The Effect of Sodium Carbonate on the Fresh and Hardened Properties of Fly Ash-Based One-Part Geopolymer

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Abstract. One-part geopolymer utilized dry activator(s) which undergo geopolymerization by “just add water” mechanism. There are wide varieties of dry binders to develop one-part geopolymer. This work presents an investigation of fresh and hardened properties of fly ash-based one-part geopolymer activated by mixture of anhydrous sodium metasilicate (Na₂SiO₃) with sodium carbonate (Na₂CO₃). The ratios of alkali activator-to-fly ash (AA/FA) were set as 0.15, 0.20 and 0.25. The substitution of Na₂CO₃ was set as Na₂SiO₃/Na₂CO₃ ratio of 1. Setting time of fresh one-part geopolymer was examined through Vicat needle apparatus. Porosity, compressive strength and microstructural properties of developed specimens were also analyzed after 28 days of curing. The result showed that the partial substitution of Na₂CO₃ resulted in a shorter setting time and lower porosity. Besides that, the one-part geopolymer activated by the mix of Na₂SiO₃ and Na₂CO₃ achieved 78.23 MPa at AA/FA ratio of 0.20. The findings suggest that Na₂CO₃ is a potential alkali activator for one-part geopolymer.

1. Introduction

Ordinary Portland cement (OPC) has monopolized the market in building and construction materials for a long time. The manufacturing process brought great negative impact on the environment. While the manufacturing of geopolymer has been reported to produce 44 to 64% lesser greenhouse gases compared to that of OPC[1]. Traditional fabrication of geopolymer involves alkali solutions that constrain in situ production. Recent research has focused on the replacement of those hazardous solutions with solid activators, and the resulting product is named as one-part geopolymer. The philosophy of one-part geopolymer is similar to traditional geopolymer. The only difference is the materials and approach to fabrication. Nematollahi et al.[2] compared fly ash-based one-part geopolymer with traditionally fabricated geopolymer and concluded that the dry binder exhibited good workability and lower density, despite that they have lower compressive strength.

To date, numerous one-part geopolymers examined were systems activated with the mixture of anhydrous sodium silicate (Na₂SiO₃) with other materials, namely sodium hydroxide (NaOH) [2-4], calcium hydroxide (Ca(OH)₂)[5], sodium oxide (Na₂O) [5], lithium hydroxide (LiOH) [5], potassium carbonate (K₂CO₃) [5] and sodium carbonate (Na₂CO₃) [6]. The combination of material would alter the fresh and harden properties of developed one-part geopolymer, usually to improve the strength, but...
cannot dispense with fresh properties. Na₂CO₃ has been a selection of alkali activator for traditionally fabricated geopolymers due to lower cost and commercial availability [7]. The addition of lower pH activating agent (Na₂CO₃), successfully prolonged the setting time of slag-fly ash-based one-part geopolymer, however, reduced the product’s compressive strength [6].

More effort should be put into the study of the properties of one-part geopolymer systems developed by combined solid activators, especially with Na₂CO₃, to obtain a potential activating agent that has excellent mechanical strength without compromise on the fresh properties. Hence, the objective of this study is to examine the effect of partially replaced Na₂SiO₃ by Na₂CO₃ solid activator use for one-part geopolymer development and compare it with those activated solely with Na₂SiO₃. Research conducted through the variation of AA/FA ratio of one-part geopolymer binder. Analysis such as setting time, porosity and mechanical strength was carried out to evaluate the fresh and hardened properties of the developed one-part geopolymers. Furthermore, the morphology analysis was done to evaluate the product microstructure.

2. Experimental Method

2.1. Material

For this research, class F fly ash was used. Fly ash (FA) employed in this study was supplied from Manjung Coal-fired power plant Perak, Malaysia. The chemical compositions of FA analyzed through X-ray fluorescence (XRF) spectrometer are presented in Table 1. Solid Na₂SiO₃ and Na₂CO₃ were used to activate the aluminosilicate precursor. Anhydrous Na₂SiO₃ of brand Alfa Aesar, in the form of 18 mesh granular was supplied by Fisher Scientific (M) Sdn. Bhd. Anhydrous Na₂CO₃ in powder form, also known as soda ash, with 99.5% purity was purchased from Chemiz (M) Sdn. Bhd.

