the bulk chemical composition of the whole fly ash. The most important factors are the quantity of reactive material present and the rate at which the reactive components enter into the hydration reaction.

The reactive components in fly ash are normally in the form of glassy phases, but the available analytical techniques cannot characterize these glassy phases directly. Bulk chemical analyses such as XRF cannot discriminate between glassy and crystalline phases. X-ray diffraction with Rietveld analysis can provide an indirect estimate of the glassy phase by calculating the difference between the XRF bulk chemistry and the overall chemistry of the crystalline phases. However, this gives only a bulk average glass composition. The computer automated scanning electron microscope (ASEM), which identifies and characterizes individual particles, shows that the chemical composition can vary widely from one particle to another. Therefore, the

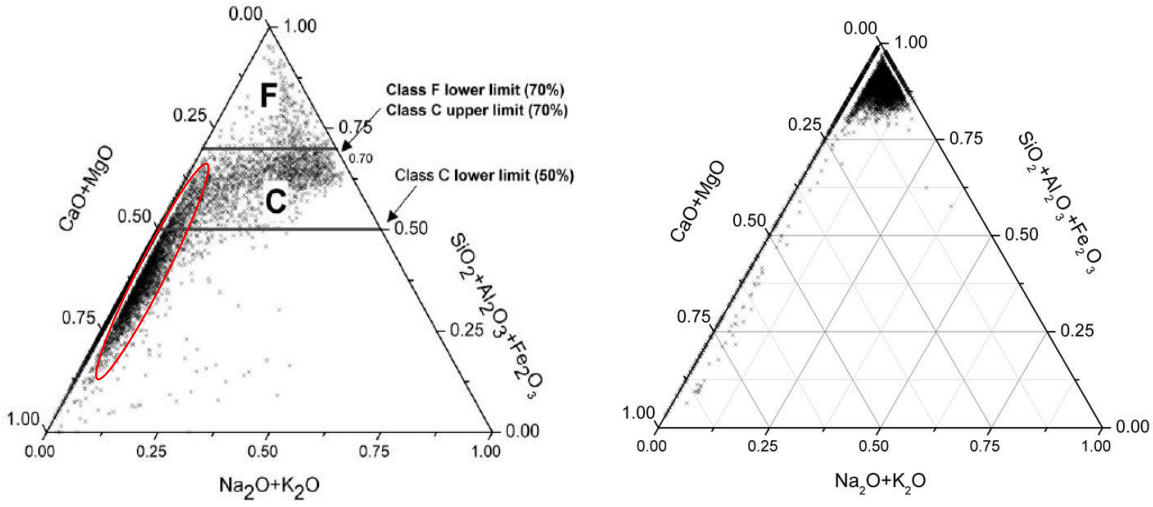
objective of this paper is to consider the possibility of a performance-based classification system based on cluster analysis of the individual particle data.

## II. PARTICLE ANALYSIS BY AUTOMATED SCANNING ELECTRON MICROSCOPY (ASEM)

As an alternative to using the fly ash bulk composition, the selected approach is based on the analysis of individual fly ash particles using Automated Scanning Electron Microscopy (ASEM) [5-7]. This measures the major elements in a selected particle and its diameters along several orientations. Glassy particles are identified using the aspect ratio, estimated from a 64 x 64 pixel micrograph of each individual particle. This is based on the concept that the glassy particles form by cooling from droplets of melted clays or other minerals, and thus would have nearly spherical shapes in contrast to the more angular shapes of the crystalline particles. The identification of crystalline particles is then confirmed using characteristic elemental ratios. A typical analysis measures about 10,000 particles. An example of ASEM analysis is shown in Fig. 1.

For better visualization of the elemental data, the particle compositions are plotted in triaxial coordinates corresponding to the three glass science categories of glass formers (right), alkali modifiers (bottom) and alkali-earth (left). Each point in the plot represents the composition of a single particle as noted above. The ASTM specification C-618 is based on the sum of the three components $Al_2O_3$+$SiO_2$+$Fe_2O_3$, with 50% specified as the lower limit for Class C ashes and 70% for Class F. This sum turns out to be the same as one of the axes of the triaxial diagram used here to plot the ASEM data. Thus, the ASTM C-618 limits plot as straight horizontal lines as shown in

Fig 1. The fly ash shown in Fig. 1 is classified as Class C based on its bulk composition. However, some particles actually plot in the Class F region. Others show significant concentrations of CaO and could be self cementing.




