Water-glass Module on Mechanical Properties of Geopolymer Recycled Aggregate Concrete

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Abstract. Geopolymer recycled aggregate concrete (GRAC) was prepared by replacing cement with geopolymer and natural aggregate with waste concrete. The effect of water-glass modules on mechanical properties of GRAC was studied. It was found that there are two kinds of bonding structures in geopolymer hydration product: C-A-S-H and N-A-S-H, they both contribute to the strength of GRAC. The value of size conversion coefficient of current national standard is inapplicable for GRAC, the calculation method of which is given in this paper. Elasticity modulus and peak stress of GRAC is proportional to water-glass modulus, and peak strain is inversely proportional and its constitutive equation was established.

Keywords. Geopolymer recycled aggregate concrete; water-glass modules; size conversion coefficient; stress-strain curve; constitutive equation.

1. Introduction
The concept of geopolymer was proposed by French materials scientist Joseph Davidovits in 1978 [1], raw materials of which are industrial residue, such as slag and fly ash. Van Deventer [2], John Provis [3], and Caijun Shi [4] make great contribution to the development of geopolymer, and the compressive strength of which can be proved to 90 MPa at present. GRAC basically does not consume natural resources, and also reuses industrial wastes. Researches have been conducted that water-glass module is the main factor affecting the mechanical properties of geopolymer [5, 6]. In this paper the effect of water-glass module on mechanical properties of GRAC, such as compressive strength, size effect, and stress-strain curve, is studied.

2. Experimental Program
2.1. Materials
Slag and fly ash were used to make geopolymer samples, the chemical composition is given in table 1. Water-glass was selected from Shandong Yousuo Chemical Technology Co., Ltd. The original modulus is 3.3, and the chemical composition of which is given in table 2. Coarse aggregate was waste concrete, and sand was natural medium-fine river sand.
Table 1. Chemical composition of slag and fly ash /wt. %.

|       | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | Na₂O | K₂O | Ignition loss |
|-------|-----|------|-------|-------|-----|------|-----|--------------|
| Slag  | 43.10 | 32.26 | 14.69 | 2.06  | 6.19| -    | -   | 0.97          |
| Fly ash | 5.51  | 48.54 | 28.35 | 6.37  | 2.42| 3.01 | 3.90| 0.96          |

Table 2. Chemical composition and property of water-glass /wt. %.

|       | Na₂O | SiO₂ | H₂O | n(SiO₂)/n(Na₂O) | pH | ρ/g·cm⁻³ |
|-------|------|------|-----|-----------------|----|---------|
|       | 7.96 | 26.1 | 66  | 3.3             | 13.1 | 1.47    |

2.2. Mix Proportion Preparation Method

This experiment mainly studied the influence of water-glass module on the mechanical properties of GRAC. Water-glass module is 0.6~2.4, the mix proportion is shown in table 3. After the mixing, GRAC was cured in standard maintenance system for 28 days. Cube concrete specimens of 100mm³, 150mm³, and 200mm³ were prepared to study its size effect. The stress-strain curves of GRAC was test by sample size is 150mm×150mm×300mm, and the loading rate is 0.01mm/min. SEM and XRD are also used to test its morphology and crystal structure.

Table 3. Test grouping and mixing proportions /kg·m⁻³.

| No.   | Water-glass module | Slag | Fly-ash | Water-glass | Water | Sand | Recycled aggregate |
|-------|--------------------|------|---------|-------------|-------|------|-------------------|
| WG06  | 0.6                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG09  | 0.9                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG12  | 1.2                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG15  | 1.5                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG18  | 1.8                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG21  | 2.1                | 315  | 135     | 54          | 126   | 681  | 1075              |
| WG24  | 2.4                | 315  | 135     | 54          | 126   | 681  | 1075              |

3. Results and Discussion

3.1. Structure of Water-Glass with Different Module

The internal structure of water-glass is shown in figure 1[7]. It can be seen that there is an electric double-layer, where ZNa⁺ is adsorbed in the dense layer, (y-z) OH⁻ is distributed in the diffusion layer. Different water-glass module is different thickness of its double-layer[7] According to the "alkali activation" theory[8] and "depolymerization condensation" theory[1], Ca, Si and Al ions in mineral raw materials are activated by OH⁻ and Na⁺ in the solution, among which geopolymer monomers, such as [SiO₄] and [AlO₄], form by Si ions and Al ions. As the concentration is saturation, these monomers converge on the precursor and undergo polycondensation reaction. Ca ions will also react with free Si ions and free Al ions. Then, geopolymer gel is formed. The hydration product of the geopolymer contains two kinds of gels, N-A-S-H and C-A-S-H.[9] N-A-S-H mainly composed of silicon and aluminum with a three-dimensional network structure, C-A-S-H is a layered calcium silicate hydrate structure mainly formed by calcium and silicon[3], which is shown in figure 2.
Figure 1. Double electron layer structure of water-glass [7].

