PAPER • OPEN ACCESS

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To cite this article: H Q Ma *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **474** 012040

View the article online for updates and enhancements.

Effects and mechanisms of slag reinforced coal gangue geopolymers

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Abstract. This paper uses alkali activators with the modulus of 1.30 to prepare coal gangue geopolymers, thereby studying the reinforcement effects of slag content on coal gangue geopolymers. Besides, XRD, TG-DTG, and SEM are introduced to analyze changes in the microstructure and further explore the change mechanisms. The experimental results show that the compressive strength of coal gangue geopolymers increases with the increase in slag content. Compared to the P.O 42.5 pure cement paste, coal gangue geopolymers can obtain higher early strength. Besides, the 28d compressive strength of coal gangue geopolymers is greater than P.O 42.5 pure cement specimens when the slag content is 20%. The geopolymer products of slag-containing coal gangue geopolymers are C-(A)-S-H and N-A-S-H gels. The two kinds of gels, which are highly compatible, jointly constitute the network-like disordered structure of polymers. The XRD, TG-DTG and SEM results are consistent with the strength analysis results.

1. Introduction

The cement industry has always been a heavy polluter among the various building materials industries. About 1.6 billion tons of cement is consumed annually, emitting 150.4 million tons of CO_2 [1-2]. Cement accounts for 5% to 8% of global CO_2 emissions [3]. Therefore, it is the development direction of modern cement industry to develop green ecological cement. Geopolymers mainly refer to inorganic polymeric aluminosilicate materials that have similar properties to cement. Studies have shown that geopolymer cement has high strength, corrosion resistance, fire resistance and better durability [4-7]. Geopolymers have become the most promising cementitious materials to replace cement due to their low carbon footprint.

Coal gangue coexists with coal, accounting for 15%-20% of coal production. Coal gangue has become one of the most significant industrial solid wastes in coal-rich countries such as China, India, Australia, and South Africa [8-10]. Currently, industrial solid wastes containing silicon-aluminum materials, including fly ash, slag, kiln dust, steel slag, and red mud, can all be used to prepare geopolymers. So far there has been little research on the coal gangue geopolymer (alkali-activated coal gangue), hydration characteristics and microstructure have also not been studied. Geng *et al.* [11] mixed 20% coal gangue into red mud to prepare high-strength red mud-coal gangue geopolymers but did not determine its optimal application parameters. Zhang [12] mixed 30% coal gangue into cement and found that the main hydration products of burned coal gangue-cement were C-S-H, C-A-H, CH, and AFM. Zhang *et al.* [13] revealed that the activation product of alkali-activated coal gangue is an amorphous alkali-aluminosilicate gel having a structure similar to that of zeolitic precursors. Yi *et al.* [14] prepared coal gangue geopolymers with sodium hydroxide and sodium silicate and found that coal gangue

geopolymers can obtain higher early strength, but the 28d strength is lower than P.O. 42.5 pure cement specimens. Through the analysis of alkali-activated slag, steel slag, and red mud, alkali-activated silicon-aluminum materials containing calcium can achieve higher strength. The differences in precursor reactants eventually result in the differences in geopolymerization products. Bignozzi *et al.* discovered that calcium could improve the mechanical properties and the microstructure of silicon-aluminum geopolymers [15]. In the process of geological polymerization, the alkali metal cation Na+ is used to charge-balance, but it is possible to balance the charge by Ca^{2+} ion rather than Na^+ in the presence of calcium source [16].

In summary, this paper uses sodium hydroxide and sodium silicate as the alkali activators to study the impact of slag as a calcium source on the strength of coal gangue geopolymers. Besides, XRD, TG-DTG, and SEM are introduced to explore the geopolymerization mechanisms further. The primary purpose of this study is to investigate the reinforcing effect of slag on coal gangue geopolymer and analysis the reaction mechanism of alkali activator slag-coal gangue.
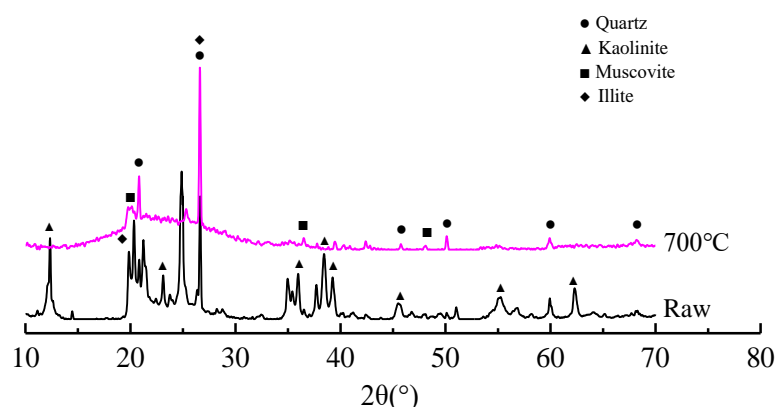
2. Experimental procedures