Table 1. Chemical composition of fly ash as determined from XRF analysis

| Chemical oxides | wt%  |
|-----------------|------|
| SiO₂            | 36.7 |
| CaO             | 19.1 |
| Al₂O₃           | 18.7 |
| Fe₂O₃           | 17.2 |
| SO₃             | 3.04 |
| K₂O             | 1.78 |
| TiO₂            | 1.68 |
| others          | 1.85 |

2.2. Sample preparation

The mix proportions of 6 fly ash-based one-part geopolymer mixes are illustrated in Table 2. Mixes M1, M2 and M3 that act as control samples were fabricated with anhydrous Na₂SiO₃ as the sole alkali activator. Whereas anhydrous Na₂SiO₃ was partially replaced with anhydrous Na₂CO₃ in mixes C1, C2 and C3. Alkali-activator-to-fly ash (AA/FA) ratios were set as 0.15, 0.20 and 0.25. While the replacement ratio of Na₂SiO₃ by Na₂CO₃ were set as 1:1. Fly ash (FA) was mixed with designated amount of solid activator(s) until homogeneous. Subsequently, water was added into the dry binder and mixed for 3 minutes. Different water-to-binder ratios (w/b) were applied for those systems, which were 0.20 and 0.25. One-part geopolymer paste was then cast into plastic moulds of 50 mm × 50 mm × 50 mm in size. The casting and compaction method was done in accordance with ASTM C109. The moulded samples were sealed with cling wrap to prevent moisture loss. Specimens were demoulded after 24 hours and left under ambient condition (30°C) for 28 days.
Table 2. Mix proportion of one-part geopolymers

| Sample Name | Binder proportion (wt%) | w/b ratio |
|-------------|-------------------------|-----------|
|             | FA | Na$_2$SiO$_3$ | Na$_2$CO$_3$ |          |
| M1          | 85 | 15.0          | -            | 0.25     |
| M2          | 80 | 20.0          | -            | 0.25     |
| M3          | 75 | 25.0          | -            | 0.25     |
| C1          | 85 | 7.5           | 7.5          | 0.20     |
| C2          | 80 | 10.0          | 10.0         | 0.20     |
| C3          | 75 | 12.5          | 12.5         | 0.20     |

2.3. Testing and analysis

Initial and final setting time of fresh one-part geopolymer was measured using Vicat apparatus in accordance with ASTM C191. Penetration of Vicat needle was recorded with 15 minutes interval until the penetration was less than 25mm deep. The reading was recorded as initial setting time. The penetration measurement continued until the final setting needle did not leave visibly mark on geopolymer’s surface. The corresponding time taken was logged as the final setting time.

Porosity of samples was determined after 28 days of curing. The percentage of pores was calculated using Equation (1).

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\text{Porosity (\%)} = \frac{M_W - M_D}{M_W - M_S} \times 100
\]  

Where $M_W$ is the samples’ weight after immersion in water, $M_D$ is the weight of dried samples after curing in oven at 85°C for 24 hours, and $M_S$ is the weight of samples suspended in water.

Compressive strength test was carried out in accordance with ASTM C109 with universal testing machine (UTM) modeled Shimadzu UH-1000kNI. Samples were tested after 28 days of ageing with loading placement of 5mm/min constant rate.

Microstructural analysis was selectively done on specimens after 28 days of ageing. Microstructures geopolymer systems were observed through Scanning Electron Microscope (SEM) modeled JEOL JSM-6460LA.

