

Activation of fly ash through nanomodification

Shiho Kawashima, Pengkun Hou, Kejin Wang, David J. Corr, and Surendra P. Shah

Synopsis: Due to the high carbon emissions that result from cement production, it is desirable to limit the cement content of concrete to make it a more sustainable material. This is possible through substantial replacement of cement with supplementary materials, such as fly ash. The positive effects of this approach are twofold. First, reducing the cement content of concrete will reduce its carbon footprint. Second, fly ash is a coal combustion by-product, so essentially a waste material, which must be stored in landfills and enclosures if unused. Therefore, the productive use of fly ash by incorporating it into building materials at high volumes can help alleviate a waste storage issue. This paper is a summary of studies performed at the Center for Advanced Cement-Based Materials - Northwestern University, in collaboration with Iowa State University, relating to the activation of fly ash through nanomodification. Through seeding effects and increased reactivity, nanoparticles can accelerate cement hydration and subsequently the production of calcium hydroxide (CH), which can help activate the pozzolanic reaction of fly ash particles. Two types of nanoparticles are discussed in this summary paper: silica (SiO_2) and calcium carbonate (CaCO_3). The study on CaCO_3 nanoparticles addresses the issue of dispersion, which is critical for nanomaterials, and the resultant effects on the hardening and early-age properties of fly ash-cement pastes. And the study on nano SiO_2 focuses on determining the mechanisms underlying the effect of the pozzolanic nanoparticle on the early-age and long-term compressive strength gain of fly ash-cement mortars.

Keywords: fly ash; nanoparticles; nanosilica; calcium carbonate; pozzolanic; microstructure; dispersion

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INTRODUCTION

Given that cement production is high in carbon emissions and that concrete is so widely utilized in construction, it is necessary to make concrete a greener infrastructural material. This is possible through substantial replacement of cement with supplementary cementitious materials, such as fly ash. The positive effects of this approach are twofold. First, reducing the cement content of concrete will reduce its carbon footprint. Second, fly ash is a coal combustion by-product, so essentially a waste material, which must be stored in landfills and enclosures if unused. Therefore, the productive use of fly ash by incorporating it into building materials at high volumes can help alleviate a waste storage issue. Although fly ash can introduce a number of beneficial rheological and long-term mechanical properties to concrete, it has effects on the early-age properties that are undesirable from a constructability standpoint. Due to its pozzolanic nature, at higher replacement levels fly ash can lead to significantly lower rate of hydration, slowed setting, and low early-age compressive strength gain.

In order to facilitate the use of fly ash, it is necessary to develop strategies to produce fly ash-cement concrete that still exhibits properties comparable to cement concrete. Numerous studies have focused their efforts on activating fly ash to improve the early-age properties, including mechanical and chemical methods (Pay et al. 1997; Fan et al. 1999; Qian et al. 2001; Goñi et al. 2003; Wang et al. 2004; Kumar et al. 2007). In the studies presented in this summary paper, the approach of nanomodification is explored. The use of nanoparticles can introduce a number of effects, such as seeding and increased reactivity, due to their fine size and corresponding high specific surface area. Therefore nanoparticles can accelerate cement hydration and subsequently the production of calcium hydroxide (CH), which can help activate the pozzolanic reaction of fly ash particles. This summary paper will highlight the results of two studies performed at Northwestern University's Center for Advanced Cement-based Materials, in partnership with Iowa State University, on calcium carbonate (CaCO_3) nanoparticles and nanosilica (nanoSiO_2). The study on CaCO_3 nanoparticles addresses the issue of dispersion, which is critical for nanomaterials, and the resultant effects on the early-age properties of fly ash-cement pastes. And the study on nanoSiO_2 focuses on determining the mechanisms underlying the effect of the pozzolanic nanoparticle on the early-age and long-term compressive strength gain of fly ash-cement mortars.

CALCIUM CARBONATE NANOPARTICLES

CaCO_3 , or limestone, powders have been found to accelerate early-age hydration, provide nucleation sites for calcium silicate hydrate (C-S-H), and produce additional hydration products (Péra et al. 1999; Heikal et al. 2000; Irassar et al. 2000; Kakali et al. 2000; Bonavetti et al. 2001). And a few studies have also demonstrated the potential of CaCO_3 nanoparticles in offsetting the retarding effects of fly ash on the early-age properties (Sato and Beaudoin 2011; Bentz et al. 2012; Gurney et al. 2013). With the use of any additive, dispersion within the cement matrix is important to achieve and it becomes increasingly more difficult with decreasing particle size. To improve the early-age properties of fly ash-cement systems with nanoparticles, it is necessary to achieve sufficient dispersion. In this study, the influence of mechanically and chemically dispersed CaCO_3 nanoparticles on the setting behavior and early-age compressive strength gain of fly ash-cement pastes was investigated. The degree of dispersion of CaCO_3 in aqueous suspension was quantitatively measured through spectrophotometry.

Experimental methods and materials

Materials – Type I Portland cement and tap water were used in all mixes, with a Class F fly ash being used in select mixes. The specific gravity of the cement and fly ash were 3.15 and 2.51 g/cm^3 , respectively. The chemical composition is presented in Table 1 and particle size distribution is presented in Figure 1. The CaCO_3 nanoparticles were in dry powder form and had a particle size range of 15 – 40 nm (0.59 – 1.58 μm) according to their manufacturer.

In this referred to study, a number of surfactants were tested to determine their suitability for dispersing and stabilizing CaCO_3 nanoparticles in aqueous solution. These surfactants included naphthalene- and polycarboxylate-based superplasticizers, anionic, amphiphilic surfactants, and nonionic, amphiphilic block copolymers. The surfactant discussed in this summary paper will be a polycarboxylate-based superplasticizer (PC).

Figure 2a shows a scanning electron microscopy (SEM) image of CaCO_3 nanoparticles treated with PC that were stirred in water. It is apparent that they were aggregated to the micron level, exceeding 20 μm (787 μm) in size. Therefore, it was necessary to mechanically break up the aggregates through sonication. Both horn and bath sonication was implemented, depending on the batch size necessary. Dry nanoparticles and surfactant were added to the water, then sonicated at a set amplitude and duration to produce the suspension. Figure 2b shows how sonication aids in dispersion. Whereas large aggregates were present in the mechanically stirred suspension (Figure 2a), none were present in the sonicated suspension (Figure 2b).

All paste samples had a water-to-binder (w/b) ratio of 0.35 and were prepared in a small upright mixer. Cement was replaced with fly ash on a mass basis. When nanoCaCO₃ was used, it was added as a suspension, which contained part or all of the mixing water, to the dry ingredients.

Table 1 – Chemical composition of cement and fly ash.

Materials	Type I Cement	Type F Fly Ash
SiO ₂	20.2	46
Al ₂ O ₃	4.7	17.8
Fe ₂ O ₃	3.3	18.2
SO ₃	3.3	2.59
CaO	62.9	8.4
MgO	2.7	0.95
Na ₂ O	/	0.59
K ₂ O	/	2.16
LOI	1.1	1.49
Total	98.2	98.2

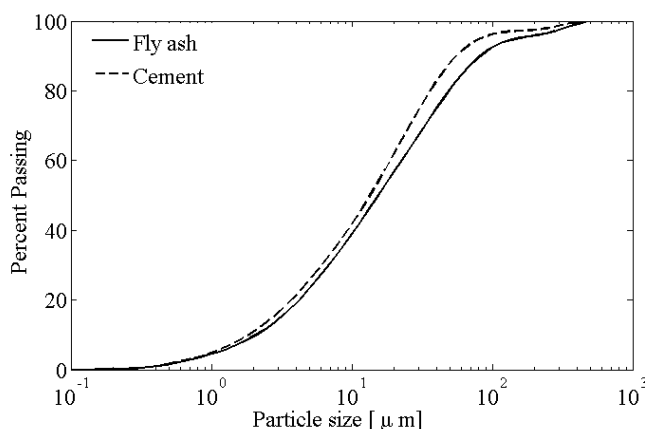


Figure 1 – Particle size distribution of cement and fly ash.

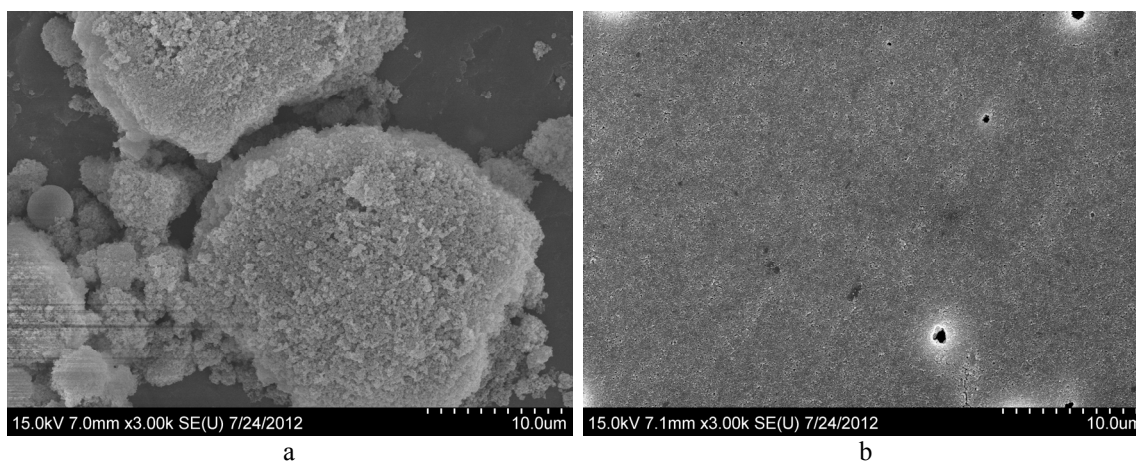


Figure 2 – SEM image, approximately 40 μm x 30 μm (1575 μin x 1180 μin), of PC-treated nanoCaCO₃ that were a) mechanically stirred in water and b) bath sonicated (Kawashima 2012).

Methods – To obtain a quantitative measure of dispersion, the absorbance spectra of centrifuged nanoCaCO₃ aqueous suspensions were measured by a spectrophotometer. It is expected that nanoparticles that are dispersed will remain in suspension, while any aggregated particles will settle to the bottom. By recording the decrease in optical density of samples before and after centrifugation, it was possible to deduce the extent of

sedimentation, which is an indicator of the quality of dispersion. Absorbance spectra readings were taken between wavelengths 380 and 800 nm (15 and 31 μm) for each sample and the absorbance at 550 nm (31 μm) was compared between samples. The details of the method can be found elsewhere (Kawashima 2012). The absorbance spectra were measured for the supernatant of nanoCaCO₃ suspensions after centrifugation and suspensions obtained immediately after sonication. The latter served as a reference point, at which the majority of nanoparticles were expected to be suspended.

Setting times of pastes were measured using the Vicat needle test, based on ASTM standard C191-08. Compressive strengths of 50 mm (2 in) cube paste samples were measured at 1, 3, and 7 d in accordance to ASTM standard C109/C109M-08.

Results

Dispersion – The influence of surfactant type and dosage, and sonication amplitude and duration on dispersion were evaluated. Here, the results of CaCO₃ nanoparticles treated with different concentrations of PC are presented. Sedimentation is defined by the following expression:

$$100\% - \frac{Abs_c}{Abs_{t=0}} \times 100\%$$

where $Abs_{t=0}$ was the measured absorbance at 500 nm (31 μm) before centrifugation and Abs_c was the corresponding absorbance after centrifugation. The results of sedimentation are shown in Table 2 for PC-treated CaCO₃ nanoparticle suspensions. All suspensions had a concentration of 0.02 % nanoCaCO₃ by mass of water and were horn sonicated at 40 % amplitude for three hours. The concentration of nanoCaCO₃ was selected to yield the desired mix proportion of cement paste samples for performance testing. The results show that at 7% PC content by mass of nanoCaCO₃, almost all the particles settle, indicating poor dispersion. However, at 17% PC, dispersion is improved. And this also marked a threshold value, from which further increase in PC content did not improve dispersion. The PC content of the paste mixes in the following tests was selected based on these results.

Table 2 – Sedimentation of CaCO₃ suspensions that were horn sonicated for 3 hours at 40% amplitude. Effect of PC content.

PC content (% by mass of nanoCaCO ₃)	Sedimentation (%)
7	99.9
17	92.3
33	92.1

Setting – The setting time of plain cement pastes were compared against pastes with 30% cement replacement with fly ash (FA), and 1% nanoCaCO₃ addition (1nC). The nanoCaCO₃ suspensions were treated with 17% PC by mass of nanoCaCO₃, based on the preceding dispersion results, and prepared either by horn sonication or mechanical stirring, each for 3 hours. The latter is a much milder method than sonication. This allowed for the effect of nanoCaCO₃ and method of dispersion to be observed. The equivalent PC dosage was added to all mixes.

