

PAPER • OPEN ACCESS

Cooling treatment of alkali solution to prolong the setting time of high calcium fly ash based geopolymers

To cite this article: O K Wattimena *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **669** 012024

View the [article online](#) for updates and enhancements.

Cooling treatment of alkali solution to prolong the setting time of high calcium fly ash based geopolymers

O K Wattimena¹, A Antoni¹, R T Surja¹, R Mintura¹ and D Hardjito¹

¹Civil Engineering Department, Petra Christian University, Indonesia

antoni@petra.ac.id

Abstract. The problem of rapid or short setting time has been reported by many researchers when utilizing high calcium fly ash as an aluminosilicate source material in the synthesis of geopolymers. Meanwhile, there are very few studies carried out to overcome this obstacle. This study was conducted to evaluate the cooling treatment of the alkaline solution to prolong the setting time of the geopolymer. Alkaline solutions with five different temperatures were used to synthesize the geopolymer paste. Each set of fresh geopolymer paste was tested using the Vicat apparatus according to ASTM C191 to measure its setting time. The results showed that a decrease in the temperature of the alkaline solutions prolonged both the initial and the final setting time of the geopolymer paste. An alkaline solution with a temperature of 9°C could double the initial setting time compared to the control mixture (31°C). In the mortar phase, the cooling treatment also increased the compressive strength of the geopolymer mortar besides longer setting time.

1. Introduction

Concrete has become a major requirement in almost all construction industries because of its strength, durability and also because of its ease to be formed as desired. The main ingredient of a concrete mixture is cement, which binds all other materials together. Portland cement is one of the most popular cement, which processed from the natural limestone. However, as globally known, the production process of Portland cement releases an amount of carbon dioxide that causes the greenhouse effect in the atmosphere. Therefore, since the global warming issue becoming world concern, numerous researches were done to develop alternatives to Portland cement [1-3].

Geopolymer concrete is one of the most promising alternative binders in concrete production. Geopolymer concrete is a synthesis product from the aluminosilicate materials (which are in the amorphous to semi-crystalline phases) [4]. Metakaolin, slag, and fly ash are widely known as some of the aluminosilicate source materials that can be used for the synthesis of geopolymer concrete. Nowadays, the use of fly ash as an aluminosilicate source material becomes more beneficial because fly ash is an abundant waste material that harmful to the environment if not used. As the waste material derived from the coal combustion, fly ash give various properties both chemically and physically, which significantly influences the synthesis of the geopolymers [5].

According to ASTM C168, fly ash was divided into two classes, class F (low calcium) and class C (high calcium). When working with class F fly ash, the geopolymer concrete produced an exceptional performance both in compressive strength and durability against severe environment [6,7]. However, when dealing with class C fly ash or fly ash with high calcium content, the fast setting time problem



arises due to the presence of calcium oxide [8]. While class F fly ash-based geopolymer concrete generally needs heat to start the geopolymerization process, the class C fly ash-based geopolymer set rapidly in minutes after the alkali solution introduced into the solid mixtures, even in the room temperature ($\pm 25^{\circ}\text{C}$).

A previous study showed that setting time of the high calcium fly ash-based geopolymer concrete influenced by both physical and chemical composition of the fly ash. It also showed that the initial temperature of the fly ash affects the setting time of the mixture, where a higher temperature of the fly ash leads to faster setting time [9]. Some research also shows that the short setting time problem could occur because of the significant amount of calcium compound in the fly ash. The presence of calcium compound makes the setting time of the geopolymer governed by the formation of CSH or CASH-like phases [10]. This rapid or short setting time problem could be a challenging problem when the high calcium fly ash-based geopolymer concrete is applied in the field.

Several studies have been conducted to provide alternatives solution addressing these setting-time problems. One study shows that increasing NaOH concentration could prolong the setting time of the geopolymer paste [11]. Another study shows a partial replacement of fly ash with diatomite or diatomaceous earth clay is beneficial as it prolongs the setting time. However, the compressive strength and the modulus of elasticity of the paste are reduced [12]. Another attempts to overcome this problem is using chemical additives like sucrose [13], borax [14], acid solutions [15]. However, some of the alternatives have a negative side effect on the other properties of the geopolymers, such as decreasing compressive strength.

