

THE INFLUENCE OF NaOH AND NaOCl ON THE CHARACTERISTICS OF FLY ASH-BASED FOAMED GEOPOLYMER

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Introduction

The Republic of South Africa relies heavily on its coal deposits to produce electricity and fuels in order to meet the ever increasing energy demands. South African power plants combust low grade brown coal and this translates to significant quantities of ash left behind after the coal combustion process (Petrik et al., 2003). The disposal of fly ash in landfills or lagoons leaves the disposed ash susceptible to leaching mechanisms thus likely to pollute the surrounding soil and ground water (Nyale et al., 2014). Geopolymer synthesis using coal fly ash, which would otherwise be treated as waste, can make a significant contribution toward environmental sustainability. Geopolymers are mineral polymers belonging to a class of three dimensional aluminosilicate materials with various arrangements of structural units such as $(-\text{Si}-\text{O}-\text{Al}-\text{O}-)\text{X}^+$ referred to as polysialate units, $(-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-)\text{X}^+$ referred to as polysialate-siloxo units or $(-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-)\text{X}^+$ referred to as polysialate-disiloxo units, where X^+ represents an alkali ion, commonly Na, which balances the charge of the tetrahedral Al (Barbosa & MacKenzie, 2003; Cioffi et al., 2003; Davidovits, 1979; Davidovits, 1999). According to Blissett & Rowson (2012), geopolymers attract interest in industrial applications such as construction, transport, mining, aerospace and metallurgy due to their excellent chemical, physical and mechanical properties such as low density, low shrinkage, high mechanical strength, micro and nano porosity, fire and chemical resistance, good thermal stability, durability and surface hardness. In the preparation of fly ash-based geopolymer, the feedstock fly ash is usually mixed with an alkali activator, such as NaOH solution, in order to obtain alumina and silica precursors necessary for the geopolymerization process (Rattanasak & Chindaprasirt, 2009). This study presents findings on foamed geopolymer synthesized from class F South African fly ash (FA) using NaOH as an alkali activator and sodium hypochlorite (NaOCl) solution as the foaming agent.

The foamed geopolymer was prepared using 100 g FA, 20 g NaOH, 38 g of 12 % NaOCl solution and 33 g H₂O (FA: NaOH: NaOCl: H₂O mass ratio of 5.00: 1.00: 1.90: 1.65) while the hydrothermal treatment conditions were 2 hours of room temperature curing followed by oven curing at 80 °C for 5 days. The impact of varying NaOH alkali activator and NaOCl foaming agent solution on the

characteristics of the synthesized foamed geopolymer such as mineralogy, porosity, compressive strength, density and surface morphology was investigated. X-ray diffraction (XRD), mercury intrusion porosimetry, compressive testing, helium pycnometry and scanning electron microscopy (SEM) were used to characterize the synthesized foamed geopolymer.

Methodology

Raw fly ash samples collected from a South African coal-fired power station were used as the starting material in this study. The foamed geopolymer was prepared by mixing class F fly ash with NaOH, NaOCl solution and ultrapure water. Analytical grade NaOH pellets (98 % purity) were supplied by Merck while sodium hypochlorite solution (12 % = NaOCl, 88 % = H₂O) was supplied by Kimix Chemicals. Table 1 shows the bulk chemical composition of the raw fly ash as determined by XRF.

Table 1. Bulk chemical composition of raw fly ash

Mass %											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	MgO	K ₂ O	P ₂ O ₅	Na ₂ O	MnO	Cr ₂ O ₃	LOI
55.21	26.85	6.20	5.53	1.64	1.56	0.58	0.38	0.10	0.05	0.03	6.27

The foamed geopolymer synthesis process was done by initially mixing fly ash with NaOH pellets and ultrapure water for 30 minutes to form a paste, before introducing NaOCl foaming agent solution into the existing paste which was mixed further for 20 minutes. The mixing was done at 150 rpm using a mechanical stirrer fitted with a Rushton turbine impeller. The resulting mixture was poured into an open mould and cured at room temperature for 2 hours then placed in an oven at 80°C for 24 hours in a sealed container. After the initial 24 hours, the resulting foamed geopolymer block was then unsealed and further cured at 80°C for 4 days in order to expel excess moisture. Table 2 shows the variation of NaOH and NaOCl during synthesis of the foamed geopolymer as well as the parameters held constant.

