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Influence of Solids-to-liquid and Activator Ratios on Calcined Kaolin Cement Powder

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Abstract

This paper summarizes the effect of activator ratio on the processing of cement powder. Geopolymer slurry was produced via alkaline activation of calcined kaolin. Once the geopolymer slurry solidified, it was crushed and ground to obtain cement powder. Ultilizing the concept of "just adding water", hardened cement paste could be produced from cement powder. This paper concluded that solids-to-liquid and sodium silicate-to-sodium hydroxide ratios have a significant effect on compressive strength of hardened cement paste. The optimum solids-to-liquid and sodium silicate-to-sodium hydroxide ratios were 0.80 and 0.20, respectively. SEM micrographs showed that a processing route to produce cement powder by "just adding water" was possible, and the structure became denser and fewer unreacted particles were observed.

Keywords: cement powder; geopolymers; activator ratio; solids-to-liquid ratio; sodium silicate-to-sodium hydroxide ratio

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1. Introduction

Geopolymers are a class of materials consisting of an amorphous, three-dimensional structure synthesized by alkaline activation of an aluminosilicate source at ambient or higher temperature through a

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geopolymerization process. Aluminosilicate sources are materials rich in Al_2O_3 and SiO_2. The geopolymerization process is an exorthermic reaction [1]. Basic steps of geopolymerization are the dissolution of solid aluminosilicate oxide in MOH solution (M = alkali metal), diffusion of dissolved Al and Si complexes to an inter-particle space, the formation of a gel phase by polymerization between silicate solution and Al and Si complexes, and lastly the hardening that occurs in the gel phase [2].

An alkaline solution is most often used in a mixture of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) [3]. Alkali hydroxide is required for the dissolution of aluminosilicates sources while sodium silicate solution acts as binder, alkali activator and dispersant or plasticizer [4]. Alkaline solutions also induce a certain amount of Si and Al atoms to dissolve the aluminosilicate sources, form monomers in solutions, and then polycondense to form a rigid framework [5]. Sodium silicate is the preferred activating solution owing to its soluble silicate content, which tends to increase the rate of the polymerization reaction [6]. The properties of geopolymers are affected by the specific surface composition of initial raw materials, the type, composition and relative amount of alkali activator and condition during the initial period of the geopolymerization process [7]. The solids-to-liquid (S/L) ratio and Na_2SiO_3-to-NaOH ratio have tremendous effect on compressive strength. Both of these ratios affect the workability of the geopolymer slurry [8, 9].

According to Xu & Deventer [10] in fly ash geopolymers, the proportion of raw materials to alkaline activator by mass should be approximately 3 to allow the geopolymerization process to occur. The alkaline activator solution formed a thick gel instantaneously upon mixing with source material. In general, calcined kaolin has a higher liquid demand than fly ash due to the difference in particle shape. Calcined kaolin has a plate-like structure while fly ash has spherically-shaped particles, which will in turn result in better workability in fly ash. Thus, a lower S/L ratio of 0.80 was suggested by Kong et al. [8], in their study on metakaolin-based geopolymers, in which this ratio provided near optimum strength and good workability. Some researchers have used a lower and higher S/L ratio of 0.30 [11] and 1.25 [12], respectively. Hardjito & Rangan [13] reported that compressive strength increases when the Na_2SiO_3/NaOH ratio increases. The Na_2SiO_3/NaOH ratio, by mass, was recommended at approximately 2.5 for fly ash-based geopolymers. For calcined kaolin geopolymers, a Na_2SiO_3/NaOH ratio of 0.24 was reported by Wang et al. [11]. According to various researches, waterglass favors the polymerization process leading to reaction product with more Si and higher mechanical strength [14]. Even so, Sathonsaowaphak et al. [15] noted that NaOH cost less than Na_2SiO_3 and therefore the mixture should utilize a low Na_2SiO_3/NaOH ratio while still maintaining its strength and workability. However, there are limited researches on the effect of Na_2SiO_3/ NaOH ratio on geopolymer synthesis.