2.1. Materials
The coal gangue selected (clay rock coal gangue) was calcined at a constant temperature of 700°C for 2 hours. Table 1 shows that the primary chemical compositions of calcined coal gangue and slag. In the experiment, the alkali activators were used 96% sodium hydroxide(NS) and sodium silicate(NS) with a modulus of 3.22 (26.5% SiO_2, 8.5% Na_2O, 65% H_2O).

Figure 1 demonstrates the XRD patterns of original and 700°C calcined coal gangue. The principal mineral components of coal gangue are kaolinite, muscovite and quartz. After high-temperature calcination, the diffraction peak of kaolinite in coal gangue decreases, and the diffraction peak of quartz increases.

Table1. The primary chemical composition of coal gangue and slag.

Materials	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	TiO_2
Coal gangue	56.56	36.78	0.62	1.95	0.22	0.42	2.10
Slag	30.58	14.04	38.43	0.35	10.57	0.57	1.93.

Figure 1. XRD patterns of original and 700°C calcined coal gangue.

2.2. Specimens preparation
The modulus of alkali activators and the liquid-solid ratio were set to 1.30 and 0.36 separately. In addition, the coal gangue was 0, 10, 20, 30, 40, and 50% replaced by slag, respectively. The geopolymer mix proportion is shown in table 2. The alkali activation solutions were prepared 24 hours before use, allowed to cool to room temperature, ensuring uniform mixing of the activator components and improve

the polymerization process. After the coal gangue and slag were uniformly mixed, we added alkali activation solutions to the mixture and mixed agitation for 3 minutes, then quickly pour the fresh paste into the steel mold (40mm×40mm×40 mm) and vibrate on the electric vibration table to remove residual air. Then covered with a thin polyethylene film, demolded after 24h of curing under standard curing conditions(curing temperature 20±2℃, humidity≥95%), the test block was moved to standard curing room until test age(1d, 3d, 7d, and 28d).

Table 2. Mix proportion of geopolymer.

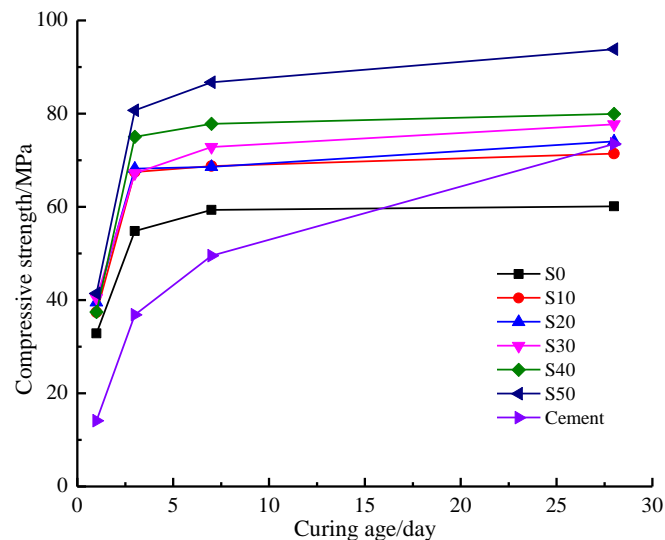| Specimens	Coal gangue: slag	Liquid-solid ratio	Alkali-activator modulus
Cement	—	0.36	—
S0	100:0	0.36	1.30
S10	90:10	0.36	1.30
S20	80:20	0.36	1.30
S30	70:30	0.36	1.30
S40	60:40	0.36	1.30
S50	50:50	0.36	1.30

a*: mass ratio

2.3. Specimens and test methods

2.3.1. Compressive strength. The compressive strength of the paste specimens was tested following the Standard for Test Method of Performance on Building Mortar. The 1d, 3d, 7d and 28d compressive strengths of each set of specimens were tested, and three specimens of each set were selected to determine the average compressive strength.