The results are shown in Figure 3. It is apparent that the addition of nanoCaCO₃, both stirred and sonicated, accelerated setting of the fly ash-cement paste. Further, sonication enhanced the accelerating effect, where it offset the delay in initial and final setting caused by the fly ash by approximately 75%. This can be attributed to improved dispersion, which likely gave rise to a seeding effect to accelerate percolation (setting). Even at relatively low additions of 1%, nanoCaCO₃ can significantly shorten setting, where its effectiveness can increase with dispersion.

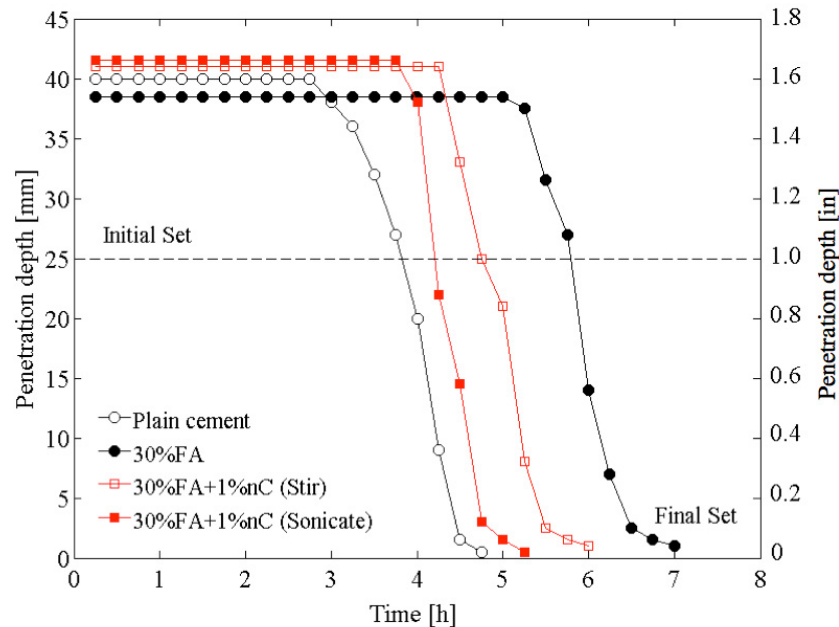


Figure 3 – Setting time of plain cement paste compared to 30% fly ash-cement paste (30%FA) with 1% nanoCaCO₃ addition (30%FA+1%nC), where nanoCaCO₃ was either stirred or sonicated in suspension (Kawashima 2012).

Early-age compressive strength gain – The 1, 3, and 7 d compressive strength gain of 30% fly ash-cement pastes with 0, 1, 2.5 and 5% addition of nanoCaCO₃ by mass of binder were compared. All suspensions were prepared by bath sonication of mixing water, nanoCaCO₃ and PC for 6 hours. The mixture proportions are given in Table 3 and the results are shown in Figure 4. By 7 d, the nanoCaCO₃ improved strength at all additions, where 2.5% led to the most enhanced effect with 20% increase compared to the control (0%nC). This can be tied to seeding and/or filler effects, of which the latter would reduce the porosity of the samples. However, 5% addition led to the smallest increase in strength at 7 d and even a slightly detrimental effect at 1 d. This can be attributed to issues of dispersion.

Recalling back to the results of the dispersion tests through photospectroscopy, Table 2, sedimentation at PC additions of 17 and 33% by mass of nanoCaCO₃ were lower than at 7%, indicating improved dispersion at the higher PC addition levels. Looking at the PC content as % by mass of nanoCaCO₃ (last column of Table 3), 5%nC only contained 7% PC. Since PC is a dispersant, the addition level was limited by the rheology of the paste sample, where excess amounts would have resulted in segregation. The lower rate of strength gain of 5%nC compared to both 1%nC and 2.5%nC, thereby, can be tied to issues of dispersion due to the insufficient amount of PC, limited by paste mix design, to treat the particles. Also, dispersion becomes increasingly more difficult at higher concentrations. Both of these factors explain the apparent threshold value that exists for nanoCaCO₃ dosage in the compressive strength results.

Table 3 – Mix composition of paste samples for compressive strength testing.

Mix	Cement, g (lb)	Fly ash, g (lb)	Water, g (lb)	NanoCaCO ₃ , g (lb)	PC	
					g (lb)	% by mass of nC
0%nC	525 (1.16)	225 (0.50)	262.5 (0.58)	0	2.5 (0.0055)	--
1%nC				7.5 (0.017)	2.5 (0.0055)	33
2.5%nC				18.8 (0.041)	3.1 (0.0068)	17
5%nC				37.5 (0.083)	3.1 (0.0068)	7

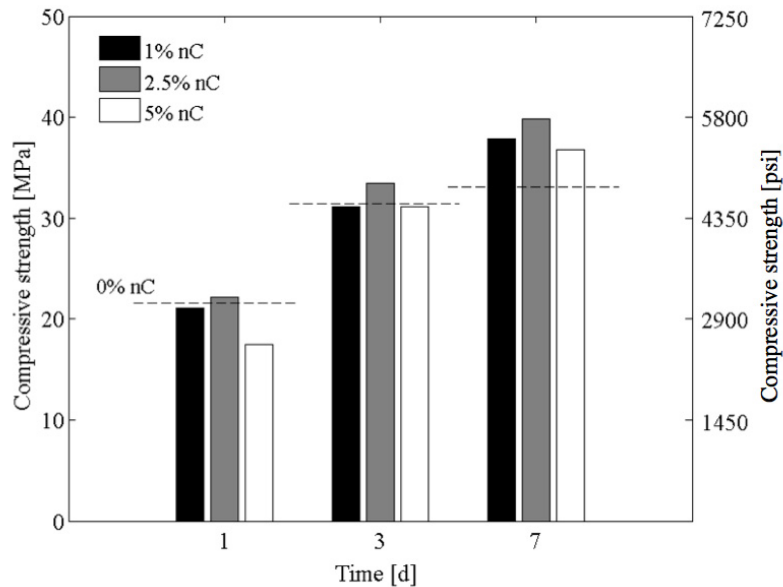


Figure 4 – Compressive strength results of fly ash-cement pastes with different nanoCaCO₃ (nC) additions compared to the control (0%nC), indicated by the dotted line. All paste samples had 30% fly ash replacement of cement (Kawashima 2012).

NANOSILICA

Numerous studies have demonstrated that nanosilica can accelerate rate of hydration of cementitious materials through seeding effects and increased pozzolanic reactivity (Björnström et al. 2004; Shih et al. 2006; Thomas et al. 2009; Gundogdu et al. 2010). Therefore, nanosilica is a good candidate to improve the hardening and early-age mechanical properties of fly ash-cement systems. However, it is important to know the effect of nanosilica on later-age strength gain, which has not been thoroughly investigated. In the study discussed here, an in-depth investigation on the mechanisms underlying the effect of nanosilica on the early-age and long-term strength gain of fly ash-cement systems was performed.

Experimental methods and materials

Type I Portland cement and tap water were used in all samples, with Class F fly ash being used in select mixes. Pastes had a w/b ratio of 0.4; and mortars had a w/b ratio of 0.5 and sand-to-binder ratio of 3. The nanosilica came in colloidal form; therefore the issue of dispersion was not investigated. The colloidal nanosilica (CNS) had an average particle size between 10 nm (0.39 µm) and 20 nm (.088 µm).

Compressive strength of 50 mm (2 in) mortar samples were measured in accordance to ASTM standard C109/C109M-08. Thermogravimetric analysis (TGA) was implemented to monitor CH content – the weight loss between 400°C (752°F) and 510°C (950°F) was considered to be the decomposition of CH. And SEM with energy dispersive spectroscopy (EDS) was performed to analyze the morphology and elemental composition of paste samples.

Results

Compressive strength gain – The compressive strength of mortars with 40% replacement of cement with fly ash and 0, 2.5 or 5% nanosilica addition by mass of binder were compared. The results are shown in Figure 5. At early age (7 d), nanosilica increased compressive strength, where strength increased with addition level. This agrees with the results of most studies, and can be attributed to the seeding effect and increased pozzolanic reactivity of the CNS. However, at 90 d, there is little measurable effect at 2.5% CNS addition and a slight reduction in strength at 5%. Therefore the results indicate that the nanosilica enhanced the early-age strength but led to a reduction in rate of strength gain over time, where the reduction was greater at higher additions, in the tested fly ash-cement systems. To explain this, the CH content and SEM-EDS results will be discussed.

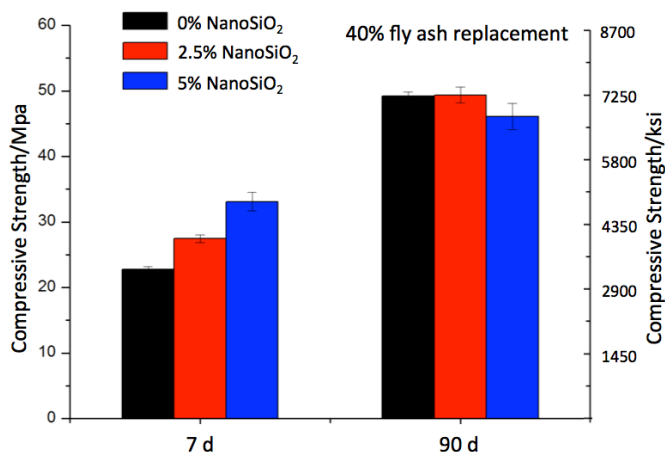
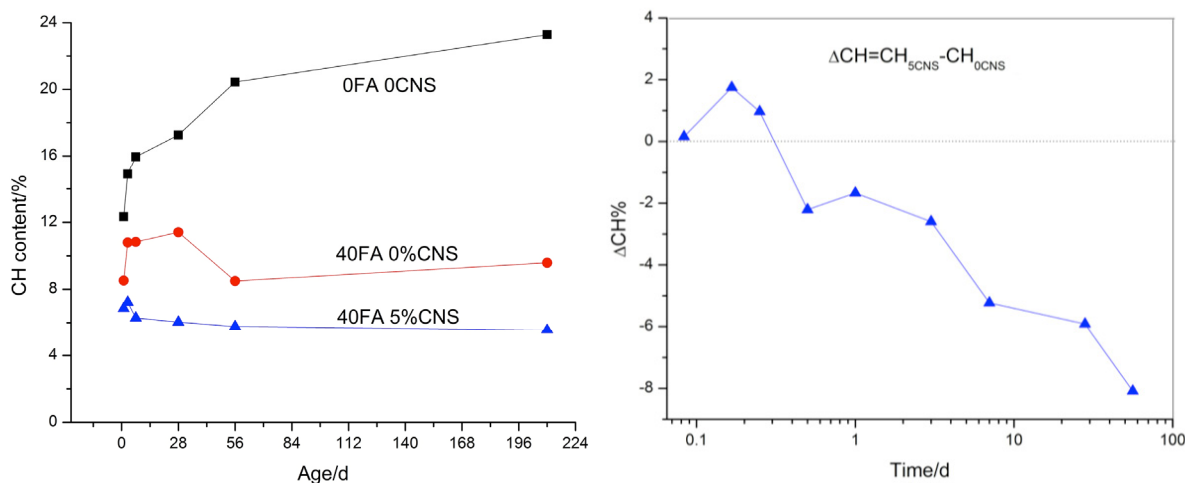


Figure 5 – Compressive strength gain of 40% fly ash-cement mortars with different CNS additions (Hou et al. 2012).