Table 2. Variation of NaOH and NaOCl during synthesis of the foamed geopolymer

Parameters	
Varied	Constant
NaOH (g)	
15	100 g fly ash + 38 g NaOCl + 33 g H ₂ O
18	Room temp curing - 2 hrs
20	Hydrothermal treatment temp 80°C
24	Hydrothermal treatment time 5 days
28	
12 % NaOCl (g)	
30	100 g fly ash + 20 g NaOH + 33 g H ₂ O
34	Room temp curing - 2 hrs
38	Hydrothermal treatment temp 80°C
41	Hydrothermal treatment time 5 days
45	

X-ray diffraction analysis was carried out on a Philips PANalytical diffractometer with a pw3830 X-ray generator operated at 40 kV and 25 mA. The mineralogical phases were identified using X'Pert Highscore plus software and relative phase amounts in weight % were estimated using the Rietveld method. Mercury intrusion porosimetry was done using an AutoPore II 9220 V3.03 series mercury porosimeter while compressive testing was performed using Amsler compression test machine with a 0 - 250 kN load cell and a resolution of 0.1 kN. Helium pycnometry was done using a Micromeritics AccuPyc 1330 V1.02 pycnometer while scanning electron microscopy was done at 20 kV using a LEO SEM 1450 series, equipped with a tungsten filament and Smart SEM V05.04 software.

Results

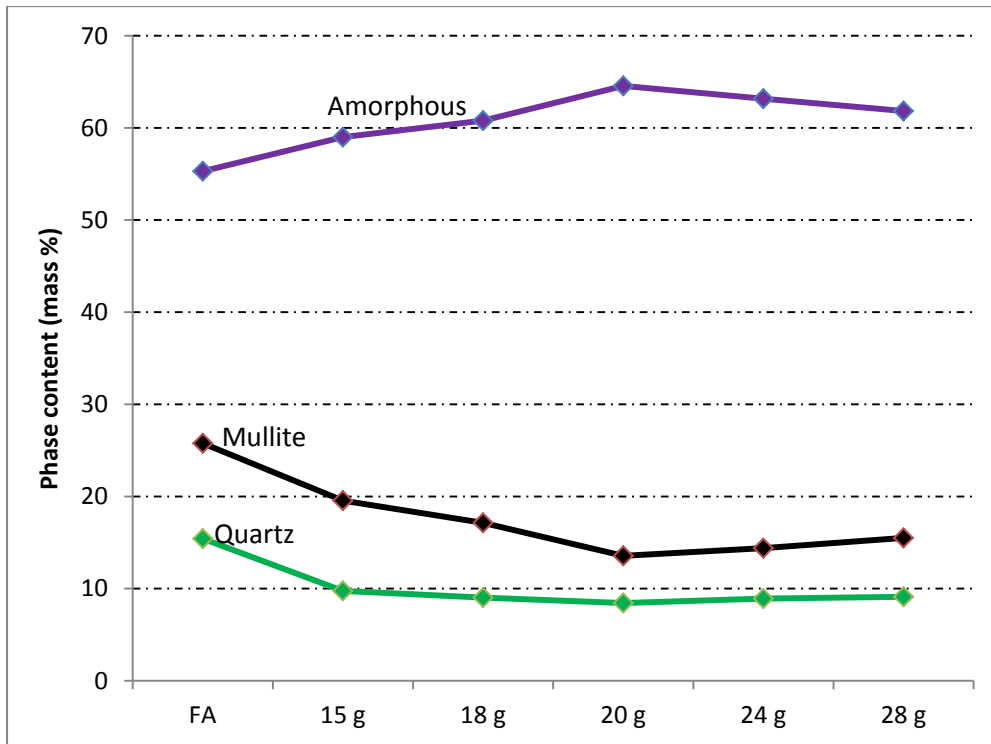


Figure 1. XRD mineral phase quantification of raw fly ash (FA) and foamed geopolymers synthesized using different quantities of NaOH (nd=not detected)

