Mechanical Properties of Geopolymer Concrete with Modified Calcium and Magnesium

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Abstract. Geopolymer concrete has better mechanical property and environmental advantages than ordinary Portland concrete. Different amount of fly ash, Ca, Mg and the proportions of mixing ingredients are researched in this paper. Contrast by mixing different ratio of calcium to magnesium (Ca-to-Mg) into the geopolymer concrete, the mechanical property was researched. The compress experiment was fulfilled, moisture reduction was measured. The experimental results show modified geopolymer concrete with Mg/Ca can enhance the ability of water retention. The compressive strength of geopolymer concrete enhanced when ratio of Mg-to-Ca was 1:1. The peak compressive strength of geopolymer concrete reached 43.7MPa when MgO and slag occupied 133% fly ash. Slag can obviously improve the mechanical properties of the geopolymers. Modified proper ratio of Ca-to-Mg can improve mechanical performance of the geopolymer gels by 52%-1461%.

Keywords. Geopolymer concrete, mechanical property, ratio of Mg-to-Ca, fly ash.

1. Introduction
Concretes are increasingly being widely used in construction sector and industrial processes especially in developing countries which affect the environment adversely [1]. The pollution of large amounts of greenhouse gases, as well as the damage to the health of workers in the industrial processes, cannot be ignored [2]. To solve the pollution problems of carbon dioxide emission from OPC, one of main tasks is to reduce or replace the concretes [3]. Geopolymer is a kind of alumino silicate cementitious material with three-dimensional network structure, which can be prepared by using industrial solid wastes and has excellent performance, is regarded as a green material [4]. They have good technical performance and cost-effectiveness in a wide range of applications [5]. Polymer concrete received considerable interest and showed to be a promising green substitute for OPC in some applications [6]. Thus, utilization of such industrial waste in concrete is a huge relive to the environment.

Geopolymer concrete have better strength, stiffness, and other mechanical properties than that of OPC-based concrete [7]. Ilknur Kara et al. found that geopolymers based on calcined clays, produced through the reaction of the calcined clay powder with an alkali source, could be replacement of the encapsulation and immobilization of Intermediate-level Wastes (ILW) [8]. Xu et al [9] carried out tests on the compressive strength and energy absorption properties of geopolymer concrete at various strain rates. They found that the addition of carbon fiber to such concrete significantly improved the strength and energy absorption properties of geopolymer concrete. Geopolymer concrete carries on like conventional concrete yet have slight increment in strength and 10-25 percent monetarily valuable than standard concrete [10]. This application of geopolymer concrete could be environmentally friendly as it helps to prevent the environmental pollution [11].
The limited research on the geopolymer concrete mix design for targeting a specific strength is identified an obstacle for their effective design and wide use. Allan et al. [12] investigated the flexural behaviour of composite beam filled with geopolymer concrete. The experimental results showed the compressive failure of concrete, followed by the compressive buckling in the pultruded composites, resulted in the failure of the geopolymer concrete in-filled pultruded composite beam. The presence of calcium oxide in the source material influences the properties [13]. Calcium dissolution from manufactured calcium silicate sources (blast furnace slag or Portland cement) at low alkalinity forms C-S-H gel in combination with the geopolymeric gel, enhancing strength [14]. H. E. Elyamany [15] et al. evaluated the performance of geopolymer mortar in magnesium sulfate solution. Results revealed that increasing curing temperature, sodium hydroxide solution molarity and decreasing alkaline solution to mixed ratio improved magnesium sulfate resistance of geopolymer mortar. Various geopolymer mortars achieved better performance in magnesium sulfate solution than OPC mortars. Previous studies have shown that the amount of vitreous calcium and magnesium plays a significant role in activation reactions and the properties of the reaction product. Before the widespread application of geopolymer concrete in civil infrastructure, a detail guideline is required for selecting the suitable concrete ingredients and determining their relative quantities.