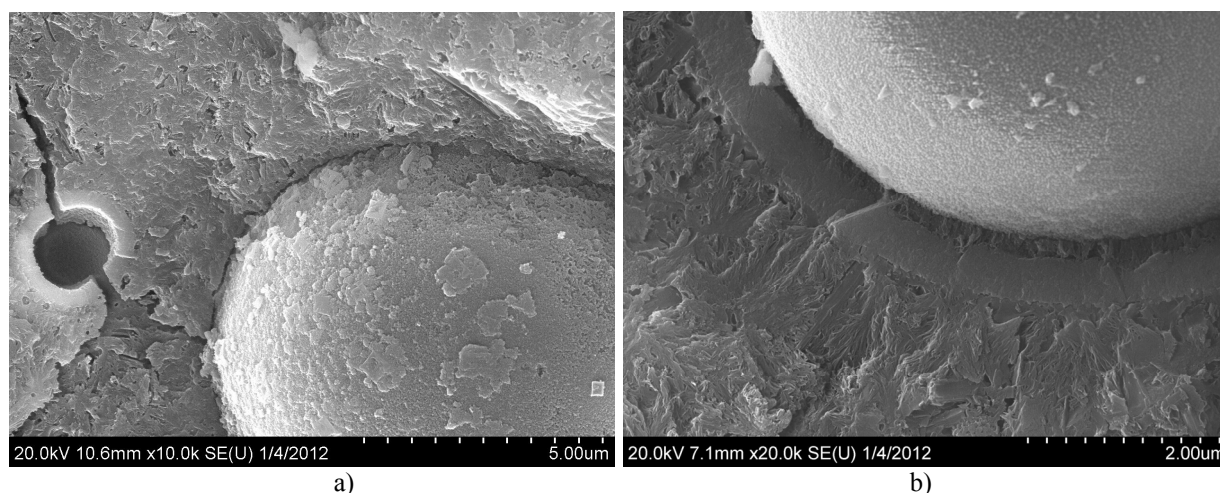
TGA – In a nanosilica-modified fly ash-cement system, both nanosilica and fly ash participate in pozzolanic reactions. Therefore, they will essentially be in direct competition with each other for CH. To observe this, the CH content over time of 40% fly ash-cement pastes with and without a 5% CNS addition were compared against that of plain cement paste. The results are shown in Figure 6a. As expected, 40% replacement of cement with fly ash (40FA 0%CNS) resulted in a substantial decrease in CH compared to the plain cement paste (0FA 0%CNS) due to reduction in cement hydration. 40FA 0%CNS exhibited an increase in CH early on, up to 28 d, but was followed by a decrease by 56 d, which can be attributed to CH consumption by fly ash. With the addition of 5% CNS (40FA 5%CNS), the overall CH content decreased even further and there was no initial increase. This can be attributed to the CH consumption by the CNS, which occurs at a higher rate than fly ash due to its increased reactivity (smaller particle size). This could also be a contributing factor for the reduction in rate of strength gain of the CNS-modified fly ash-cement mortars presented in the preceding section – the higher rate of CH consumption by CNS left less CH for the fly ash to consume to sustain long-term strength gain that is typically characteristic of fly ash-cement systems.

Figure 6b shows the difference in CH content between cement pastes with 5% and 0% CNS in a logarithmic scale to capture the CH content very early on, within 24 h. There is an initial spike that is apparent within the first few hours, which indicates that the 5% CNS addition led to accelerated rate of cement hydration. This can be tied to the seeding effect. Then the CH content drops dramatically – that can be attributed to the pozzolanic reactivity of the CNS. Both of these phenomena explain the increase in early-age compressive strength (7 d) measured in mechanical testing.



a) b)
Figure 6 – TGA results: a) CH content of plain cement paste (0FA 0CNS) and 40% fly ash-cement paste (40FA) with 0% and 5% CNS (Hou et al. 2013) and b) difference in CH content between cement pastes with 5% CNS and 0% CNS additions (Hou et al. 2013).

SEM-EDS – The compressive strength gain of the fly ash-cement mortars (Figure 5) suggest that the hydration mechanisms of nanosilica-modified systems may be different from those of control pastes. Figure 7 presents SEM images of the microstructure of 7 month old fly ash-cement pastes with and without CNS. There was an apparent coating around the fly ash in the sample with CNS (Figure 7b) that was not present in the control paste (Figure 7a). EDS results at 15 different areas of the compacted coating structure revealed an average Ca/Si ratio of 1.38, which was smaller than that of the adjacent C-S-H gel of 1.66. It has been reported that C-S-H gel with a low Ca/Si ratio is less permeable (Garrault and Nonat 2001). And in other work, nanosilica hydration gel has been observed to seal off C_3S particles from the pore solution and stop hydration (Thomas, Jennings et al. 2009). Thus, it was deduced that the outer layer of compacted hydrates, which was formed by the pozzolanic reaction of nanosilica and CH, hindered ion diffusion and thus hindered fly ash hydration at later ages. This can, thereby, partially explain the reduction in rate of strength gain exhibited by the nanosilica-modified fly ash-cement mortars.



a) b)
Figure 7 – SEM images of 7 month old fly ash-cement samples with (a) and without (b) CNS (Hou, Wang et al. 2012).

CONCLUSIONS

This was a summary paper that discussed two studies pertaining to the use of nanoparticles to facilitate the replacement of cement with fly ash to lead to a greener infrastructural material. It was demonstrated in each of these studies that nanoparticles, such as $CaCO_3$ and SiO_2 , can help to offset the retarding effects fly ash has on the hardening and early-age compressive strength by contributing to seeding effects and increased reactivity. The effect of nano $CaCO_3$ was enhanced through dispersing the particles in aqueous solution through chemical and mechanical methods. And the results of mechanical testing agreed well with the dispersion results obtained through photospectroscopy. It may be possible to further enhance dispersion by tailoring the architecture of the polycarboxylate-based superplasticizer (i.e. alter the number of repeatable units in the anionic backbone and length of side chains) for $CaCO_3$ nanoparticles, which can be the topic of future work. Also, although early-age properties were the focus of the present work, later-age strength development should be investigated to determine the long-term effects of $CaCO_3$ nanoparticles. The mechanisms underlying the effect of nanosilica on fly-ash cement systems were investigated. Increase in early-age compressive strength was attributed to the seeding effect and high rate of CH consumption by the nanosilica, while the decrease in rate of strength gain over time was attributed to a compact coating of calcium silicate hydrate gel that forms around fly ash particles and hinders their subsequent ability to participate in pozzolanic reactions.

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Determining the potential of a fly ash for geopolymer formation by examining dissolution of glassy phases in a caustic solution

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Abstract:

Geopolymers are made from natural or waste aluminosilicate powders that come from a variety of sources and have highly variable compositions. These powders are mixed with caustic 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. Previous research has suggested that scanning electron microscopy and multispectral image analysis (SEM-MSIA) can be used to identify and quantify the glassy phases in fly ash and allows for the determination of how these phases dissolve over time in caustic solutions. In this study, a Class F fly ash was analyzed for phase content using x-ray diffraction and Rietveld analysis (RQXRD) and SEM-MSIA, which identified multiple glassy phases in the fly ash. Next, the fly ash was suspended in 8 M 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 for this fly ash, all of the glassy phases identified were reactive in the alkaline solution and decreased in amount after being subjected to the sodium hydroxide solution. Two distinct reaction products were identified for this fly ash as well.

Introduction:

Geopolymers are an aluminosilicate-based cementing material that can be used instead of portland cement as a binder for concrete. By mixing aluminosilicate powders with caustic activating solution, a cementitious material is created that can be tailored to the particular application for which it is intended [1]. The main difficulty in using fly ash as the precursor material for geopolymer cements is that it is difficult to determine whether a given fly ash will react sufficiently with the activating solution. Characterization of fly ash using analytical methods such as x-ray diffraction (XRD) and scanning electron microscopy (SEM) may help predict its reactivity. There is some evidence that the vitreous alumina content of a fly ash may affect its reactivity as a geopolymer, and this quantity can be calculated by subtracting the amount of crystalline alumina-bearing minerals obtained using quantitative XRD (QXRD) from the bulk oxide composition of fly ash [2]. It is also known that there are multiple glassy phases within a fly ash sample, and it is important to identify these glasses since they can react differently when exposed to caustic solutions [3]. Thus, how the silica and alumina are bound within the fly ash is important. Several researchers [4, 5, 6, 7] have used SEM x-ray point counting methods to establish the chemical composition of the various glasses within fly ash in an attempt to better understand its internal structure and potential for reactivity.

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A combined method of fly ash dissolution and x-ray mapping analysis may be a promising option for testing the reactivity of fly ash. This method was used by Chancey [3] and Aughenbaugh et al. [8] to examine the reactivity of a fly ash in cement pore solutions. The fly ash is mixed in a dilute suspension for discrete period of times, and then the solid material is separated from the solution for analysis. In the study presented here, the method was modified to mimic the dissolution-precipitation process that occurs in geopolymerization [9, 10], using a highly caustic solution. It should be noted that the solution used in this study is in stark contrast to the acidic solutions often used to assess how much of the fly ash is available to react [11, 12]. In the study presented here, a different fly ash was used than in the prior work [3, 4, 8, 10]. The fly ash was examined 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 [13] from Atikokan Thermal Generating Station, Ontario Canada was selected for the study. Table 1 lists the oxide analysis and loss-on-ignition (LOI) for the Atikokan fly ash. The activating solution for the materials was 8 mol/L NaOH solution, like that used by Fernández-Jiménez et al. [2], and was made from 50 mass % prepared NaOH solution (ACS reagent grade) diluted with ultrapure water ($18.5 \pm 0.5 \text{ m}\Omega\text{-cm}$).

Table 1: Atikokan fly ash oxide composition from x-ray fluorescence spectroscopy, as reported from manufacturer in mass %

Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	SO ₃	TiO ₂	LOI
21.58	47.66	12.30	4.21	0.89	2.70	1.93	1.20	0.97	0.76

When cured at 23° C, geopolymer mortars made from Atikokan fly ash and 8 mol/L NaOH had relatively low strength at 7 d and moderate strength at 28 d when compared to mortars made with nine other fly ashes that were mixed and cured under identical conditions (unpublished data). For the geopolymer mortars tested in the experimental program, low strength was defined as less than 1 MPa, moderate strength was defined as 1 MPa to 14 MPa, and high strength was defined as greater than 14 MPa. These are relatively low strengths for cementitious materials but are expected values for geopolymers made using Class F fly ash and cured at 23°C. Most geopolymer studies use high temperature curing, which increases compressive strength [9, 14] The Atikokan 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 diffractometer³. The x-ray source produced Cu-K α 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

³ 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

phases. The scans were run from 10° to $70^\circ 2\theta$ with a step size of $0.02^\circ 2\theta$. The crystalline phases were identified using files from the inorganic crystal structure database⁴, and Rietveld analysis was completed with TOPAS Academic version software (Coelho⁵). Zinc oxide (ACS 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 and others [3, 4]. 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 10 kV accelerating voltage, and the 1024 x 768 EDS maps were collected using 256 μ s dwell time per pixel with a line average of 2. Each map took approximately 6 minutes to collect, and after four maps were collected and summed, the data collection was complete. Multispectral image analysis has been described for minerals [15] and fly ash [3, 4] and the specific process used is summarized briefly here. The raw x-ray maps in 16-bit form contained count information for the element at each pixel location. Initial data manipulation was completed on the 16-bit maps using Octave⁶, in order to properly scale the x-ray maps relative to each other when viewed in 8-bit (0-255) format. Typically, the silicon had the highest counts, so all other maps were scaled based on the maximum value found in the silicon map (i.e. for a maximum count of 80, 80 was scaled to 255). After rescaling, the images were smoothed using ImageJ⁷ and if low-signal noise needed to be removed, Octave code was used to find the pixels below a threshold value and replace them with zero values. The maps were then stacked digitally using Multispec⁸. 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 specimens in this study consisted of fly ash in its original state and solid residue of the fly ash after selective dissolution in the caustic 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) in a room at 23° C that rotated the samples end-over-end at approximately 10 rpm until the desired time had elapsed. At 28 d, the sample was removed from the rotisserie and the solid material was separated from the liquid under vacuum using a 2.7 μ m filter paper on a Buchner funnel. The solid 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. The residue after this dissolution technique was

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

⁵ <http://www.topas-academic.net/>

⁶ Octave, <http://www.gnu.org/software/octave/>

⁷ ImageJ, <http://rsbweb.nih.gov/ij/>

⁸ Multispec, <https://engineering.purdue.edu/~biehl/MultiSpec/>

analyzed for changes in the amounts of the glassy phases present with the goal of identifying the reactive glasses in the fly ash.

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 [2] that the amount of vitreous alumina, in particular, affects the reactivity of the fly ash. Fernández-Jiménez et al. [2] tested two fly ashes, one with a vitreous alumina content of 20.45 mass % and another with 14.11 mass %, with the same vitreous silica content of 50 mass %. Geopolymers made from the ash with higher vitreous alumina outperformed the ash with lower vitreous alumina content in terms of degree of reaction, as measured by hydrochloric acid dissolution of reaction products. The Atikokan fly ash examined in this study had a vitreous alumina content of 18.71 ± 1.27 mass % (Table 2). This implies that the fly ash may perform well as a geopolymer, since its vitreous alumina content is closer to that of the well-performing fly ash tested by Fernández-Jiménez et al. [2]. It should be noted that the vitreous silica content of the Atikokan fly ash was 41.49 ± 1.38 mass %, which was lower than the 50 mass % vitreous silica content studied in both samples by Fernández-Jiménez et al. [2]. These specimens were tested at 23° C; however, Fernández-Jiménez et al. [2] cured their specimens at 85° C, which was much hotter than the samples in this study and the reaction pathways are somewhat different at higher temperatures [9]. Therefore, more research is necessary on the relationship between vitreous alumina and silica content and geopolymer performance.

