Effect of nano-TiO₂ content on the flexural strength and compressive strength of dry-Mixing CDG-Slag based geopolymer paste

Kai Wang, Xiaoxiong Zha*

School of Civil and Environmental Engineering, Harbin Institute of Technology
Shenzhen, Shenzhen, Guangdong, China.

zhahero@126.com, cewangkai@126.com

Abstract. In this paper, the effects of nano-titanium dioxide (TiO₂) content on the 28-day flexural strength and 28-day compressive strength of Completely decomposed granite (CDG) and slag based geopolymer paste was investigated, using the dry-mixing method. The calcium hydroxide, sodium carbonate and solid sodium silicate were used as the alkali activator. The results show that with the increase of nano-titanium dioxide content increasing from 0 to 2.0%, the compressive strength and flexural strength gradually increase. In addition, the surface of geopolymer paste gradually became smooth. What’s more, the geopolymer paste microstructure was characterized by using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Microanalysis, details of the research process and analysis are presented throughout the paper.

Keywords. Geopolymer paste, CDG, Slag, Nano-TiO₂, Compressive strength, Flexural Strength

1. Introduction
In 1976, Professor Davidovits investigated the solid-phase synthesis of a mineral blockpolymer by low temperature polycondensation of alumino-silicate polymers (Davidovits, 1976), and the synthetic alkali aluminosilicate material was firstly named as geopolymer in 1979 (Davidovits, 1979). As a new kind of construction material, geopolymer shown great potential in replacing ordinary Portland cement (OPC), owing to its high early strength and significant reduction of CO₂ emission in practical production (Cheng, Lo et al., 2018; Ribeiro, R.A.S., et al. 2016; Usman and Sam, 2017; Sathanandam, Awoyera, et al., 2017). Studies have already shown that the addition of calcium has a generally positive effect on the mechanical behaviour of geopolymer binder. (Yip, Lukey, et al., 2008; Ling, Wang, et al., 2019) In addition, researches all over the world have been carried out on the calcium enriched slag cementitious materials. Since the completely decomposed granite (CDG) mainly consists of aluminosilicates, in which the alumina tetrahedron could react with the silica tetrahedron, under the activation effect of the alkali metal ion. The component CDG can be used as the alumina-silicate precursor in geopolymer manufacturing process. Besides, study has already shown that the CDG can be used as the main cementitious material in geopolymer (Zha and Zhu, 2018). In recent years, researchers investigated the effect of adding nano-TiO₂ on the strength and drying shrinkage of
geopolymer paste, the results shown that nano-TiO$_2$ enhances both the early and later compressive strength of geopolymer. (Ping, Chun, et al., 2016)

In this study, the 28-day flexural strength and compressive strength of dry-mixed geopolymer paste on considering the variation of nano-titanium dioxide content were conducted. The completely decomposed granite (CDG) and slag were used as the cementitious materials. The calcium hydroxide, sodium carbonate and solid sodium silicate were used as the alkali activator. Since traditional alkali activator sodium hydroxide may release large amounts of heat in geopolymerisation process, the alkali activator adopted in the test could successfully eliminate potential safety hazards. In addition, the dry-mixing method could achieve the purpose of cementitious materials mixing well and evenly with the solid alkali activator, which is helpful for the occurrence of later geopolymerisation process.

2. Materials and methods

Based on the X-ray fluorescence (XRF) analyses method, chemical composition of the materials CDG and slag were successively obtained, and the main chemical components are presented in Table 1. It can be seen from the table that the CDG mainly contains SiO$_2$ and Al$_2$O$_3$, while the granulated blast furnace slag mainly contains SiO$_2$, Al$_2$O$_3$ and CaO. Since the materials CDG and slag are rich in silicon and aluminium, they can be chosen as the cementitious materials.

| Cementitious materials | Chemical composition |
|------------------------|----------------------|
|                        | SiO$_2$ (%)          | Al$_2$O$_3$ (%) | Fe$_2$O$_3$ (%) | CaO (%) | MgO (%) | TiO$_2$ (%) | Na$_2$O (%) | K$_2$O (%) |
| CDG                    | 45.71                | 36.92           | 8.96            | 0.49    | -       | 4.40        | -           | 2.96       |
| Slag                   | 31.57                | 15.27           | 0.23            | 43.18   | 6.68    | 0.74        | 0.45        | 0.21       |

