Influences of Sodium Silicate Modulus on Mechanical Properties and Microstructure of Fly Ash Geopolymer

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Abstract. In order to explore the water glass modulus that can make the fly ash base polymer the highest strength and the best performance, fly ash is used as the raw material to prepare alkali-activated fly ash-based geopolymer test blocks. Through unconfined compression test, SEM test, XRD test, the influence of different water glass modulus and age on its mechanical properties is studied. The results are as follows. When the sodium silicate modulus is 1.1, the strength of fly ash-based geopolymer is the highest, reaching 6.1MPa after 28 days of curing. With the growth of age, the strength of fly ash-based geopolymers continues to increase. It is observed from the SEM test that when the modulus is 1.1, the structure is dense, the porosity is small, the alkali excitation effect is obvious, and the reaction is relatively complete.

1. Introduction
Geopolymer is a new type of green building material, referred to as geopolymer. It is an amorphous three-dimensional network structure polymer formed from silicon-alumina raw materials under the action of an alkali activator. In 2019, the global cement trade volume was about 280 million tons[11], and the price of cement is high. To achieve the same strength effect, some cheap substitutes can be found. As an industrial waste, fly ash has a global output of approximately 1.143 billion tons in 2016[2]. If we can make full use of it, not only can we reduce industrial waste, but also greatly reduce the consumption of cement, which will kill two birds with one stone. Therefore, the research of geopolymer materials represented by fly ash has received extensive attention from scholars at home and abroad[3,8]. The factors that affect the mechanical properties of geopolymers include the properties of the raw materials themselves, the concentration and type of alkali activator, curing temperature, water-to-binder ratio (solid-to-liquid ratio), curing time, etc.

Different researchers use different raw materials. For example, kaolinite[9,11], slag, and fly ash are used as raw materials. Some scholars combine them to study mechanical properties and obtain certain research results. Zhao Renda et al.[12] obtained a large amount of research and found that the total drying shrinkage strain of slag-based polymer concrete is larger than that of fly ash-based polymer concrete. If the same material is taken from different factories, its performance will be different. Liang Jianjun et al.[13] selected 6 different types of fly ash and 1 type of slag, and studied the effects of their chemical composition, activity and ash body fineness on the setting time and strength of alkali-excited geopolymers, and they concluded the higher the content of calcium, iron and aluminum in fly ash, the shorter the setting time. There is also research on increasing the strength of geopolymers by adding some other substances to the raw materials: Wang Chunxue et al.[14] used steel slag and fly ash as raw materials.
materials to study the compressive strength of different content of steel slag on fly ash base polymers. It is concluded that the geopolymer structure formed when the steel slag content is 30% is the densest and the porosity is the lowest. Geopolymers have been extensively studied in foundation reinforcement: Liu Songyu et al.\cite{15} studied the role of industrial waste lignin in improving silt roadbeds, and compared them with lime improvement, and found that the quality of lignin solidified and improved silt roadbeds meets the secondary standard in conclusion. The strength of the geopolymer generally increases with time. Li Hui et al.\cite{16} used fly ash as a raw material and NaOH as an activator to explore the effect of curing conditions on fly ash. The results showed that the strength of the fly ash test block increased with time. Peng Hui et al.\cite{17} used the orthogonal test method to study the influence of alkali activator concentration and curing temperature on the mechanical properties of metakaolin, and concluded that the alkali activator concentration has the greatest influence on it. At the same time, with the increase of curing time, the strength continues to increase. There are many types of alkali activators, and the combination of NaOH and water glass is generally used as the alkali activator, and the effect of alkali excitation is remarkable. Rao Shaojian et al.\cite{18} used sodium water glass as an alkali stimulator to study the influence of the solid phase composition of sodium water glass on the compressive strength of geopolymers, and found that when the modulus is 1.5 and the content of Na2O is 10%, the soda water glass has the best excitation effect on the geopolymer. Xue Caihong et al.\cite{19} prepared fly ash-based geopolymers by adding NaOH to water glass to adjust its modulus. It is concluded that the strength of the geopolymer is the highest when the water glass modulus is 1.2, the molar ratio of silicon to aluminum is 1.96, and the curing temperature is 60°C. Long Tao et al.\cite{20} used needle-like sodium hydroxide and sodium silicate as alkali activators, and replaced natural coarse aggregate with recycled coarse aggregates, and compared and analyzed the difference in mechanical properties between geopolymer recycled concrete and ordinary recycled concrete, and concluded that at different ages, the strength of geopolymer recycled concrete is higher than that of ordinary recycled concrete.