(a) Coal Creek Fly Ash (b) Cayuga Fly Ash

Figure 1: Composition of all spherical particles of (a) Coal Creek and (b) Cayuga fly ash in glass coordinates

This plot also illustrates the inadequacy of the current ASTM C-618 classifications, which do not take into account the CaO or alkali contents of the fly ash. It is often stated that Class C ashes are higher in calcium than Class F, even though the CaO content is not given explicitly. This statement is apparently based on the constant sum properties of chemical compositional data discussed below. In other words if the sum $Al_2O_3$-$SiO_2$-$Fe_2O_3$ decreases, then the CaO content must increase in compensation. However, this is strictly true only for the four component system: $Al_2O_3$-$SiO_2$-$Fe_2O_3$ -CaO. Since the sum $Al_2O_3$-$SiO_2$-$Fe_2O_3$ is at the top vertex and the CaO is at the left vertex, this actually defines a binary system, and hence all the data points

would have to plot along the left triaxial axis in Fig. 1. However, as can be seen, the data are scattered all across the upper half of the triangle, indicating little or no correlation between CaO and $Al_2O_3$+$SiO_2$+$Fe_2O_3$. This is the result of the presence of the additional components $Na_2O$ and $K_2O$ which add more degrees of freedom.

## III. CLUSTER ANALYSIS

Figure 1 also gives some idea of the dispersion in the particles' chemical compositions. A mean chemical composition for the all particles can be calculated, but it would have such large compositional variances as to be meaningless. However, in the plot, several clusters can be observed whose derived statistics would indicate far better in class compositional similarity. For example, as shown by the red outline, there is an elliptical cluster running parallel to the CaO+MgO axis below $SiO_2$+$Al_2O_3$+$Fe_2O_3$ ≈ 0.60. These clusters reflect the chemical compositions of the precursors of the glassy particles, i.e. different clay minerals. Each of these clusters would have a characteristic glass chemical composition, and hence a characteristic reactivity. This suggests the possibility of predicting the reactivity of the overall fly ash in terms of the fractions and characteristic reactivities of these clusters.

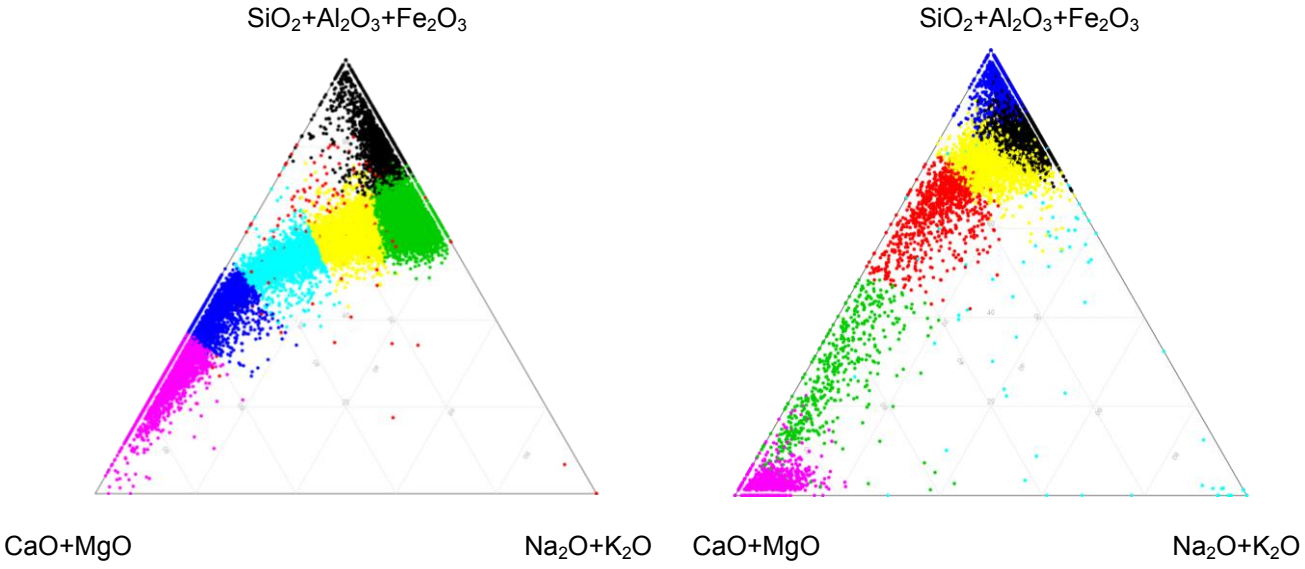
Each cluster is defined by its weighted compositional centroid and the boundary in chemical composition space which encloses all the members of the cluster. This space would have as many dimensions as the number of major chemical constituents, which can consist of as many as 7 and thus the boundary would be a hypersurface. The ellipse shown in Fig 1a is actually a projection of the hypersurface onto the 2 dimensional planes. The centroid is strictly a geometrical concept; it is the center of

symmetry of shape of the boundary. It can also be regarded as the mean chemical composition of the cluster, provided that this mean is calculated correctly as discussed below.