3. Result and Discussion

3.1. Setting time

Figure 1 shows the initial and final setting time of one-part geopolymer mixes. In general, final setting time of all mixes increased with increasing AA/FA ratio. Besides that, the setting time of mixes involved Na$_2$CO$_3$ (mix C1, C2, C3) was shorter than those without Na$_2$CO$_3$ (mix M1, M2 and M3). The result contradicted to those reported by Ma et al. [6], whereby the system involved Na$_2$CO$_3$ possessed one-part geopolymer paste with longer setting time. According to Hajimohammadi [8], lower pH generally decreases the dissolution rate of aluminosilicate materials. Supposing Na$_2$CO$_3$ with lower pH value would lead to a lower dissolution of fly ash, drive less available silica for geopolymerization. However, the result in this study showed otherwise. The only explanation for the opposite result obtained was due to the type of Na$_2$SiO$_3$ used in this research. Instead of Na$_2$SiO$_3$ powder, this project utilized 18 mesh granular Na$_2$SiO$_3$ which required longer time to be hydrolyzed when water was added, only then sufficient to initiate geopolymerization. Suppose that if Na$_2$SiO$_3$ powder applied, the initial and final setting time of one-part geopolymer would be shorter than the C-series mixes. This scenario is similar to the research done by Antoni et al. [9], where geopolymer with lower pH value experienced advanced setting rate due to the particle size of raw materials. Nevertheless, this would not be a major factor that affects the hardened properties of one-part geopolymer because the Na$_2$SiO$_3$ would be hydrolyzed eventually as curing proceeds as long as sufficient water is supplied.
Figure 1. Initial and final setting time of one-part geopolymer mixes.

3.2. Porosity
From Figure 2, it can be observed that porosity generally decreased with increasing AA/FA ratio. Besides that, one-part geopolymer system involved Na₂CO₃ has lower porosity even with a higher w/b ratio than M-series system. The finding corresponded to Ma et al. [6], by which increasing dosage of Na₂CO₃ in slag-based one-part geopolymer caused slight reduction in total porosity. Noteworthy that pores can be classified into harmful (pore diameter > 50nm) and harmless (pore diameter < 50nm) pores [10]. Hence it does not indicate that structure with more total porosity would cause properties deterioration. The theory shall be reflected in the compressive strength result.

Figure 2. Relationship of porosity to AA/FA ratio of one-part geopolymer

The porosity difference between mix M1 and C1 was only 1.41%, which was not significant. Meaning Na₂SiO₃/Na₂CO₃ ratio of 1 at AA/FA ratio of 0.15 did not bring great influence towards the matrix of fly ash-based one-part geopolymer. On the other hand, at AA/FA ratio of 0.20 and 0.25, the impact of Na₂CO₃ towards products’ physical property was more obvious. The porosity differences of M2 and C2 were 5.23%, whereas M3 and C3 were 3.58%.

3.3. Compressive strength
Figure 3 illustrates the compressive strength of two one-part geopolymer systems. Fly ash-based one-part geopolymer activated by Na₂SiO₃ or Na₂SiO₃-Na₂CO₃ displayed similar trend towards the
compressive strength, whereby they achieved the highest mechanical strength at AA/FA of 0.20, and both systems possessed lower strength at AA/FA of 0.15 and 0.25.

At AA/FA of 0.15, the compressive strength of M1 and C1 was 37.7 MPa and 22.5 MPa, respectively. The result is in line with Ma et al. [6] that the participation of Na₂CO₃ declined the strength of slag-based one-part geopolymer. At AA/FA ratio of 0.20, the compressive strength of M2 and C2 was 83.6 MPa and 78.2 MPa, respectively. The difference in strength between M2 and C2 mixes was minor. This indicates that for both systems, AA/FA ratio of 0.20 is the ideal mix proportion that promoted dissolution of aluminosilicate precursor and supported optimum geopolymerization.

But for both AA/FA ratios (0.15 and 0.20), the total porosity differences go against the knowledge that the rise of porosity causes deterioration in geopolymer’s strength [11]. Similar finding was demonstrated by Ma et al. [6] whereby the total porosity hardly correlates well with 28 days strength acquired. This may be due to lower amount of harmful pores present in the structure of M-series one-part geopolymer, as discussed in section 3.2. The speculation could be answered by microstructural analysis in section 3.4.

