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# Effect of calcium aluminate cement on geopolymer concrete cured at ambient temperature

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## HIGHLIGHTS

- Geopolymer incorporating calcium aluminate cement can cure at ambient conditions.
- CAC replacement ratio significantly affects the strength development of geopolymer.
- Taguchi method can be used to develop optimised geopolymer mixture.
- Geopolymer concrete with CAC has reasonably good mechanical properties.

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## ABSTRACT

This paper aims to investigate the mechanical performance of fly ash-based geopolymer concrete cured at ambient temperature by incorporating a certain amount of calcium aluminate cement (CAC) as an extra source of Al and Ca. An orthogonal array design was employed to obtain the optimum mix proportions, where the considered factors include the CAC replacement ratio (at 3 levels of 5, 10, and 20%), sodium hydroxide (NaOH) concentration (at 3 levels of 10, 12, and 14 M) and alkali activator to binder ratio (at 3 levels of 35, 40 and 45%). The results show that the CAC replacement ratio plays an important role in the strength development, whereas the alkali activator to binder ratio has a significant influence on the workability of mortars. Two optimal mixes were proposed to achieve the highest strength and best workability, respectively. Meanwhile, another mix was developed to achieve a balance between strength and workability. Based on these optimum proportions, the corresponding geopolymer concrete was tested for compressive strength, splitting tensile strength, flexural strength and elastic modulus. It is found that the Australian standard AS 3600 can predict the elastic modulus of the geopolymer concrete with reasonable accuracy, whereas the American code ACI 318 gives reasonable predictions for the splitting tensile strength. The flexural strength of the geopolymer concrete is underestimated by both AS 3600 and ACI 318.

## 1. Introduction

Climate change caused by greenhouse gas emissions is a critical environmental issue facing the world today. Ordinary Portland cement (OPC), intensively used in making conventional concrete, is responsible for approximately 5–7% of total greenhouse gas emissions [1]. Geopolymer concrete is a new type of concrete in which an alkali-activated aluminosilicate binder replaces the OPC binder for reducing greenhouse gas emissions. In comparison with the OPC binder, geopolymer binders normally exhibit earlier strength gain [2], higher resistance to fire [3] and excellent durability [4]. The formation of geopolymer involves chemical synthesis between aluminosilicate raw materials and alkali solution (usually hydroxide, metal silicate or acid salts) [4]. The reacted product is a type of long-chain inorganic polymer material whose microstructure is amorphous to semi-crystalline [4].

The most commonly used aluminosilicate material is fly ash, which is an industry by-product obtained from coal-fired power plants. In Australia, most fly ashes are low-calcium fly ash (ASTM class F) suitable for making geopolymers. Temuujin et al. [5] found that the calcium content in the mix has significant influence on the geopolymer mechanical properties. The presence of calcium leads to the formation of C-S-H, which promotes the strength development of geopolymers. Without enough calcium oxide in the mix, a moderate curing temperature is required for the alkali-

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activation of fly ash-based geopolymers [6]. However, the heat curing procedure will restrict the field application of geopolymer concrete. To cope with this issue, some investigations [6–10] have been conducted to eliminate the need for heat curing. These studies have proven that fly ash-based geopolymers have the ability to harden at ambient temperature if extra calcium is incorporated in the system. Previous researches have mainly focused on using either OPC or ground granulated blast-furnace slag (GGBFS) as the source of extra calcium. Khan et al. [11] studied the workability and compressive strength of low calcium fly ash-based geopolymer mortar blended with slag, hydrated lime and ultra-fine fly ash. The ambient cured fly ash-slag geopolymer obtained the highest compressive strength which was greater than 100 MPa at 28 days. The microstructure of the fly ash-slag geopolymer was also denser than that of other geopolymer mixtures. In contrast, the compressive strength of geopolymer was moderately affected by the addition of hydrated lime and ultra-fine fly ash. Nath and Sarker [6,12] reported that as little as 5% OPC can be added to the mixture to ensure fly ash-based geopolymer concrete to set and harden at ambient temperature, and the compressive strength increases with increasing amount of OPC. Meanwhile, durability of geopolymer concrete could also be improved because of the reduction in the water absorption, porosity and chloride permeability [6–8]. Hadi et al. [9] proposed an optimal mixture composition for geopolymer concrete with GGBFS cured at ambient temperature. This ambient cured geopolymer concrete showed higher ductility, as compared to heat cured geopolymer concrete.