In the k means method of cluster analysis,[8] the number, k, of clusters is specified in advance. The algorithm then assigns all the members of the data set into one of these clusters based on some distance metric in the composition space. For the purposes of this paper, the distance metrics used were Euclidian, following the rules of orthogonal vector space geometry. Once all the members have been assigned, the cluster boundary is drawn around the extreme values of the cluster. In this approach, outliers are generally defined by single particle clusters (i.e., groups with only one compositional member). For the purposes of summarization and compositional modeling, such outliers are generally ignored.

As an example of cluster analysis the ASEM data for some fly ashes from an Iowa State University study were used. The open source implementation of S, known as R [9] includes cluster analysis software, which was used to identify the clusters in the ASEM data by the k-means method. This was based on 7 constituents: $K_2O$, $Na_2O$, CaO, MgO, $SiO_2$, $Al_2O_3$ and $Fe_2O_3$. The number, k, of clusters was also limited to 7. It is worth noting that, while the number of clusters is arbitrary, decreasing the number of clusters tends to reduce the precision of in class statistics. Consequently, increasing the number of clusters reduces the summarization and predictive power of the derived clusters. The value chosen here represents a balance between these two considerations, although it is derived only through empirical study. The clusters obtained by using k-mean method on spherical particles of Cayuga and Coal Creek fly

ashes are shown in Fig. 2. There are seven clusters found in the analysis of each fly ash appearing in Red, Magenta, Green, Blue, Cyan, Yellow and Black.




(a) Coal Creek (b) Cayuga

Figure 2: Clusters of spherical particles of (a) Coal Creek fly ash and (b) Cayuga fly ash in $CaO+MgO$-$SiO_2+Al_2O_3+Fe_2O_3$-$Na_2O+K_2O$ coordinates

Table 1 Classification of Glassy Phase based on Cluster Analysis of Coal Creek Fly Ash

| Cluster No. | Color | Name | Number (%) |
|---|---|---|---|
| 1 | Black | Si-Al-Fe glass | 9.57 |
| 2 | Red | Trace element | 1.00 |
| 3 | Green | Si-Al-Fe glass | 32.67 |
| 4 | Blue | CAS glass | 11.85 |
| 5 | Cyan | CAS glass | 11.93 |
| 6 | Magenta | Ca rich glass | 15.64 |
| 7 | Yellow | CAS glass | 17.34 |

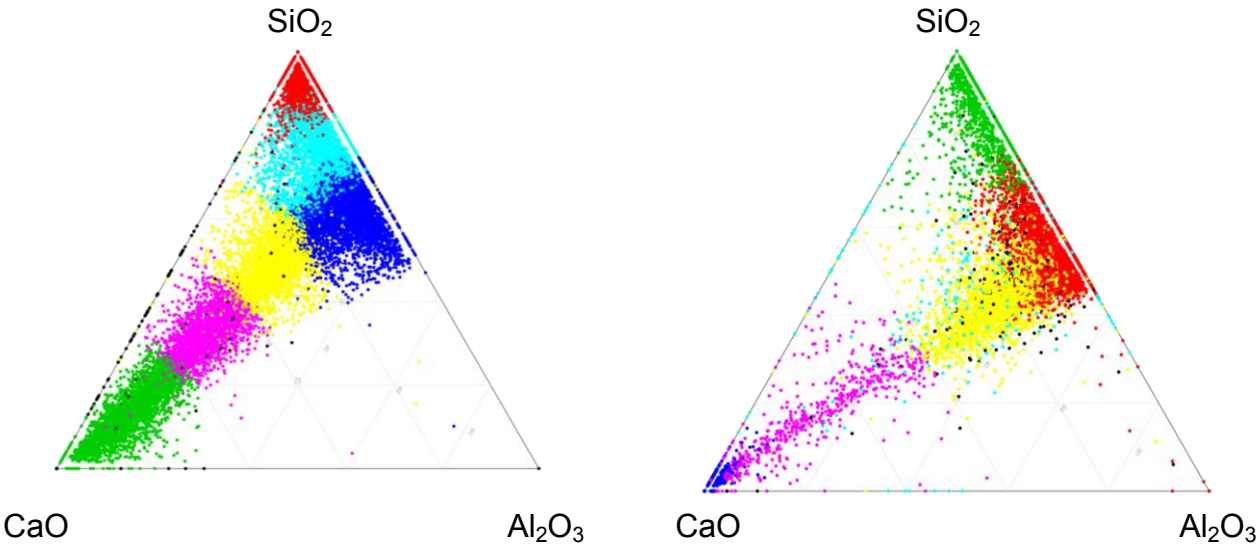
Table 2 Classification of Glassy Phase based on Cluster Analysis of Cayuga Fly Ash

