



Application Research of Alkali Activated Ternary Geopolymer in the Field of Engineering Materials

Lijuan Su*, Siqu Li, Siyao Wu

School of Civil Engineering, Liaoning Technical University, Fuxin 123000, China

*Corresponding author: E-mail:lisiqu1909543254@qq.com

Abstract. In order to help achieve the "dual carbon" goal in the cement industry, new engineering materials are actively introduced into green buildings, and a new type of multi solid waste low-carbon cementitious material is developed to replace traditional cement. This article uses granulated blast furnace slag (GBFS), fly ash (FA), municipal solid waste incineration fly ash (MSWI FA), NaOH, and liquid water glass to prepare ternary geopolymer cementitious materials, and explores the influence of various ratios between cementitious systems on mechanical properties. And X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) were used to analyze its microstructure, revealing its macroscopic mechanical properties and microstructure evolution mechanism. The macroscopic results indicate that the modulus of water glass has a significant impact on the flow properties of cementitious materials; The compressive strength of the specimen shows a peak with the increase of water glass modulus and alkali content. The microscopic results show that with the increase of curing age, the hydration products of the specimens are mainly calcium silicate hydrate gel (C-S-H) and calcium aluminosilicate hydrate gel (C-A-S-H). The gel products increase, forming a dense structure, significantly enhancing the strength characteristics of engineering materials.

Keywords: engineering materials; Geopolymer; Strength characteristics; Microstructure

1 Introduction

In recent years, with the rapid development of China's economy, the scale of urban construction and infrastructure construction have continued to expand, and the amount of cement concrete used in various projects is enormous and continues to grow. However, the production process of cement not only consumes a large amount of energy, but also generates a large amount of greenhouse gases such as carbon dioxide. Replacing traditional cement with low-carbon cementitious materials using diverse solid waste can not only significantly reduce environmental pollution, but also effectively reduce carbon emissions. In addition, by using industrial waste as raw materials, it is possible to reduce the consumption of natural resources and achieve

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resource utilization^[1]. This new type of green engineering material has minimal environmental pollution during production and use, which is in line with the concept of sustainable development.

Geopolymer is a new type of inorganic polymer, which has environmental protection properties and is widely used in industrial fields. It refers to a class of natural or artificial composite silicate solid engineering materials processed by certain processes using clay and other non-polar minerals as raw materials, which are mainly used in building materials, civil engineering and construction industry^[2]. Compared with traditional cement, geopolymer not only shows lower CO₂ emission in the production process, but also has higher early strength, better volume stability, stronger erosion resistance and impermeability, and excellent durability, so it has been widely used in the field of building engineering materials^[3]. Ma Wei et al.^[4] prepared alkali-excited slag-flyash-silica fume geopolymer concrete (ASFSGC), and studied its workability, quasi-static mechanical properties and impermeability. Kong Fanlong et al.^[5] studied the influence of different slag content on the rheological properties and strength of the base polymer of CFB fly ash, as well as the reaction mechanism of slag-fly ash composite geological polymerization. In this paper, a new type of engineering material is studied, and the effects of material mix ratio, sodium silicate modulus and alkali amount on the new engineering material are systematically analyzed. Hope to provide a new direction for the development of engineering materials in the future.

2 Materials and Testing

2.1 Raw Materials

MSWI FA: It uses circulating fluidized bed waste incineration fly ash produced by Fuxin Municipal Waste Incineration Plant. MSWI FA is brown in color and has a granular texture. It contains a very small amount of unburned metal and glass products. The crystal composition analysis of MSWI FA using X-rays is shown in Figure 1. The MSWI FA was analyzed for particle size using a laser particle size analyzer, as shown in Figure 2. Fly ash: The coal ash residue generated during the combustion process of a power plant in Henan Province is mainly derived from fine ash in the flue gas. Slag: S95 grade slag produced by a water purification company in Shenyang is used. The slag is white in color, with a density of 3.1g/cm³ and no obvious particle texture. The particle size of slag is relatively small, mainly concentrated between 1-10 μm. The main chemical composition of each raw material is shown in Table 1.