(a) N-A-S-H structure  (b) C-A-S-H structure

Figure 2. Two main hydration products of geopolymer [3].

3.2. Water-glass Module on Compressive Strength of GRAC

The influence of water-glass module on the compressive strength of GRAC is shown in figure 3. As water-glass module is too high (n=2.4), the electric double-layer structure of water-glass is very thin, and there is not enough Na\textsuperscript{+} and OH\textsuperscript{-} to activate the mineral raw materials, so it does not condense and cannot form strength. However, as water-glass module is 0.6, the polycondensation reaction occurs in advance, flashing occurs, the strength is extremely low or there is no strength. Moreover, as water-glass module is gradually reduced from 2.1 to 0.9, the compressive strength of the GRAC gradually increases. It is because that as water-glass module decrease, the concentration of hydroxide and sodium ions in the system gradually increases, so that more Ca, Si, and Al ions can be activated in the system, generating more zeolite and hydrate calcium silicate which lead to a tighter and complete structure of hydration products. Thus, the strength of GRAC gradually increases.

Figure 4 presents the XRD patterns of geopolymer cementing materials under different water-glass module conditions. The main hydration products of geopolymer are calcium silicate hydrate (Tobermorite 9A, PDF card number: 89-6458), a type containing calcium zeolite (Zeolite, PDF card number: 38-0232) and mulite (Mulite, PDF card number: 74-2419). It can be seen that the hydration products of geopolymer are layered structure (C-A-S-H) and net structure (N-A-S-H). As water-glass module changes, mullite and zeolite in the geopolymer change significantly, while the calcium silicate hydrate basically does not change, indicating that the strength of the geopolymer depends on the N-A-S-H gel content. And the N-A-S-H gel content increases with decreasing modules. The higher the N-A-S-H gel content, the more complete the geopolymer network structure and the higher the overall strength of the structure.
Figure 3. Compressive strength of GRAC on water-glass module.

Figure 4. X-ray diffraction pattern of geopolymer on different water-glass module.

Figure 5. SEM micrographs of different water-glass modules of GRAC.

Figure 5 shows the micro-structure images of GRAC as water-glass module is 2.1, 1.5, and 0.9 respectively. It can be seen from figure 5(a), as a result of small diffusion layer of water-glass under high module (2.1), there are not enough free Na⁺ and OH⁻ to activate the raw material, and the hydration product of geopolymer is very loose. As water-glass module is 1.5, shown in figure 5 (b), the structure is more denser, this is because there are more free Na⁺ and OH⁻ caused by the thick electron layer of water-glass. As water-glass module is 0.9, shown in figure 5 (c), the structure becomes very dense. Point A and B in figure 5 (c) is two different gel structure of the geopolymer hydration product, which is shown in figure 5 (d) and figure 5 (e), and figure 5 (f) is the EDS of these two gel. It shows that point A and B is different both in morphology and elementary composition, which evidences the XRD and strength analysis.

3.3. Water-glass Module on the Size Conversion Coefficient

The compressive strength of GRAC with different side length cube specimens (100mm³, 150mm³, 200mm³) is shown in figure 6. According to the current national standard “Standard for Test Methods for Mechanical Properties of Ordinary Concrete” GB/T50081, the standard specimen refers to a cube
specimen with a side length of 150mm, and the size conversion coefficient \((\alpha)\) of other non-standard specimens is as shown in equation (1) and equation (2):

\[
a_{100} = f_{cu,150}/f_{cu,100} \\
a_{200} = f_{cu,150}/f_{cu,200}
\]  

(1)

(2)

The influence of water-glass module on the size conversion coefficient of GRAC is given in figure 7. The national standard stipulates that \(a_{200}=1.05, a_{100}=0.95\) (the horizontal dotted line). However, it should be noted that none of the data in figure 7 is between 0.95-1.05, indicating that the standard of ordinary cement concrete does not apply to the size conversion coefficient of GRAC. This may be attributed to the fact that geopolymers are different from cement, and the properties of recycled aggregates are also different from natural aggregates. It can be seen directly that when the water-glass module reach 0.9-1.5, the size conversion coefficient of the two sizes of specimens change relatively smoothly; while the water-glass module reach 1.5-2.1, the size conversion coefficient changes drastically. Therefore, this article uses a segmented method to calculate the size conversion coefficient of GRAC. The segment point selects the water-glass module \((\alpha)\) =1.5. And linear fit the size conversion factor, the result is: \(0.6\leq\alpha\leq1.5, a_{200}=0.79063+0.23305\alpha; a_{100}=1.0293+0.0737\alpha; 1.5\leq\alpha\leq2.4, a_{200}=0.845-0.0833\alpha, a_{100}=1.22951-0.19296\alpha.\)

![Figure 6](image1.png) **Figure 6.** Compressive strength of GRAC on different sizes.

