Effect of water glass on setting time and mechanical properties of fly ash slag geopolymer

Tianling Du¹,a*, Yin Liu²,b

¹Research Institute of Highway Ministry of Transport Beijing, China
²Research Institute of Highway Ministry of Transport Beijing, China

a*Corresponding author’s e-mail: 1042736537@qq.com, b-e-mail: tl.du@rioh.cn

Abstract—In this paper, the effects of different modulus and content of water glass(sodium silicate solution) on the setting time and mechanical properties of geopolymer were studied, and the internal reaction mechanism was analyzed. Studies show that the setting time (initial setting and final setting) of fly ash slag geopolymers increases with the rise of the modulus of sodium silicate solution, and the compressive strength increases first and then decreases with the rise of the modulus. The optimal modulus range is 1.2 ~ 1.5. With the increase of the water glass content, the setting time of the slurry material becomes shorter. When the water glass content increases to more than 20%, the compressive strength tends to decrease. This article analyzes the hydration and solidification reaction process of the polymer of fly ash slag geopolymer under water glass excitation.

1. INTRODUCTION

Geopolymer is an alkali-activated gelling material. It is a three-dimensional network aluminosilicate. Polymer composed of crystalline phase and amorphous phase. Geopolymers have excellent properties, such as mechanical properties, low shrinkage, fire resistance, and low energy consumption. They have attracted widespread attention and research from scholars at home and abroad[1-2]. The raw materials for the preparation of geopolymers are very extensive, mainly come from industrial waste residues containing active aluminosilicates, such as fly ash, slag, coal gangue, metakaolin, red mud, among which fly ash and slag are generally materials for research. In engineering practice, in addition to strength as the main property, setting time is another important factor to ensure the completion of preparation, mixing, transportation and pouring operations. Therefore, studying the factors and mechanisms that affect the setting time and mechanical properties of geopolymers has laid the foundation for improving our technology for the preparation of geopolymers from fly ash slag.

Many researchers have studied the factors affecting the strength of geopolymers. For the selection of alkaline stimulants, it is generally considered that the combination of sodium silicate aqueous solution and sodium hydroxide has better excitation effect[3-5]. Zheng Rongjuan et al.[6] studied the effect of sodium silicate modulus on the strength of metakaolin soil polymers, and concluded that compressive strength of the slurry could reach the highest when the sodium silicate modulus was between 0.75 and 1.5. Peng Hui et al.[7] studied the effect of using sodium hydroxide and water glass as a composite alkaline activator on metakaolin soil polymers, and the results showed that the mechanical properties and setting time of geopolymers increased with the increase of sodium hydroxide. Increase then decrease. Cao Dingguo et al.[8] studied the influencing factors of the setting time of geopolymers and
concluded that the base material, the modulus of the stimulant, the amount, the curing temperature, etc. have a greater effect on the setting time. Within a certain range, the setting time increases with the increasing the modulus of activator, decreases with the increasing the amount of the activator, and decreases with the increasing temperature.

In this paper, water glass and sodium hydroxide composite activator were used to prepare fly ash and slag geopolymer. The setting time and mechanical properties of geopolymer were studied by different modulus and dosage of water glass, and the reaction mechanism of fly ash and slag geopolymer was revealed.

2. RAW MATERIALS AND TEST METHODS

2.1. raw materials

2.1.1. fly ash
The chemical composition of fly ash is silicon-aluminum oxide, and its chemical activity depends on the glass content [9]. The chemical composition of fly ash used in this paper is shown in Table 1. The glass content of fly ash is above 80%, which provides sufficient raw materials for the hydration reaction.

| TABLE 1 | CHEMICAL PROPERTIES OF MATERIALS |
|---------|--------------------------|
| content | SiO₂ | Na₂O | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | MnO | TiO | Loss on ignition |
| Water glass | 66.3 | 24.1 | 0.6 | 0.2 | 0.1 | - | 0.17 | 0.41 | 0.57 | - |
| Fly ash | 52.1 | 0.94 | 29.1 | 7.0 | 2.7 | 0.9 | - | - | 4.35 |
| Slag | 31.3 | - | 18.6 | 0.6 | 34.6 | 9.3 | - | - | - |

2.1.2. flag
Blast furnace granulated slag is a kind of waste slag discharged from the blast furnace when smelting pig iron. Its chemical composition is shown in Table 1. It can be seen from the chemical composition of slag that the content of CaO is more than 30%, which is one of the main active components of slag.

The calculated basic coefficient of slag is 0.879, which is acidic slag. The slag has a quality coefficient of 1.935. According to the provisions in GB / T203-2008, a quality coefficient greater than 1.6 is a premium product and has a high activity [10]. The calculation method is as follows:

\[
\text{basic coefficient} = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}
\]

\[
\text{quality coefficient} = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MgO} + \text{TiO}_2}
\]

2.1.3. water glass
Water glass is sodium silicate solution (the following are called water glass). It consists of silicon dioxide and alkali metal oxides. Its molecular formula is Na₂O · nSiO₂. N is the modulus of water glass that is the ratio of SiO₂ and Na₂O. The sodium silicate solution used in this paper is prepared by adding sodium hydroxide with a high modulus (2.8) to a low modulus. It’s baume is 38°degree and a solid content of 63%. Sodium hydroxide uses industrial tablets with a purity of 99%.
2.2. Test method

2.2.1. Setting time test
According to GB/T1346-2011 test method of cement water consumption, setting time, stability test method. The testing equipment is a Vicat instrument(Fig.1). The test mold is a truncated cone with a depth of 40mm ± 0.2mm, a top inner diameter of φ65mm ± 0.5mm, and a bottom inner diameter of φ75mm ± 0.5mm (Fig. 2).