Stimulating agent: Alkaline activators are obtained by compounding liquid water glass and sodium hydroxide. Liquid water glass is provided by a chemical technology company in Shenyang, with a modulus of 3.2, a Baume degree of 38, a SiO₂ content of 27.00%, Na₂O content of 8.50%, and a solid content of 38; Sodium hydroxide particle analysis provides commercially available sheet-like samples with a purity greater than 99% for a chemical reagent company in Fuxin City, used to adjust the liquid water glass modulus; Water: Laboratory tap water.

Table 1. Main components of experimental materials

Ingredients (%)	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	Na ₂ O	MgO	SO ₃	Others
Fly ash	12.6	30.2	5.35	45.1	0.31	1.22	2.36	2.86
MSWI FA	24.49	17.46	5.29	25.36	5.43	5.33	5.63	1.79
Slag	40.61	14.84	0.39	29.27	1.18	8.53	3.96	1.67

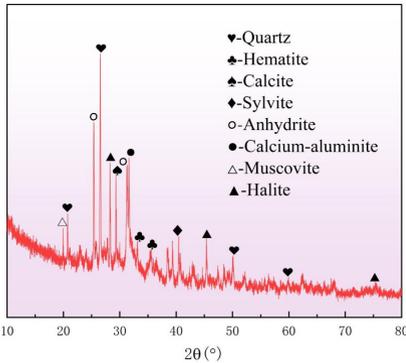


Fig. 1. XRD pattern of MSWI FA

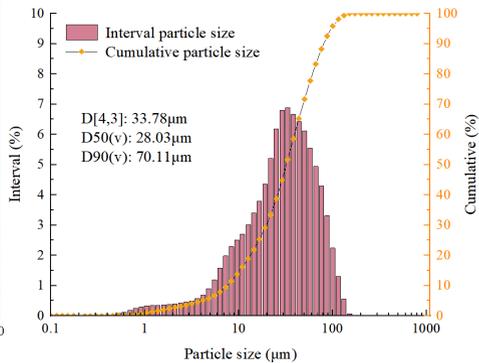


Fig. 2. Particle size distribution of MSWI FA

2.2 Sample Preparation

Mixing ratio design: Taking the content of MSWI FA, the modulus of water glass and the content of alkali (the proportion of Na₂O in the activator to the total mass of MSWI FA and slag) as variables, the experimental ratio was set by controlling variables, as shown in Table 2.

Preparation of geopolymer: MSWI FA, slag and fly ash required by the test design were separately weighed, liquid water glass, NaOH and water were measured and prepared into alkali solution, and then poured into a glass and stirred evenly. Pour the geopolymer paste into the 40mm×40mm×40mm triple mold while stirring, scrape off the excess paste with a flat ruler, and then vibrate with a shaking table for 3min. After 24 hours of curing at room temperature, the mold was removed, and the samples were put into the YH-60b standard cement constant temperature and humidity standard curing box for curing. The curing temperature was 20°C, the humidity was above 95%, and the curing was until the specified age.

Table 2. Test mix ratio

MSWI FA content/%	Water glass modulus	Alkali content/%
10, 20, 30, 40	1.2	6
30	1.0, 1.1, 1.2, 1.3	6
30	1.2	2, 4, 6, 8

2.3 Testing Methods and Processes

(1) Compressive strength test: Polish the two ends of the cured cylindrical specimen flat and place it on a computer-controlled electronic universal testing machine (testing machine model: Jinan Times Assay WDW-100E). Load it by displacement loading at a loading rate of 0.5mm/min. Take the average compressive strength of three identical specimens as the final compressive strength of the ratio, as shown in Figure 3.

(2) Flow performance analysis: The flowability and flowability loss of freshly mixed slurry shall be determined in accordance with the "Test Method for Homogeneity of Concrete Admixtures" (GB/T 8077-2000). Place the truncated cone circular mold (with an upper diameter of 36mm, a lower diameter of 60mm, and a height of 60mm) on a smooth glass plate placed horizontally. Inject fresh slurry into the truncated cone circular mold, lift the mold vertically upwards and start timing, allowing the slurry to flow naturally for 30 seconds. Measure the two diameters of the slurry perpendicular to each other with a ruler, and take the average diameter as the flowability, as shown in Figure 4.

(3) Microscopic testing: XRD (model: Rigaku Ultima IV; Japan) is used to analyze the mineral composition of raw materials and samples; FTIR (model: Thermo Scientific Nicolet iS10) is used to analyze the molecular structure and chemical bonds of materials; SEM (German Carl Zeiss SUPRATM55) is used to observe the microscopic morphology and elemental composition of the sample.