Table 2: Atikokan fly ash crystalline and bulk amorphous content expressed as mass %

Crystalline Phases		Amorphous Phases	
Phase name	Mass %	Phase	Mass %
Quartz	5.039 ± 1.6	Bulk Amorphous	79.72 ± 1.2
Mullite (3:2)	4.00 ± 1.8	Vitreous Alumina	18.71 ± 1.3
Hematite	0.49 ± 0.1	Vitreous Silica	41.49 ± 1.4
Anhydrite	0.24 ± 0.1		
Periclase	0.512 ± 0.1		

Six phases were identified in the Atikokan fly ash using SEM-MSIA⁹: quartz, aluminosilicate, C-A-S, C-A-S 1 (low Al), iron-rich, and voids, as shown in Table 3. The NaOH-exposed fly ash (28 days) did not appear to contain the low aluminum C-A-S phase, but it contained a high-aluminum C-A-S 2 and two types of reaction product. The intensity ratios from x-ray maps for each of the phases containing calcium, aluminum, and silicon are given in Table 3.

⁹ Cement chemistry notation is used for defining the glasses: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, f = FeO, $\bar{S}$ = SO₃, M = MgO, N = Na₂O, K = K₂O, and H = H₂O. Dashes are used to signify that the stoichiometry of the glass is not indicated in the name of the glass.

Table 3: Approximate phase intensity ratios for glass in the Atikokan fly ash

Phase designation	S / A	C / S
Aluminosilicate	0.95	-
C-A-S	0.56	0.2
C-A-S 1 (low Al)	1.28	1.0
C-A-S 2 (high Al)	0.88	0.8
Reaction1	0.65	0.2
Reaction 2	1.56	0.9

[10 kV operating conditions]

Phase-assignment images for the unexposed Atikokan fly ash and the 28-day exposed fly ash are shown in Figure 1. The crystalline phases recognized using MSIA included quartz, which was distinguished due to its angular morphology and high intensity silicon pixels, and an iron-rich phase with spherical morphology that was thought to contain the hematite identified by x-ray diffraction. Phase amounts are shown in Table 4. From the phase amounts in Table 4, it is surprising to note that the quartz decreased over time since it has been reported to be non-reactive [16]. This could be an artifact of selecting the fields-of-view for imaging and analysis. In the initial specimen, the field of view contained rather large quartz inclusions, 5 area% (which is approximately 14 mass % of quartz if one assumes that the area of polished fly ash cross-sections is equal to volume [17] and a quartz has a density of 2.64 g/cm³). The Rietveld results in Table 2 showed that quartz should have been present at approximately 5 mass % at 0 d. Therefore, the results from this method should be interpreted for qualitative trends in phase amounts, not quantitative amounts, unless a representative number of images are analyzed, which was not done in this study.

Of note in Table 4 is the dramatic decrease in the quantity of the aluminosilicate phase ($S/A = 0.95$) after 28 days of exposure to NaOH solution. This difference is so great that the trend can be considered independent of field-of-view artifacts. Similarly, the C-A-S phase ($S/A = 0.76$) decreased greatly from 0 d to 28 days. Since the other C-A-S phase varied in composition from specimen to specimen (low Al and high Al), it cannot be directly compared, however the phase found in the 28-day specimen was present in lower amount. A calcium aluminosilicate reaction product was found in the 28 d sample with two general compositions, a higher calcium reaction product ($C/S = 0.9$) and a lower calcium reaction product ($C/S = 0.2$). The actual composition of these reaction products was not measured, and they are only noted to be some type of reaction product of the materials in the system, as they were identifiable phases in the x-ray maps. The reaction product was an interesting observation, but identifying trends in the dissolution of glassy phases identified in the raw material fly ash was the primary goal of this dissolution study. The iron-containing phase was very minor in both the 0 d and 28 d specimens, thus not considered to have greatly influenced the solubility of the fly ash.

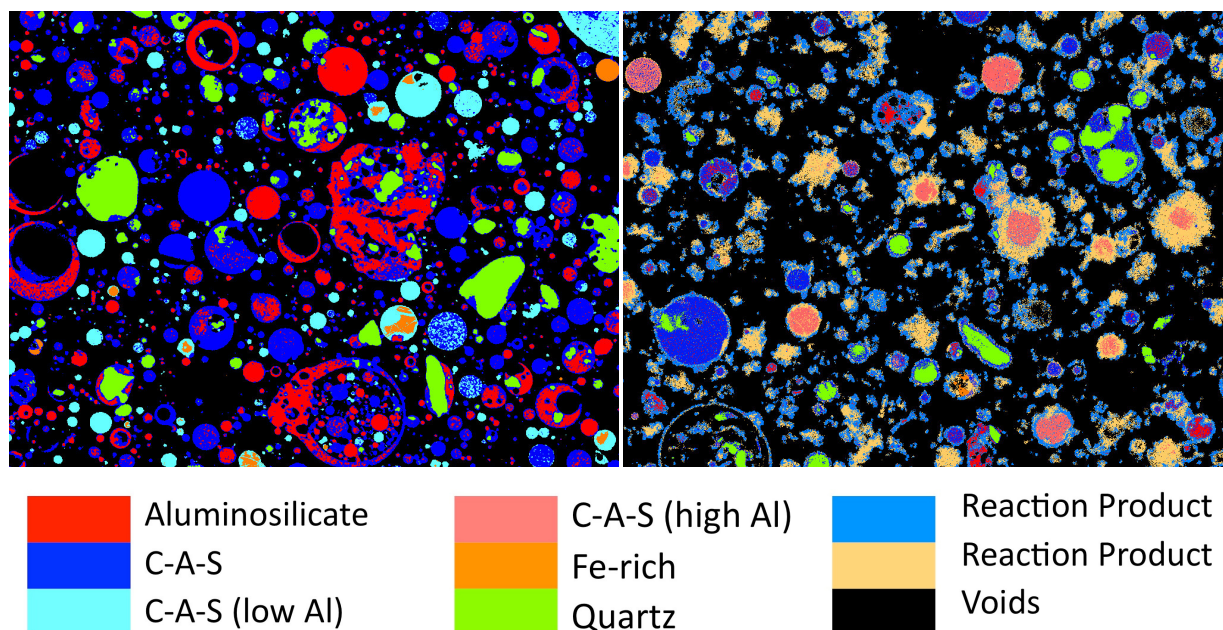


Figure 1: Untreated Atikokan fly ash phase assignment map (left), 28 d treated Atikokan fly ash phase assignment map (right).

Table 4: Area percentages of phases identified in Atikokan fly ash before and after 28 days of treatment with 8 M NaOH solution, based on a single measurement

Phase	Area Percentage of 1024 x 900 map	
	0 days	28 days
quartz	5.64	2.202
Aluminosilicate	10.02	1.238
C-A-S	20.57	4.063
C-A-S (low Al)	5.25	-
C-A-S (high Al)	-	1.801
Fe-rich	0.57	0.041
Reaction Product 1	-	12.182
Reaction Product 2	-	13.846
voids	57.95	64.627

Discussion:

Hemmings and Berry [16] published a detailed paper discussing the glass in fly ashes in which they 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, and calcium, sodium, potassium, and magnesium serving 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 [16]. These concepts are applied in the discussion of results from this dissolution study of the glasses identified in the Atikokan fly ash.

The aluminosilicate phase ($S/A = 0.95$) decreased greatly from the untreated sample to the 28 d sample. The C-A-S phase ($S/A = 0.56$, $C/S = 0.2$) also decreased from 0 d to 28 d. We speculate that the C-A-S phase ($C/S = 0.2$) has dissolved and reformed as reaction product on the surface of the particles (Reaction Product 2, $C/S = 0.9$). The low-Al C-A-S phase ($S/A = 1.28$) identified in the untreated specimen does not appear in the 28 d specimen; however, a high-Al C-A-S phase ($S/A = 0.88$) does. The high-Al C-A-S phase ($S/A = 0.88$) was surrounded by the high-Ca reaction product ($C/S = 0.9$), which also contained more silicon than aluminum ($S/A = 1.56$). This suggests that silicon may have dissolved from the particles (C-A-S low Al) and reacted near the surface of the particle, leaving a higher-aluminum C-A-S glass behind. Additionally, a slightly different composition of reaction product ringed the high-Ca reaction product (Reaction 2) and other particles in the 28 d specimen, and its composition was higher aluminum and lower calcium ($S/A = 0.65$, $C/S = 0.2$). The morphology of particles that this reaction product encircled tended to be more circular, implying that minimal dissolution occurred, and potentially these particles served as reaction nuclei rather than as sources for the aluminum and silicon ions; i.e. they were of low reactivity. The iron-rich particles were present in very small amounts in each data set, and are not thought to influence the reaction greatly, as they are typically considered inert [16].

Of the crystalline phases noted in Table 2, the quartz was easily identified using SEM-MSIA. The iron-rich particles are thought to be the hematite, which was measured in very small quantity by XRD and not thought to have affected the reaction kinetics. Anhydrite was not identified with SEM, but it was present in very small quantity and would have been highly reactive when exposed to the NaOH. The mullite cannot easily be identified through SEM analysis, and it is present in high enough quantity that further research will need to be completed to determine how it is incorporated into fly ash particles. The periclase was not identified in SEM-MSIA.

When comparing these results to those for the LEGS fly ash [10] from the Limestone Electric Generating Station Jewett, TX, some differences are apparent. First, the number of phases found in the LEGS fly ash was higher and included two aluminosilicates, two calcium-aluminosilicates, and two alkali-modified aluminosilicates. This compares to one aluminosilicate phase and two calcium-aluminosilicates found in the Atikokan fly ash. The S/A intensity ratio of the aluminosilicates seems to show a trend that increasing the S/A ratio improves reactivity of the glass. The LEGS A-S 1 glass with a 0.36 S/A was not reactive, while the LEGS A-S 2 with 0.77 S/A was reactive, and the Atikokan Aluminosilicate with 0.95 S/A was also reactive. The C-A-S phase found in the Atikokan fly ash has a similar S/A ratio as the moderate-Ca C-A-S found in the LEGS fly ash, and both were found to dissolve under the experimental conditions. Analysis of additional fly ashes may prove that the presence of this glass is a good indicator that a fly ash will react favorably in caustic conditions.

Conclusions:

A fly ash that has been shown to make a high-strength geopolymer was exposed to NaOH in dilute proportions (5 solution-to-powder ratio) for 28 d 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 an aluminosilicate phase, two C-A-S phases, an iron-rich phase, mullite, and quartz.
- All of the glassy phases appeared reactive in this fly ash.
- The C-A-S particles appeared to have leached silicon and calcium based upon the appearance of a material surrounding these particles that was high in these two elements.

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 aluminosilicate and C-A-S 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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List of Figures:

Figure 1: Atikokan fly ash pixel assignments map (left) and after 28 days of NaOH exposure (right)

WASTE GLASS FOR USE IN GEOPOLYMERS

Mary U. Christiansen and Lawrence L. Sutter

Synopsis: Waste glass is considered for use in a geopolymer binder systems based on the high Si content, amorphous framework structure, adequate hardness and widespread availability. A lack of Al within the system, however, must be taken into account, as Si/Al and Na/Al ratios have been shown to affect properties such as setting time, compressive strength and microstructure. Metakaolin and fly ash were added to a glass-based system, lowering the Si/Al and bringing Na/Al closer to unity. Mortars made using 100% glass as well as 25 and 50% of fly ash or metakaolin by mass were activated with 10M NaOH and cured at 80°C for 24 hours. Microstructural characterization of fracture surfaces and thin sections as well as compressive strength and degree of reaction data was collected. The 100% glass mixture (Si/Al – 8.39, Na/Al – 1.61) and 25% metakaolin (Si/Al – 4.96, Na/Al – 0.97) mixtures showed a dense, continuous microstructure. The 25% MK mix resulted in a 1-day f'_c of above 5000 psi (35 MPa), while the 50% metakaolin mixture (Si/Al = 3.45, Na/Al – 0.69) developed little strength and had a low-density microstructure, possibly due to the high water demand. Mixtures containing fly ash resulted in reasonable compressive strengths and moderately dense microstructures.