| Cluster No. | Color | Name | Number (%) |
|---|---|---|---|
| 1 | Black | Si-Al-Fe glass | 44.55 |
| 2 | Red | CAS glass | 7.00 |
| 3 | Green | Ca rich glass | 3.86 |
| 4 | Blue | Si-Al-Fe glass | 11.82 |
| 5 | Cyan | Hi Alkali glass | 0.78 |
| 6 | Magenta | Ca rich glass | 6.35 |
| 7 | Yellow | Si-Na glass | 25.65 |

It can be seen that the boundaries of the clusters in the Coal Creek fly ash are clearly separated from one another except for the black cluster, which overlaps with other clusters. This may be because the particles in the black cluster have significant amounts of the other elements, such as Ti, that are not shown as individual axes in the diagram. A higher number k of clusters would be needed to separate this widely dispersed black cluster into more precisely defined clusters. However, each cluster would then contain only a small number of particles. Each cluster in this fly ash contains a similar number of particles although the green cluster, which is the Si-Al-Fe glass, has the highest number of particles accounting for 33% of all particles. The average composition of this cluster is 56% Si-Al-Fe and 28% alkali content, which indicates high reactivity of the particles.

There are only two major clusters in Cayuga fly ash; black and yellow. The black cluster accounts for 45% of the total particles. It has high Si-Al-Fe content and low Ca-Mg and Na-K content which is considered aluminosilicate glass. Their high Si-Al-Fe content indicates low reactivity of the cluster. The wide dispersion of the cyan class seems to indicate that more clusters would better define the class.

In order to relate the clustering observed in the ASEM data to conventional mineralogical analysis, the cluster data are also plotted as oxides in a $CaO$-$Al_2O_3$-$SiO_2$ ternary diagram. Note that the colors in this $CaO$-$Al_2O_3$-$SiO_2$ diagram do not represent the same clusters as found in the $CaO+MgO$-$SiO_2+Al_2O_3+Fe_2O_3$-$Na_2O+K_2O$ diagrams in Fig 2. The ternary diagram suggests that the clusters arise from the original chemical compositions of the inorganic minerals in the coal. This could be either clay minerals or other minerals such as quartz or pyrites. For example, the clay mineral kaolinite[10] has the formula $Al_2Si_2O_5(OH)_4$ for an $Al_2O_3$:$SiO_2$ ratio of 1:2 and no CaO. Thus it could be a source for the blue cluster in Coal Creek and the red cluster for Cayuga. The common clay mineral montmorillonite has idealformula:$Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ and it could be a source for the yellow cluster in Coal Creek and the yellow cluster in Cayuga. The Na content in this mineral could volatilize during the melting process.




(a) Coal Creek (b) Cayuga

Figure 3: Clusters of spherical particles of (a) Coal Creek fly ash and (b) Cayuga in $CaO$-$Al_2O_3$-$SiO_2$ coordinates

The majority of the clusters found in Coal Creek fly ash are the green, blue, cyan magenta and yellow clusters. The difference between these clusters is the CaO and $SiO_2$ content for which as CaO decreases the $SiO_2$ content increases in compensation. They have similar $SiO_2/Al_2O_3$ ratios in which $SiO_2$ is greater than $Al_2O_3$. The major clusters in Cayuga fly ash; blue, magenta, black and cyan, also differ by the CaO content. They have similar $SiO_2/Al_2O_3$ ratios and $Al_2O_3$ is almost equal to the $SiO_2$ content.