Fig. 3. Compressive strength test



Fig. 4. Fluidity test

3 Results and Discussion

3.1 Analysis of Compressive Strength

3d, 7d, and 28d compressive strength tests were conducted on specimens with different mix proportions, and the test results are shown in Figure 5. From the data in the figure, it can be seen that the overall trend of compressive strength of slag fly ash based ternary geopolymer varies with the dosage of MSWI FA, the modulus of alkali activator, and the alkali dosage. That is, the unconfined compressive strength of each mix proportion specimen decreases with the increase of MSWI FA dosage, and shows

a trend of first increasing and then decreasing with the increase of alkali activator modulus and alkali dosage. The reason for this is that when the dosage of MSWI FA increases, due to the weak chemical activity of MSWI FA itself, the degree of polymerization reaction in the system decreases, and MSWI FA particles are difficult to be fully and effectively excited. Therefore, the increase in MSWI FA dosage leads to a decrease in the compressive strength of the specimen; An increase in the modulus of water glass helps to improve the early strength of the specimen. This is because an increase in the modulus of water glass can bring more abundant $[\text{SiO}_4]^{4-}$ to the system, leading to the formation of more complex polymers from silicates, which then transform into a structurally complex three-dimensional network skeleton. However, too high sodium silicate modulus will reduce the solubility of Ca^{2+} in the system, thus reducing the C-S-H gel generated by hydration and reducing the compressive strength of geopolymer [6].

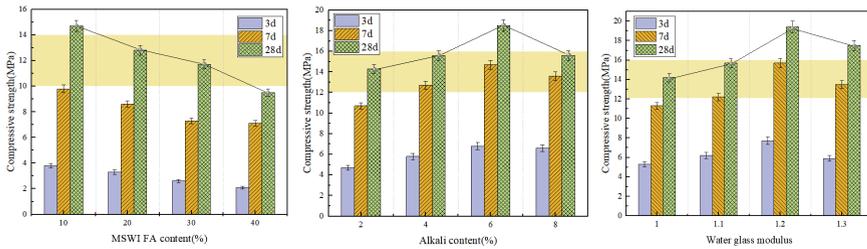


Fig. 5. The influence of various factors on the compressive strength of cementitious materials

3.2 XRD and FTIR Testing of Optimal Mix Proportion Samples

The XRD patterns of some samples at different ages are shown in Figure 6(a). From the figure, it can be seen that the X-ray diffraction peak shapes of MSWI FA solidified bodies are basically the same at different ages, with the difference being that the peak values of reaction product content have changed. After analysis, the diffraction peak near 26.6° is SiO_2 , which gradually decreases with the extension of curing age. This indicates that active SiO_2 continuously participates in the polymerization reaction, generating amorphous phase products through the cleavage of Si-O bonds and the polymerization reaction of active substances such as Ca^{2+} and Al_2O_3 in the system. With the increase of curing age, the diffraction peak of calcium sulfate dihydrate gradually decreased, which may participate in the hydrolysis polymerization reaction in the system and produce a small amount of ettringite (Aft) and other products. Figure 6(b) shows the Fourier infrared spectra of some samples. The absorption bands at 3604cm^{-1} and 1650cm^{-1} are related to the stretching vibration of O-H in the crystal water and the bending vibration of H-O-H in the interlayer water. The interlayer water is usually adsorbed on the polymer surface or filled in the pores of gel products and is not easy to flow freely, playing a certain role in bearing weight. The C-O asymmetric stretching and bending vibration peaks in CO_3^{2-} appear around 1400cm^{-1} and 890cm^{-1} , which reflects the presence of a certain amount of calcite in the sample. The spectrum in the range of 900cm^{-1} - 1200cm^{-1} is generally an asymmet-

ric stretching vibration of Si-O-Si or Si-O-Al structure, so the peak near 970cm^{-1} in the figure is the asymmetric stretching vibration peak of Si(Al)-O bond. Based on relevant literature, it can be judged that this is the characteristic peak of C-(A)-S-H or N-A-S-H gel^[7]. With the increase of curing age, more gel products appear in the cured body, which is conducive to the improvement of strength characteristics of engineering materials.