Keywords: alkali activation, fly ash, geopolymer, metakaolin, sodium hydroxide, waste glass

Biography: ACI student member Mary Christiansen is a PhD Candidate at Michigan Technological University in Houghton, Michigan. She earned her BS in Architectural Engineering in 2008 and MS in Structural Engineering at the Milwaukee School of Engineering in Milwaukee, Wisconsin in 2008. Ms. Christiansen's research interests include geopolymers and other sustainable binders created from waste products.

ACI member Dr. Lawrence Sutter is a Professor in the Michigan Tech Transportation Institute (MTTI) with expertise in concrete-making materials and durability. He serves as Secretary of ACI Committee 232 on Fly Ash and is a member of ASTM Committees C01 (Cement) and C09 (Concrete) and chairs ASTM Subcommittee 9.24 on Supplementary Cementitious Materials.

INTRODUCTION

An increased consideration of sustainability throughout society has resulted in a surge of research investigating sustainable alternatives to existing construction materials. Much of this research has focused on developing new binder systems, such as geopolymers, to supplement ordinary portland cement (OPC) concrete, which has come under scrutiny because of the CO₂ emissions inherent in its production (Shi, Jimenez et al. 2011). OPC production is reported to be responsible for 5-8% of global anthropogenic carbon emissions annually (Scrivener and Kirkpatrick 2008).

Geopolymers are produced from the alkali activation of a powdered aluminosilicate source by an alkaline solution such as NaOH or KOH; sodium silicate is also often included if sufficient silica is unavailable. Geopolymerization begins when an aluminosilicate source is dissolved by the alkali hydroxide and hydrolyzed within the solution. Upon reaching a certain Si concentration in solution, polycondensation occurs, where silicate and aluminate monomers polycondense with each other to form oligomers and later polymers (Fernandez-Jimenez, Palomo et al. 2005; Shi, Jimenez et al. 2011). As network connectivity increases, syneresis, or the expulsion of water from the hardening gel, occurs, resulting in a dense three-dimensional matrix of tetrahedrally linked aluminosilicates.

Geopolymer binders have shown great potential as a building construction material, offering similar mechanical (Fernandez-Jimenez, Palomo et al. 2006) and durability (Fernandez-Jimenez, Garcia-Lodeiro et al. 2007) properties to OPC. Additionally, geopolymers have the added value of a considerably smaller carbon footprint, with reported CO₂ emission reductions of up to 80% as compared to OPC (Davidovits 1994; Duxson, Provis et al. 2007).

GEOPOLYMER SOURCE MATERIALS

Since silica and alumina are the two most common elements in the Earth's crust after oxygen, there are seemingly endless natural materials that could be used as geopolymer source materials. However, not all of these materials would be successful, as the success of the source material has been found to depend a great deal on the following properties:

- Adequate Si and Al content – there must be enough Si and Al to form the geopolymer matrix
- Availability of the Si and Al – the rate at which the Si and Al becomes available must be rapid enough for polycondensation to occur
 - Structure – an amorphous, framework structure is favored for ease of dissolution (Xu and Van Deventer 2000); crystalline phases typically remain unreacted in the final matrix
 - Particle size and shape – affects ease of dissolution and rheology/water demand of the mixture
- Homogeneity – physical or compositional variability can affect reliability and reproducibility of the final product
- Hardness – important if complete dissolution does not occur and unreacted particles remain embedded in the matrix (Xu and Van Deventer 2000).

Alkali activated high-Ca slags have been used as building construction materials since early in the middle of the 20th century (Shi, Krivenko et al. 2006; Sofi, van Deventer et al. 2007), however “geopolymers” are typically considered to consist of low-Ca systems made primarily of Si and Al, such as those materials shown on the Si-Al side of the ternary diagram in Figure 1.

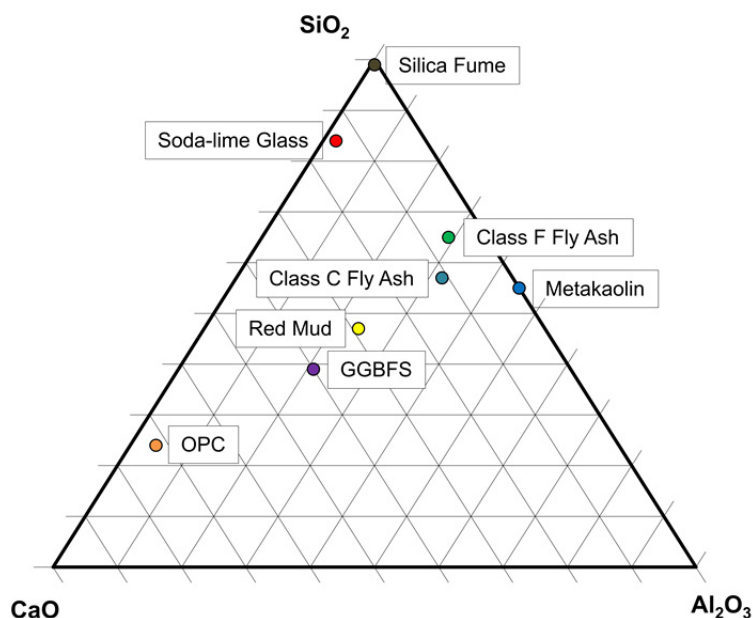


Figure 1 – Typical composition of common source materials used in geopolymers and OPC.

Since the early 1990s, metakaolin (Palomo and Glasser 1992; Rahier, Van Mele et al. 1996) and fly ash (Wastiels, Wu et al. 1994; Fernandez-Jimenez and Palomo 2003) have been the most commonly used source materials to produce geopolymers. Metakaolin-based geopolymers are not generally considered for structural or construction applications due to the low strengths and high water demand of the particles (Duxson, Fernandez-Jimenez et al. 2007). Metakaolin also requires an initial heat treatment, which contributes to carbon emissions and fuel requirements.

Fly ash has been shown to be a successful geopolymer source material (Fernandez-Jimenez, Palomo et al. 2006). However, it is extremely heterogeneous in nature and often contains crystalline phases such as mullite, hematite, quartz, etc. which do not react during geopolymerization (Diamond 1986; Hemmings and Berry 1986). This variability diminishes the reproducibility of a mixture and makes it difficult to predict performance behavior. The long-term availability of fly ash is also unknown, especially with the threat of being labeled a hazardous material.

Other materials such as kaolinite (Davidovits 2008), naturally occurring aluminosilicate minerals (Xu and Van Deventer 2000; Xu and Van Deventer 2002), cement kiln dust (Babaian, Wang et al. 2003; Buchwald and Schulz 2005), silica fume (Brew and MacKenzie 2007), natural pozzolans such as volcanic ash (Varela, Teixeira-Pinto et al. 2009) and red mud (Pan, Li et al. 2003; Zhang, He et al. 2010) have also been explored. This research considers the use of waste glass for geopolymer production.

WASTE PACKAGING GLASS

Waste glass could include any number of glass types but most prevalently consists of packaging glass, which made up 81% of all glass in the municipal solid waste stream in 2010 (US EPA 2010). Compositionally, packaging glass is considered to be a soda-lime glass, containing roughly 72% SiO₂, 13% CaO, 12% Na₂O (Glass Packaging Institute 2012). The high amorphous Si content can dissolve quickly and easily in basic solutions when ground to sufficient fineness (Iler 1979). Glass also typically has a significant Na content, which aids in dissolution and plays an important role in the geopolymer network formation when Al is present. The calcium content of glass is moderate and similar Ca concentrations in fly ash geopolymers have been shown to improve compressive strength through the formation of C-S-H (calcium silicate hydrate) alongside or integrated into the geopolymer matrix (Yip, Lukey et al. 2005; Guo, Shi et al. 2010).

Structurally, glass is amorphous with a framework structure, which increases the ease of dissolution. It is also hard, rated as 5.5 on Moh's hardness scale. Crushed glass particles typically display a conchoidal fracture resulting in sharp edges and smooth planes, further grinding has been found to even out the particle shape (Polley, Cramer et al. 1998). Packaging glass is relatively homogenous in composition and has most of the desirable components needed to create a geopolymeric binder.

Sodium silicate

Sodium silicate, or waterglass, is often included in the activating solution in a geopolymer cement mixture to account for a deficiency in available silica or if the Si is not able to dissolve into solution fast enough for polycondensation to occur. The presence of waterglass, or soluble silica, in an optimal dosage has been shown to enhance the hardened properties of GPC (Fernández-Jiménez and Palomo 2005; Steveson and Sagoe-Crentsil 2005; Criado, Fernandez-Jimenez et al. 2007).

Glass provides a substantial source of silica, and has the potential to create very high Si/Al content without the need for soluble silica (Cyr, Idir et al. 2012). This is beneficial environmentally because the production of sodium hydroxide and sodium silicate are the main contributors to CO₂ emissions associated with geopolymer cement (Duxson, Provis et al. 2007).

Glass recycling

Waste glass, or cullet, can be collected and remelted with other raw materials to form new glass, offering glass manufacturers significant cost, energy and fuel savings (Glass Packaging Institute 2012). However, impurities such as borosilicate glass, ceramics, stone, porcelain, metal containers, dishware, etc. can wreak havoc on the glass production machinery and cause defects in the final product due to their higher melting temperatures (Glass Packaging Institute 2012).

The time and costs associated with color sorting and removing impurities from single-stream or curbside recycling program waste glass streams to meet the strict requirements of glass manufacturers often exceed the savings. There are only 48 glass manufacturing plants and 76 cullet processors in the United States (Glass Packaging Institute 2012) and the transportation costs to get the cullet to a recycler makes glass recycling unfeasible in many locations (Polley, Cramer et al. 1998; Glusing and Conradt 2001; Zeiger 2008).

Due to the aforementioned limitations, glass recycling within the United States has reached a plateau over the past 20 years, as can be seen by the gray portion in Figure 2. In 2010, only 27% of the 11.53 million tons (10.46 metric tons) of glass generated in the municipal solid waste (MSW) stream was recovered (US EPA 2010).

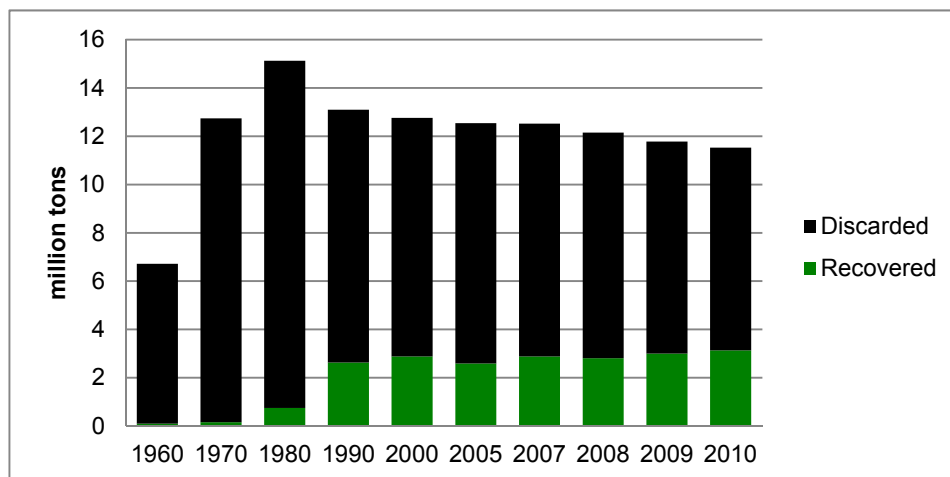


Figure 2 – Relationship between recovered and discarded glass in MSW from 1960-2010. Black represents discarded glass, gray represents recovered glass (US EPA 2010).

Other markets do exist for this unacceptable glass including the production of fiberglass insulation and blasting media as well as in decorative use applications (Pascoe, Barley et al. 2001; US EPA 2010; Glass

Packaging Institute 2012; Turner February 25, 2013). These markets often have compositional limitations of their own and none are robust enough to handle all the waste glass generated. Efforts to include glass in OPC concrete as either a cement replacement or aggregate have been successful in some cases, but issues with ASR (alkali-silica reactivity), poor workability, high water demand and poor bonding with the OPC matrix and aggregates are common and must be dealt with proactively (Meyer, Baxter et al. 1996; Shi and Zheng 2007).