This paper presents our study of the influence of S/L and Na_2SiO_3/NaOH ratios on the synthesis of cement powder. The study focused on the effect of these parameters on compressive strength results. SEM analysis was also performed.

2. Experimental Methods

2.1. Materials

The kaolin used was purchased from Associated Kaolin Industries Sdn. Bhd,, Malaysia with minimum 40% of particles sized less than 2 µm. Calcined kaolin was obtained by dehydroxylation of kaolin at 800°C for 2 hours. It was used as the Si-Al cementitious materials. The NaOH powder had 99% purity and was made in Taiwan under the brand name of Formosoda-P. A technical grade Na_2SiO_3 solution was supplied from South Pacific Chemicals Industries Sdn. Bhd. (SPCI), Malaysia with a chemical composition of 30.1% SiO_2, 9.4% Na_2O and 60.5% H_2O with a weight ratio $SiO_2/Na_2O = 3.2$, specific gravity at 20°C = 0.0014 g/cm^3 and viscosity at 20°C = 0.4 Pa·s. Distilled water was used throughout.

8M of NaOH solution was prepared and allowed to cool down to room temperature. The alkali activator solution was prepared by mixing NaOH solution and Na_2SiO_3 solution at a ratio that ranged between 0.12 – 0.28 until clear solution was obtained. The solution was prepared for minimum 24 h prior to use.

2.2. Synthesis

Calcined kaolin was mixed well with alkali activator solution at a S/L ratio ranging between 0.4 – 1.2 for a few minutes by using mechanical mixer, thus forming a homogeneous slurry. The fresh geopolymer paste was then poured into steel molds. The dimension of the steel molds was 50mm × 50mm × 50mm. The samples were compacted as described in ASTM C109 [16]. The molded samples were sealed with a film to prevent moisture loss. All specimens were heated undisturbed in an oven at 80°C for 3 hours. The solidified geopolymer samples were then pulverized using a mortar and pestle, grinder, and then passed through a sieve mesh to obtain cement powder at a fixed particle size.

2.3. Test method and Analysis

The compressive strengths were measured according to ASTM C 109/C 109M – 08 [16] by using the Instron machine series 5569 Mechanical Tester. The cement powder had water added to produce cement paste and tested for its compressive strength. A minimum of three specimens were tested to evaluate the 7th day strength gain for the specimens.

A JSM-6460LA model Scanning Electron Microscope (JEOL) was utilized to reveal the microstructure and the various degrees of reaction at different S/L and Na_2SiO_3/NaOH ratios.The specimens were cut into small pieces and coated with platinum by using an Auto Fine Coater, model JEOL JFC 1600 before the examination.

3. Results and Discussion

3.1. Cement Powder

Fig. 1a shows the microstructure of the synthesized cement powder. The microstructures of the synthesized cement powder of varying ratios were almost similar. Large parts of unreacted raw materials were still being observed as indicated by the plate-like structure. Only a very small portion of the raw materials was activated with growth of small particulates on the surface of raw materials. This cement powder later had water added to produce cement paste for compressive strength and SEM analysis.

3.2. Effect of S/L ratios

Fig. 2a displays the compressive strength at the 7th day of the resulting cement paste from cement powder with varying S/L ratios ranging from 0.4 to 1.2. Strength peaked at a S/L ratio of 0.8 and dropped gradually as the ratio increased. No strength results were recorded for the S/L ratio of 0.4 and 1.2 since the mixes had extremely low viscous to allow for molding and was of very limited workability for good compaction, respectively. The ratio of S/L of 0.8 provided optimum workability and thus led to optimal strength. Optimum workability resulted in homogeneous slurry. The strength measured has confirmed that a 0.8 S/L ratio has optimum activator content that allows for dissolution of raw materials while not hindering the polycondensation rate during the geopolymer synthesis. Thus, when water was added to the cement powder to produce cement paste, the water content will accelerate the polycondensation process due to the continual dissolution of residual raw materials and hydrolysis of generated Al^{3+} and Si^{4+}.