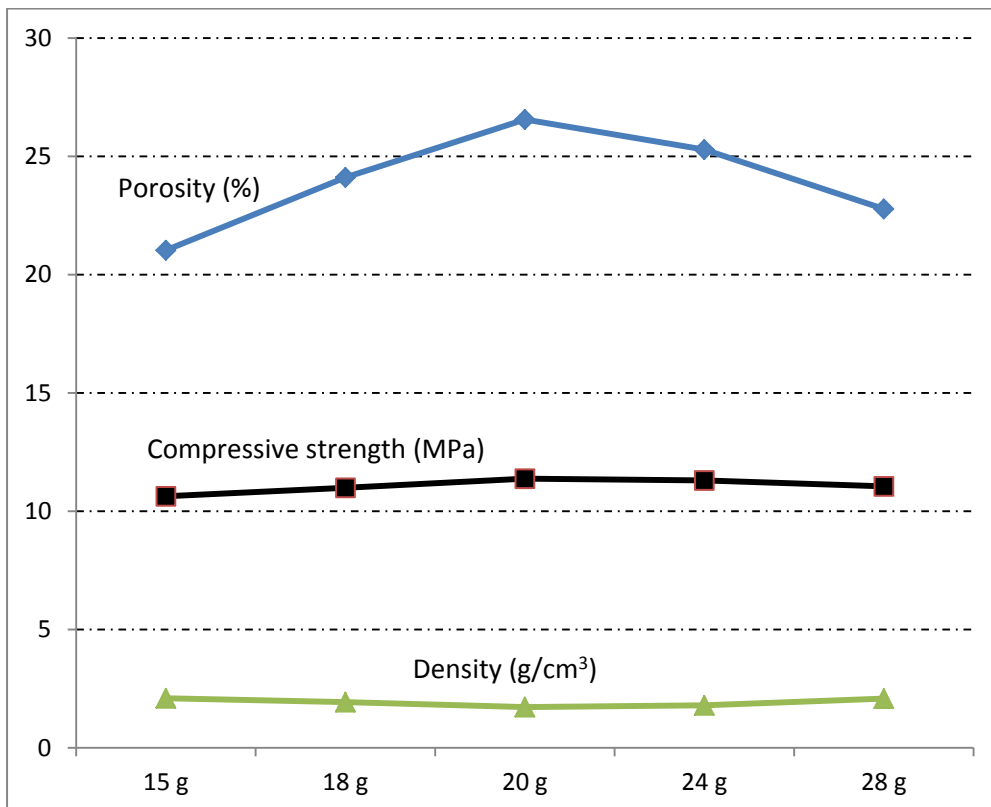


Figure 2. Porosity, compressive strength and density of foamed geopolymers synthesized using different quantities of NaOH

