

# Assessment of the glassy phase reactivity in fly ashes used for geopolymer cements

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## Abstract:

Geopolymer cements have not found widespread use as a portland cement replacement, in part due to the difficulty in proportioning mixtures in a reliable manner. Unlike portland cements, which are mixed with water, geopolymer cements contain caustic activating solutions, which must be selected carefully to optimize strength and durability. Geopolymer cement can be designed by tailoring caustic solution composition to the reactive phase composition of the solid component of the mixture; however, assessing which phases are reactive is challenging for complex and heterogeneous solids such as fly ash. The present work focuses on applying a scanning electron microscopy and multispectral image analysis (SEM-MSIA) method to identify and quantify the reactive glassy phases in fly ash and to determine how these phases dissolve over time in a caustic activating solution. The fly ash was selected based upon its oxide contents and was analyzed for phase content using x-ray diffraction and Rietveld analysis (RQXRD) and SEM-MSIA. The MSIA method identified multiple glassy phases in the fly ash. Next, the fly ash was suspended in 8 mol/L NaOH, and tested at various time intervals with SEM-MSIA to track changes in the amounts of each individual glassy phase initially identified in the fly ash. The results showed that an aluminosilicate glass (C-A-S) with a moderate amount of calcium appeared to be the most reactive between 0 and 28 days for a Class F fly ash. Other phases that were identified in the fly ash included a high-Ca C-A-S glass, two aluminosilicate glasses with different S/A ratios, two alkali-modified A-S phases, and an iron-containing glass.

## Introduction:

Geopolymers are an aluminosilicate-based cementing material that can be used instead of portland cement as a binder for concrete. The material is formed by mixing an aluminosilicate powder with a caustic activating solution, commonly an alkali hydroxide and/or alkali silicate (Davidovits 1991). A large body of the research on geopolymer cements has been completed using metakaolin as the aluminosilicate source (Barbosa et al. 2000, Rowles and O'Connor 2003, Duxson et al. 2007), which serves as a model geopolymer precursor due to its nearly pure aluminosilicate composition with little crystalline material. Fly ash can also be used as an aluminosilicate source for geopolymer formation since it contains a large proportion of reactive glassy aluminosilicates, and it has an added environmental benefit of being a recycled material.

A major challenge in using fly ash as the sole geopolymer precursor material for concrete is that it is difficult to determine whether a given fly ash will react sufficiently with the activating solution. One chemical method for testing reactivity is hydrofluoric acid dissolution, which measures the reactive silica content of the fly ash by comparing the

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weight of the treated material to the original sample weight (Kilgour and Diamond 1988, Fernández-Jiménez et al. 2006a). However, the acid requires extreme care in handling, and it does not represent the highly caustic environment that the fly ash is subjected to in geopolymer formation. Analytical methods of fly ash characterization include x-ray diffraction (XRD) and scanning electron microscopy (SEM). There is some evidence that the vitreous alumina content of a fly ash may affect its reactivity as a geopolymer, which is calculated by subtracting the amount of crystalline alumina-bearing minerals obtained using XRD from the bulk oxide composition of fly ash (Fernández-Jiménez et al. 2006b). It is also known that the glassy phases are varied within a fly ash sample, and it is important to identify these glasses since they can react differently when exposed to caustic solutions (Chancey 2008). Thus, how the silica and alumina are bound within the fly ash is also important. Several researchers (Williams et al. 2005, Chancey et al. 2010, Dhole 2010, Kruse 2012) have used SEM x-ray point counting methods to ascertain the chemical composition of the various glasses within fly ash in an attempt to better understand its internal structure and potential for reactivity.

Combining the methods of fly ash dissolution and x-ray mapping analysis may be a promising option for testing the reactivity of fly ash. Since the reaction of fly ash to form a geopolymer is a dissolution-precipitation process (Duxson et al. 2007), a dissolution method using a caustic solution instead of an acidic solution can be used to assess how much of the fly ash is available to react (Chen-Tan et al. 2009; Chancey 2008; Pietersen 2003). The reacted material can then be separated from the solution for analysis. The work presented in this paper examined a fly ash using x-ray mapping in its initial state and after 28 days exposure to 8 mol/L sodium hydroxide. These results were used to determine approximately how much of the fly ash was reacting in such conditions and to find out which of the phases that were identified in the original fly ash were the most reactive.

