Effect of Water-Solids Ratio on the Compressive Strength and Morphology of Fly Ash-Waste Glass Geopolymer Mortars

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ABSTRACT

On a global scale, the production of portland cement is responsible for a significant portion of annual anthropogenic greenhouse gas emissions. While the use of fly ash in portland cement concrete can reduce portland cement consumption, geopolymer technology has the potential to completely eliminate portland cement in some concrete. Geopolymers are made from the combination of an aluminosilicate source (fly ash, waste glass, metakaolin, etc.) with a highly concentrated alkali activating solution (sodium hydroxide, sodium silicate, etc.). The effect of the water-solids ratio on compressive strength and morphology of fly ash/waste glass-based geopolymer mortars was investigated. Geopolymer mortars made of fly ash and varying replacement levels of waste glass were activated with 10M NaOH. Three water-solids ratios were examined for each mixture. Water in geopolymer mixtures acts primarily as a transport mechanism for dissolution to occur and is not bound in the reaction products. The importance of the water-solids ratio was found to be dependent on the mixture composition. Strength gain profiles showed very high gains within 24 hours followed by little strength gain thereafter, regardless of the water-solids ratio. The morphology of the geopolymer mortars was also examined.

1. INTRODUCTION

Geopolymers are produced by combining an aluminosilicate source with a highly concentrated alkali solution. Typical aluminosilicate sources include industrial waste byproducts (fly ash or slag), metakaolin, powdered waste glass, etc. Geopolymerization consists of a three-stage process. The first stage is known as dissolution, where the aluminosilicate source is broken down by the alkali solution. The rate of dissolution depends on the pH level of the activating solution and is generally higher in aluminosilicate sources with more disordered or amorphous structures [1]. The second stage is polymerization, where the individual alumina and silica monomers polymerize together in increasing speciation to create a N-A-S-H (similar to C-S-H in portland

cement). The final stage consists of further growing, reorganizing and crystallization of the gel into a monolithic material [1-3].

While the chemical composition of the aluminosilicate source generally affects the overall performance of the geopolymer, given the correct mixture design and curing methods, geopolymers can sometimes outperform portland cement concrete [2, 4, 5]. Tensile strengths are similar to values expected with portland cement concrete, whereas compressive and flexural strengths tend to exceed PCC values [4]. However, the major advantage concrete made with geopolymer has over portland cement is the reduced carbon footprint. During the production of geopolymers, there is no calcination process, nor is there the need to heat a kiln, therefore carbon emissions are reduced significantly as compared to PCC production [5]. Geopolymers also typically involve high volumes of waste materials in their mixtures that would otherwise be disposed of in a landfill.

Geopolymers are still a relatively new technology and are viewed suspiciously by many because they do not contain portland cement. One major obstacle facing geopolymer technology is the prevalent use of prescriptive specifications. Some geopolymer mixtures could potentially outperform their portland cement counterparts, but if the specification states a "minimum cement content", it excludes using the geopolymer [5]. Variability within the available aluminosilicate sources (chemical composition, reactivity, etc.), which can affect the mechanical properties of the geopolymer, is a valid concern [6]. Other unknowns include the exact geopolymerization process, the effect of water/solids ratio, whether water is included in the final product, etc.

It is a well-known fact that water is required for portland cement to properly hydrate and workability for ease of placement. The optimal water-cement ratio in portland cement concrete theoretically allows for 100% hydration and adequate workability. Higher water-cement ratios will typically lead to decreased compressive strength due to the presence of voids leftover from excess water present in the mixture. The effect of the water-solids ratio on the compressive strength and microstructural development was studied here for a series of fly ash-waste glass geopolymer mortars activated with two different activators.

2. EXPERIMENTAL

2.1. Materials

The geopolymers used in this research were created by mixing various quantities of fly ash and waste glass powder with activators including sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The chemical compositions for each of the materials used are shown in Table 1.

Table 1. Weight percent oxide chemical compositions of the materials used, as determined by XRF.