Depart from the fact that the chemical reaction involved in the polymerization process is an exothermic reaction, in addition, using cold water in conventional concrete, that use Portland cement, has also been generally applied to reduce the rate of hydration and extend the setting time of the concrete, especially when working with mass concrete. This study was done to evaluate the cooling effect of both the solid material and the alkaline solution to the setting time of the geopolymer paste and also the compressive strength of the hardened mortar.

2. Materials, mix-design, and methods

2.1. Materials and mix design

All geopolymer made in this study use fly ash obtained from Paiton steam power plant in East Java, Indonesia as the source of aluminosilicate material. An XRF test (showed in Table 1) was done to find out the chemical composition of the fly ash and the Loss on Ignition (LoI) value is also shown. A pH value of 11.2 (tested using a pH meter immersed in a solution consisting of 20 grams of fly ash and 80 grams of distilled water) also confirmed the high calcium content in the fly ash. The physical properties of the fly ash given by PSA (Particle Size Analysis) showed that 10% of the fly ash particle having a diameter smaller than $0.67\ \mu\text{m}$, 50% of the fly ash particle having diameter smaller than $6.72\ \mu\text{m}$, and 90% of the fly ash particle having diameter smaller than $35.95\ \mu\text{m}$. The fly ash had a specific surface area (SSA) of $570.14\ \text{cm}^2/\text{g}$ and the specific gravity of 2.753.

Table 1. Chemical composition of the fly ash from XRF test

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	LoI
% weight	34.29	16.62	15.38	18.18	7.52	1.35	2.97	1.63	0.36

Alkali solution was prepared using sodium hydroxide (NaOH) and type 52 sodium silicate (Na₂SiO₃). 8M sodium hydroxide solution was made by dissolving 24 grams of sodium hydroxide flakes into distilled water until the solution volume reaches 75ml, while the sodium silicate used was 60 grams, so that the mass ratio of 2.5 between sodium silicate liquid and sodium hydroxide solid was obtained. All the alkali solution was kept until reaching room temperature before further process. Then, for some alkali solution was kept in the freezer for a specific time to decrease its temperature before mixed with the fly ash. For the geopolymer paste, the mixture consists of 300 grams of fly ash, 75 ml of sodium

hydroxide, and 60 ml of sodium silicate. Sand from Lumajang quarry, East Java, Indonesia was used to make geopolymer mortar with fly ash and sand mass ratio of 1:2.

2.2. Methods and testing

Alkali solutions with five different temperatures were used to make five sets of geopolymer paste. Right before the alkali solution come into contact with the fly ash, the temperature of the solution was measured using a digital thermometer. Both the initial and the final setting time of each geopolymer paste was tested using the Vicat apparatus as described by ASTM C191 [16]. For compressive strength test, geopolymer mortar was made and cast into 5×5×5 cm cube molding. The compressive strength test was carried out by crushing three cube samples at testing age of 3, 7, 14, and 28 days.

3. Results and discussions

The initial alkali solution temperature was 31°C in the room temperature and before entered the freezer for further cooling. This alkali solution was also used to make the control geopolymer paste. The initial setting time of the control geopolymer paste was about 14 minutes, while the final setting time was 26 minutes. The initial setting time was similar to the previous study for a similar pH of fly ash [17]. This result confirmed that the setting time of high calcium fly ash-based geopolymer is strongly affected by the pH value of the fly ash.

Table 2. Initial and final setting times for different activator solution temperature

Activator Solution Temperature (°C)	Initial Set (mins)	Final Set (mins)	Set Temperature of the paste (°C)	
			Outside	Inside
31	14	26	-	-
22	20	-	28	30.7
19	25	48	-	-
9	28	42	-	-
7	36	-	25	28.8

By cooling the alkali activator solution, it was shown that both the initial and the final setting times of the geopolymer paste could be prolonged. Figure 1 shows the strong correlation between the setting time of the geopolymer paste and the alkali activator solution temperature. The cooling treatment might prolong the setting time of the geopolymer paste probably because, in a lower temperature, the chemical reaction runs slowly, especially in the general polymerization. However, polymerization reactions, especially in the condensation phase, require heat to be able to take place. Figure 2 confirmed that a geopolymer paste was not able to harden when it stored in the freezer, while the sample stored in the room temperature starts to set after the geopolymer paste reaches 25°C at about 40 minutes.