Besides OPC and GGBFS, calcium aluminate cement (CAC) is also one of the commonly used cementitious materials rich in calcium. CAC is suitable for applications requiring high resistance to aggressive chemicals, high early strength, resistance to high temperature, resistance to abrasion, and low ambient temperature placement [13]. But different from OPC and GGBFS, CAC also contains a high amount of alumina ($Al_2O_3$), which may further promote the hardening of geopolymers at ambient temperature. The alumina plays an important role in the alkali-activation of fly ash. The geopolymerisation mechanism of alkali-activated fly ash involves the polycondensation reaction to produce polymeric Si-O-Al bond, which is responsible for the strength development of geopolymers. CAC can supply reactive Al in the activation process and thus may promote the reaction. Meanwhile, when extra calcium was available, formation of Al-substitute calcium silicate hydrate (C-(A)-S-H) was observed in [14], suggesting that this reaction product contributes to the strength development of geopolymer. Criado et al. [4] also drew a conclusion that the amount of the aluminosilicate gel during geopolymerisation is controlled by the amount of $[Al(OH)_4]^-$ tetrahedral groups which are able to attract positive charge groups. Meanwhile, the number of $[Al(OH)_4]^-$ tetrahedral groups is dependent on the available amount of aluminium to react with the alkaline activator. Therefore, CAC can theoretically be used as an admixture for developing ambient-cured geopolymers as it can supply extra aluminium and calcium to geopolymeric systems. Fernández et al. [15] investigated the performance of alkali-activated metakaolin blended with CAC. They found that the calcium and aluminium in the CAC were successfully taken up into the aluminosilicate gel, i.e., the main product of the metakaolin-based geopolymer. However, the samples investigated in the study were cured at 85 °C. No study has been reported to date on alkali-activated fly ash blended with CAC cured at ambient temperature.

The aim of this paper is to investigate mechanical properties of fly ash-based geopolymeric materials cured at ambient temperature by partially replacing fly ash with CAC. It is envisaged that properties of the geopolymers could be significantly affected by the mixing parameters, such as the concentration of alkali solution, activator to binder ratio and CAC replacement ratio. Because of the need for extensive experimental work, it is difficult to consider all possible combinations when studying the influences of different parameters. However, through a properly designed experimental program using the Taguchi method, the amount of experimental work could be effectively reduced. This has been proven by successfully developing mix design for OPC blended fly ash-based geopolymer concrete and GGBFS blended fly ash-based geopolymer concrete [9,16–18].

In the current study, the Taguchi method with an L9 ($3^3$) orthogonal array was used, which requires only 9 mixture designs for analysing the three important mixing parameters. Firstly, the influence of different factors on workability was analysed based on mini-slump tests of fresh geopolymer pastes. In order to eliminate the influence of aggregates, geopolymer paste samples were also prepared for microstructure analysis and the measurements of initial and final setting times. Then, salient parameter analysis on the 7-day and 28-day compressive strengths was conducted on geopolymer mortar samples. Afterwards, geopolymer concrete samples were prepared based on the salient parameter analysis results of the mortar samples. Finally, mechanical properties of the geopolymer concrete samples were measured and the test results are compared with predictions of existing design codes for OPC concrete.

## 2. Experimental investigation

### 2.1. Materials

ASTM type F (low calcium) fly ash was used in this research for making geopolymers. There are different types of CAC with different amounts of alumina (40–80%). Normal CACs with 40–50% alumina can be used in a wide range of applications, such as self-levelling floor or non-shrink grouts. CACs with 70–80% alumina, such as Secar 71, are primarily employed for high duty refractory mortars and concretes. In this investigation, Secar 71 with an alumina content of 75.3% was chosen because: (1) a high content of alumina might promote geopolymerisation for strength development; and (2) CAC with a high content of alumina might help to keep the high fire-resistance of geopolymer concrete. However, further studies can be conducted to investigate the influence of using other types of CAC. X-ray fluorescence (XRF) spectroscopy analysis was performed to obtain the chemical composition information of the binding materials (fly ash and CAC). The results of the XRF analysis are presented in Table 1. Clearly, the fly ash contains mainly $SiO_2$ (quartz) and $Al_2O_3$ (aluminium oxide), whereas the CAC has high alumina oxide content and calcium oxide (CaO) content but very low quartz content. Blaine fineness of the CAC and fly ash are 3800 and 3410 $cm^2/g$, respectively.

Locally available river sand and crushed limestone (nominal sizes of 10 and 20 mm) were used as fine aggregate and coarse aggregate, respectively. The aggregates were used in a saturated surface dry condition. The grading curves of the aggregates are shown in Fig. 1, indicating that both fine and coarse aggregates meet the grading requirements of the ASTM C33 standard [19].

Alkali activator was made by mixing sodium hydroxide solution and sodium silicate solution at a constant ratio of 1:2.5. This ratio was selected based on the results of setting time and compressive strength of geopolymer obtained in our preliminary experiment [20]. A suitable ratio would ensure the obtained mixture exhibiting a proper setting time in the fresh state and an acceptable compressive strength in the hardened state. This ratio of 1:2.5 has also been widely used by previous researchers as an optimum value [6,9,10]. Sodium hydroxide pellets were dissolved in tap water to produce 10, 12 and 14 M concentration solutions. Sodium silicate (grade D) with a modulus silicate ratio (Ms) of 2 (where $Ms = SiO_2/Na_2O$,