	Waste Glass	Class F Fly Ash	NaOH Flake	Sodium Silicate
H_2O	-	0.06%	22.53%	62.31%

SiO$_2$	60.25%	51.10%	-	28.70%
Al$_2$O$_3$	12.19%	15.61%	-	-
Fe$_2$O$_3$	0.31%	5.73%	-	-
CaO	21.72%	15.11%	-	-
MgO	3.01%	4.97%	-	-
SO$_3$	0.01%	0.76%	-	-
Na$_2$O	0.87%	2.44%	77.48%	8.99%
K$_2$O	0.08%	2.27%	-	-
P$_2$O$_5$	0.04%	0.22%	-	-
TiO$_2$	0.89%	0.25%	-	-
LOI	0.59%	0.20%	-	-

Fly ash
An ASTM C618 Class F fly ash was selected based on its moderate alumna and calcia contents (15.61% Al$_2$O$_3$ and 15.11% CaO).

Glass
Waste glass classified as consumer source (CS) glass was used. The glass was collected from a glass recycling plant that specializes in making fiberglass insulation. The glass is 100% amorphous and contained no crystalline silica; the median size of the glass particles was 3-4µm [7].

NaOH
Reagent grade 100% sodium hydroxide flake was mixed with deionized water to create a 10M activating solution. The 10M NaOH activating solution was the main activating solution used in this research. The NaOH solution was prepared the day before mixing to allow the temperature and solution to equilibrate.

Sodium silicate
Reagent grade Na$_2$SiO$_3$ was used in combination with NaOH to make an additional activator.
Sand
ASTM C778 graded quartz sand was used to create the mortars.

2.2. Mixture Design

All mixtures were designed with a fine aggregate to aluminosilicate ratio of 3 and an activator to aluminosilicate ratio of 0.5 Five combinations of aluminosilicates were considered, the first containing 100% fly ash (100FA), the next containing 25% replacement with glass by mass (75FA25G), then 50% (50FA50G) and so on until the last mixture contained 100% glass (100G). Each combination was investigated using NaOH as the activator and three different water-solids ratios. An additional five mixtures made of the same aluminosilicate proportions and activated with a sodium hydroxide to sodium silicate ratio of 1:1 were also investigated. **Error! Reference source not found.** shows the SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ molar ratios of all of the mixtures. A SiO$_2$/Al$_2$O$_3$ molar ratio of 2-5 and a Na$_2$O/Al$_2$O$_3$ molar ratio of around 1 are typical [2, 8]; these values are slightly higher due to the high SiO$_2$ content in the glass.

Table 2. SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ ratios of the five mixtures investigated.

	100FA	75FA25G	50FA50G	25FA75G	100G
SiO$_2$/Al$_2$O$_3$ (molar) NaOH	5.56	6.14	6.80	7.54	8.39
Na$_2$O/Al$_2$O$_3$ (molar) NaOH	1.42	1.46	1.51	1.55	1.61
SiO$_2$/Al$_2$O$_3$ (molar) NaOH:SS = 1	6.34	6.97	7.67	8.47	9.39
Na$_2$O/Al$_2$O$_3$ (molar) NaOH:SS = 1	1.08	1.10	1.12	1.14	1.17

The water-solids ratio investigated in this research can be defined as the ratio of total mass of water (water in activating solution and additional water) to the total mass of geopolymer solids (aluminosilicate source and solids in activating solution). Due to mixture design constraints (activator/aluminosilicate ratio, molarity of NaOH), the minimum water-solids ratio for mixtures activated with sodium hydroxide was 0.350 and 0.305 for those activated with sodium hydroxide and odium silicate. Three water-solids ratios were selected for each geopolymer. To determine the lowest water-solids ratio used for each mixture, water was added to the minimum and increased by 0.025 until a reasonable mixture consistency was achieved, from there two additional ratios were determined by increasing the ratio by 0.025. Those mixtures containing higher quantities of fly ash were observed to require less water due to the "ball-bearing" effect that fly ash tends to have on mixtures.