According to Kong et al. [8], S/L ratio contributed to the porosity level of the hardened geopolymer paste. At a low S/L ratio of 0.6, there was more activator content, and the mix was also very viscous, easing workability and providing good homogeneity. Many air bubbles, however, will embed into the structure after hardening [17]. Thus, the increased porosity in the system caused decline in strength. In this study, porosity measurements were not taken, hence, it does not confirm the conclusion made by the authors. From the SEM micrographs, it was obvious that the microstructure of paste with a S/L ratio of 0.6 (**Fig. 1b**) consisted of more voids than that of a S/L ratio of 0.8 (**Fig. 1c**). These voids were believed to have been left as result of water evaporation. Only a slight activation of calcined kaolin could be observed on the particle surface. Additionally, as activator content increased, the excess OH^- concentration left in the system weakens the structure of paste formed, while the excess Na^+ content will react with CO_2 by atmospheric carbonation [18]. All these factors affect the geopolymerization process and led to a reduction in strength. In contrast, at a high S/L ratio, the mixture was of low viscosity [8, 19]. This caused difficulty in compacting and molding the paste into the mould where failure in providing good compaction can seriously depress the compressive strength of the cement paste due to non-homogeneity. Thus, the microstructure of paste from a S/L ratio of 1.0 also revealed large voids as result of poor compaction (**Fig. 1d**). On the other hand, the excess amount of liquid activator assisted in providing a higher dissolution rate of raw materials; however, this will hinder the polycondensation rate as the diffusion of dissolved species is difficult. Large parts of unreacted materials were observed in the microstructure (**Fig. 1b, 1c** and **1d**), but were much less than that in cement powder (**Fig. 1a**). The process of powder synthesis must be optimized; otherwise the addition of water to produce cubes will not produce high strength. Consequently, it is preferable to reduce the amount of solution within a range where workability does not deteriorate.

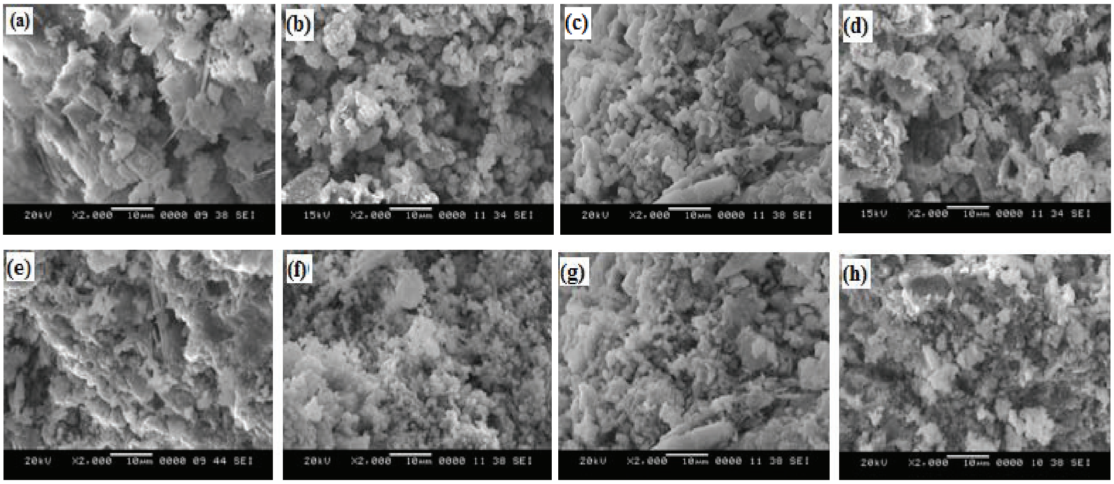

Fig. 1: SEM micrographs of (a) cement powder; cement paste with S/L ratios of (b) 0.6, (c) 0.8 and (d) 1.0; and cement paste with Na2SiO3/NaOH ratios of (e) 0.12, (f) 0.20, (g) 0.24 and (h) 0.28.

