

Quantitative Characterization of Fly Ash Reactivity for use in Geopolymer Cements

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Abstract

The ability to characterize the reactivity of fly ashes is an essential part of making use of this aluminosilicate-rich waste product in geopolymer binders. Most fly ash reactivity investigations only consider the bulk reactivity of the ash because of incomplete information on the constituent phases. This study used a new method for characterizing fly ash and the resulting geopolymer reaction products that combines Rietveld quantitative x-ray diffraction (RQXRD) and scanning electron microscopy coupled with multispectral image analysis (SEM-MSIA) to quantitatively characterize both crystalline and glassy phases. The combined information from these methods gives quantitative mass fractions of each independent crystalline and glassy phase in any material analyzed, including unreacted fly ash, partially reacted fly ash, and geopolymer reaction products. The method was used in the present study for characterizing fly ashes prior to alkali-activation and to identify the reaction products formed in a geopolymer paste. The different phases in fly ash were shown to react differently in the alkaline environment required for geopolymerization.

Originality

Obtaining accurate, quantitative compositional information on the glassy phases in fly ash is essential in order to understand their behavior in geopolymer binders. The proposed characterization protocol is a novel way to determine this information using analytical equipment that is already used in cementitious materials analysis. The drawback of traditional fly ash chemical characterization by oxide analysis is the inability to identify and quantify individual glassy phases, not to mention to discern their different reactivities. By using this method to characterize the multiple glassy phases present in fly ash as opposed to assuming them to be uniform, a more targeted method for designing activating solutions can be developed.

Chief contributions

The work contributes a new way of determining and quantifying the multiple reactive phases in fly ash instead of chemical testing or oxide analysis. This method has been used to show that the reactivities of different glassy phases within fly ash are not the same, thus the typical assumption that the bulk amorphous content is incorporated into the geopolymer microstructure can be refined based upon improved raw material characterization. By using the RQXRD and SEM-MSIA method to characterize fly ash glassy phases, the relationships between activator and glass reactivity can better defined to engineer a material with improved properties.

Keywords: geopolymer, fly ash, SEM

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1. INTRODUCTION

Geopolymer cements are a relatively new aluminosilicate-based cementing material that can be used in place of ordinary portland cement in concrete construction (Davidovits 1991). The development of geopolymers came from the necessity of new construction materials that were strong, durable, and non-flammable. Since their initial discovery, geopolymers have moved into the forefront of a search for green building materials. Interest in new green building materials has come from an increased scrutiny on the environmental impacts of manufacturing cement; Damtoft *et al.* (2008) reported that cement production accounts for 5 % of the global CO₂ emissions resulting from human activity. Geopolymers are considered environmentally friendly cements since they can be made with waste materials such as fly ash from coal burning power plants or blast furnace slag from iron and steel processing. Fly ash, in particular Class F fly ash (ASTM C 618 2008), consists of mainly aluminosilicate glasses with minor presence of crystalline phases such as quartz, mullite, hematite and maghemite. It consists of 60 % -80 % x-ray amorphous glasses (McCarthy *et al.* 1990), which may be available to form the geopolymer structure under highly caustic conditions.

To synthesize geopolymers, an aluminosilicate powder is mixed with an activating solution such as sodium or potassium hydroxide. Mixtures are often designed using solution-powder ratios or water-powder ratios (Bakharev 2005). A more exact technique is to use oxide ratios to optimize the chemistry of the system such that a strong, durable material is formed. The literature has many recommendations for the ratios that lead to proper polymerization and strength such as: $M_2O/SiO_2 = 0.2-0.48$, $SiO_2/Al_2O_3 = 3.3-4.5$, $H_2O/M_2O = 10-25$, and $M_2O/Al_2O_3 = 0.8-1.6$, where M is an alkali metal (Khale and Chaudary 2007), with many other refinements (Fletcher *et al.* 2005; Duxson *et al.* 2005a, Duxson *et al.* 2005b, Duxson *et al.* 2007c). The difficulty in determining these ratios is that only the reactive portion of the fly ash and/or activating solution should be considered, and determining the reactive constituent of fly ash is difficult. In some work, an acid dissolution method is used to determine reactive silica (Fernandez- Jiménez *et al.* 2006). Alternately, the reactive phases in fly ash have been calculated by subtracting the amount of each crystalline phase from the bulk x-ray fluorescence (XRF) chemistry of the fly ash (Fernández-Jiménez *et al.* 2006, Soare and Garcia-Luna 2008). Although these methods give an indication of potential reactivity, they do not necessarily represent the caustic environment of geopolymer formation. Thus, an improved method to analyze fly ash reactivity, in particular in caustic environments, is needed.