Within the current literature, there has been surprisingly little research performed on the alkali activation of waste glass. The work of Cyr et al. was the first study that considered a system of 100% waste glass (Cyr, Idir et al. 2012). Other research has included waste glass in the geopolymer recipe, but not as the main ingredient (Grutzeck and Marks 1999; Carvalho, Carvalho et al. 2008; Kourtí, Rani et al. 2010; Cyr, Idir et al. 2012; Hao, Lin et al. 2012; Lin, Shiu et al. 2012).

GEPOLYMER STOICHIOMETRY

The Al content of a geopolymer, or more specifically, the Si/Al and Na/Al molar ratios, have been shown to affect the set time, compressive strength and microstructure of the subsequent binder; where in most cases the presence of Al can drastically improve the performance of the geopolymer (Fernandez-Jimenez, Palomo et al. 2006). A number of research projects have used reagent grade sodium aluminate as an alumina source for reaction with Si-rich materials, however sodium aluminate can be fairly expensive (Phair and Van Deventer 2002; Brew and MacKenzie 2007; Hajimohammadi, Provis et al. 2008; Gluth, Lehmann et al. 2012)

Si/Al

While the optimal Si/Al ratio in a geopolymer varies slightly depending on the source material and other parameters of the mixture, in general a Si/Al ratio of around 1.8-2.0 or so in the final matrix is considered to be a good goal for metakaolin or fly ash geopolymers (Duxson, Provis et al. 2005; Fernandez-Jimenez, de la Torre et al. 2006). There exists an optimum Si/Al ratio for each system where mechanical properties are highest (Duxson, Provis et al. 2005). Very low Si/Al systems ($\text{Si/Al} \leq 1$) generally have low compressive strengths, with some Al remaining in solution in accordance with Lowenstein's avoidance principle, which states Al-O-Al bonds are not favored naturally (Lowenstein 1954). Extremely high Si/Al systems ($\text{Si/Al} > 24$) have been found to develop elastic-like properties, with failure occurring through deformation rather than brittle failure (Fletcher, MacKenzie et al. 2005). However, aluminosilicate binders synthesized with Si/Al ratios from 0.5 to 300 have been studied and mixes with Si/Al up to 16 have exhibited high compressive strengths (Fletcher, MacKenzie et al. 2005)

With regard to microstructure, it has been found that low Si/Al systems ($\text{Si/Al} \leq 1$) generally produce a matrix consisting of many tiny precipitates densely packed together (Fletcher, MacKenzie et al. 2005). Alternately, the microstructure of high Si/Al systems ($\text{Si/Al} \geq 3$) is typically more uniform and individual particles are difficult to distinguish. Porosity in low Si/Al systems is generally in the form of large interconnected pores, whereas in higher Si/Al systems, porosity is more uniform and consists of small, isolated pores (Stevenson and Sagoe-Crentsil 2005). As porosity can be closely linked to compressive strength, it is no surprise that the less porous samples with higher Si/Al ratios and more soluble silica also had higher compressive strengths as compared to low Si/Al systems that contain coarser porosity (Stevenson and Sagoe-Crentsil 2005).

Na/Al

The ratio of alkali (sodium or potassium) to alumina has also been found to be very important to the success of a geopolymer mixture. Monovalent alkali cations (Na^+ or K^+) present in the geopolymer system allow trivalent alumina to be incorporated into the gel matrix in tetrahedral coordination alongside tetrahedral silica. Structurally, the role of Al is similar to that of Si, where it acts as a network former, linking tetrahedrally with other Si and Al ions through oxygen bridges.

Since the alkali cations are included in the final aluminosilicate matrix in a charge balancing capacity, ideally, the available Na/Al ratio will be as close to unity as possible. It has been found that in gels synthesized under basic conditions, only an equal amount of Al and Na will be included in the gel. Additionally, Na NMR-MAS does not show Na associated with non-bridging oxygen, meaning the Na is

only associated with Al as a charge balancer (Duxson, Lukey et al. 2005). Na^+ ions are believed to exist in a solvated state in between openings in the matrix where they balance the charge (Barbosa, MacKenzie et al. 2000).

Should excess Al exist ($\text{Na}/\text{Al} < 1$), it has been found to remain in the pore solution as aqueous $\text{Al}(\text{OH})_4^-$ (Duxson, Lukey et al. 2005). Na^+ ions have also been found in the pore solution with aqueous Al in an attempt to maintain charge neutrality. Excess Na^+ ions in the pore solution ($\text{Na}/\text{Al} > 1$) have been known to react with the atmosphere to form deleterious carbonates (Duxson, Lukey et al. 2005), which can lead to expansion, cracking or efflorescence. In very high Si/Al systems where the Na/Al is also very high, Na^+ ions present in the pore solution have been found to be easily leached away from the hardened product in water resulting in a substantial loss of compressive strength (Cyr, Idir et al. 2012).

Glass geopolymer stoichiometry

Waste packaging glass generally lacks Al in the system; typically containing only 2-3% Al_2O_3 by mass (Glass Packaging Institute 2012). In the case of a 100% packaging glass geopolymer activated simply with an alkali hydroxide, there exist limits within the stoichiometry with regard to Si, Al and Na. Figure 3 illustrates the maximum Si/Al and Na/Al ratios in a system activated by 10M NaOH where metakaolin replaces glass incrementally by mass. As the concentration of the activator increases the already very high Na/Al ratio will continue to increase as well, moving farther away from unity. If sodium silicate were added, this would affect the Na/Al in the same way, and would only serve to further increase the Si/Al ratio as well.

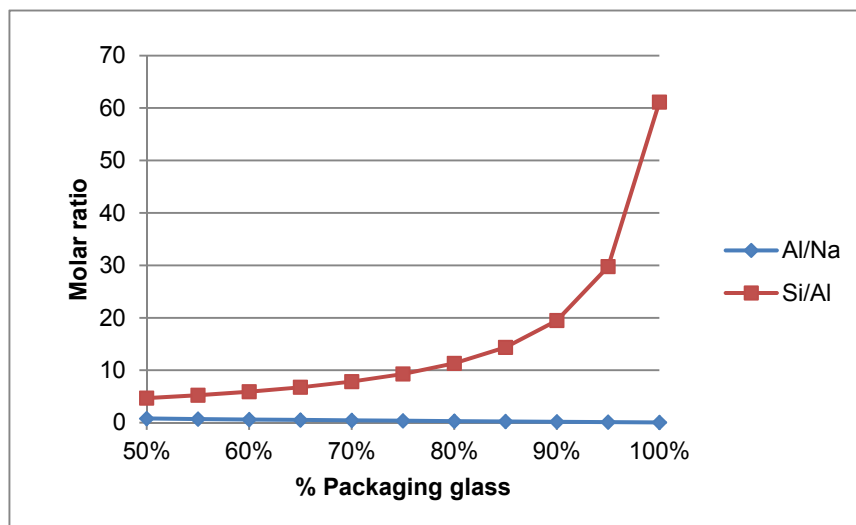


Figure 3 – Theoretical stoichiometry of packaging glass-metakaolin geopolymer activated with 10M NaOH.

EXPERIMENTAL

Materials

This research considered a consumer source (CS) glass as the principle source material. Metakaolin and fly ash replace 25 and 50% of the glass to provide Al to the system. It should be noted that the glass used in this research contains a higher Al and lower Na content than is typical of packaging glass. The source materials were activated with a 10M NaOH solution. The materials used in the experimental program are detailed below. Table 1 shows the wt% oxide composition of the glass, metakaolin and fly ash.

Table 1 – Composition of glass powder, metakaolin, fly ash and quartz sand.

	CS glass	Typical packaging glass*	Metakaolin	Fly ash	Quartz sand
SiO_2	60.25%	72%	51-53%	39.2%	99.7%
Al_2O_3	12.19%	2%	42-44%	20.3%	0.06%

Fe ₂ O ₃	0.31%	0%	<2.20%	8.12%	0.02%
TiO ₂	0.89%	0%	<3.0%	1.24%	0.01%
CaO	21.72%	12%	<0.20%	14.3%	<0.01%
SO ₄ , SO ₃	3.01%	0%	<0.50%	3.22%	0%
P ₂ O ₅	0.04%	0%	<0.20%	0.56%	0%
MgO	3.01%	1%	<0.10%	3.53%	<0.01%
Na ₂ O	0.87%	13%	<0.05%	5.84%	<0.01%
K ₂ O	0.08%	0%	<0.40%	1.10%	<0.01%
LOI	0.59%	-	<0.50%	1.19%	0.1%

*This composition included for comparison only, this glass was not used in this research.

Glass – Consumer source (CS) glass powder made from 100% recycled glass from a glass recycling plant that specializes in making fiberglass insulation was used. The glass is 100% amorphous, containing no crystalline silica (Turner July 27, 2012). The median size of the glass particles was 3-4µm.

Metakaolin – High reactivity metakaolin derived from pure kaolin clay, Al₂Si₂O₅(OH)₄, was used. The median size of the metakaolin was less than 4-5µm.

Fly ash – An ASTM C618 Class C fly ash was chosen for use based on its high alumina content (20.39% Al₂O₃), which helped to lower the Si/Al and Na/Al ratios. It was also chosen because it is considered unusable as a supplementary cementitious material in OPC production due to its high alkali content (6.56% Na₂O_{eq}).

NaOH – Reagent grade 100% sodium hydroxide in the form of solid flake was used to create the activator solution. The NaOH solution was prepared the day before mixing to allow the temperature and solution to equilibrate. In general, the higher the alkalinity of the activating solution, the higher the resulting compressive strength, however this is not always the case (Provis and vanDeventer 2009). Prior experimentation found activation with 10M NaOH as compared to 5M NaOH to yield higher compressive strength in 100G mortars under similar experimental conditions to this research.

Sand – ASTM C778 graded quartz sand was used to create the mortars.

Methodology

Mortar production – Mortars were prepared using a baseline 3:2:0.5 ratio of sand to glass to activator solution by mass, respectively. The mortars were prepared by first mixing the dry ingredients for 1 minute, then mixing in the activator for 3 minutes in a 20-quart all-purpose mixer. Paste samples were collected for degree of reaction measurements before the sand was added slowly over 2 minutes followed by an additional five minutes of mixing. Flow, unit weight and temperature were measured. The mortars were then consolidated into 2 in by 4 in cylinders using a vibration table, struck off and cured for 24 hours in sealed boxes containing open water at 176°F (80°C) and 95% relative humidity. All cylinders were demolded at 24 hours and the samples were cured at 76°F (24°C) in sealed storage containers at 90-95% relative humidity until the time of testing or analysis.

Figure 4 shows the relationship between the Si/Al and Na/Al molar ratios of the raw materials in the five mixes considered in this research, where metakaolin or fly ash replaced 25% and 50% of glass by mass. Mixtures were named according to the materials used, where 75G25MK means 75% glass, 25% metakaolin by mass.

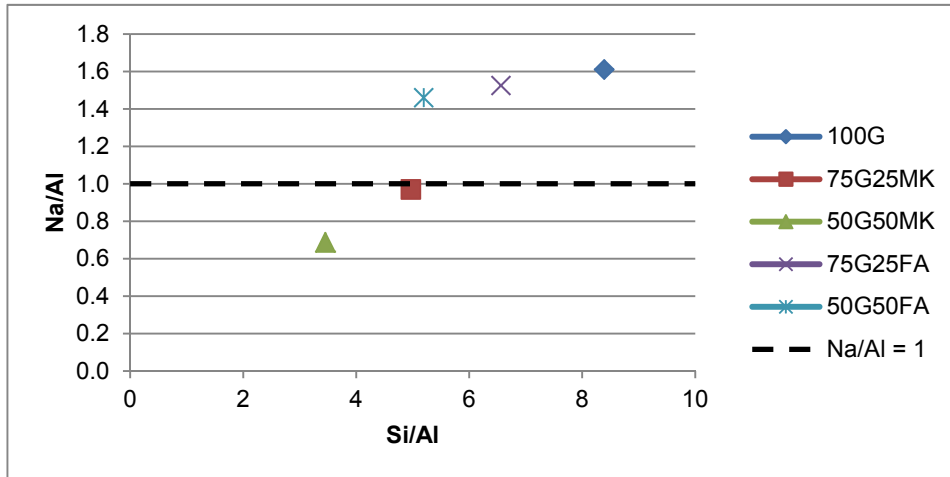


Figure 4 – Molar stoichiometry of the unreacted source materials and activator solution of the five mixtures. The dashed line represents the point where $\text{Na/Al} = 1$.