![Figure 1 Vicat](image1)
![Figure 2 Round mold](image2)

Since geopolymer materials are different from Portland cement, the setting time of the slurry is calculated from the addition of the activator. Pure pulp is introduced into the round mold, and placed in a standard curing box for maintenance after demoulding.

2.2.2. Mortar test
According to GB/T17671-1999 test method of cement mortar strength (ISO method), the test piece of cement mortar is prepared with fly ash slag instead of cement material, and then it is put into the curing box for curing after demoulding.

2.2.3. Test plan
The modulus of water glass has a large influence on the setting time. In order to study the influence of the modulus and the amount of water glass on the setting time and strength, six kinds of water glass modulus (0.5, 1.0, 1.2, 1.5, 2.0, 2.5) and five kinds of water glass amounts (5%, 10%, 15%, 20%, 25%) are selected for experimental research. In the mixing ratio, the water-binder ratio is 0.5, the fly ash and slag ratio are listed as 1:1, and the water glass content is 20%.

3. TEST RESULTS AND DISCUSSION

3.1. Effect of setting time

3.1.1. Influence of water glass modulus
The modulus of water glass has a great influence on the setting time of polymer materials of fly ash slag geopolymer. The change rule of setting time with the modulus of water glass is shown in Fig.3: with the gradual increase of modulus, the initial setting time increases gradually. In the actual test, when the modulus is 0.5, the initial setting occurs in a few minutes, even flash setting.
Figure 3  Influence of modulus

When the water glass modulus is 0.5, the solution has a strong alkaline environment, and there are more $OH^-$ in the solution, which makes the Si-O and Al-O bonds in fly ash and slag quickly break and dissolve and react to produce a large amount of hydration products. The slurry quickly coagulated and hardened, and the initial coagulation phenomenon occurred. As the hydration products continued to increase, the final coagulation quickly appeared. On the other hand, the dissolution rate of Ca$^{2+}$ in slag is faster than that of Si$^{4+}$ and Al$^{3+}$. The formation of Ca(OH)$_2$ with $OH^-$ is easy to form CaCO$_3$ with CO$_2$ in the air. These products are wrapped around the particles to prevent further hydration. It can be seen that the content of slag has a certain effect on the setting time.

When the water glass modulus gradually increases, the ratio of SiO$_2$ and Na$_2$O is changed, the content of SiO$_2$ in the solution gradually increases, the alkalinity of the solution gradually weakens, the excitation effect on the powder gradually decreases, and the hydration reaction speed and the amount of produced products is reduced. Therefore, the initial setting time of the slurry is relatively delayed, and the corresponding final setting time is also prolonged.

In conclusion, the modulus of water glass has a great influence on the setting time of geopolymer. In practical engineering application, modulus should be selected reasonably in combination with strength target, construction time and other factors.

3.1.2. Influence of water glass concent

As shown in Fig.4, the setting time of the slurry will gradually shorten with the increase of the content of sodium silicate when the modulus of the activator is fixed at 1.2.

Figure 4  Influence of amount

When the modulus of water glass is constant, the amount of NaOH is constant. The amount of water glass in the solution actually reflects the concentration of Si$^{2+}$ and $OH^-$. If the content is large, the corresponding large amount of $OH^-$ is provided, which will accelerate the breakage of the Si-O and Al-O bonds of the powder. The reaction speed is fast. The generated products are mostly wrapped on the surface of the powder particles, preventing further dissolving of particles. So it shows a shorter
setting time. On the contrary, when the content of water glass is low, the concentration of $OH^-$ is less, the speed of dissolving $Si^{4+}$ and $Al^{3+}$ is slow, so the setting time of slurry is slow.

3.2. Effect of strength

3.2.1. Influence of water glass modulus

As shown in Fig. 5, the strength of water glass increases first and then decreases as the modulus increases. When the modulus is in the range of 1.2 ~ 1.5, the intensity reaches the maximum value.