Chancey and others (2010) introduced a novel method for quantifying the composition of fly ash. In this approach, Rietveld quantitative x-ray diffraction (RQXRD) and scanning electron microscopy coupled with multispectral image analysis (SEM-MSIA) were used to show that there were multiple glassy phases present in a particular fly ash and the phases were compositionally varied. Chancey (2008) also showed that the individual glassy phases in fly ash reacted differently when subjected to the caustic environments similar to those found during geopolymer formation. By applying this method to geopolymers, the reactivity of fly ashes can be determined, and a protocol for selecting activators for a particular fly ash can be developed. The present study initially tested reactivity by evaluating compressive strength of mortar cubes, and compared the results for each geopolymer to the fly ash compositions found using the Chancey's method.

2. MATERIALS AND METHODS

Two Class F (ASTM C 618) fly ashes were chosen for this study. The oxide analysis data are presented in Table 1. Both fly ashes were produced at power plants in Texas and are named according to the plant. The total sum of oxide constituents does not equal 100 %, as the fly ashes have some trace elements that were not identified through inductively coupled plasma optical emission spectroscopy (ICP-OES). Each lot of fly ash was produced in 2005 at separate coal-burning power plants. The activator selected for mortar cube compressive strength studies was 8M NaOH solution. The solution was made from a prepared 10M solution diluted with ultrapure water to the proper molarity.

Table 1: Oxide composition of the fly ashes based upon a single analysis. (courtesy of Savannah River National Laboratory, Aiken, SC)

Oxide	Oxide Composition (wt. %)	
	Coletto Creek	LEGS
Al ₂ O ₃	20.98	17.80
CaO	12.77	10.70
Fe ₂ O ₃	4.85	7.74
K ₂ O	1.20	1.43
MgO	3.42	2.31
Na ₂ O	1.53	0.45
SO ₄	0.32	0.40
SiO ₂	48.15	54.14
TiO ₂	1.04	1.20
total:	95.49	96.24

Mortar cubes were prepared according to ASTM C109 (2007). The solution to powder ratio for the mortar cubes was 0.4. The curing process of the geopolymer mortars varied from the method outlined in ASTM method C109. The mortar cubes were cured in a 100 % humidity fog room at room temperature (23 °C). Instead of demolding at 24h as per ASTM C109, the mortar cubes were demolded at 3 d, since the geopolymer mortars had often not gained sufficient strength for handling by 24h. Upon demolding, the mortar cubes were placed in airtight plastic storage bags and kept in a temperature controlled 23 °C room until testing. Compressive strength testing was completed at 7d and 28d.

Quantitative characterization of the crystalline portion of each fly ash was completed using x-ray diffraction and Rietveld analysis. The x-ray source produced Cu-K α radiation and operated at 40 kV and 30 mA. Relatively lengthy scan times were used to increase the x-ray counts at each step for better resolution of phases. The scans were run from 10° - 70° 2 θ with a six second dwell time at each step and a step angle of 0.02° 2 θ . The total scan time was approximately six hours. Due to the large amorphous content in fly ash, an internal standard was used for Rietveld analysis. Rutile was interground with the fly ashes as 10 % by mass of the sample. Qualitative identification of the crystalline phases was completed using the Inorganic Crystal Structure Database. Quantification of phases was completed using the Rietveld method.