At AA/FA ratio of 0.25, the compressive strength of both systems decreased compared to AA/FA ratio of 0.20. Increase the amount of activator would enhance geopolymerization reaction until maximum was reached, subsequent reaction reduced when alkalis were further added [12]. In this case, AA/FA ratio of 0.25 is considered as activator overload. While mechanical strength of C3 was higher than M3. The excess amount of Na₂SiO₃ supplied to the dry binders hindered structure formation of one-part geopolymer [13], subsequently delayed setting time of M3 and deteriorated the mechanical strength.

In short, the addition of Na₂CO₃ affects the compressive strength of one-part geopolymer depending on the AA/FA ratio. The dosage of Na₂CO₃ as alkali activator for one-part geopolymer should be further experimented through Na₂SiO₃/Na₂CO₃ ratio, as that might be a more crucial factor to the properties of one-part geopolymer other than AA/FA ratio.

3.4. Microstructural analysis
Figure 4 presents the SEM micrographs of four selected specimens analyzed after 28 days of curing. Pores, unreacted or partially reacted raw materials as well as micro-cracks were present in these specimens. The difference between microstructure of M2 (figure 4a) and C2 (figure 4c) are the portion of geopolymer matrix, pore size and amount of unreacted fly ash. From the microstructure of M2 and C2, C2 processed more compact geopolymeric structure than M2. However, larger pore size was observed from specimen C2, compared to that of M2. This explained that even when porosity of M2 was higher than C2 by 5.23% (figure 2), the compressive strength of M2 was still higher. Larger pore size reduced strength of geopolymer [14]. Besides that, as M2 showed the presence of partially reacted
fly ash, more unreacted fly ash can be observed from C2. This was due to the rapid setting of C-series mixes that prevented further dissolution and polycondensation of remaining fly ash [15]. The larger pore size and more unreacted fly ash were the reasons that the mechanical strength of mix C2 was lower than M2 by 5.4 MPa.

As for mix M3 (figure 4b) and C3 (figure 4d), both specimens displayed similar microstructure except M3 which showed more and broader crack lines. Cracks presented in M3 hindered the growth of compressive strength to only 32.11 MPa but not higher. This corresponded to the mechanical strength result obtained (figure 3) and proved that geopolymer with excess Na2SiO3 content required longer setting time, thereafter underwent poorer structure development, as mentioned in section 3.3.

4. Conclusion
The effect of AA/FA ratio and involvement of Na2CO3 as alkali activator for fly ash-based one-part geopolymer were investigated. Increasing AA/FA ratio from 0.15 to 0.25 delayed the setting time especially in one-part system activated with only Na2SiO3. While the presence of Na2CO3 resulted in rapid hardening of one-part geopolymer. The porosity generally decreased with increasing AA/FA ratio for both systems. The porosity of Na2SiO3-activated one-part geopolymer was higher indicating that the addition of Na2CO3 reduced the pores content. Furthermore, AA/FA ratio of 0.20 was the ideal activator amount to produce high strength one-part geopolymer, which achieved 83.59 MPa for solely Na2SiO3-activated one-part geopolymer as well as 78.23 MPa for Na2SiO3- and Na2CO3-activated one-part geopolymer. Pores, unreacted or partially reacted raw materials as well as micro-cracks were present in the selected specimens. The analysis leads to the conclusion that the partial substitution of Na2SiO3 by Na2CO3 at the ratio of 1:1 is a potential activator mix for fly ash based-one part geopolymer.

Figure 4. SEM micrographs of (a) M2; (b) M3, (c) C2 and (d) C3 after 28 days of curing (magnification x1000)

Acknowledgement
The authors of the present work wish to acknowledge the funding support from “Partnership for Research in Geopolymer Concrete” (H2020-MSCA-RISE-2015-689857-PRIGeoC) sponsored by the European Union.
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