2.3. Methodology
Mortar production
The aluminosilicate(s) were mixed together for three minutes to ensure a well-blended mixture. The activating solution was then added slowly over a period of one minute. For mixtures using sodium silicate in the activating solution, the sodium silicate and sodium hydroxide were mixed prior to being added to the dry ingredients. The activating solution and aluminosilicate blend was allowed to mix for three minutes before any additional water was added. This created a geopolymer paste used in the degree of reaction tests. To produce the mortars used for compressive strength, silica sand was added slowly over a period of two minutes. The mixtures were then allowed to mix for an additional six minutes.

Following mixing, the mortars were placed in cylindrical molds in two lifts, vibrated for 30 seconds and cured at 80°C and 95% relative humidity for 24 hours in sealed containers containing open water. At 24 hours the cylinders were demolded and placed in 24°C sealed storage containers at 90-95% relative humidity until the time of testing or analysis.

Compressive Strength
Compressive strength was then measured at 1, 7, 28, and 56 days. As specified by ASTM C39, compressive strength was measured using a constant loading rate of 156 kN/s. Cylindrical specimens with a 2:1 aspect ratio were used and all values reported are the average of three samples.

Microstructural characterization

Microstructural analysis of the hardened mortar samples was performed using a JEOL JSM-6490LV scanning electron microscope (SEM). Secondary electron imaging on gold-coated fracture surfaces was performed on samples that were all over 100 days old.

3. RESULTS AND DISCUSSION

Results from compressive strength testing showed that the water-solids ratio did affect the compressive strength of the mortars to some degree. However, it seems that how important the water-solids ratio is depends primarily on the mixture composition. For example, the 100G mixture was not affected greatly by the water-solids ratio, but the 50FA50G mixture seemed to be more dependent on how much water was added. Figure 1 shows the effect of the water-solids ratio on compressive strength after seven days.
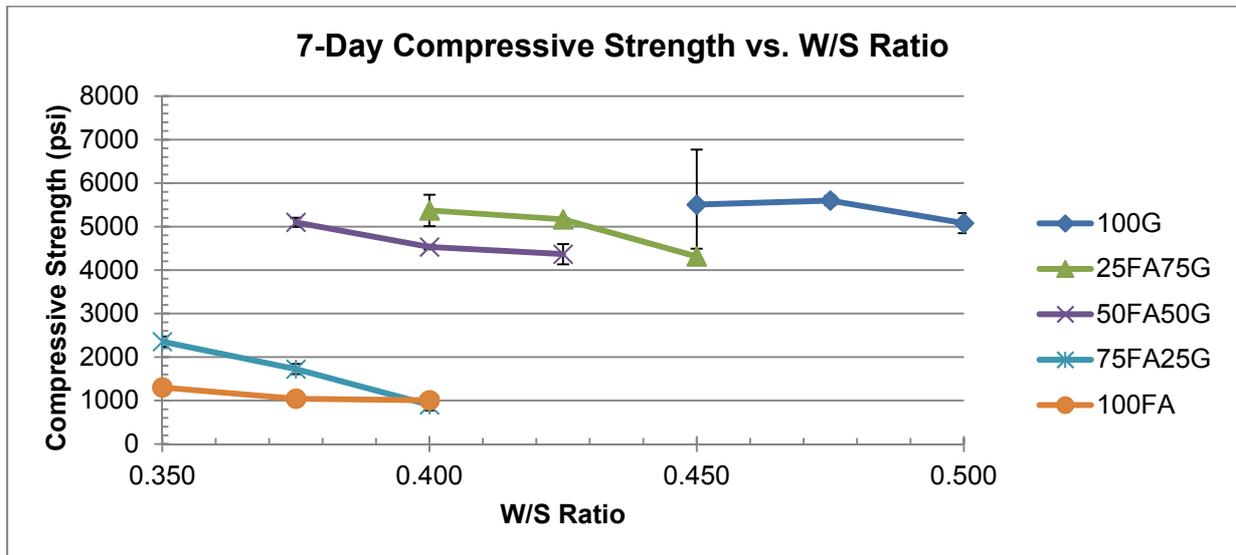

Figure 1. 7-day compressive strength vs w/s ratio for mixtures activated with NaOH.

As stated previously, the lowest water-solids ratio that could be achieved was 0.350 for sodium hydroxide (NaOH) mixtures. These restrictions are believed to have affected the 100FA and 75FA25G mixtures and could be the reason for such low strengths.