To characterize and quantify the glassy phases in fly ash, the SEM method outlined in Chancey *et al.* (2010) was followed and is summarized here. The fly ashes were epoxy mounted and polished flat for x-ray mapping. The scanning electron microscope used for this work had a field emission electron source. Two silicon-drift EDS detectors were used for elemental mapping. Silicon drift detectors allow for faster signal processing such that high x-ray count rates can be collected in less time than with conventional Si(Li) detectors (Goldstein *et al.* 2003). The microscope was operated at 15kV accelerating voltage, and the specimen was positioned in the chamber such that the two EDS detectors collected a total of approximately 80,000 counts per second (cps). The maps were collected slowly, with 256 μ s dwell time for each pixel and a 1024 x 1024 map size. This resulted in a scan time of around 4.5 minutes for a single pass. In order to decrease the noise in the images, approximately 14 passes were made over the specimen for a total data collection time of just over one hour. The following elemental maps were collected for each specimen: Ca, Al, Si, Fe, Na, Mg, K, O, C, and S. Post-processing was completed using ImageJ¹, a freely available image processing program.

The image processing methodology was outlined in Chancey (2010), and further information on the identification of phases from x-ray maps can be found in Lydon (2005). In general, the images were smoothed and the background cut to decrease the noise in each image. The images were virtually stacked using Multispec². Only three images in the stack can be viewed at once, as red,

¹ ImageJ, <http://rsbweb.nih.gov/ij/>

² Multispec, <https://engineering.purdue.edu/~biehl/MultiSpec/>

green, and blue channels. By viewing all combinations of the stacked images, the phases present in the fly ash could be identified and phase classes established. Multispec allowed for phase designations to be assigned to particular pixels as training fields. The software used these training fields to assign every pixel in the image to a particular phase. Once the phase areas were quantified by Multispec, the phase densities were used to solve for mass quantities of each phase in the fly ash. The density selected for glassy phases was 2.5 for non alkali-modified phases and 2.4 for alkali-modified phases after Hemmings and Berry (1987) and Pieterse (1993). The crystalline constituents were calculated based upon their known densities from the literature.

3. RESULTS AND DISCUSSION

To gain an initial understanding of the fly ashes' reactivities, geopolymer mortars were made with each fly ash using identical sodium hydroxide solutions and solution-to-powder ratios (s/p). The activating solution was 8M NaOH with a 0.4 s/p. The compressive strength results are shown in Figure 1. It was observed that the Coletto Creek fly ash formed a stronger geopolymer than the LEGS fly ash under identical mixing and curing conditions. At seven days, the LEGS fly ash did not reach 1.0 MPa, while the Coletto Creek fly ash had a compressive strength of 5.6 MPa. At 28 days, the Coletto Creek fly ash far exceeded the LEGS in compressive strength, reaching a value of 20 MPa compared to 10.5 MPa. Given that the oxide compositions for the two fly ashes appeared similar (Table 1), the need for further investigation into the chemistries of the two materials was apparent.