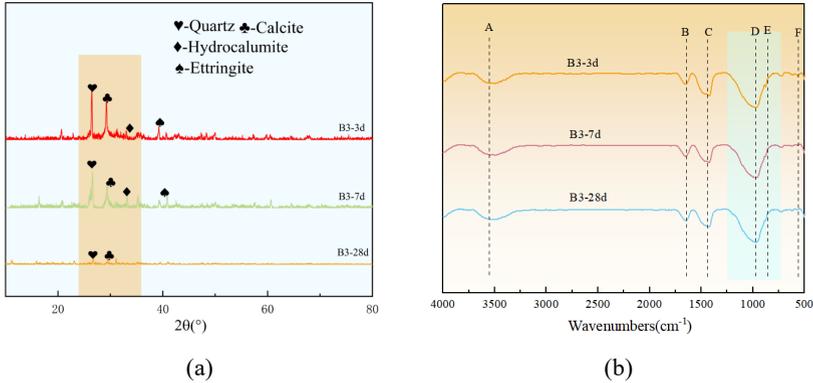


Fig. 6. XRD, FTIR spectra and peak separation at different age groups

3.3 SEM testing of Optimal Mix Proportion Samples

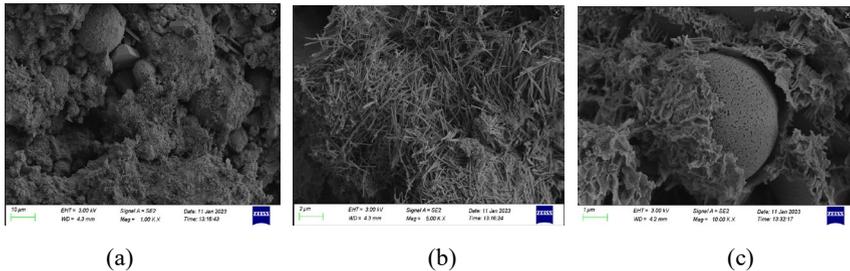


Fig. 7. Microstructure of specimens at different ages

This time, B3 group samples were selected for scanning and comparative analysis, and the microstructure characteristics of different age groups were observed as shown in Figure 7. It can be seen from 7 (a) that the surface morphology of the solidified body is dense, and gel like substances wrap raw materials that are not completely reacted. It can be seen from 7 (b) that clusters or needle like substances grow on the surface of spherical particles. It is preliminarily judged that the surface of spherical particles reacts with alkali activator to generate zeolite and other substances, which are closely linked with surrounding gel products. Figure 7 (c) shows the dense structure in the solidified body more clearly, and a large number of cluster products fill the gaps in the test block, making the gel tightly wrapped with the raw material. A large

number of layered products are stacked and covered on the surface of the material, overlapping with ettringite, connecting the two parts of the raw material particles together, enhancing the system density, reducing the negative impact of pores, and resulting in a denser structure^[8].

4 Conclusion

(1) Based on comprehensive compressive structure and microscopic analysis, a suitable engineering material ratio was obtained: MSWI FA: fly ash: slag ratio of 3:3:4, modulus of 1.2, and alkali content of 6%.

(2) The compressive strength of ternary geopolymer increases first and then decreases with the increase of water glass modulus and alkali content, and gradually decreases with the increase of MSWI FA content. It is due to the increase in the modulus of water glass and the amount of alkali used that more $[\text{SiO}_4]^{4-}$ dissolves in the system, forming more complex polymers. However, too high alkaline concentration and water glass modulus will reduce the solubility of Ca^{2+} in the system, thus reducing the strength of C-S-H gel. The analysis of the microstructure of the geopolymer by SEM, XRD and FTIR shows that the more C-S-H gel produced by the ternary geopolymer, the more compact its structure and better strength characteristics.

(3) The application of alkali activation technology in the field of engineering materials is extensive and diverse. In addition to being used for the preparation of building materials such as alkali activated fly ash cementitious materials, the recycling of concrete, and the active preparation of lightweight concrete, this experiment further expands the application field of this technology by preparing a new type of engineering material through alkali activated technology. This new type of material not only inherits the high strength and durability of traditional cement engineering materials, but also has better environmental performance and resource utilization efficiency.

In summary, this experiment successfully prepared a new type of engineering material, and through in-depth research on its properties, laid the foundation for its wide application in the engineering field. In the future, we will continue to explore the application of alkali activation technology in the preparation of other new engineering materials, promoting innovative development in the field of engineering materials.

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