The aim of this paper is to determine reasonable amounts of blended ingredients and ratio of Mg/Ca to improve the performance of the geopolymer. To determine a direct relationship between blended ingredients and the mechanical properties of geopolymer concretes.

2. Preparation of Materials and Specimens
As it is necessary to develop a rigorous, but still easy method for a geopolymer concrete mix design, a general composition shown in table 1 is proposed. Composition used in the fabrication of geopolymer concrete specimens are main shown in follows: fly ash, slag(Among them, CaO>35%), Mg powder(MgO>90%), molar ratios of SiO₂/Na₂O is 3.02 in sodium silicate, (H₂O/Na₂O =37.8%, Na₂O occupied 2.81% in Sodium silicate). Sodium hydroxide(NaOH, occupied 0.70%), water (occupied 6.41%), coarse aggregates(diameter size is about 4-8 mm, occupied 30.46%), fine aggregates(sand, occupied 39.73%).

The mass proportion of each group is shown in brackets. Among them, mass ratios of Ca occupied the whole ingredients are listed with '*' signal in the slag rank brackets and mass ratios of Mg occupied the whole ingredients are listed with '#' signal in the MgO rank brackets.

The main propose is to find how to improve the mechanical properties of geopolymer with different composition. A large number of samples with various ratios of slag and MgO to fly ash, ratios of Ca-to-Mg were investigated. In this paper, there are 21 groups of the compositions of experimental geopolymer concrete as shown in table 1.

Table 1 indicates mix proportions of composed materials in the different groups. The percentage of slag (CaO>35%) and MgO (Mg>90%) occupied fly ash is varied from 0 to 150%. In group D0, ratio of slag and MgO to fly ash is 0. In group D1-1~ D1-5, ratio of slag and MgO to fly ash is 3:4(75%). In group D2-1~ D2-5, ratio of slag and MgO to fly ash is 1:1(100%). In group D3-1~ D3-5, ratio of slag and MgO to fly ash is 4:3(133%). In group D4-1~ D4-5, ratio of slag and MgO to fly ash is 3:2(150%).

In group D1-1~ D4-1, there is only Ca and there isn’t Mg, among them there are Ca>35% in the slag. In group D1-2~ D2-2, ratio of Ca-to-Mg is 1:0.25. In group D1-3~ D3-3, ratio of Ca-to-Mg is 1:0.5. In group D1-4~ D4-4, ratio of Ca-to-Mg is 1:1. In group D1-5~ D5-5, ratio of Ca-to-Mg is 1:2.

The mixed raw was stirred enough. The highly viscous pastes obtained were poured into 150mmx150mmx150mm plastic molds. The samples were then vibrated to release any residual air bubbles. Subsequently, the specimens were thrown and relieved for 28 days and tested for mechanical properties. All the specimens are prepared, cured, and tested under an average temperature of 20°C.

The mass proportion of each group is shown in brackets. Among them, mass ratios of Ca occupied the whole ingredients are listed with '*' signal in the slag rank brackets and mass ratios of Mg occupied the whole ingredients are listed with '#' signal in the MgO rank brackets.
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Table 1. The composition of geopolymer with different ratio of Ca/Mg.

| Group | Fly ash (g) | Slag (g) | MgO (g) | NaOH (g) | Sodium silicate (g) | Water (g) | Coarse aggregate (g) | Sand (g) |
|-------|-------------|----------|---------|----------|--------------------|-----------|---------------------|---------|
| D0    | 6004(19.89%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D1-1  | 3545(11.36%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D1-2  | 3545(11.36%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D1-3  | 3545(11.36%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D1-4  | 3545(11.36%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D1-5  | 3545(11.36%) | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D2-1  | 3029(9.42%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D2-2  | 3029(9.42%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D2-3  | 3029(9.42%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D2-4  | 3029(9.42%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D2-5  | 3029(9.42%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D3-1  | 2658(8.52%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D3-2  | 2658(8.52%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D3-3  | 2658(8.52%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D3-4  | 2658(8.52%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D3-5  | 2658(8.52%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D4-1  | 2482(7.96%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D4-2  | 2482(7.96%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D4-3  | 2482(7.96%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D4-4  | 2482(7.96%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |
| D4-5  | 2482(7.96%)  | 0        | 219     | 876      | 2000               | 9504      | 12395               |