Two geopolymer mortars were made to investigate the effect of cooling treatment towards the geopolymer compressive strength. The control sample (FAG-CT) was synthesized using materials in the room temperature condition. For the second sample (FAG-CL), all materials were pre-treated by storing in the freezer until the temperature of the material close to 0°C before finally being synthesized.

Table 3 shows the compressive strength for each testing age and also the average density of each sample. The higher density on the FAG-CL sample indicates that the fresh mortar has more workability compared to the control sample. The 28-days compressive strength of the FAG-CL sample was 65.20 MPa, and it was about 20 percent higher when compared to FAG-CT sample, which has the compressive strength of 54.27 MPa. Higher compressive strength of the FAG-CL sample could be either because of the increased density or because of the better chemical reaction processes. Not only at 28-days compressive strength, but the cooling treatment also provides higher compressive strength at an early age of 3 days.

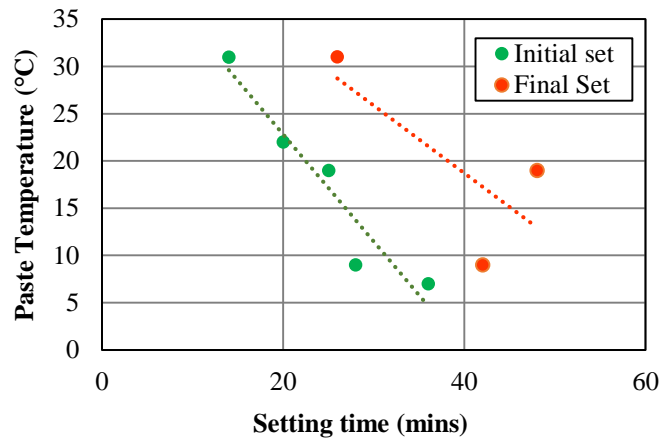


Figure 1. Setting time of geopolimer pastes

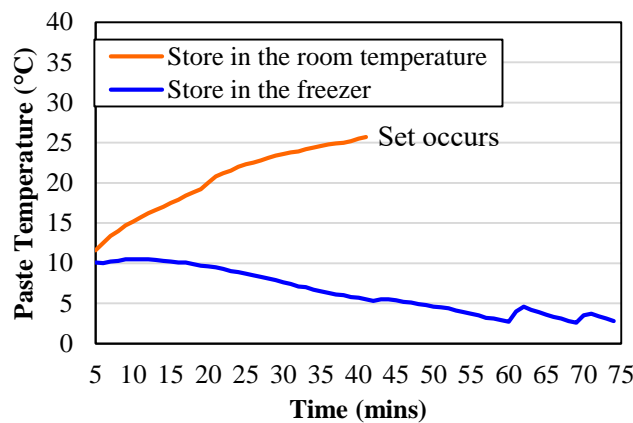


Figure 2. The internal temperature of the geopolimer paste

Table 3. Compressive strength & density of geopolimer mortar

Sample	Compressive Strength (MPa)				Density (kg/m ³)
	3 days	7 days	14 days	28 days	
FAG-CT	30.80	37.33	47.60	54.27	2.344
FAG-CL	38.67	47.47	53.33	65.20	2.417

In contrast to the low calcium fly ash-based geopolymers whose the compressive strength of the concrete is not influenced by age [6], high calcium fly ash-based geopolymers show the development of strength along with age. As shown in Figure 3, both the FAG-CT samples and the FAG-CL samples showed strength development as well as conventional concrete (which use Portland cement). For FAG-CT sample, the compressive strength development for 3, 7, and 14 days was 56.75%, 68.78%, and 87.71% respectively. While for FAG-CL sample, the compressive strength development for 3, 7, and 14 days was 59.31%, 72.81%, and 81.79%. The strength development indicates that the chemical reaction occurred in high calcium fly ash-based geopolimer is not only the polymerization but also the hydration reaction due to the presence of calcium compound in the fly ash.