Compositional data statistics

A complication of working with compositional data is the constant sum property. If a chemical composition is given in terms of a set of mass fractions, $x_1$, $x_2$, $x_3 \ldots x_d$, then by definition:

$$\sum_{i=1}^{d} x_i = 1 \qquad (1)$$

This constant sum property implies that there are only $d$-1 independent variables since:

$$x_d = 1 - \sum_{i=1}^{d-1} x_i \qquad (2)$$

Consequently, it is not correct to calculate a mean composition of a set of samples by simply calculating the means of the individual $x_i$.

Aitchison[11] proposed a way to overcome this problem by calculating a set of ratios:

$$r_i = \frac{x_i}{x_d} \qquad i \neq d \qquad (3)$$

Then the mean composition and the variances of a set of samples can be calculated in terms of these ratios. For convenience, Aitchison used the logs of these ratios to

calculate the means, consequently this technique is known as the logratio method. As a result the mean computed from the logratio is the geometric mean rather than the arithmetic mean, but in many cases this is more appropriate when dealing with geological data sets.

The use of ratios rather than mass fractions to describe a chemical composition may initially be hard to understand, but the two sets of coordinates are equivalent. As shown in Fig 4a for a hypothetical sample composition A, in a ternary phase diagram the ratio is a line. Since there are two possible ratios that can be calculated for the three components, the result is a pair of lines. Their intersection defines the position of the data point.

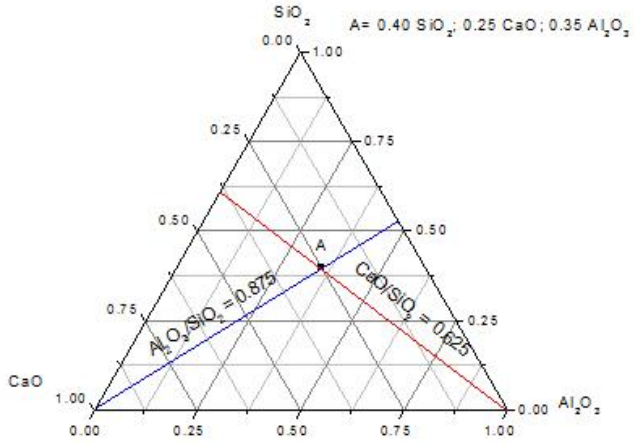



Fig. 4a: Illustration of the equivalent of mass fraction and ratio coordinates for hypothetical composition A.

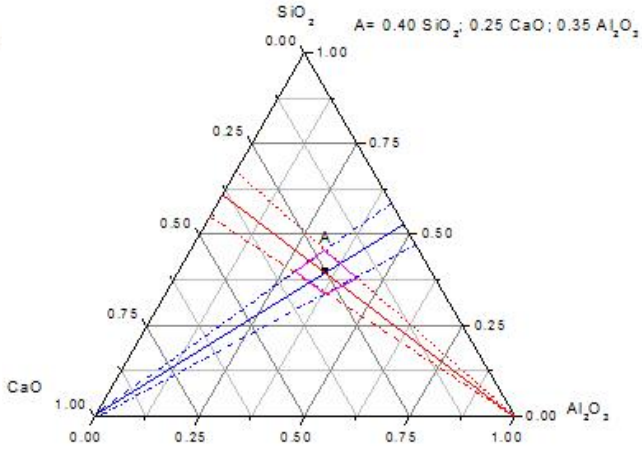



Fig. 4b: Illustration of variances in ratio coordinates

The logratio method also calculates variances, $\sigma_i^2$, in terms of ratios. This produces a confidence interval $\pm \sigma_i$ around $r_i$ which plots as a pair of lines bracketing the line for $r_i$ as shown in Fig 4b. The intersections of these line pairs form a polygon which defines a region of confidence around the point *A.*

Clusters vs Standard Glass Compositions

The k means cluster analysis algorithm avoids the constant sum issue because it uses an iterative geometric method which compares the distances between pairs of data points to find the centroid of the data set. However, there would some problems with a fly ash classification system based directly on clusters. The set of clusters is specific to a given data set. This means that the cluster centroids and boundaries would vary from one fly ash sample to another, as illustrated in Figs. 2 & 3. In other cases, the number k may even be different. Consequently, it would not be possible to compare fly ashes using their respective sets of clusters.

However, it would be possible to define a set of standard clusters and then to evaluate how well a data set fits that standard set. This set would be developed by statistical analysis of the clusters analyzed from a variety of actual fly ashes. The specifications of these standard clusters would also take into account geochemical constraints such as clay mineral chemistry. Since the centroid of each of these standard clusters would be a specific chemical composition, this also defines a set of standard glasses. An example of such a standard set of glasses is given in Table 3 [12].