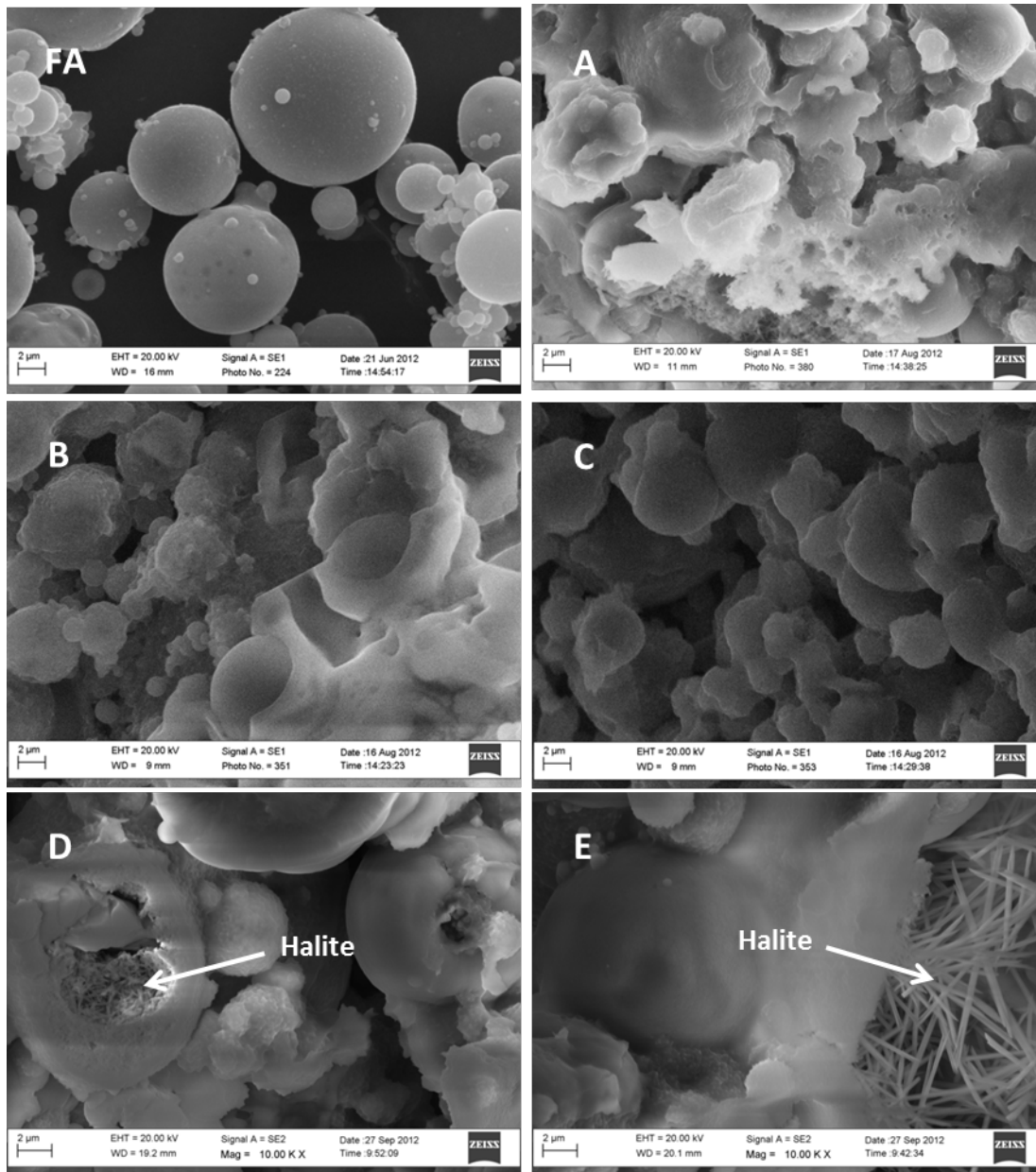


Figure 3. SEM images of raw fly ash (FA) and foamed geopolymers synthesized using different quantities of NaOH (A=15 g, B=18 g, C=20 g, D=24 g, E=28 g)