Nowadays, fly ash is widely used in engineering construction, but the effective utilization rate is low. Alkali activator can improve the activity of fly ash. In order to explore the most suitable alkali activator modulus, different water glass modulus and Age-old fly ash-based geopolymer test block, to study the influence of different sodium silicate modulus and age on its compressive strength, and use unconfined compressive test, SEM test, XRD test to characterize the sample to explore their rule.

2. Materials and Methods

2.1. Experiment material

The fly ash used in the test was taken from a coal-fired power plant in Zhengzhou City, Henan Province. It is a low-calcium fly ash with a cement-colored powder appearance. It is composed of SiO2, Al2O3, CaO and Fe2O3. The specific content is shown in Table 1. The liquid water glass (sodium silicate) used in the experiment comes from a company in Nanchang, and its main components are sodium oxide (9.03%) and silicon oxide (24.7%), with a modulus of 2.8 and a wave density of 38. Use NaOH to adjust the modulus of water glass. The NaOH used is produced by a company in Tianjin and is a white uniform granular solid. The ratio of test water and water glass is 1:1.

| Ingredient | SiO2 | Al2O3 | CaO | Fe2O3 | K2O | TiO2 | MgO | Na2O | SO3 | P2O5 |
|------------|------|-------|-----|-------|-----|------|-----|------|-----|------|
| contents   | 54.94| 34.86 | 2.63| 2.52  | 1.76| 1.25 | 0.779| 0.475| 0.313| 0.232|

Table 1 Main components of fly ash
2.2. Experiment method

Assuming that the fly ash is taken as mg, the water comes from two parts, the water in the water glass and the added water, and the water glass and water are both a, and the specific content is calculated by the following formula [21]:

\[
\frac{\text{Proportion of water in water glass} \times a + a}{\text{Proportion of solids in water glass} \times a + m} = \text{Water} - \text{binder ratio}
\]  (1)

Solve the amount of water and water glass added according to this formula, and set the water glass modulus to 0.8, 1.1, 1.3, 1.5. Based on this, the amount of NaOH added to the water glass is solved. The specific test plan is shown in Table 2.

Table 2 Testing programs

| Water glass modulus | 0.8 | 1.1 | 1.3 | 1.5 |
|---------------------|-----|-----|-----|-----|
| NaOH/%              | 29.464 | 18.248 | 13.648 | 10.272 |

Pour NaOH into the weighed water glass solution to adjust the water glass modulus, and pour the adjusted water glass and water into the fly ash. Use a mixer to stir the alkali-activated fly ash pure slurry evenly, and pour it into a triple test mold to form. Make three parallel samples for each group of samples, and place them on a vibrating machine to vibrate and ram. The test block was allowed to stand for 24 hours, then demoulded, and cured to 7 d, 14 d, and 28 d age respectively. Then use the SANS universal testing machine for unconfined compressive strength test.

Use the SEM testing machine to do the micro test. Take the uniform internal sample after the unconfined experiment and cut it into blocks of appropriate size. After drying, break it into two rectangular parallelepipeds with natural cross-sections, blow off the surface powder, and plate gold on the cross-sections. Otherwise, the accumulation of electric charge on the surface of the cross-section will cause electric discharge, which will affect the image quality. The magnifications are 500 times, 800 times, 1000 times and 1500 times respectively. Take part of the powder and pass it through a 0.02 mm sieve. After drying, use a D/max2500PC X-ray diffractometer for X-ray diffraction experiment (XRD) to analyze the phase and structure of fly ash. The scanning range is 5° ~ 95°.