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In group D2-1~D2-5, ratio of slag and MgO to fly ash is 1:1 (100%). In group D3-1~D3-5, ratio of slag and MgO to fly ash is 4:3 (133%). In group D4-1~D4-5, ratio of slag and MgO to fly ash is 3:2 (150%).

In group D1-1~D4-1, there is only Ca and there isn’t Mg, among them there are Ca>35% in the slag. In group D1-2~D4-2, ratio of Ca-to-Mg is 1:0.25. In group D1-3~D4-3, ratio of Ca-to-Mg is 1:0.5. In group D1-4~D4-4, ratio of Ca-to-Mg is 1:1. In group D1-5~D4-5, ratio of Ca-to-Mg is 1:2.

The mixed raw was stirred enough. The highly viscous pastes obtained were poured into 150mmx150mmx150mm plastic molds. The samples were then vibrated to release any residual air bubbles. Subsequently, the specimens were thrown and relieved for 28 days and tested for mechanical properties. All the specimens are prepared, cured, and tested under an average temperature of 20°C. The fly ash concrete with modified ratio of Mg/Ca were cast in cube 150 mm×150 mm×150 mm, some of them were shown in figure 1.

![Figure 1](image1.jpg)

(a) before decoding  (b) experimental specimens

**Figure 1.** Photographs of fly ash geopolymer specimens.

The compressive strength test for cubes was conducted using pressure testing machine (WAW-1000D) to accurately measure displacement and strain under loading, as shown in figure 2. The shapes were performed in compressive testing machine at the rate of 2 mm/min and recorded the data automatically.

![Figure 2](image2.jpg)

**Figure 2.** Experiment on universal mechanical experiment machine.
3. Results and Discussions

3.1. Effects of the Amounts of Fly Ash, CaO and MgO on Compressive Strength

Ratios of MgO and Slag to fly ash are modified while certain amounts of the geopolymer gels are kept constant. The compressive strength test results of geopolymer concrete modified with amount of Mg and Ca are shown in figure 3. The horizontal axis indicates the ratio of MgO and Slag to fly ash which range from 0% to 150%. The vertical axis is the failure compressive stress of the sample. The experimental results show the compressive strength of geopolymer is increasing with increasing amount of the Ca and Mg until the ratio slag and MgO to fly ash is reached 133%. Totally the compressive strength reached the peak value in each group D3-1~D3-5. With increasing of CaO, the compactness of geopolymer is improved and the speed of solidification is accelerated [15]. The compressive strength of geopolymer concrete of fly ash is the most optimum when the slag and MgO occupied 133% of the fly ash (namely ratio of slag and MgO to fly ash is 4:3 in group D3-4). Because the number of calcium and magnesium cations maintain at the optimal ratio, the mechanical properties of cementitious materials are reinforced with the improvement of the reaction rate of raw materials.

![Figure 3. Compressive properties of geopolymer concrete with different amount of MgO and slag.](image)

3.2. Analysis on the Effects of Ca/Mg Ratios

The composition of specimen can be classified into main solids which can’t be evaporated includes fly ash, NaOH, sodium silicate, Mg, slag, and water which can be evaporated. The totally moisture reduction was almost happened after demoulding so that moisture reduction can be measured simply by weight.

Rate of moisture reduction (Δ) is calculated as follows:

\[ \Delta = \frac{M_0 - M_1}{M_0} \times 100\% \]  

(1)

\( M_0 \): mass of the specimen when the sample is ready in the mould in grams;

\( M_1 \): mass of the specimen after demoulding in grams.