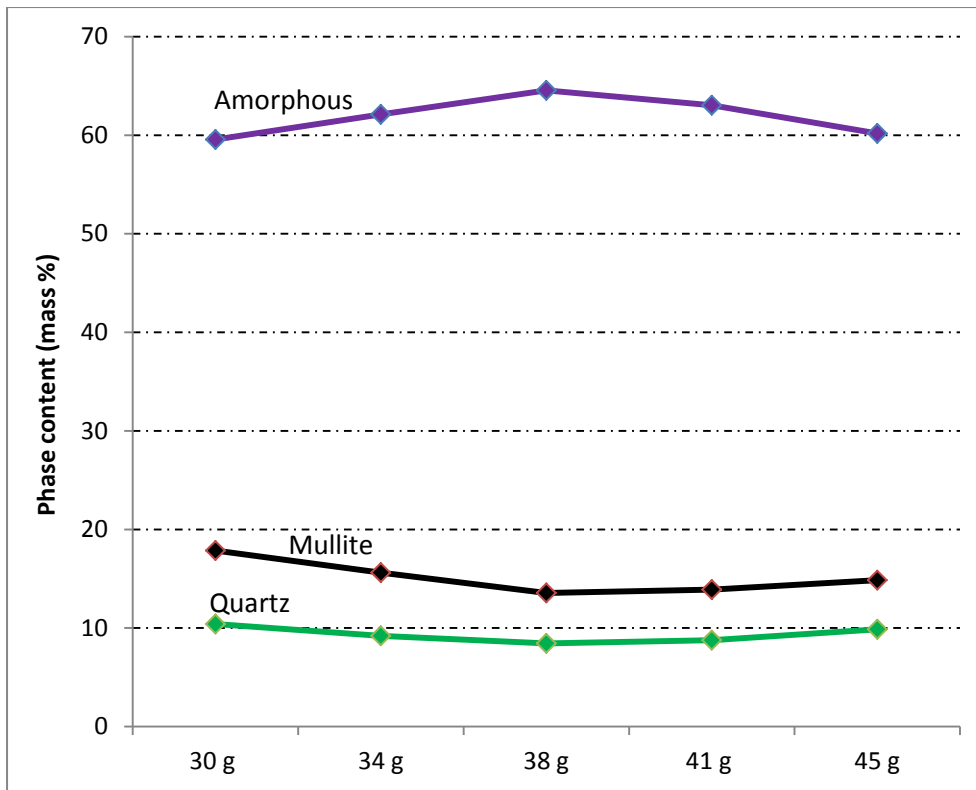


Figure 4. XRD mineral phase quantification of foamed geopolymers synthesized using different quantities of NaOCl foaming agent solution

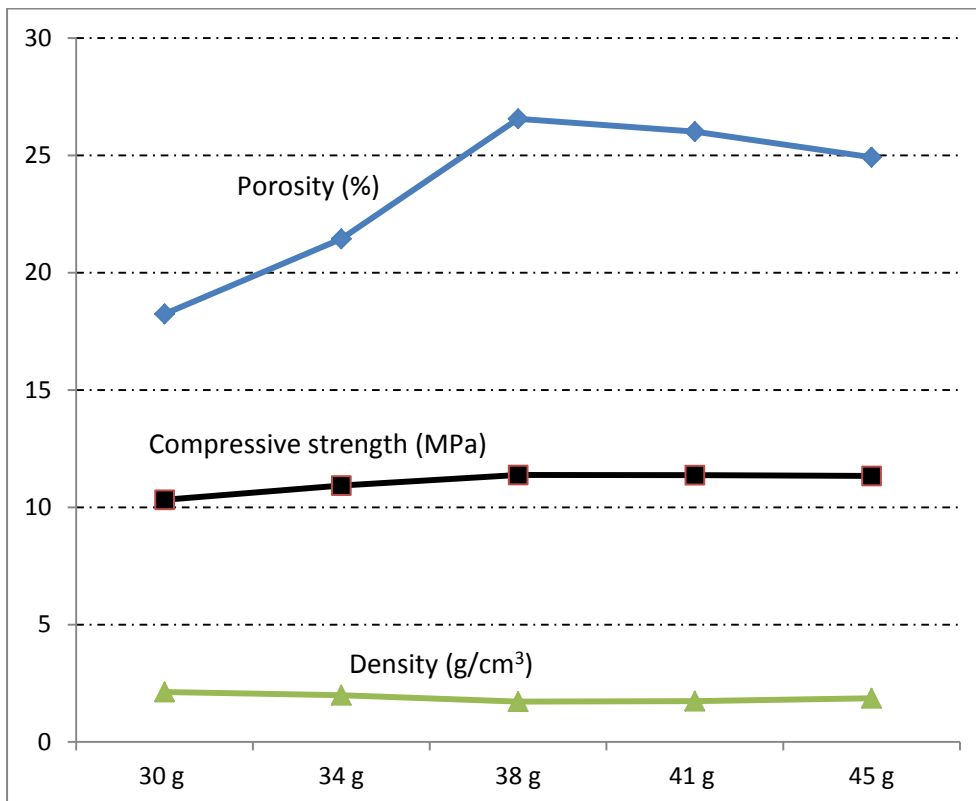


Figure 5. Porosity, compressive strength and density of foamed geopolymers synthesized using different quantities of NaOCl foaming agent solution