## Materials & Methods:

A Class F fly ash (ASTM C618) from Limestone Electric Generating Station (LEGS) in Jewett, Texas was selected for the study. The fly ash was chosen based on its oxide composition, which was similar to those of fly ashes that performed well in studies in Australia (Lloyd 2008). Table 1 lists the oxide analysis and loss-on-ignition (LOI) for the LEGS fly ash from the mill sheet provided by the material supplier. The activating solution for the materials was 8 mol/L NaOH solution, like that used by Fernández-Jiménez et al. (2006b), which was made from 50 wt. % prepared NaOH solution (ACS reagent Grade) diluted with ultrapure water ( $18.5 \pm 0.5 \text{ M}\Omega\text{-cm}$ ).

Table 1: LEGS fly ash oxide composition from x-ray fluorescence spectroscopy

Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	LOI
17.8	54.14	10.7	7.74	1.43	2.31	0.45	0.4	1.2	0.09

When cured at 23° C, geopolymer mortars made from LEGS fly ash and 8 mol/L NaOH had relatively low strength at 7 days and moderate strength at 28 when compared to mortars made with nine other fly ashes also mixed with 8 mol/L NaOH activating solution (unpublished data). For the geopolymer mortar, low strength was defined as less than 1 MPa, moderate strength was defined as 1-14 MPa, and high strength was defined as greater than 14 MPa. While these are relatively low strengths for cementitious materials including

geopolymers, these were the result of the low-temperature curing regime. The LEGS fly ash was selected for this study due to its moderate reactivity in terms of compressive strength.

Rietveld analysis of XRD data was used to calculate the amount of bulk glassy phase in the fly ash after subtracting the amounts of the identified crystalline phases. X-ray diffraction analysis was performed using a Siemens D500 x-ray diffractometer<sup>3</sup>. The x-ray source produced Cu-K $\alpha$  radiation and operated at 40 kV and 30 mA. A long dwell time of 6 seconds per step was used to increase the x-ray counts at each step for better resolution of phases. The scans were run from 10° 2 $\theta$  to 70° 2 $\theta$  with a step size of 0.02° 2 $\theta$ . The crystalline phases were identified using files from the inorganic crystal structure database<sup>4</sup>, and Rietveld analysis was completed with TOPAS Academic version software (Coelho). Zinc oxide (reagent grade) was used as an internal standard and interground with the fly ash at 10 % by mass using ethanol as a dispersant and an agate mortar and pestle.

SEM-MSIA includes x-ray mapping of selected elements on epoxy-mounted fly ash specimens. Full details on the preparation process were published by Chancey (2010). X-ray mapping was completed using a field emission SEM fitted with two energy dispersive spectroscopy (EDS) detectors, which collected approximately 60,000-80,000 counts per second. The microscope was operated at 15 kV accelerating voltage, and the EDS maps were collected with a 256  $\mu$ s dwell time per pixel and a 1024 x 1024 map size. Each scan was run for approximately one hour, or 14 passes of the field of view. Multispectral image analysis has been described for minerals (Lydon 2005) and fly ash (Chancey et al. 2010) and is only summarized briefly here. The raw x-ray maps were smoothed using ImageJ<sup>5</sup> and they were then stacked digitally using Multispec<sup>6</sup>. Three maps were viewed simultaneously as red, green, and blue channels; by changing which elemental maps were turned on, the user gained familiarity with the composition of the fly ash. Groups of pixels were then selected in regions of varied composition (based on appearance of the 3-channel RGB image) and were defined as the training field for various phases in the fly ash. The Multispec program then assigned every pixel in the image to one of the defined fields from which an area percentage of each phase was calculated. The volume of spherical fly ash particles was assumed equal to the area (Bentz and Rémond 1997); after converting to volume, published densities were used to calculate weight percentages of each phase present.

The fly ash was analyzed in its original state as well as after 28 days of exposure to NaOH solution. The dissolution method was performed as follows: 2 g fly ash was mixed with 10 mL 8 mol/L NaOH solution. These were mixed in non-reactive plastic vials, sealed with a screw-cap lid, and placed on a laboratory rotisserie (LabQuake) that rotated the samples end-over-end at approximately 10 rpm until the desired time had elapsed. At 28 days, the sample was removed from the rotisserie and the solid material was separated from the liquid under vacuum using a 2.7  $\mu$ m filter paper on a Buchner funnel. The solid

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<sup>3</sup> Certain commercial materials and equipment are identified to adequately specify experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose

<sup>4</sup> FIZ/NIST Inorganic Crystal Structure Database (ICSD)<http://www.nist.gov/srd/nist84.cfm>

<sup>5</sup> ImageJ, <http://rsbweb.nih.gov/ij/>

<sup>6</sup> Multispec, <https://engineering.purdue.edu/~biehl/MultiSpec/>

material was dried for approximately an hour in air, then scraped from the paper into a vial and placed in a vacuum desiccator for complete drying.