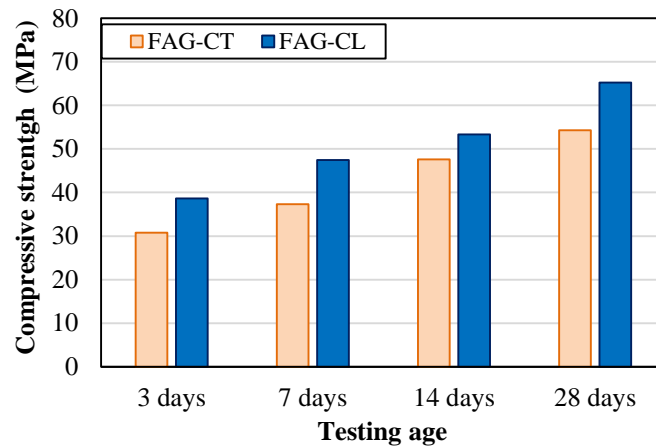


Figure 3. Strength development of geopolymer mortar

4. Conclusions

From the above study, it can be concluded that the cooling treatment of alkali solutions and the constituting materials can prolong the setting time of high calcium fly ash-based geopolymer. The lower temperature of the material would prolong the initial and final setting time of the geopolymer. However, it should be noted that high calcium fly ash-based geopolymer cannot harden under freezing conditions i.e., below 0°C. The cooling treatment can also increase the compressive strength of the geopolymer mortar both at an early age and at 28-days compared to the room temperature specimens.

In an industrial perspective, using high calcium fly ash as geopolymer precursors could give more benefit both in saving time and cost because it does not need the application of heat to start the geopolymerization reaction, and the casting process can be shortened.

Regarding the rapid setting time problem of high calcium fly ash-based geopolymer concrete, by using cooling treatment, it is more likely to be applied in the precast concrete industry or for repair material, where short setting time and high early age compressive strength are expected. In addition, the cooling treatment is also a more promising method to prolong the setting time of high calcium fly ash-based geopolymer concrete compared to the use of chemical additive as it did not reduce the compressive strength of the concrete.

References

- [1] Davidovits J 1991 *J Therm Anal* **37** no 8 1633–1656
- [2] Palomo A, Grutzeck M W, and Blanco M T 1999 *Cem Concr Res* **29** no 8 1323–1329
- [3] Berry M, Cross D, and Stephens J 2009 World of Coal Ash Conference
- [4] Davidovits J 2015 *Geopolymer Chemistry & Application* (Morrisville: Institute Geopolymere)
- [5] Wattimena O K, Antoni, and Hardjito D 2017 *AIP Conference Proceedings* **1887** 020041
- [6] Hardjito D and Rangan B V 2005 *Development and properties of low-calcium fly ash-based geopolymer concrete* (Perth, Australia: Curtin University of Technology)
- [7] Song X J, Marosszeky M, Brungs M, and Munn R 2005 *Int. Conf. Durab. Build. Mater. Components LYON* 17–20
- [8] Topark-ngarm P, Chindaprasirt P, and Sata V, 2014 *J. Mater. Civ. Eng* **27** no. 2011 1–7
- [9] Antoni, Wijaya S W, and Hardjito D 2016 *Mater. Sci. Forum* 841, 90–97
- [10] Chindaprasirt P, De Silva P, Sagoe-Crentsil K, and Hanjitsuwan S 2012 *J. Mater. Sci* **47** no. 12 4876–4883
- [11] Hanjitsuwan S, Hunpratub S, Thongbai P, Maensiri S, Sata V, and Chindaprasirt P 2014 *Cem. Concr. Compos* **45** 9–14
- [12] Phoo-Ngernkham T, Chindaprasirt P, Sata V, and Sinsiri T 2013 *Indian J. Eng. Mater. Sci* **20** no.4 310–318

- [13] Kusbiantoro A, Ibrahim M S, Muthusamy K, and Alias A 2013 *Procedia Environ. Sci* **17** 596–602
- [14] Antoni, Wijaya S W, Satria J, Sugiarto A, and Hardjito D 2016 *Mater. Sci. Forum* **857** 416–420.
- [15] Antoni, Herianto J G, Anastasia E, and Hardjito D 2017 *AIP Conf Proc* **1887** 020042
- [16] ASTM C191-18a 2018 *ASTM International*
- [17] Antoni, Satria J, Sugiarto A, and Hardjito D 2017 *MATEC Web Conf* **97**, 01026