Table 3: Set of Standard Glasses

| Glass | SCL | SCM | SCH | SCF | SCFK | SCB | SYH | SYF | SYQ | SYB |
|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 17.46 | 14.69 | 13.98 | 14.28 | 16.38 | 16.54 | 23.71 | 26.80 | 9.59 | 25.99 |
| CaO | 4.79 | 13.15 | 25.35 | 3.51 | 7.75 | 13.83 | 22.40 | 4.07 | 1.34 | 4.61 |
| $Fe_2O_3$ | 5.77 | 6.28 | 7.30 | 5.53 | 5.07 | 5.40 | 7.28 | 10.83 | 2.02 | 12.11 |
| $K_2O$ | 6.50 | 4.63 | 2.18 | 7.34 | 2.73 | 2.35 | 0.12 | 2.92 | 1.78 | 2.07 |
| MgO | 1.86 | 2.52 | 3.43 | 1.23 | 5.70 | 3.36 | 4.81 | 3.44 | 0.24 | 1.01 |
| $Na_2O$ | 15.61 | 10.43 | 6.09 | 11.06 | 2.24 | 4.33 | 0.11 | 1.35 | 0.34 | 0.86 |
| $SiO_2$ | 47.93 | 48.20 | 41.57 | 56.94 | 60.13 | 53.59 | 41.40 | 50.45 | 84.69 | 53.35 |

Given the standard chemical compositions, it would then be possible to make specimens of the glasses. These would then be characterized for density and reactivity.

Development of a Performance-based Classification System

A performance-based classification system could be developed using a set of these standardized glass compositions. In this approach, for a total number, N, of glassy particles analyzed by ASEM, each particle would be assigned to a standard glass class, based on its chemical composition. Then for *k* number of standard glass classes:

$$N = \sum_{i=o}^{k} n_i \tag{4}$$

where $n_i$ is the particle count in the $i^{th}$ class. The $n_o$ class is introduced to account for those outlier particles that could not be assigned to any of the standard set within the specified tolerances.

The $n_i$ themselves can be plotted as a histogram, but for comparison between different fly ashes they should be normalized to give fractions or percentages i.e. $f_i = n_i/N$. It should be noted these are number fractions. To convert them to mass fractions it is necessary to use the individual particle radius and the density of the glass.

$$x_i = \frac{\sum_{j=1}^{n_i} r_j^3 \rho_i}{\sum_{i=1}^{k} \sum_{j=1}^{n_i} r_j^3 \rho_i} \tag{5}$$

where $x_i$ is the mass fraction, $r_j$ is the radius of the $j^{th}$ particle and $\rho_i$ is the density of the $i^{th}$ standard glass. It is necessary to use this approximation because the ASEM system does not measure the density of the individual particles.

Since the reactivities of the standard glass types would be known, either the $f_i$ or the $x_i$ can be used to predict the performance of the fly ash and thus make up a performance-based classification system. Rather than deal with a set of individual reactivities, it may be more desirable to use a single composite reactivity index. Depending on how the reactivities are defined, this could be a mass-based index:

$$A_m = \sum_{i=1}^{k} a_i m_i \tag{6}$$

where $A_m$ is the reactivity index based on mass and the $a_i$ are the reactivities of the individual glass types.

However, because the reactions take place at the solution/glass interface, a more appropriate index may be based on surface areas:

$$A_s = \sum_{i=1}^{k} a_i s_i \tag{7}$$

where $s_i$ are the surface area fractions, given by:

$$s_i = \frac{\sum_{j=1}^{n_i} r_j^2}{\sum_{i=1}^{k}\sum_{j=1}^{n_i} r_j^2} \tag{8}$$

In this case, the $a_i$ are surface area normalized reactivities. Another advantage of the surface-based reactivity index is that avoids the need to specify particle densities.

## V. CONCLUSIONS

The availability of data on individual fly ash particles provided by the ASEM makes it possible to identify characteristic clusters of glass particles with similar compositions. These clusters can then be used to develop a standard set of fly ash

glass compositions. The density and reactivity of each of these glasses would then be determined experimentally. This standard set of glasses can then form the basis of a classification system for fly ashes using mass or surface –based fractions. Finally, a composite reactivity index can be calculated from the individual glass reactivities.

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