## Results:

Results from x-ray diffraction and Rietveld analysis from three independent replicate samples are shown in Table 2. From these data, the crystalline phases were subtracted to reveal the amount of each oxide in “vitreous” phases. It has been suggested in the literature (Fernández-Jiménez et al. 2006b) that the amount of vitreous alumina, in particular, affects the reactivity of the fly ash. Fernández-Jiménez et al. (2006b) tested two fly ashes, one with a vitreous alumina content of 20.45 wt. % and another with 14.11 wt. %, with the same vitreous silica content, and found that geopolymers made from the ash with higher vitreous alumina outperformed the ash with lower vitreous content in terms of degree of reaction, for the same vitreous silica content. The LEGS fly ash examined in this study had a vitreous alumina content of  $(15.87 \pm 0.4)$  wt. % (Table 2). This implies that the fly ash should not be as reactive as a geopolymer, since its vitreous alumina content is closer to that of the poorly reactive fly ash tested by Fernández-Jiménez et al. (2006b). It should be noted that the vitreous silica content of the LEGS fly ash was  $40.29 \pm 1.89$  wt. %, which was lower than the 50 wt. % vitreous silica content studied in both samples by Fernández-Jiménez et al. (2006b). Additionally, Fernández-Jiménez et al. (2006b) cured their specimens at 85° C, which was much warmer than the samples in this study and the reaction pathways are somewhat different at higher temperatures (Duxson et al. 2007).

Table 2: LEGS fly ash crystalline and bulk amorphous content

	Quartz	Mullite (2:1)	Magnetite	Anhydrite	Periclase	Bulk Amorphous	Amorphous Vitreous Alumina	Vitreous Silica
Weight	12.54	3.63	0.92	0.34	0.12	72.44	15.87	40.29
%	$\pm 1.98$	$\pm 0.52$	$\pm 0.12$	$\pm 0.08$	$\pm 0.12$	$\pm 1.76$	$\pm 0.40$	$\pm 1.86$

Nine phases were identified in the fly ash using SEM-MSIA<sup>7</sup>: quartz, A-S 1 (high aluminum), A-S 2, C-A-S 1 (high Ca), C-A-S 2 (moderate Ca), N-A-S, K-A-S, iron-rich, and voids. The intensity ratios from x-ray maps for each of these phases are given in Table 3.

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<sup>7</sup> Cement chemistry notation is used for defining the glasses: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, f = FeO,  $\bar{S}$  = SO<sub>3</sub>, M = MgO, N = Na<sub>2</sub>O, K = K<sub>2</sub>O, and H = H<sub>2</sub>O. Dashes are used to signify that the stoichiometry of the glass is not indicated in the name of the glass.

Table 3: Phase intensity ratios for glass in a LEGS fly ash

Phase designation	S / A	C / S / A
A-S 1 (high Al)	0.36	-
A-S 2	0.77	-
C-A-S 1 (high Ca)	1.1	4.74 / 1.74 / 1
C-A-S 2 (moderate Ca)	0.61	1.14 / 1 / 1.4
N-A-S	0.79	-
K-A-S	1.14	-

[15 kV operating conditions]

Phase-assignment images for the unexposed LEGS fly ash and the 28-day exposed fly ash are shown in Figure 2. The images were used to calculate mass percentages of each phase, shown in Figure 3. No reaction product was noted in the specimen after 28 days exposure to NaOH. Since it was assumed that glassy phases would dissolve over time when exposed to the NaOH and that the quartz was nonreactive (Hemmings and Berry 1988), it was expected that the relative amount of quartz in the solid material would increase with exposure time to the sodium hydroxide solution. This was observed in the raw data. Thus, the quartz was used as an internal standard, and the amount of quartz in the reacted specimen was set to the same value as that in the raw specimen with the remaining phases adjusted proportionally. This enabled calculation of the amount of fly ash that dissolved in the sodium hydroxide. The amount of quartz calculated in the original fly ash was 10.7 wt. % calculated using MSIA and 12.5 wt. % using Rietveld analysis. The quartz calculated using MSIA on the 28-day exposure sample was 15.3 wt. %, resulting in a scale factor of 0.7 for the remaining phases. The results showed that about 30 wt. % of the fly ash dissolved from the original sample.