Varying the components of the mortars affected not only the stoichiometry of the mixtures (Si/Al , Na/Al , $\text{H}_2\text{O/Na}_2\text{O}$) but also the water content and color as well, as seen in Figure 5. The spherical particles of the fly ash drastically reduced the water demand when they replaced the more angular shaped glass particles. Alternately, the sheet-like structure of the metakaolin particles greatly increased the water demand when it replaced the glass. Additional water was added during mixing so that all of the mortars would achieve a similar flow. The liquid to solids ratio (not including the sand) is shown along with the theoretical stoichiometry of the raw mixes in Table 2. These ratios will not be realized in the actual geopolymer reaction products unless 100% dissolution occurs. The unreactive portion of the fly ash was not determined.

Table 2 – Molar stoichiometry (including unreacted source materials and activator solution)

Mix ID	Si/Al	Na/Al	$\text{H}_2\text{O/Na}_2\text{O}$	Na/Si	Liquid/solid ratio
100G	8.39	1.61	16.1	0.19	0.504
75G25MK	4.96	0.97	17.6	0.20	0.540
50G50MK	3.45	0.69	20.4	0.20	0.617
75G25FA	6.56	1.53	14.6	0.23	0.504
50G50FA	5.19	1.46	12.3	0.28	0.464

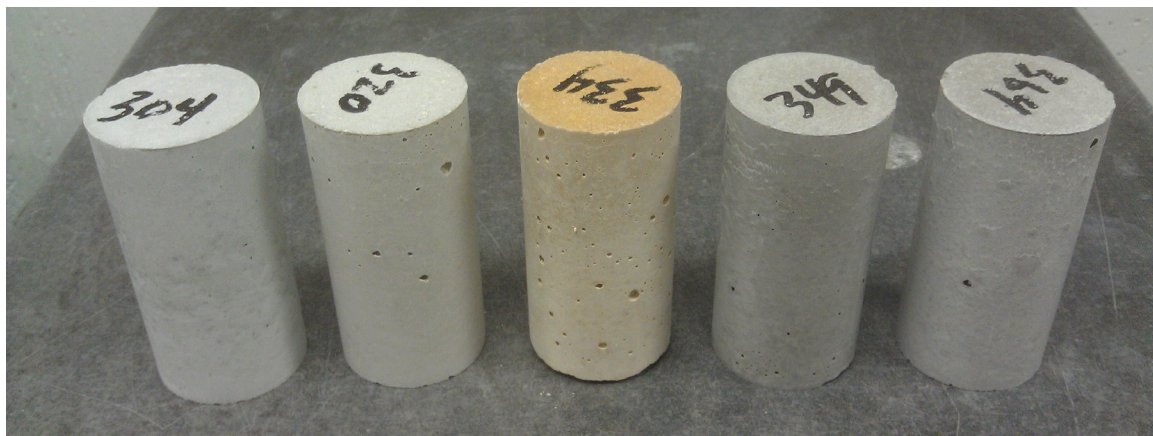


Figure 5 – From left to right: 100G, 75G25MK, 50G50MK, 75G25F, 50G50FA.

Microstructural analysis – Microstructural analysis by way of secondary electron imaging on carbon coated fracture surfaces was performed with a FEI XL-40 Environmental Scanning Microscope (ESEM) at 1, 3 and 7 days. Thin sections were prepared by polishing samples using consecutively finer media. Backscatter electron imaging on carbon coated thin sections was performed at 84 days (3 months).

Degree of reaction – The degree of reaction is a measure of the dissolved/reacted source material as a function of time and was measured on paste to avoid the affects of the graded sand in the experiment. During mixing, a sample of the paste was collected prior to the addition of the sand. The paste was cured alongside the mortar samples under the same conditions.

The degree of reaction experimental procedure was based on a currently used method (Fernandez-Jimenez, de la Torre et al. 2006; Criado, Fernandez-Jimenez et al. 2007; Criado, Fernández-Jiménez et al. 2010) and consists of reacting one gram of ground paste with 200mL of 20:1 HCl by volume for 3 hours on a magnetic stir plate. The solution is then filtered, washed, dried overnight at 100°C and calcined at 1000°C for one hour. The HCl dissolves the amorphous geopolymer and any zeolites that have formed (Granizo, Alonso et al. 2002), so a gravimetric measurement of the remaining unreacted particles gives the degree of reaction, α . The degree of reaction was measured at 1 and 7 days.

Compressive strength – As specified by ASTM C39, compressive strength was measured on an 810 Material Test System (MTS) material testing system, using a constant loading rate of 35 pounds per second (156 kN/s). Specimens were cylindrical with a 2:1 aspect ratio. All values reported are the average of three samples. Compressive strength was measured at 1, 3 and 7 days.

RESULTS and DISCUSSION

Electron microscopy on both fracture surfaces and thin sections revealed the differences within the microstructures of the five mortars. Figure 6 shows the fracture surface of the five mixtures at 3 days. The 100G and 75G25MK mixtures, which also yielded the highest compressive strengths (see Figure 14), appeared dense and homogenous, with angular voids most likely remnant of unreacted glass particles that were pulled out during sample preparation.

The mixture containing 50% metakaolin appeared to be made up of aggregated pieces of reaction product intermingled with unreacted glass rather than a monolithic structure as was found in the others. The aggregated microstructure was similar to that found in low Si/Al systems ($\text{Si}/\text{Al} = 1.15, 1.4$) found in other research concerning the Si/Al ratio of metakaolin geopolymers (Duxson, Provis et al. 2005). The microstructure of the mixtures containing fly ash appeared dense for the most part, with partially reacted fly ash particles or remnant voids from particles present.

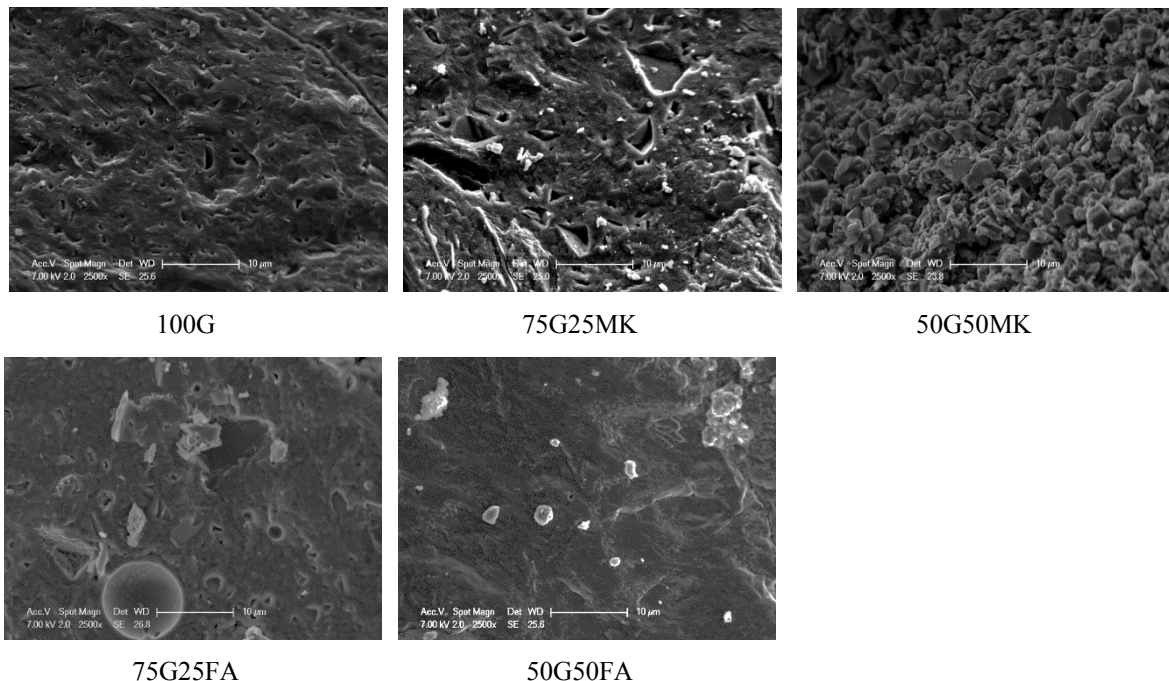


Figure 6 – Comparison of fracture surfaces after 3 days of five mixtures starting at top left, 100G, 75G25MK, 50G50MK, and bottom left, 75G25FA, 50G50FA.

Backscatter electron micrography on the five mixtures further elucidated the differences in microstructure, as seen in Figure 7. The 100G mortar showed a uniform geopolymer microstructure embedded with unreacted glass particles. Most of the glass particles had a very thin reaction rim around them, as seen in Figure 8; this reaction rim was not found in the other mixtures.

The 75G25MK mixture yielded the highest compressive strength, yet appeared less dense in both secondary and backscatter analysis. It is possible that the Si/Al or Na/Al ratios played a role in this case; in particular, the Na/Al ratio of this mix was the closest of all the mixtures to 1. The 75G25FA mixture also appeared to have a uniform, dense microstructure, however the compressive strength of this mix was lower than the 100G and 75G25MK mixtures. Both the 50MK and 50FA mixtures have a less dense structure, as illustrated by the underlying black areas where no product is present. More unreacted particles were also evident, where unreacted metakaolin particles were identified by EDS in the 50G50MK mixture.

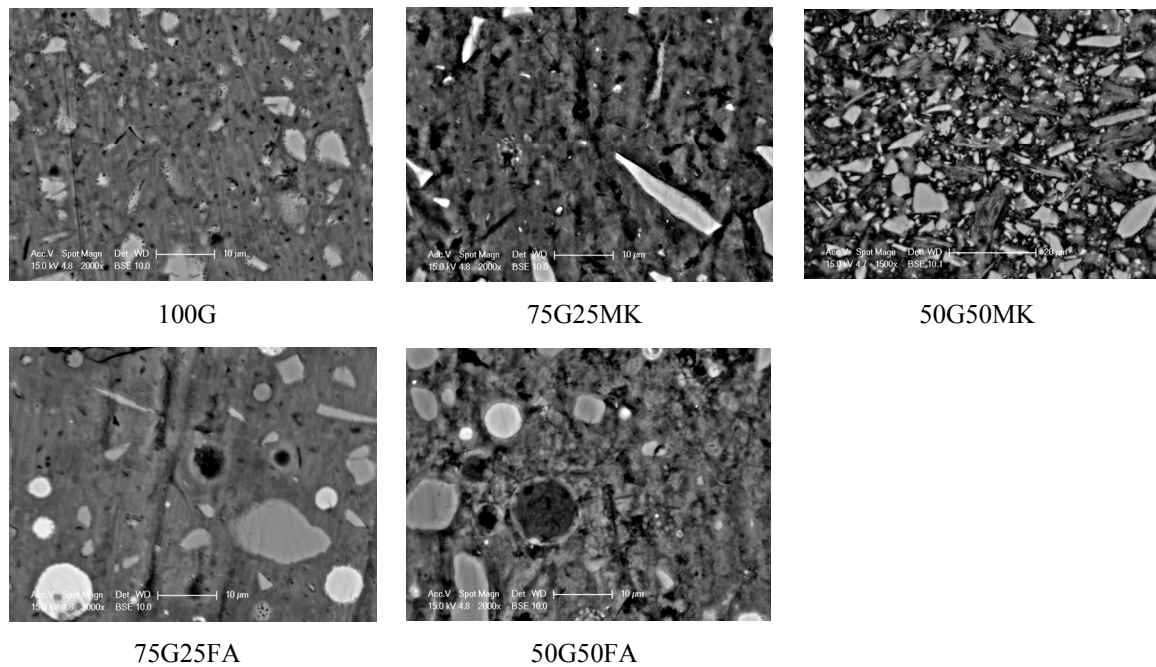


Figure 7 – Backscatter comparison of groundmass at 84 days (three months) of five mixtures starting at top left, 100G, 75G25MK, 50G50MK, and bottom left, 75G25FA, 50G50FA.

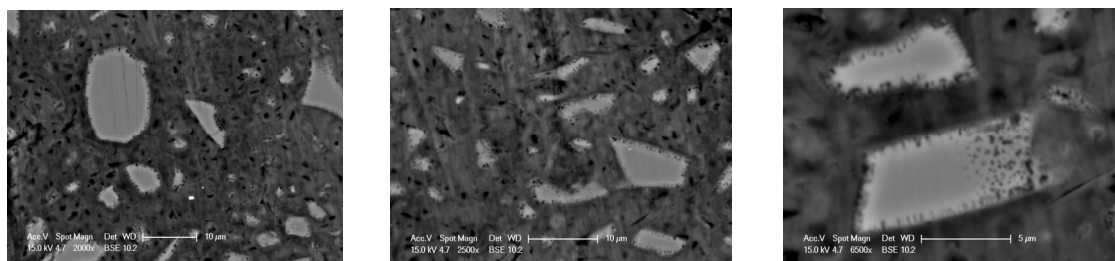


Figure 8. Backscatter electron images of the reaction ring around glass particles in 100G matrix at various magnifications.