3.3. Effect of $Na_2SiO_3/NaOH$ ratios

Fig. 2b shows the compressive strength of r cement paste from cement powder with various $Na_2SiO_3/NaOH$ ratios. An increase in activator ratio up to 0.20 favored compressive strength. Compressive strength reached a maximum at a $Na_2SiO_3/NaOH$ ratio of 0.20, and decreased with subsequent increases in this ratio. The compressive strength measured was in agreement with Villa et al. [20] where strength reached the highest level at an optimum $Na_2SiO_3/NaOH$ ratio and further increments in this ratio did not increase strength. The measured compressive strength, however was in contradiction to that concluded by Hardjito et al. [13], who claimed that a high ratio of $Na_2SiO_3/NaOH$ by mass, results in high compressive strength. According to Villa et al. [20], when the activator ratio increased, this led to an increase in sodium silicate content which tends to increase the occurrence of geopolymerization reactions. The use of more sodium silicate led to more silica gel and thus contributed to the high strength recorded at a $Na_2SiO_3/NaOH$ ratio of 0.20. By comparing the microstructures of resulted cement paste with various $Na_2SiO_3/NaOH$ ratios, all the samples showed that the geopolymerization process continued to occur after the addition of water. Samples with a $Na_2SiO_3/NaOH$ ratio of 0.20 (**Fig. 1f**) displayed more geopolymeric gel with more intervening materials. Again, large parts of unreacted materials were observed in the structure (**Fig. 1e, 1f, 1g** and **1h**), but were much less than that in cement powder (**Fig. 1a**). Conversely, as expected, there was a reduction in strength as Na_2SiO_3 increased, which was probably due to the inhibition of the geopolymerization reaction through the Al-Si phase precipitation which avoids contact between reacting materials and the activating solution, meaning that excess sodium silicate hinders water evaporation and structure formation [8]. Thus, samples of high $Na_2SiO_3/NaOH$ ratio showed very little geopolymeric gel (**Fig. 1h**). Furthermore, workability depended on the ratio by mass of $Na_2SiO_3/NaOH$. Sodium silicate ordinarily is very viscous in nature. Therefore, an increasing ratio of $Na_2SiO_3/NaOH$ tends to lower the flow of the mix. Similarly to the S/L ratio, when this happened, a less workable mix produced high porosity. As a workaround, extra water or superplasticizer is needed to obtain mixes with suitable workability.

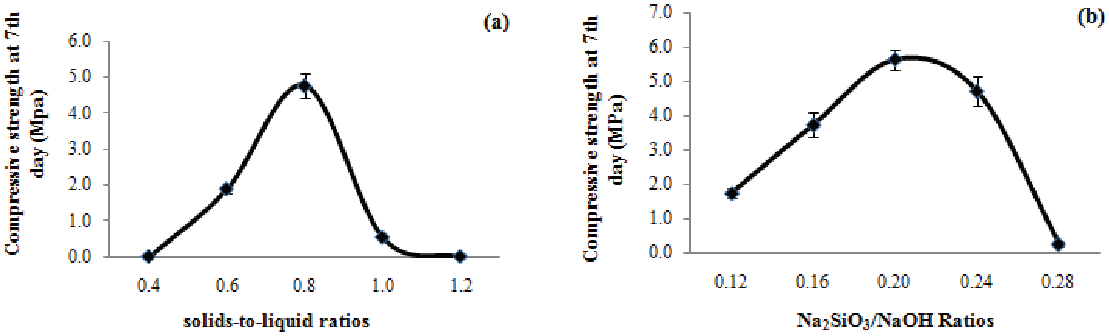

Fig. 2: Compressive strength at 7th day at various (a) solids-to-liquid (S/L) ratios and (b) sodium silicate-to-sodium hydroxide ($Na_2SiO_3/NaOH$) ratios.

4. Conclusion

The findings of this study are summarized as follows are:

- Both S/L and $Na_2SiO_3/NaOH$ ratios affect the compressive strength and workability of geopolymer paste.
- The optimal S/L and $Na_2SiO_3/NaOH$ ratios to produce cement powder were 0.80 and 0.20, respectively, leading to highest strength.
- The compressive strength of samples maximized at an optimum and then decreased gradually for subsequent increases, which was supported by SEM analysis.

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