For nearly all mixtures, the majority of compressive strength gain occurred in the first 24 hours, as shown in Figure 2 and Figure 3. This was consistent throughout all of the mixtures that used NaOH as the activating solution. However, mixtures that used sodium silicate showed an increase of strength over time, which is consistent with other studies [9].
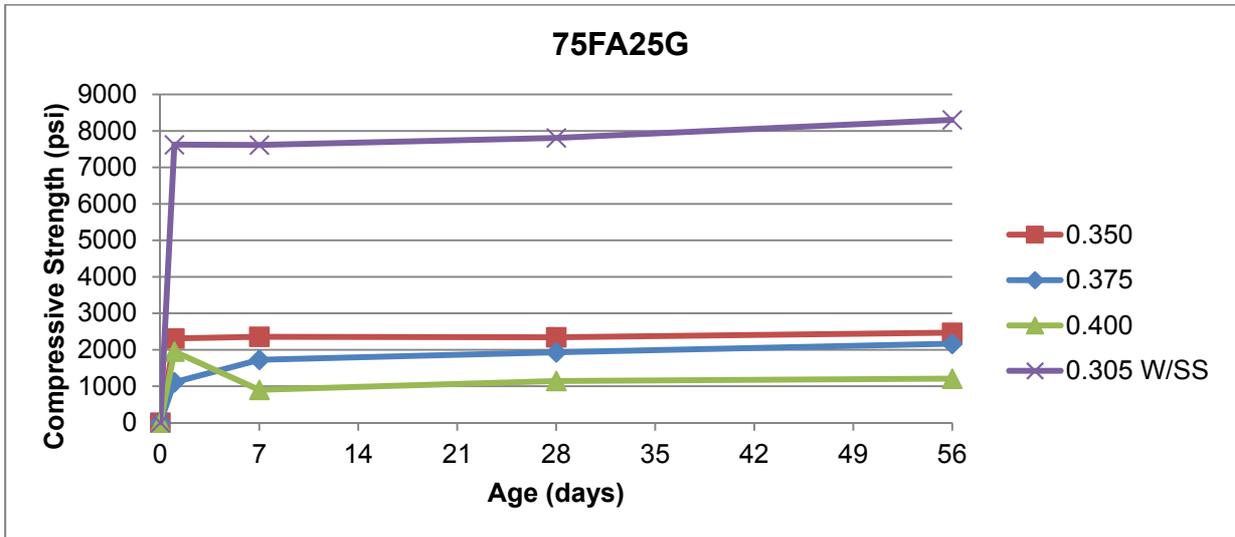
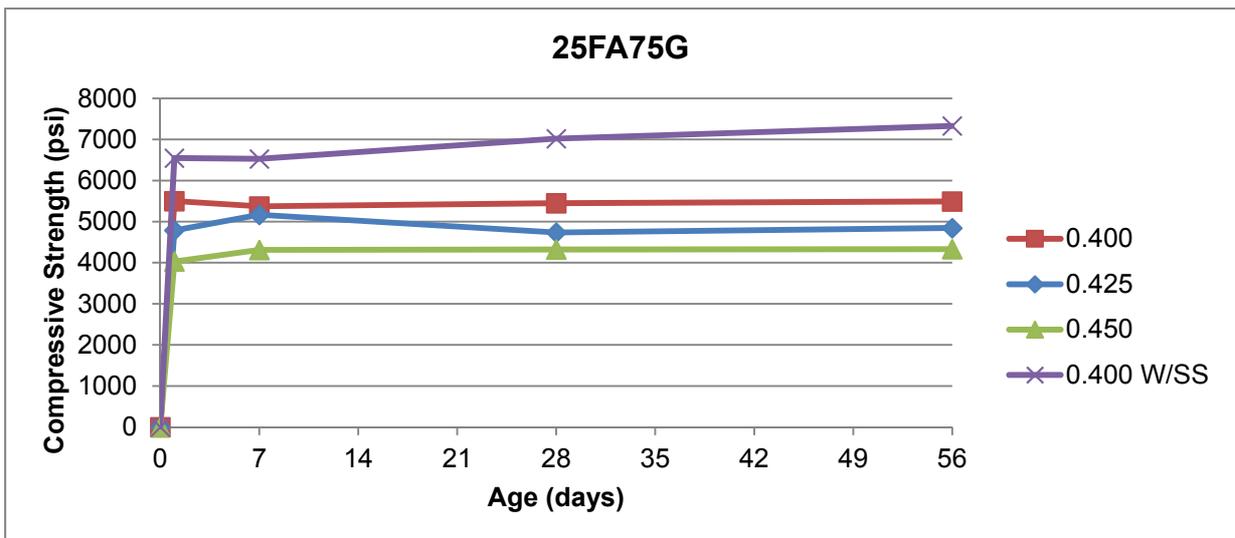**Figure 2. Compressive strength gain over 56 days for 75FA25G mixtures.**