As shown in Figure 3, the A-S 2 phase ( $S/A = 0.77$ ) decreased after 28 days of exposure to the NaOH. Similarly, the C-A-S 2 phase ( $S/A = 0.61$ ) decreased greatly from 0 to 28 days. N-A-S phase (sodium aluminosilicate) entirely disappeared by 28 days. The C-A-S 1 phase did not significantly change from 0 days to 28 days. Likewise, the K-A-S phase (potassium aluminosilicate) and the iron-containing phase stayed approximately even from 0 to 28 days. The A-S 1 ( $S/A = 0.32$ ) phase increased from 0-28 days. As previously discussed, the quartz was set to equal its initial amount at 28 days, so its plot shows no change from 0 to 28 days

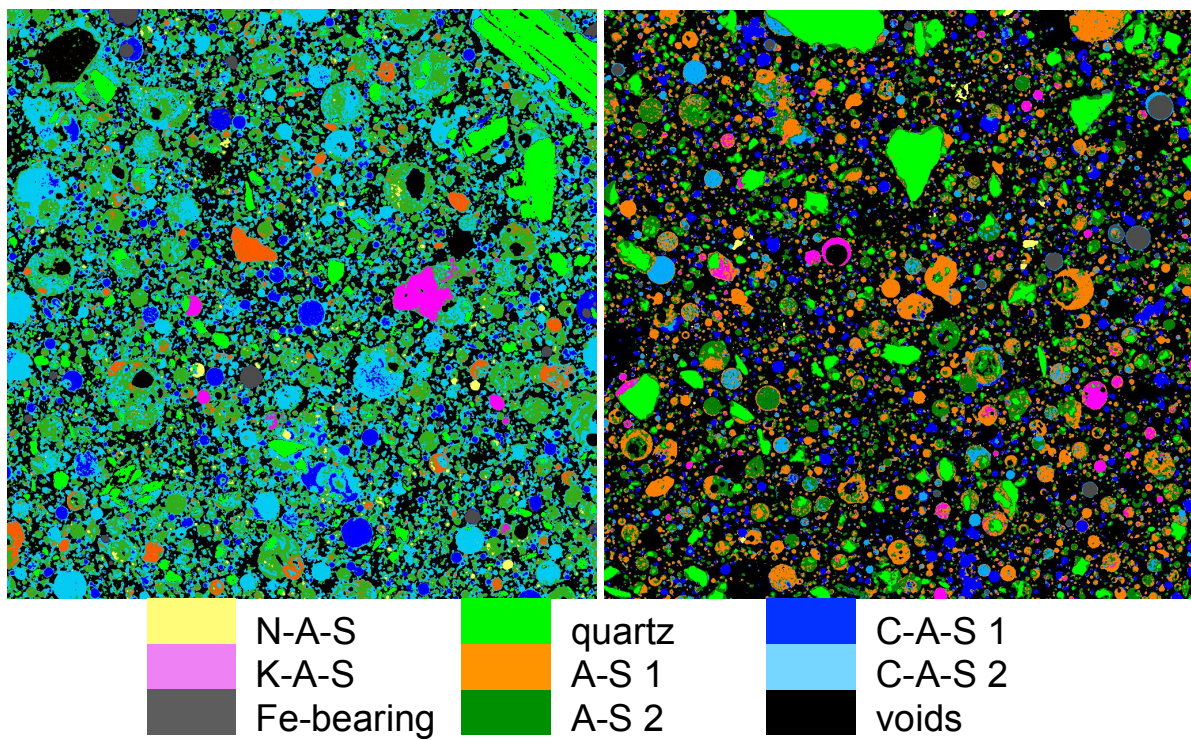


Figure 2: LEGS fly ash pixel assignments map (left) and after 28 days of NaOH exposure (right)