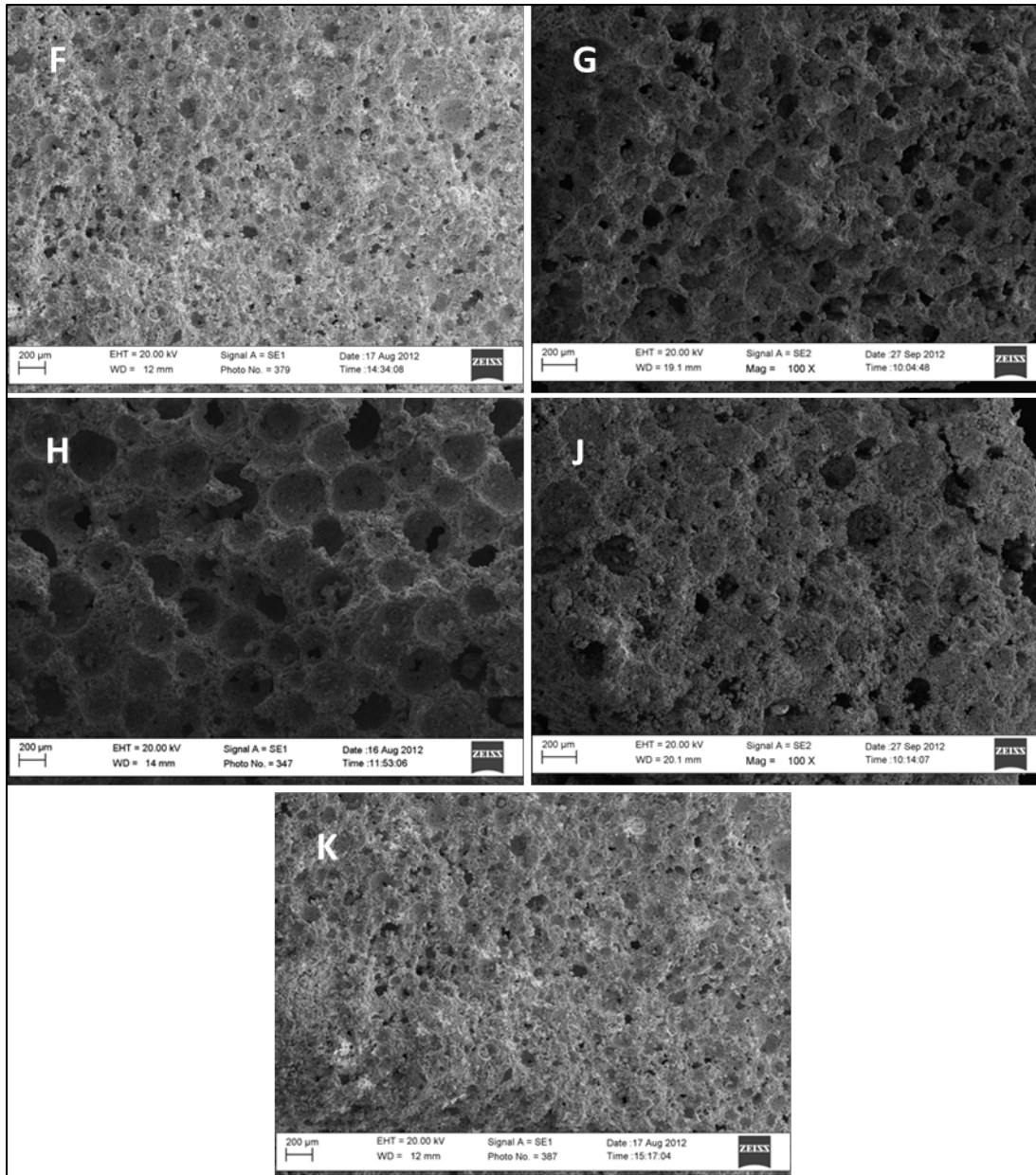


Figure 6. SEM images of foamed geopolymers synthesized using different quantities of NaOCl foaming agent solution (F=30 g, G=34 g, H=38 g, J=41 g, K=45 g)

Discussion

The mineral phase quantification data presented in Figure 1 showed that 20 g NaOH resulted in the highest conversion of the glassy component and crystalline mineral phases of the original feedstock fly ash into amorphous aluminosilicate matrix. This was evident since the foamed geopolymer sample produced using 20 g NaOH not only had the highest amorphous glassy silicate content (64.55 ± 1.38 mass %), but also had the lowest content of mullite (13.55 ± 0.75 mass %) and quartz (8.43 ± 0.33 mass %) compared to the other foamed geopolymer samples (Figure 1). The amorphous glassy silicate content showed inverse proportionality to mullite and quartz content, and also the increase in amorphous content correlated

directly with the increase in NaOH up to 20 g. The results presented in Figure 1 suggested that NaOH content lower than 20 g was not sufficient to achieve the highest level of alkali activation of the feedstock fly ash, with 15 g NaOH achieving amorphous content of only 58.99 ± 1.41 mass %. The results also showed that NaOH content higher than 20 g may have been in excess with respect to the water present in the synthesis mixture and this high amount may have inhibited the alkali activation process of the feedstock fly ash, resulting in a decrease in amorphous content. It was noted that using 20 g NaOH resulted in a foamed geopolymer product that had higher amorphous glassy silicate content (9.26 mass % increment) and significantly less mullite (12.21 mass % decrement) and quartz (6.99 mass % decrement) compared to the original fly ash (Figure 1).