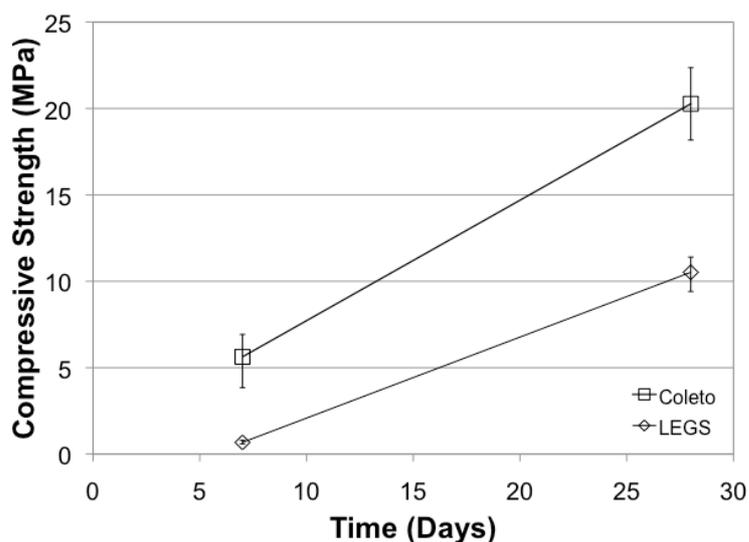


Figure 1: Compressive strengths of geopolymer pastes made with 8M NaOH (0.4 s/p). Error bars represent a \pm 1s of the mean.

Crystalline phases were identified by Rietveld analysis, which is shown in Figure 2. The amorphous content of the Coletto Creek fly ash was approximately 82 %. The fly ash also contained quartz, mullite, hematite, and periclase in small amounts. The LEGS fly ash amorphous content was approximately 86 %, and the crystalline constituents included mullite, hematite, magnetite, quartz, and anhydrite.

Scanning electron microscopy with x-ray mapping was completed in order to analyze the glassy phases in each fly ash. To illustrate the process of analyzing the images, the Coletto Creek fly ash will serve as an example. A backscattered electron image was recorded for visual identification of phases by looking at the brightness of particular particles and regions. The relative darkness or lightness of a pixel or region is indicative of different average atomic number of the region, thus a differing phase. Elemental maps were collected to determine the composition of the particular phases in the fly ash, and they were analyzed in the method of Chancey *et al.* 2010.