2.3.2. Microstructure. Microscopic tests for this test included X-ray diffraction (XRD), Thermogravimetric analysis (TG-DTG), scanning electron microscopy analysis (SEM). The XRD test used the German Bruker D8 X-ray diffractometer, and the specimen was continuously scanned at 5° to 70° (2θ°) with a step size of 0.02°. The TG-DTG test used the German Netzsch STA 449 F3 thermal analyzer, the experiment was carried out under a nitrogen atmosphere to 600°C, and the heating rate was 10°C/min. The SEM test used the field emission scanning electron microscope (SU8010; Hitachi; Japan) to observe surface morphology of the broken specimens.

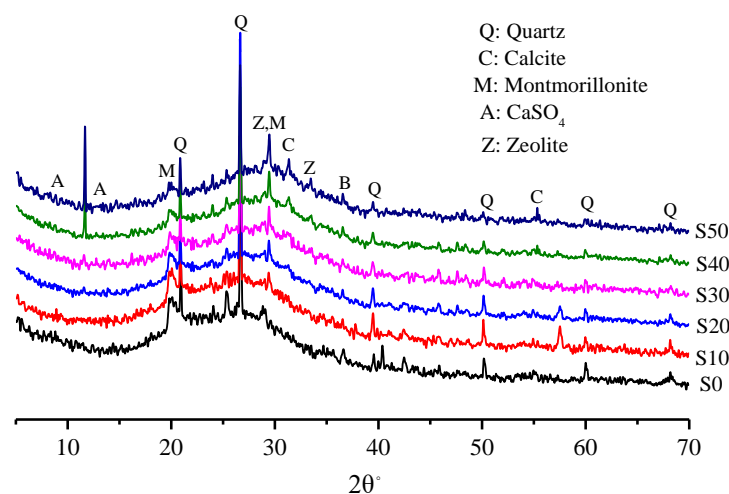## 3. Results and Discussion

3.1. Compressive strength

Figure 2 exhibits the compressive strength of pure cement specimens and specimens with different slag contents. It can be seen that the compressive strength of coal gangue geopolymers increases with the increase of slag content. In comparison with S0 specimens, specimens with the slag content of 10, 20, 30, 40 and 50% exhibited an increase in compressive strength by 18.78, 23.17, 29.22, 32.93, and 55.98%, respectively. Besides, coal gangue geopolymers achieved higher initial strength, thereby enjoying higher 1d, 3d, and 7d compressive strengths. The compressive strength of geopolymers increased slowly from the 7th day, and their 7d compressive strength reached 95% of the 28d compressive strength. However, the 28d compressive strength value of P.O 42.5 cement specimens was 48.42% greater than their 7d compressive strength value. Besides, geopolymers had a greater 28 compressive strength than P.O 42.5 cement specimens when the slag content was 20%. Therefore, coal gangue geopolymers are more suitable for projects that require high early strength. The increase in slag content tends to bring a more substantial increase in the compressive strength.