Moisture reduction of the specimens after demoulding was measured as shown in figure 4. It can be seen that the evaporation of water decreased and the water retention strengthened with increase of modified amount of the Ca and Mg. The minimum decrease water was the group D3-4 which weighs reduced only occupied 0.78%. Only 67.1 g water was evaporated which water retention was 96.6%. The water retention ability of Geopolymer modified with Ca and Mg is better than that of Portland cement.
One of main roles of CaO for plastic shrinkage concrete is water retention and substitution for water. There are low participation and slow speed when CaO are mixing with hydration reaction. It slows down the totally responsible process and reduces water of hydration. CaO powder have smoothly surface, round edges, dense structure, little pores and cracks, poor hydrophilic and water holding capacity. The Portland concrete have poor water retention, easy to drain, fast evaporation of water [16]. Calcium ions in soluble calcium components are involved in generating C-SCI gel which works jointly with geopolymers to improve the cement and pore connectivity [17]. The substitution effect of CaO powder is positive, the plastic shrinkage of concrete decreases, the anti-cracking effect increases, and the plastic shrinkage of concrete increases. The negative effect plays an important role, which increasing the plastic shrinkage of concrete and decreasing the crack. The limited volume expansion after MgO hydrated compensates the plastic shrinkage deformation of geopolymer concrete. At the same time, the absorb water ability of geopolymer is increasing which shows good water absorption and holding capacity. It can effectively reduce the drainage and water evaporation for the excellent water retention of MgO. It is shown that the MgO plays a prominent role in controlling the plastic shrinkage of cementitious materials.

The fly ash specimens with modified ratio of Ca-to-Mg were conducted compressive experiment by pressure testing machine as shown in figure 2. The maximum compressive stress is shown in figure 5. The compressive strength of geopolymer without Ca and Mg is 2.8 MPa (group D0). The compressive strength of fly ash with slag (group D3-1) is 28.8 MPa. The maximum compressive strength of geopolymer with modified ratio of Ca/Mg(1:1) is 43.7 MPa (group D3-4). It can be seen
that peak compressive strength of geopolymer with modified ratio of Ca/Mg(1:1) can enhance by 1461% than pure fly ash, and reinforced by 52% than pure slag.

Slag can obviously improve the mechanical properties of the geopolymers. In addition, the proper ratio of Ca and Mg can improve the performance of the geopolymer gels by 52%-1461%. It shows that the peak compressive strength of geopolymer concrete reached 43.7 MPa with modified ratio of Ca-to-Mg is 1:1 when MgO and slag occupied 133% fly ash as shown in figure 5. Namely, modified proportion of Ca-to-Mg can improve mechanical performance of geopolymer cementitious.

4. Conclusion

By contrast with ordinary Portland concrete, geopolymer modified with amount of slag and ratio of Ca-to-Mg can improve the mechanical performance. Geopolymer concrete with modified Ca and Mg is a kind of environmental material which has prosperous application for its better mechanical performance.

Overall our experimental focused on two variables that amount of slag and MgO, and ratio of Ca/Mg affected both moisture reduction and compressive strength of geopolymer gels. Based on experimental outcomes, the following conclusions are drawn:

- The slag and MgO can improve the compressive strength of the geopolymer concrete. The amount of slag and MgO occupied fly ash 133%, each element has the highest participation. The compressive strength of the geopolymer concrete was increased with increasing amount of slag and MgO and reached peak when it occupied fly ash 133%.
- Modified the ratio of Ca to Mg is 1:1, slag can significantly improve the compressive strength of the geopolymer concrete.
- The compressive strength of the geopolymer concrete with MgO and slag occupied fly ash 133%, ratio of Ca-to-Mg is 1:1, its compressive strength increased from 2.8 MPa to 43.7 MPa.

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