2.1. Cementitious materials

The residual soil, completely decomposed granite (CDG) used in the test is widely distributed in southern China. According to the Code for Highway Engineering Geological Investigation (JTG-C20-2011), the soil is defined as the quaternary loose deposits remaining in situ after the granite is weathered, called the completely decomposed granite residual soil. The CDG used in this test contains sand and gravel clay, showing a middling brown red color. After dried, the clod was grinded into powder, making it possible for the CDG and slag to react fully with the alkali-activator. The CDG sample used in the test is shown in Figure 1(a).

The blast furnace slag used in the test was the S-95 grade granulated blast furnace slag powder, a by-product in steel-making industry. The slag powder sample is shown in Figure 1(b).

![CDG](image1.png) ![Slag](image2.png)

**Figure 1.** Cementitious materials used in the experiment

2.2. Alkaline activator and nano-titanium dioxide

When the tradition alkali activator, strong sodium hydroxide reacts with water, huge amounts of heat may be released, thus causing many potential safety hazards. This paper optimizes the alkali activator
system and the mixing process. Calcium hydroxide, anhydrous sodium carbonate and solid sodium silicate were used as the alkali activator. In addition, the dry-mixing method was adopted in preparing the CDG and slag based geopolymer paste. The calcium hydroxide and anhydrous sodium carbonate are in white colored powder, water-soluble. The solid sodium silicate is white crystalline particle. The nano-titanium dioxide is a white powder, with the particle size ranging from 20 nm to 30 nm. The alkali activator and nano-titanium dioxide are presented in Figure 2.

![Figure 2. Alkaline activator and nano-titanium dioxide used in the experiment](image)

### 3. Experimental methods

#### 3.1. Preparation of geopolymer specimens

In the preparation of geopolymer paste specimens, the weighted CDG, Slag, calcium hydroxide, anhydrous sodium, solid sodium silicate and nano-titanium dioxide were placed in the cement paste mixer, and the six solid materials were mixed evenly. Then, the weighted water was injected into the mixture. Subsequently, the mixed materials were stirred for 2 mins until the geopolymer paste is developed. The stirred slurry was then poured into the test piece of 40mm × 40mm × 160mm, and the moulded geopolymer paste specimens were cured at ambient temperature. The 28-day flexural strength and compressive strength were successively measured by using the universal testing machine. The related test data were recorded.

Accordingly, the 12 specimens in this part were classified into four groups, which were labelled as B1, B2, B3, B4. In each group, 3 specimens were prepared, for the purpose of minimizing the influence of accidental errors on tests results. In addition, the nano-titanium dioxide dosage varies from 0 to 2%. The activator modulus is 1.5, the water-paste ratio is 0.5. Details of the mix ratio design were presented in Table 2, which is shown as follows.

| Specimen label | TiO₂(%) | TiO₂(g) | CDG(g) | Slag(g) | Ca(OH)₂(g) | Na₂CO₃(g) | Na₂SiO₃(g) | H₂O(g) |
|----------------|--------|--------|--------|--------|------------|-----------|-----------|--------|
| B1             | 0      | 0      | 900    | 600    | 60         | 87        | 177       | 750    |
| B2             | 0.5    | 7.5    | 900    | 600    | 60         | 87        | 177       | 750    |
| B3             | 1.0    | 15     | 900    | 600    | 60         | 87        | 177       | 750    |
| B4             | 2.0    | 30     | 900    | 600    | 60         | 87        | 177       | 750    |

#### 3.2. Determination of the specimen strength

The determination of the flexural strength (R_f) requires a folding clamp, and the method of use is shown in Figure 3(a). The method for measuring the compressive strength (R_c) of the geopolymer paste is to put the half-cuboid after the fracture test of the fracture test into a compression clamp, so
that the pressure receiving surface of the test piece is 40 mm×40 mm, and the use method is shown in Figure 3(b).

\[ R_f = \frac{1.5 \times F_f}{l} \]  \hspace{1cm} (1)

\[ R_c = \frac{F_c}{A} \]  \hspace{1cm} (2)

In which, \( F_f \) is the load when the test piece is broken, \( l \) is the distance between the two supporting cylinders below the clamp, \( b \) is the length of the square section of the test piece, \( F_c \) is ultimate load when the compressed test piece is damaged, \( A \) is the pressure area of the test piece.