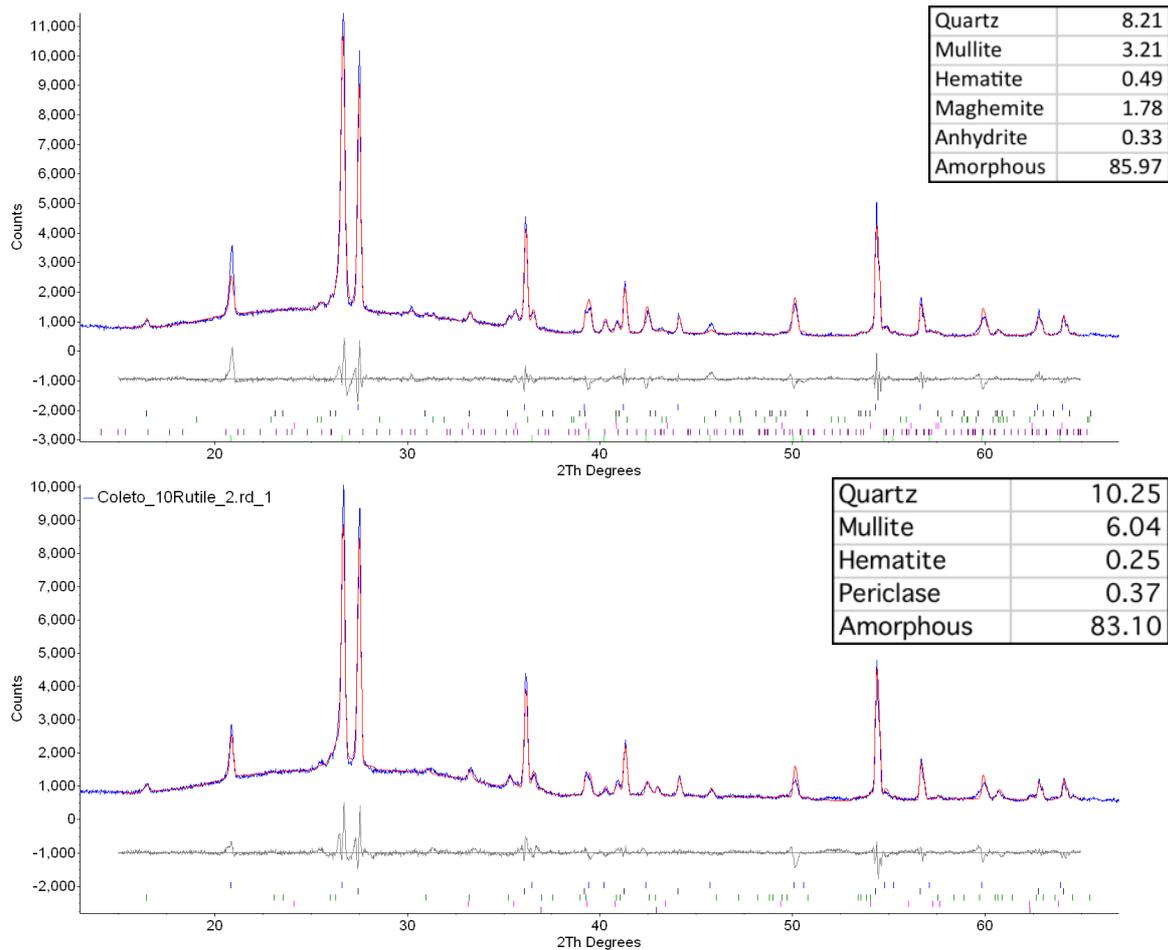


Figure 2: Rietveld analysis for LEGS fly ash (top) and Coletto Creek fly ash (bottom). Blue is the measured pattern, red is calculated.

The overlaid elemental maps produced images with each phase classified and identified in the image by color (Figure 3). The identical phases across the two types of fly ash are shown with the same name and color in each map. The relative proportions of each phase are shown in Figure 4. The Coletto Creek fly ash, which formed a stronger geopolymer at both 7 and 28 days had a larger proportion of alkali-modified aluminosilicates and the A-S 1 and A-S 2 glassy phases. The A-S¹ 1 phase was comprised of nearly equal proportions of aluminum and silicon, while the A-S 2 phase was much more strongly aluminum, with a Al/Si intensity ratio using 15kV accelerating voltage of 3.5:1. The Coletto Creek C-A-S phase differed in composition from the LEGS fly ash C-A-S phase, and it was present in a smaller amount. There was a much greater proportion of N-A-S in the Coletto Creek fly ash, as well as an additional phase, Mg-modified aluminosilicate.

Table 2: Glassy phase intensity ratios (SEM accelerating voltage = 15kV)

Phase designation	Al / Si	Ca / Al / Si
A-S 1	3.4	n/a
A-S 2	0.9	n/a
C-A-S	n/a	1.2 / 0.4 / 1
C-A-S 1	n/a	1.3 / 0.6 / 1
N-A-S	0.7	n/a
K-A-S	0.6	n/a
Mg-A-S	3.7	n/a

¹ Cement chemist convention is used; C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, f = FeO, \bar{S} = SO₃, M = MgO, N = Na₂O, K = K₂O, and H = H₂O.