The results of the degree of reaction experiments are shown in Figure 9. Relatively low degree of reaction was found for all of the samples tested at up to 7 days, with the exception of the 50G50MK mixture, which was much higher. This higher degree of reaction is believed to be due to the higher water content of the

mixture, where more liquid allowed for more lability of the hydroxyl ions within the mixture. Metakaolin is also easily dissolved in an alkaline solution (Davidovits 2008), which could be why the two mixtures containing metakaolin have the highest degree of reaction.

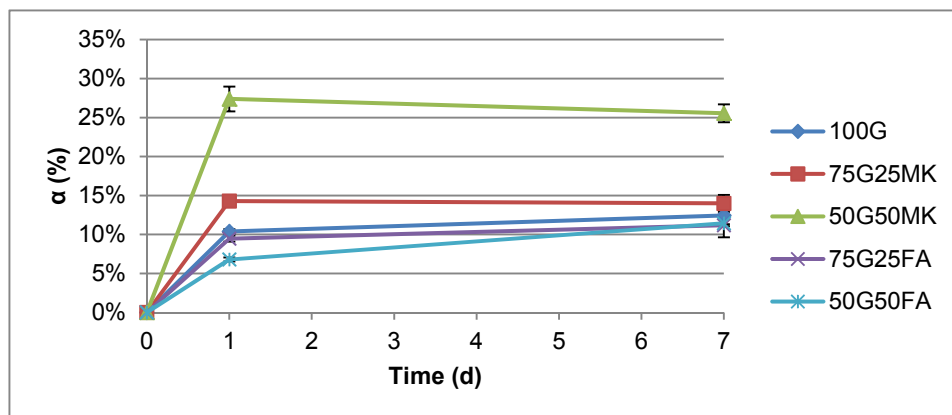


Figure 9 – Degree of reaction versus curing time. Each data point is the average of two tests. Error bars were calculated from the $SD/\sqrt{n}$, where SD is standard deviation and n is the sample size.

It should be noted that mixes are typically designed based on the stoichiometric amounts of Si, Al, Na, etc. in the source materials; however whether or not the desired Si/Al ratio, etc. is realized or not depends on the degree of reaction as well as the content of nonreactive phases (i.e. mullite, quartz, etc. in fly ash). The stoichiometry reported previously is not the same stoichiometry that will be found in the reaction products unless 100% degree of reaction is reached and all of the available ions are combined into the final matrix. This was not found to be the case and since most of the mixes contained two source materials, it is impossible to determine the actual dissolution of each material and therefore the stoichiometry without EDS.

All of the mortars showed unreacted particles embedded within the matrix even after 3 months. This does not coincide with data from Cyr et al, who reported 100% dissolution of the glass after 56 days, however prolonged curing was employed in that research, which could have led to higher dissolution. Figure 10 shows some backscatter electron images of unreacted or partially reacted fly ash particles found in the 50G50FA mixture. Fly ash often contains crystalline or unreactive particles such as that shown on the right below, and in Figure 11. The percentage of reactive phases present should be calculated to determine the compositional contributions of a given fly ash.

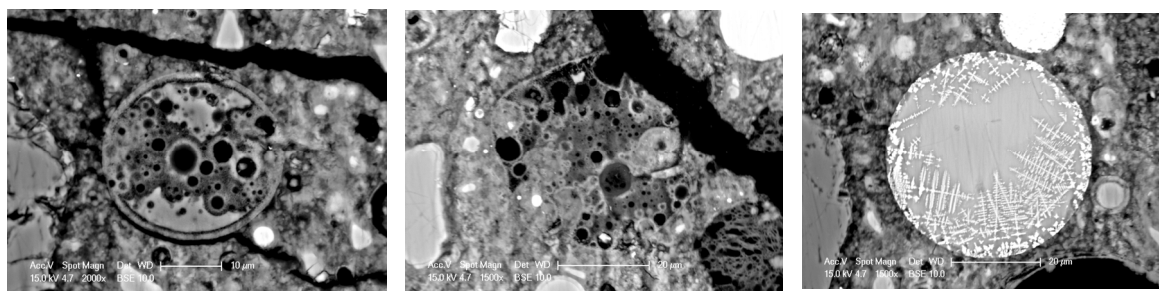


Figure 10 – Unreacted and partially reacted fly ash particles in 50G50FA mixture. The image on the right is a barely reacted cenosphere, in the middle is a partially reacted cenosphere and on the right an unreacted Fe-rich particle.

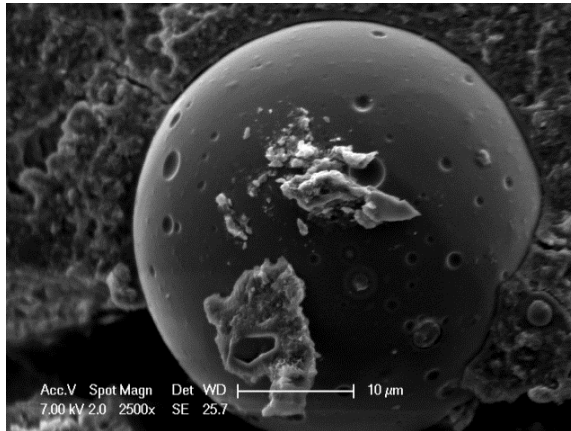


Figure 11 – Unreacted fly ash particle in matrix.

Secondary electron imaging on fracture surfaces also found the presence of zeolites. Geopolymers are said to be the amorphous analogues to zeolites (Duxson, Provis et al. 2005), where both can be synthesized in similar conditions, with zeolites requiring higher temperatures, more time and a higher liquid/solid environment. Zeolites were found in all of the mixes, particularly in the mortar containing 50% metakaolin, this could be due to the higher water/solids ratio, where the excess water available may have allowed for more organization to occur, and thus zeolite formation. Most of the zeolites were found within air voids or in voids left behind from unreacted particles. It is unknown if the zeolites exist within the matrix or if they just form on the surface in air or in voids. Figure 12 shows examples of the types of zeolites found in the samples at 7 days.

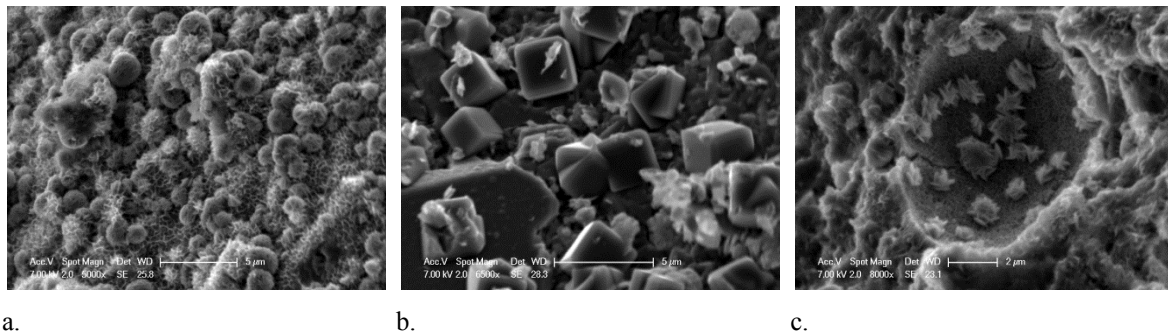


Figure 12 – Examples of zeolites found in the samples at 7 days. From left to right: zeolites in the 100G sample, zeolites found in the 50G50MK specimen, and zeolites found in a void in the 50G50FA sample.

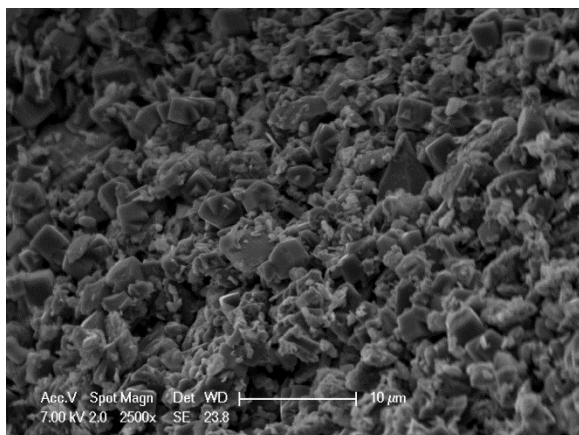


Figure 13 – Fracture surface of 50G50MK, showing many unreacted glass particles embedded in a matrix rich in zeolites.

Compressive strength results are shown in Figure 14. In nearly all cases, there was a very slight decrease in compressive strength from 1 to 7 days. The 75G25MK mixture had the highest compressive strength overall, followed by the 100G mixture and then the mixes containing fly ash. The highest strength could be due to the addition of the Al to the system through the metakaolin. Of the four samples that performed adequately in terms of compressive strength, this sample also had the highest degree of reaction, which is most likely attributed to the metakaolin particles, which dissolve easily in basic solutions.

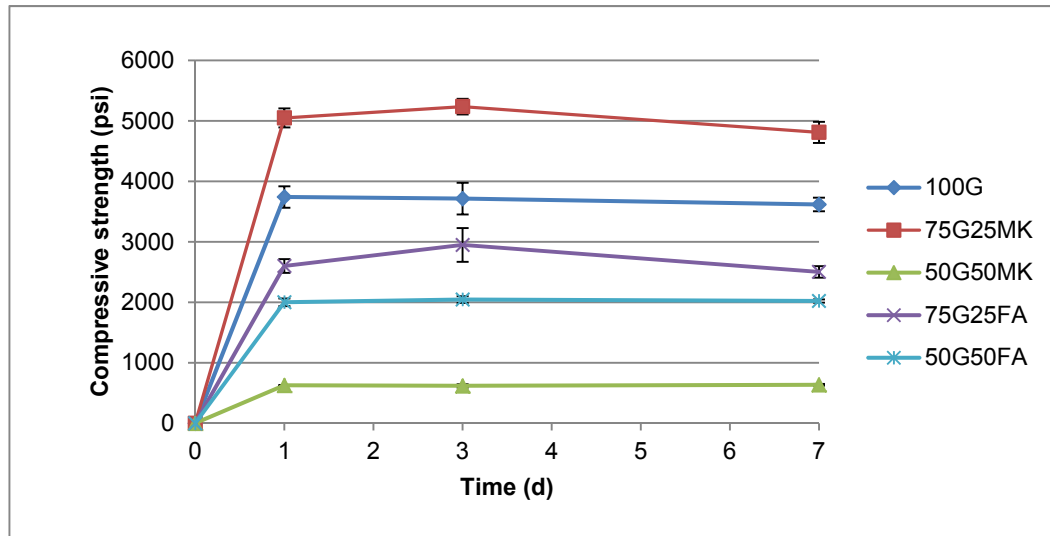


Figure 14 – Compressive strength versus curing time. Each data point is the average of three tests. Error bars were calculated from the $SD/\sqrt{n}$, where SD is standard deviation and n is the sample size.

The mixture containing 50% metakaolin exhibited extremely low compressive strengths, crumbling apart easily upon fracture. It is possible that the high water demand of the mixture led to the high degree of dissolution since the water allowed for easier dissolution. However, this extra water left behind a low-density microstructure upon drying and hardening, which is most likely the reason for the extremely low compressive strength. The high quantity of zeolites found in these samples is also consistent with a system requiring a high water content. Zeolites are more likely to form in environments where the liquid/solid ratio is high.

Water in a geopolymer mixture is not chemically bound within the reaction products, but rather exists alongside them in gel pores. This is different than the case with OPC, where water is chemically bound in the calcium-silicate-hydrate (Provis and vanDeventer 2009). Despite this fundamental difference, the water/binder ratio in both OPC and GPC is very important when it comes to fresh and hardened concrete properties. In both systems, a high liquid/solid ratio can result in increased porosity, which has been linked to lower compressive strength (Hardjito and Rangan 2005; Steveson and Sagoe-Crentsil 2005).

CONCLUSIONS

Geopolymers made of glass has a significantly smaller carbon footprint than ordinary portland cement and also has the potential to utilize vast quantities of waste materials. Glass-based geopolymers also have the potential to produce a quality alternative binder capable of reaching high strengths at only 24 hours, as well as to create a stable market for waste glass, which will help to relieve pressure from the municipal waste stream and put a valuable material to good use. Further, the high Si and Na contents that waste glass offers without the addition of sodium silicate allow for activation with just an alkali hydroxide, further lowering the carbon footprint of the binder.

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