The foamed geopolymer sample produced using 20 g NaOH showed optimum properties since it had the highest porosity (26.56 %) and compressive strength (11.38 Mpa), and was also the lightest showing the least density (1.72 g/cm^3) (Figure 2). It was interesting to see that the sample with the highest amorphous glassy silicate content (i.e. 20 g NaOH) also had the highest porosity and compressive strength, which suggested that the level of alkali activation of the feedstock fly ash influenced the porosity and compressive strength of the product. This finding supported Atmaja et al., (2011) who reported that the amorphous phase content may have an influence on the mechanical strength of geopolymer such that the higher the amorphous phase, the higher the mechanical strength. It was also noted that the density of the synthesized foamed geopolymer reduced with increasing porosity (Figure 2).

Comparing the SEM images of the foamed geopolymer samples synthesized using different quantities of NaOH with the SEM image of the raw fly ash (Figure 3); it was evident that the NaOH used in the synthesis process was responsible for the alkali activation of the original fly ash which resulted in the conversion and aggregation of the previously smooth cenospheres. The agglomerated surface morphology of the foamed geopolymer was as a result of a continuous aluminosilicate gel matrix formed during alkali activation of the feedstock fly ash (Williams & van Riessen, 2010). The SEM images presented in Figure 3 also suggested that NaOH content higher than 20 g may have led to significant presence of halite (NaCl) mineral phase in the geopolymer product, evidenced by the “needle-like” structures believed to be NaCl crystals.

The mineral phase quantification data presented in Figure 4 showed that using 38 g of 12 % NaOCl solution achieved the highest level of alkali activation of the feedstock fly ash, resulting in the highest content of amorphous glassy silicate phase and the lowest content of mullite and quartz in the foamed geopolymer matrix compared to the other NaOCl quantities. The addition of NaOCl quantities higher than 38 g may have had a diluting effect on the NaOH alkali activating agent due to the higher water content, resulting in lower amorphous content (Figure 4). It is

noteworthy that the formation of halite mineral phase and sodalite zeolite phase in the geopolymer product increased with higher NaOCl quantity (Figure 4).

It was clear from the data presented in Figure 5 that 38 g 12 % NaOCl solution produced the foamed geopolymer sample with the highest porosity and compressive strength, and lowest density compared to the other quantities of NaOCl used. Although the addition of NaOCl solution quantities higher than 38 g may have been expected to achieve higher porosity, this was not the case since the higher amount of NaOCl solution introduced more water into the synthesis mixture making the slurry thin leading to loss of foaming bubbles.

The SEM images in Figure 6 presented the surface morphology of the foamed geopolymer samples at a magnification able to show pore variation. It was clear that there was a systematic increase in pore size as the quantity of 12 % NaOCl solution increased from 30 g (Figure 6F) to 34 g (Figure 6G) such that 38 g (Figure 6H) produced larger pores compared to the other quantities of NaOCl solution used. The decrease in pore size for NaOCl solution quantities higher than 38 g (see Figure 6J & K) suggested that the higher quantity of NaOCl solution may have produced smaller bubbles in the slurry, resulting in the formation of much smaller pores.

Conclusions

The quantity of NaOH used during synthesis determined the level of alkali activation of the feedstock fly ash and had a significant impact on the amorphous glassy silicate content and compressive strength of the geopolymer product. There was a systematic increase in amorphous glassy silicate content as the quantity of NaOH increased. The increase in amorphous glassy silicate content showed a direct correlation with the decrease in mullite and quartz content. The compressive strength of the geopolymer product improved with increasing amorphous glassy silicate content.

The amount of NaOCl foaming agent solution used influenced the porosity and density of the synthesized products. There was an increase in pore size as the quantity of NaOCl foaming agent solution increased. Also, the density of the foamed geopolymer reduced with increasing porosity.

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