3. Test results and analysis

3.1. Unconfined compressive strength

Table 3 shows the corresponding unconfined compressive strength values of geopolymer test blocks under different water glass moduli and ages. Figure 1 is a histogram of the influence of different curing ages and water glass modulus on the unconfined compressive strength of geopolymers. The horizontal axis is the water glass modulus and the vertical axis is the unconfined compressive strength.

Table 3 Unconfined compressive strength corresponding to different modulus and age

| Water glass modulus | 0.8 | 1.1 | 1.3 | 1.5 |
|---------------------|-----|-----|-----|-----|
| Unconfined 7 d      | 0.92 | 1.774 | 1.48 | 0.71 |
| Compressive strength/MPa | 14 d | 3.35 | 2.92 | 0.74 |
| 28 d               | 2.55 | 6.1 | 2.95 | 1.5 |
It can be seen from Figure 1 that the water glass modulus and curing age have a significant impact on the mechanical properties of fly ash. The specific effects are as follows: As the modulus of water glass increases, the compressive strength first increases and then decreases, and the highest compressive strength corresponds to the modulus of 1.1, which shows that the excitation effect is the best. Alkali activator can depolymerize the glass body in fly ash, that is, the Si-O and Al-O bonds in the glass body are broken, SiO$_4$ tetrahedron and AlO$_4$ tetrahedron are quickly released, and polycondensation reaction occurs at the edge of the glass body to form amorphous Phase N-A-S-H gel. Therefore, when the alkali activator is selected appropriately, the performance of fly ash can be significantly improved. When the modulus of water glass is too large and the pH is too high, Al(OH)$_4$-, (OH)$_2$SiO$_2$-$^2$-, (OH)SiO$_3$-$^3$- will be formed, which is not conducive to the formation of N-A-S-H gel and reduces the impact of polymerization. However, when SiO$_2$ reacts to form amorphous silicate, it will affect the formation of N-A-S-H gel, which is not conducive to the strength of the fly ash test block. Overall, the water glass modulus has a significant impact on the unconfined compressive strength of fly ash-based geopolymers.

The selected curing ages are 7 d, 14 d, and 28 d. As the age increases, the unconfined compressive strength shows an increasing trend. In this test process, the longer the age, the higher the strength of the fly ash test block. When the modulus is 0.8 and 1.1, the age has the most obvious influence on the compressive strength of the fly ash test block, and the alkali is not excessive at this time. The 14 d compressive strength is significantly higher than 7 d, while the 28 d compressive strength is significantly higher than 14 d, which shows that as time increases, N-A-S-H gel fills the pores of the fly ash test block more and more fully, and the polymerization effect is better. When the modulus is 1.3 and 1.5, the age has little effect on the compressive strength of the fly ash test block, but with the increase of time, the strength continues to increase. Part of the reason is that SiO$_2$ reacts to form amorphous silicate, which is then exposed to the air. The CO$_2$ reacts with H$_2$O to form silicic acid colloid, which has a certain cementing and filling effect on the particulate matter in the fly ash test block, and has a certain effect on the increase of the strength.