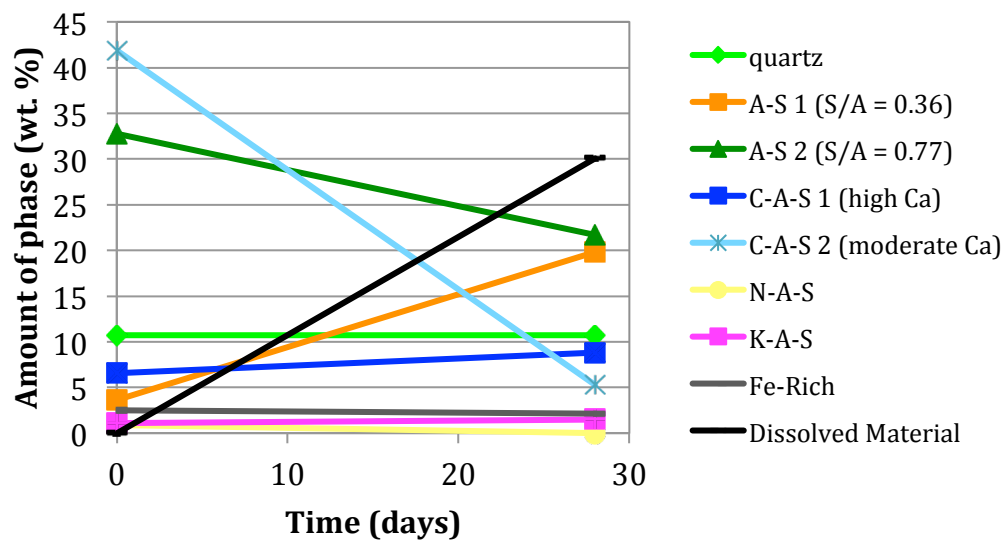


Figure 3: LEGS fly ash after 28 days of reaction with 8mol/L NaOH solution pixel assignments map and weight % phase distribution plot

### Discussion:

Hemmings and Berry (1988) discussed the glass in coal fly ashes and described the ideal glass structure for silicon-based glasses as pure silica tetrahedra with short-range order; while aluminum can substitute with silicon nearly interchangeably, calcium, sodium, potassium, and magnesium serve as network-modifiers in the system. Both substitution and modification lead to increased disorder in the glass network, which causes the glass to be reactive under certain conditions (Hemmings and Berry 1988). These concepts are applied in the discussion of results from this dissolution study of LEGS fly ash.

Due to their assumed disordered nature, it was surprising that the K-A-S and high-Ca C-A-S 1 phases did not seem to have reacted at 28 days. However, the both the K and Ca are considered contaminants that change the reaction mechanism of the glass (Duxson et al. 2007). Based on the results, the K-A-S and C-A-S 1 glasses present in the LEGS fly ash seem to be chemically bound in such a way as to prohibit reaction with the NaOH. The disordered N-A-S phase was fully reacted and not detectable at 28 days, which was as expected. Similarly, the moderate Ca C-A-S 2 phase decreases greatly after exposure to NaOH, and thus may be the most reactive phase in the LEGS fly ash. The other phase that dissolved in the presence of NaOH was the A-S 2 ( $S/A = 0.77$ ) glass, which decreased somewhat at 28 days. Thus, the N-A-S, C-A-S 2, and A-S 2 phases show promise as phases to look for in potential raw materials for use in geopolymers. Further studies of other ashes may help prove the hypothesis that these particular glassy phases are desirable in ashes used for geopolymer cements activated with NaOH.

The results showed that the amount of iron-containing phases does not change with 28 days of exposure to concentrated NaOH. Iron is an important cation in geopolymer formation, but little is known about its exact effect on the reactions in geopolymer formation (Duxson et al. 2007), which was not studied here. Thus, these phases may be nonreactive in geopolymer formation from LEGS fly ash, but further study is necessary.

The increase in the A-S 1 ( $S/A = 0.36$ ) glass is difficult to explain. The intensity ratio shows that the aluminum is present in relatively large amounts in this phase, while the silicon is present in relatively low amounts. It is hypothesized that the relative proportions of the A-S 1 glass may inhibit dissolution. Additionally, it is possible that leaching of other phases occurred, which left behind material with similar composition to the A-S 1 phase. Measurement of the actual composition of the A-S 1 phase and the other glassy phases will be necessary to test this hypothesis.

## **Conclusions:**

A fly ash that has been shown to make a moderate-strength geopolymer was exposed to NaOH in dilute proportions (6.4 solution to powder ratio) for 28 days in an attempt to determine its reactivity under the caustic conditions encountered in geopolymer production. Using RQXRD and SEM-MSIA, it was found that:

- The fly ash consisted of two aluminosilicate phases and two calcium-aluminosilicate phases, along with quartz, an iron-containing phase, and two alkali-modified aluminosilicates: potassium-modified and sodium-modified.
- The most reactive phase in the system appeared to be a moderate-calcium aluminosilicate glass (C-A-S 2,  $S/A = 0.61$ ). The A-S 2 ( $S/A = 0.77$ ) and N-A-S glassy phases also dissolved.

- It is unclear why the A-S 1 phase increased and the K-A-S phase did not react.

The method described in this paper is proposed as a technique to assess the reactivity of phases in fly ash and determine the potential of the fly ash for geopolymeric reactivity. From these results, the presence of glasses such as C-A-S 2 and A-S 2 indicate promising starting materials for geopolymers. More work is necessary to characterize a variety of fly ashes using the same process and compare the results to a measure of reactivity, such as the amount of geopolymer formed or the compressive strength development.



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