![Figure 5 Influence of modulus](image)

When the water glass modulus is low (0.5), the alkalinity of slurry is strong. The Si-O and Al-O bonds in the powder quickly dissolve in a strong alkali environment, and $Ca^{2+}$ dissolves first. Dissolved products interact to form oligomers and gels form between the oligomers that cover the on the surface of the particles that preventing the powder particles from dissolving and the hydration reaction from further progressing, which affects the development of strength. When the water glass modulus is increased to 1.2 ~ 1.5, the products gradually form as the reactants continue to dissolve. The formation of C-S-H gel promotes the formation of $OH^-$, which promotes the sufficient dissolution of $Ca^{2+}$, $Al^{3+}$, $Si^{4+}$ and deep polymerization reactions. Polymerization and destruction are matched. So the large number of gel structures generated can also fill the pores and make the structure denser, so the strength is high. When the modulus is increased to 2.0 and above, the $OH^-$ in the solution is relatively small, the amount of $Si^{4+}$ and $Al^{3+}$ dissolved is less, the reactants are formed less, it is difficult to form macromolecular aggregates, and the silicon dioxide in the solution is greatly increased. Although hardened body is formed, its strength is low. Therefore, the slurry appears with lower strength. REE, Barbosa et al. [11-12] showed that the concentration of NaOH not only determines the rate of raw material decomposition, but also determines the rate of product. Although excessive NaOH accelerates the rate of polymerization, the strength of geopolymer will be further reduced.

In summary, When the water glass mold is gradually increased to 1.2 to 1.5, the compressive strength can reach the highest value.

3.2.2. Influence of water glass concentration

As shown in Fig. 6, the compressive strength of the fly ash slag geopolymer increases with the increase of the content of water glass, but above 20%, the strength will not increase, or even decrease.
The amount of water glass determines the concentration of SiO₂ and Na₂O in the solution. When the content is low, less OH⁻ is introduced, which does not provide a favorable excitation effect. There are fewer reactants and products, which is not good for strength. When the amount of water glass is gradually increased, there are more OH⁻, and the excitation speed is accelerated, which causes a large number of Al-O and Si-O bonds to break. The dissolution rate and quantity of Al³⁺ and Si⁴⁺ also increase accordingly, forming more hydrated calcium silicate gels and hydrated calcium aluminosilicates and other products, which overlap and to form a polymer structure with a certain strength. However, when the content exceeds 25%, a large amount of products are quickly generated to coat the surface of the particles, preventing the hydration reaction from proceeding further, which is not conducive to the improvement of strength.

In summary, when the content of water glass exceeds 20%, the strength will decrease. Considering economic factors, it is not easy to exceed 20%.

3.3. Geopolymer reaction mechanism of fly ash slag

The reaction of fly ash slag geopolymer is mainly the reaction process between solid phase fly ash and slag particles and sodium silicate activator solution.

When water glass is used as an activator, the hydrolysis reaction of water glass should first generate NaOH and Si(OH)₄. At this time, Ca²⁺, Mg²⁺ were first dissolved on the surface of the slag, and then adsorbed OH⁻ in alkali medium that cause damage to the surface structure. Ca(OH)₂ reacts with glass micelles H₄SiO₄⁻ to form a C-S-H gel, see equation (1). As the alkalinity of the solution increases, Si-O and Al-O bonds in the slag glass are broken. Dissolved Si⁴⁺ and Al³⁺ the -Si-OH and -Al-OH monomers are formed, which interact to form initial oligomers and this oligomers form gel particles with increase of oligomer concentration. The formation of a hydrated calcium silicate gel promotes the continuous ionization of OH⁻, and promotes the depolymerization continues, the oligomer concentration gradually increases, forming gel particles on the surface of the raw material . At the same time, the alkaline metal Na²⁺ participates in the reaction and the gelatin particles are dehydrated and condensed to form larger gel particles, see equation (2), equation (3). The polymerization products re-polymerize and overlap with each other, eventually forming an aluminosilicate network structure, finally the strength is formed.

\[
4OH⁻ + 2H₂SiO₄⁻ + 3Ca²⁺ \rightarrow C-S-H + 2H₂O \quad (1)
\]

\[
n(OH)_₃ \cdot Si-O-Al-O(OH)_₃ \xrightarrow{NaOH} \{Na\}_n[Si-O-Al-O-Si]_n + 3nH₂O \quad (2)
\]

\[
n(OH)_₃ \cdot Si-O-Al-O-Si[OH]_₃ \xrightarrow{NaOH} \{Na\}_n[Si-O-Al-O-Si-O]_n + nH₂O \quad (3)
\]
Function of mineral powder: the quality coefficient of slag selected in this paper is greater than 1.6 (see Table 1), with high activity. In the polymer system of fly ash and slag, slag has a great promotion effect on the depolymerization of raw materials.

The water glass solution can not only provide the OH- needed for depolymerization of raw materials, but also provide the silicate ion group needed for polymerization reaction.

4. CONCLUSION

(1) The modulus of water glass has a significant effect on the setting time and mechanical properties of fly ash and slag ground polymer. The setting time of the slurry increases with the increase of the modulus of the water glass when the dosage is constant. Compressive strength generally increases first and then decreases with the increase of modulus of water glass. In order to ensure the best strength performance, the modulus range of water glass is recommended to be between 1.2 and 1.5.

(2) The setting time of slurry increases with the increase of water glass content. There is an optimal content of 20% for the influence of the content of water glass on the strength, which will not increase but decrease when the content exceeds.

(3) The alkalinity of the solution is an important factor affecting the mechanical properties and setting time of geopolymers. When the modulus and content of water glass change, it is actually the alkalinity of the solution has changed, so it directly affects the number of product and reaction speed.

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