3.2. The microstructure of geopolymers

Figure 2 shows the microstructure of fly ash test blocks with a modulus of 1.1 at different ages. The sphere in the picture is fly ash particles, and the N-A-S-H gel is wrapped on the surface. The bright white outside the N-A-S-H gel is the phenomenon of frosting. It can be seen from Figure 2 that with the increase of time, the polymerization reaction becomes more and more complete, and the N-A-S-H gel wraps more and more comprehensively, from obvious granular solids to fully cemented block solids. On the whole, it changes from a spherical shape to an irregular corroded shape, and small pores gradually disappear. In the end, only the large pores between the blocks are left. This shows that as the age increases, the porosity of the test block decreases and the strength increases. At 7 d, the fly ash particles are still obvious, with large or small particle sizes, and a small amount of N-A-S-H gel is
coated on the surface, which is not compact. At 14 d, the geopolymer sample is frosted and the reaction proceeds further, and the surface of the spherical particles is covered with a small amount of N-A-S-H gel. At 28 d, the reaction has proceeded sufficiently, there are almost no spherical fly ash particles, and the color becomes lighter, indicating that part of the water in the structure has evaporated, and the fly ash block shows obvious signs of corrosion. The N-A-S-H gel tightly surrounds the fly ash particles. As explained above, the longer the time, the more complete the reaction, the better the cementing effect, and the higher the strength of the geopolymer.

Figure 3 shows the microstructure of geopolymers with moduli of 0.8, 1.1, 1.3 and 1.5 at 28 d. The microstructure of the geopolymer with a modulus of 0.8 looks smooth, with some N-A-S-H colloids on the surface and uneven distribution, and some crystals are small particles accumulated around the fly ash particles, with many pores, and some small cracks due to drying. Some fly ash particles have strip gels on the surface. Geopolymers with a modulus of 1.1 have a rough surface and are severely corroded. Small salt particles are precipitated. The fly ash particles are completely cemented by the N-A-S-H gel. The particles are densely connected, with few and small pores. The microscopic morphology of the geopolymer with a modulus of 1.3 is similar to that with a modulus of 1.1. The difference is that when the modulus is 1.3, the cementation is not complete, and part of the N-A-S-H gel wraps the fly ash particles and is not on the same plane as the surrounding solids. And less dense than 1.1 modulus. The microstructure of the geopolymer with a modulus of 1.5 is more dispersed, mainly when the modulus is at 1.5, excessive alkali affects the formation of N-A-S-H gel, resulting in insufficient colloid to cement the fly ash particles. Therefore, the graph in Figure 3 (d) looks more dispersed and the fly ash particles are relatively complete. As explained above, as the modulus of the water glass increases, the strength of the geopolymer first increases and then decreases. When the modulus is 1.1, the excitation effect is the best. When the modulus is 1.5, the excitation effect is the worst.
3.3. Phase composition

Figure 4 shows the diffraction patterns of geopolymers with different moduli at 28 d. As the modulus of water glass increases, the sharp peaks of the samples shift, indicating that the amorphous glass phases of geopolymers with different moduli are different. New substances are produced. The analysis shows that the new substance is calcite. The stronger the alkalinity, the higher the calcite content. The chemical formula of calcite is CaCO₃. When the alkalinity is reasonable, Ca²⁺ combines with other substances to form ettringite crystals, which play a filling role and increase the strength of the test block by increasing the density. The reaction equation is [22]:

\[
6\text{Ca}^{2+} + 2\text{Al}^{3+} + 12\text{OH}^- + 3\text{SO}_4^{2-} + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]

(2)

When the alkali content is too high, calcium hydroxide reacts with carbon dioxide in the air to form calcium carbonate precipitate, which is calcite powder. Calcite powder is not conducive to the formation of gel and reduces the strength of fly ash base polymer. The analysis in Figure 4 shows that the higher the modulus, the greater the probability of calcite appearing, which is consistent with the theory in the above cited literature.
(2) It can be seen from the microscopic test that after excitation, the surface of fly ash is covered by N-A-S-H gel. Water glass of suitable modulus reacts with fly ash to form a gel to fill the pores of the fly ash geopolymer sample. The main reason for the increase in the strength of the geopolymer is the filling effect and the cementing effect.

(3) It can be obtained from the X-ray diffraction test that the geopolymer samples in this research contain mullite, quartz and calcite. Among them, the increase in the modulus of water glass makes it difficult to generate cementitious materials, and the probability of calcite is increased. Because the generated calcite is powdery and difficult to cement, the compressive strength of fly ash geopolymers is reduced. Therefore, the modulus of water glass should not be too high, and 1.1 is the best.

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