![Figure 7](image2.png) **Figure 7.** Size conversion coefficient on water-glass modules.

3.4. Stress-Strain Curves of GRAC

Figure 8 presents stress-strain curves of GRAC on different water-glass modules. It can be observed that the stress-strain curve of GRAC has the same pattern to the ordinary cement concrete’s, which can be divided into up-portion and down-portion. Figure 9 shows the influence of water-glass module on the elastic modulus, peak stress and corresponding peak strain of GRAC. It can be observed that the elastic modulus increases with the increasing of water-glass module. As water-glass module were reduced from 2.1 to 0.9, the elastic modulus increased. The reason for this observation is that the increase in the water-glass module will reduce the internal porosity of the geopolymer cementing material, forming a denser structure. The decrease in the water-glass module will also significantly increase the peak stress, and the trend is directly proportional to the water-glass module. As water-glass modules reduced to 0.9, the peak stress is increased to 1.38 times compared with the water-glass module is 2.1. The analysis of the compressive strength of GRAC shows that the water-glass module decrease, and the content of Na\(^{+}\) and OH\(^-\) in the system increases, which activates freer [SiO\(_4\)] and [AlO\(_4\)]. Hence, the formed skeleton structure is more complete, the higher the compressive strength, the higher the peak stress and the lower the peak strain.
3.5. Establishment of Constitutive Equation

The stress-strain curve of GRAC under uniaxial compression has similar geometric characteristics to the ordinary portland cement concrete (in Figure 8). Thus, the stress-strain behavior model of Guo Zhenhai concrete uniaxial compression is adopted in this paper, as shown in equation (3).

\[
y = \begin{cases} 
  \frac{ax + (3-2a)x^2 + (a-2)x^3}{b(x-1)^2 + x} & 0 \leq x < 1 \\
  x & x \geq 1
\end{cases}
\]  
(3)

where \(a\) is up-portion parameter, \(b\) is down-portion parameter. The parameter \(a\) and \(b\) are related to the water-glass module, calculated using the equations (4) and (5):

\[
a = 2.2026 - 0.7466m + 0.1340m^2
\]  
(4)

\[
b = 10.3277m - 5.5359
\]  
(5)

Combining equations (4), (5) and (6), and then introducing \(x = \varepsilon/\varepsilon_{pr}\), \(y = \sigma/\sigma_{pr}\), constitutive equation of compressive strength of GRAC with water glass module as variable was obtained, as shown in equation (6):

\[
\sigma = \begin{cases} 
  f_{pr} \times [(2.02026 - 0.7466m + 0.1340m^2) \times (\frac{E}{E_{pr}} - 2 \frac{E^2}{E_{pr}^2} + \frac{E^3}{E_{pr}^3}) + 3 \frac{E^2}{E_{pr}^2} - 2 \frac{E^3}{E_{pr}^3}] & (\varepsilon \leq \varepsilon_{pr}) \\
  f_{pr} \times \frac{\varepsilon/\varepsilon_{pr}}{(10.3277m - 5.5359) \times (\varepsilon/\varepsilon_{pr} - 1)^2 + \varepsilon/\varepsilon_{pr}} & (\varepsilon \geq \varepsilon_{pr})
\end{cases}
\]  
(6)

4. Conclusions

Water-glass has an electric double-layer structure, high module results in a thin layer and low module results in a thick layer, the thickness of the electric double-layer in water-glass dominates the alkali activate effect and the mechanical strength of GRAC. There are two different gel structure in geopolymer hydration product, C-A-S-H and N-A-S-H, they both contribute to the compressive strength of GRAC.

Size conversion coefficient of GRAC cannot adopt the value specified in the current national standard "Standard for Test Methods for Mechanical Properties of Ordinary Concrete" GB/T50081. The calculation method of size conversion coefficient of GRAC is given in this paper.

GRAC exhibits similar stress–strain behavior to ordinary portland cement concrete, the elastic modulus and peak stress of GRAC are inversely proportional to the water-glass module, the peak

Figure 8. Stress-strain curves of GRAC on different water-glass module.

Figure 9. Elastic modulus, peak stress and peak strain of GRAC on different water-glass module.
strain is proportional to the water-glass module. Moreover, the constitutive equation of the compressive strength of GRAC based on the water-glass module is given.

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