Figure 3. Compressive strength gain over 56 day for 25FA75G mixtures.

The compressive strength of sodium silicate mixtures also seemed to be affected by the chemical composition of the mixture. The 100G mixture exhibited similar strengths to those using sodium hydroxide as an activator. As fly ash content increased however, the mixture activated with a combination of sodium silicate and sodium hydroxide resulted in increased compressive strength results, as can be seen in Figure 2.

Microstructural analysis via electron microscopy showed the differences in microstructure that occurred between the various mixtures and their varying water-solids ratios. As shown in Figure 4, the microstructure of each mixture tended not to change too dramatically as water-solids ratio changed. This is in line with the similar findings from compressive strength testing. Variations between the mixtures (i.e. ratio of fly ash to glass) however, were quite apparent.
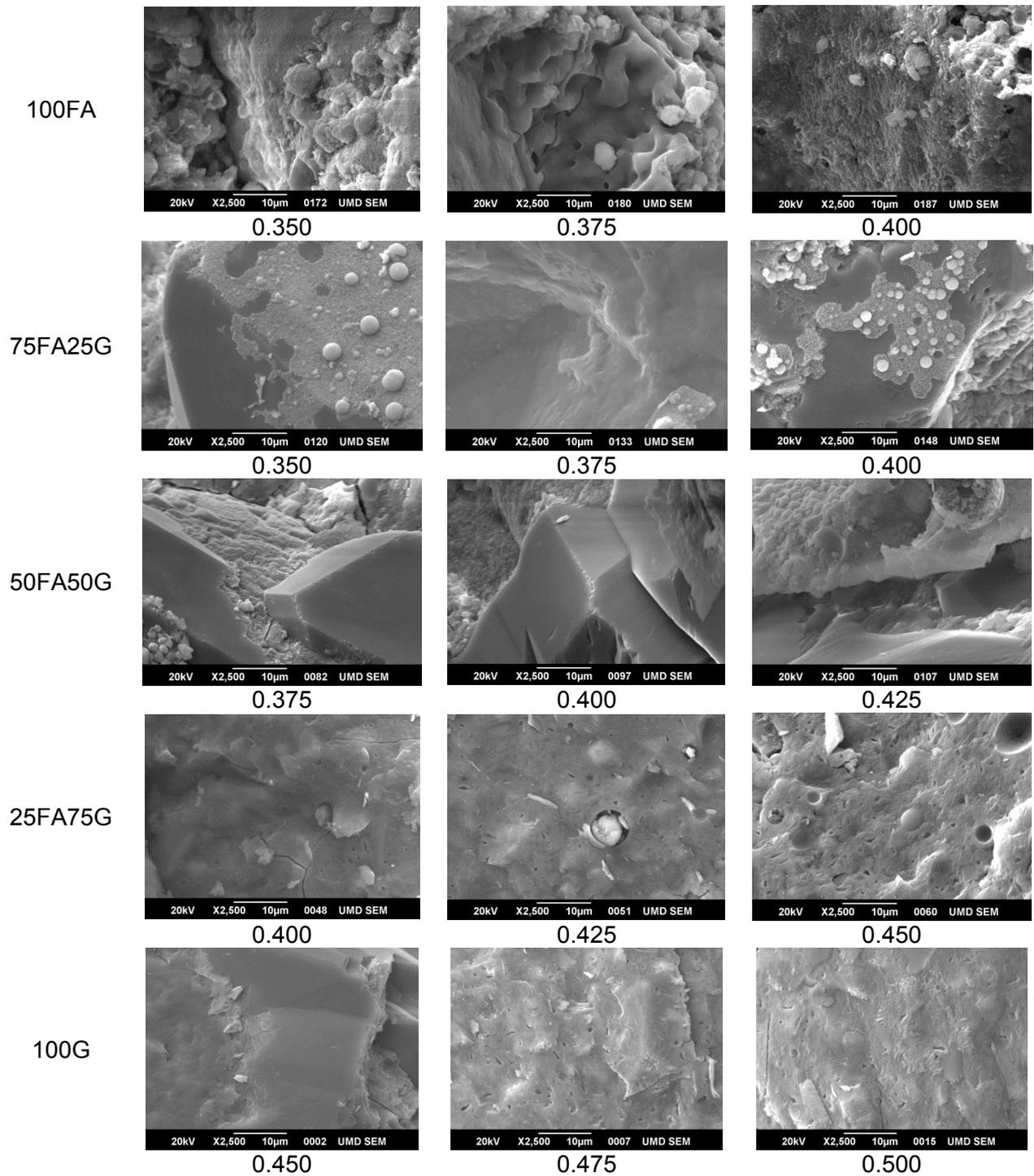
Figure 4. Secondary electron imaging of the five geopolymer mixtures activated with NaOH at each water-solids ratio tested. Mixtures activated with NaOH:sodium silicate of 1 are not shown here.