![Figure 3. Strength measurement methods](image)

(a) Flexural strength  (b) Compressive strength

### 4. Results and discussions

#### 4.1. Effect of nano-titanium dioxide content on the flexural strength and compressive strength

It can be observed that with the increase of nano-titanium dioxide content, the outer surface of geopolymer paste became smoother and smoother, the small holes on the outer surface decrease significantly. Twelve specimens were placed on the universal testing machine for the flexural test and compressive test. The average values of flexural strength and compressive strength of the specimens were obtained from the measured values of three specimens in the corresponding group. Based on the test results, the relationship curves of 28-day flexural strength and 28-day compressive strength with the content of nano-titanium dioxide are drawn respectively, as shown in Figure 4.

![Figure 4. 28-day flexural strength and compressive strength versus TiO$_2$ content curves](image)

(a) Flexural strength-TiO$_2$ content curve  (b) Flexural strength-TiO$_2$ content curve

**Figure 4. 28-day flexural strength and compressive strength versus TiO$_2$ content curves**
It can be seen from Figure 4(a), 4(b) that, the flexural strength and compressive strength increase as the nano-titanium dioxide content varies from 0 to 2.0%. When the nano-titanium dioxide content is 2.0%, the ultimate flexural strength and compressive strength are successively obtained, which equal to 3.08 MPa and 13.75 MPa. Compared with that of specimens without adding nano-titanium dioxide, the increasement of flexural strength and compressive is 12.82% and 9.91%. This can be explained by the fact that the nano-titanium dioxide has good dispersion, thermal stability. The fine particles can fill the micro-voids in the geopolymerisation process. Therefore, the geopolymer paste is much denser, thus improving the flexural strength and compressive strength.

4.2. Microstructure characterization
To investigate the chemical composition and microstructure of the geopolymer paste specimens, a series of specimen samples were observed and analysed by using the Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Microanalysis. Limited by length, Figure 5(a), 5(b) only show the EDX spectra and SEM image of specimen B3. The results show that the geopolymer paste samples mainly contain silicon, aluminium and calcium. What’s more, the proposition of elements silicon, aluminium and calcium range from 8.0% to 12.8%, 5.7% to 9.2%, and 2.1% to 7.4%, respectively. In addition, the proportion of element titanium varies from 0.2% to 1.4%. On the other hand, the results also indicate that the CDG and slag are rich in silicon and aluminium elements, thus proving the possibility of CDG and slag being as the cementitious materials in preparing geopolymer. Figure 5(b) shows that there are huge amounts of uniformly distributed fine particles formed in the tested samples. In addition, many needle-shaped and bar-shaped crystals are formed, filling the capillary cavity, thus improving the specimen strength. Additionally, there are N-A-S-H and C-S-H gels generated, proving the feasibility of sodium carbonate, calcium dioxide and anhydrous sodium silicate being as the alkali activator when preparing geopolymer materials.

5. Conclusion
This paper investigated the 28-day flexural strength and 28-day compressive strength of CDG and slag-based geopolymer paste specimens, in considering of the nano-titanium dioxide content. Additionally, the dry-mixing method was adopted. Sodium carbonate, calcium dioxide and anhydrous sodium silicate were chosen as the alkali activator. When the nano-titanium dioxide content is 2.0%, the ultimate flexural strength and compressive strength are successively obtained, which equal to 3.08 MPa and 13.75 MPa. Compared with that of specimens without adding nano-titanium dioxide, the increasement of flexural strength and compressive is 12.82% and 9.91%. This can be explained by the fact that the nano-titanium dioxide has good dispersion, thermal stability. The fine particles can fill the micro-voids in the geopolymerisation process. Therefore, the geopolymer paste is much denser, thus improving the flexural strength and compressive strength. On the other hand, through the SEM and EDX analysis, huge amounts of N-A-S-H and C-S-H gels were generated, proving the feasibility of
sodium carbonate, calcium dioxide and anhydrous sodium silicate being as the alkali activator and CDG, slag being the cementitious materials when preparing geopolymer materials.

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