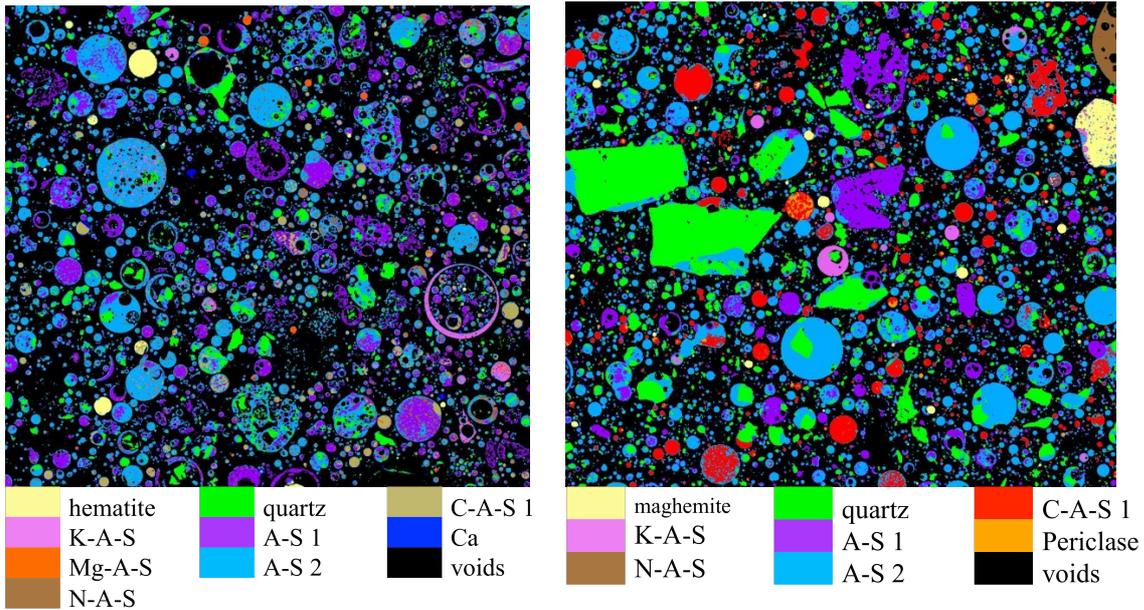


Figure 3: Coletto Creek fly ash (left) and LEGS fly ash (right) assigned phase composition maps

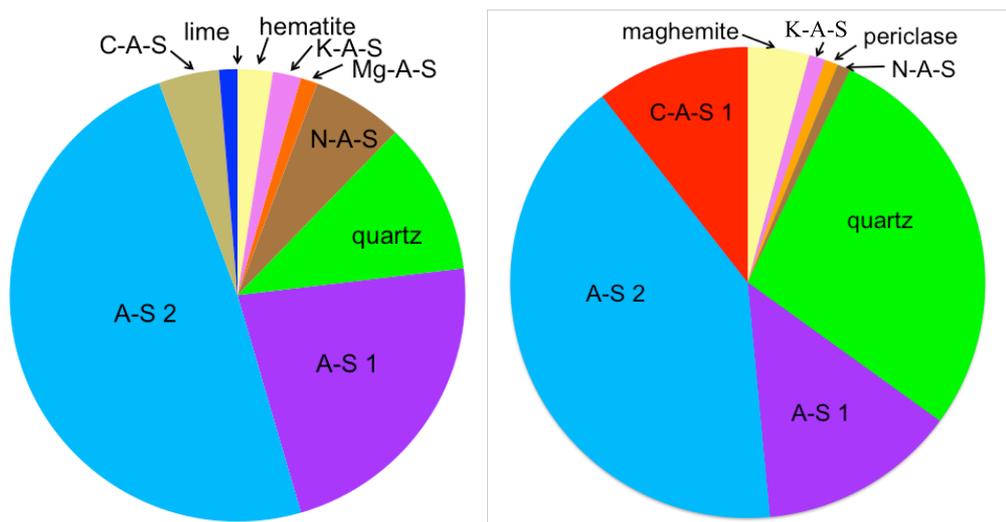


Figure 4: Proportion of phases in Coletto Creek fly ash (left), LEGS fly ash (right) (based on a single measurement)

The larger quantity of alkali-modified aluminosilicate material is thought to be one of the reasons that the Coletto Creek fly ash formed a stronger geopolymer than the LEGS fly ash at seven and 28 days. The large proportion of the A-S 2 phase is also a potential reason for the improved strength of the Coletto Creek geopolymer. Further replicate studies of the fly ashes will allow for statistical analysis of these data to help prove this hypothesis.

4. CONCLUSIONS

The use of XRD/SEM-MSIA methodology to classify the crystalline and glassy phases of fly ash allowed for the impacts of fly ash chemistry on geopolymer formation to be better understood. By identifying the chemistry of the reactive constituents of the fly ash, activating solutions will be better tailored to an individual aluminosilicate source. The alkali-modified aluminosilicate phases appear to be one contributing factor to the improved strength in Coletto Creek fly ash geopolymers as compared to LEGS fly ash geopolymers.

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