The two mixtures containing the most fly ash also showed the most zeolites, which are crystalline phases that typically form in the presence of excess water [9, 10]. Figure 5 shows examples of the zeolites found in the 100FA and 75FA25G mixtures.
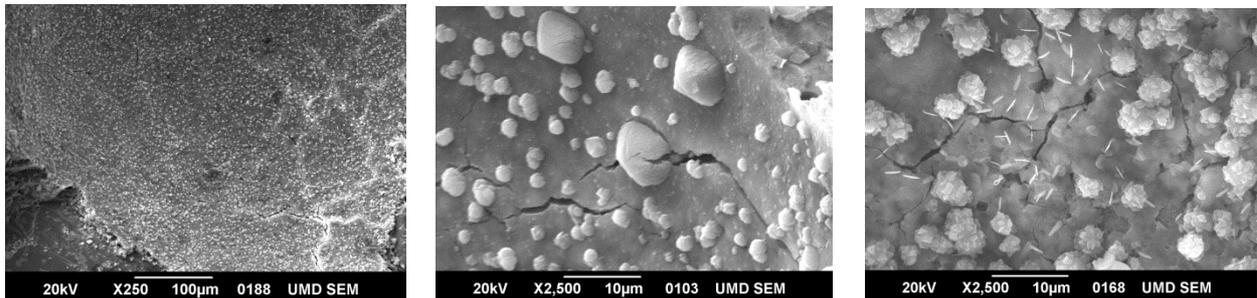
Figure 5. Zeolites found in 100FA and 75FA25G mixtures.

4. CONCLUSIONS

Geopolymer mortars made of varying ratios of fly ash and glass were investigated with regard to water-solids ratio. It was found that the water-solids ratios tested in this research did not have a significant impact on the compressive strength or microstructure of the mortars. However, mixtures containing higher amounts of fly ash demonstrated surprisingly low compressive strengths and high presence of zeolites, indicating that perhaps the water-solids ratio was too high in this case.

The presence of sodium silicate in the activator allowed for a lower water-solids ratio and in most cases resulted in considerably higher compressive strength as compared to mixtures activated with just NaOH, however it is likely that this is due to the presence of the pre-dissolved silica rather than the lower water-solids ratio. Further research including a wider range of water-solids ratios and degree of reaction experiments that would help quantify the amount of dissolution occurring is planned and will likely help paint a clearer picture with regard to importance of the water-solids ratio in geopolymers.

5. REFERENCES

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