Figure 2. The compressive strength of specimens with different slag content and cement.
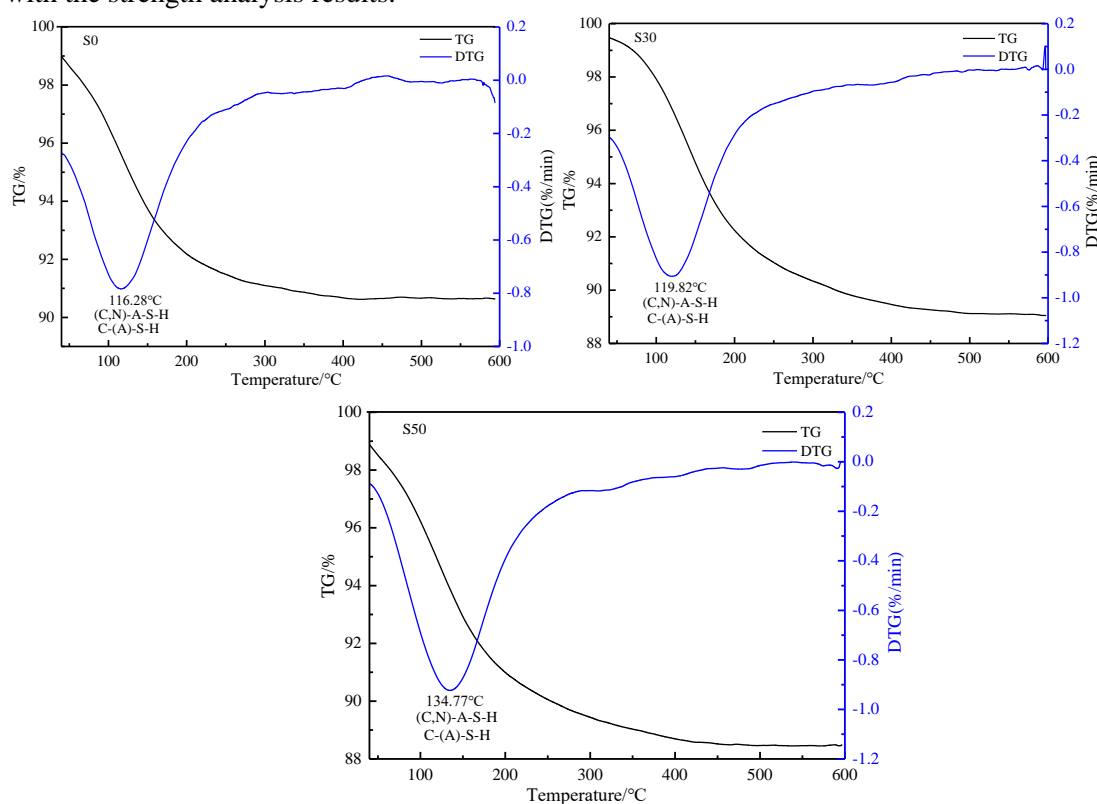
3.2. XRD analysis

Figure 3 demonstrates the XRD patterns of specimens with different slag contents. In the figure, sharp and broad peaks between 20° and 30° are essentially the characteristic reflections of amorphous geopolymers, indicating the dominant position of SiO_2 and Al_2O_3-containing components. Besides, the diffraction peaks of quartz in the original coal gangue still exist, there is also the formation of new minerals such as $CaAl_5Si_{20}O_{10}\cdot4H_2O$, $NaAlSiO_2\cdot H_2O$, and $AlSi2O5\cdot xH_2O$. It can be seen from the figure that the diffraction peak of zeolite phases enhances while that of quartz weakens with the increase in slag content. According to the analysis of XRD patterns by Jade, there are diffraction peaks of calcium zeolite $(Ca[Al_2Si_3O_{10}]\cdot3H_2O$, PDF#29-0809). Namely, calcium alumino-silicate is generated in this process. The availability of additional reactive calcium would have increased the amount of reactive calcium favorable for the formation of C–S–H gel [17]. As the slag content increases, the amount of active substances involved in the alkali-activated reaction increases, thereby improving the chemical reactivity. It not only reduces the content of inert quartz in the mixture but also increases the amount of calcium alumino-silicate produced. The experimental results are consistent with the strength analysis results.

Figure 3. The X-ray diffraction patterns of specimens with different slag content

3.3. TG-DTG analysis

Figure 4 shows the TG-DTG curves (40°C to 600°C) of specimens with the slag content of 0%, 30% and 50% separately. Weight loss of the specimens, which is mainly manifested as the water loss of zeolite minerals and the binding gel. Specifically, specimens with the slag content of 0%, 30%, and 50% reached the weight loss peaks at 116.28°C, 119.82°C and 134.77°C respectively, which indicates that the weight loss peak temperature increases with the increase in slag content, due to modification of the structure of coal gangue geopolymer gel by incorporation of slag and the formation of C–A–S–H gel whose free water is more tight to the structure [16]. The peaks at 110°C-250°C are related to the dehydration of the (C, N)-A-S-H gel and ettringite. Weight loss of the three specimens below 250°C was 7.50%, 8.43%, and 8.83% respectively while the total loss of the three specimens was 8.39%, 9.83%, and 10.98% respectively. As the slag content increases, the amount of hydrous aluminosilicate gels (mainly calcium aluminum silicate gels) increases accordingly. The growth in hydrous aluminosilicate gels densifies the structure of geopolymers and improves the compressive strength, which is consistent with the strength analysis results.
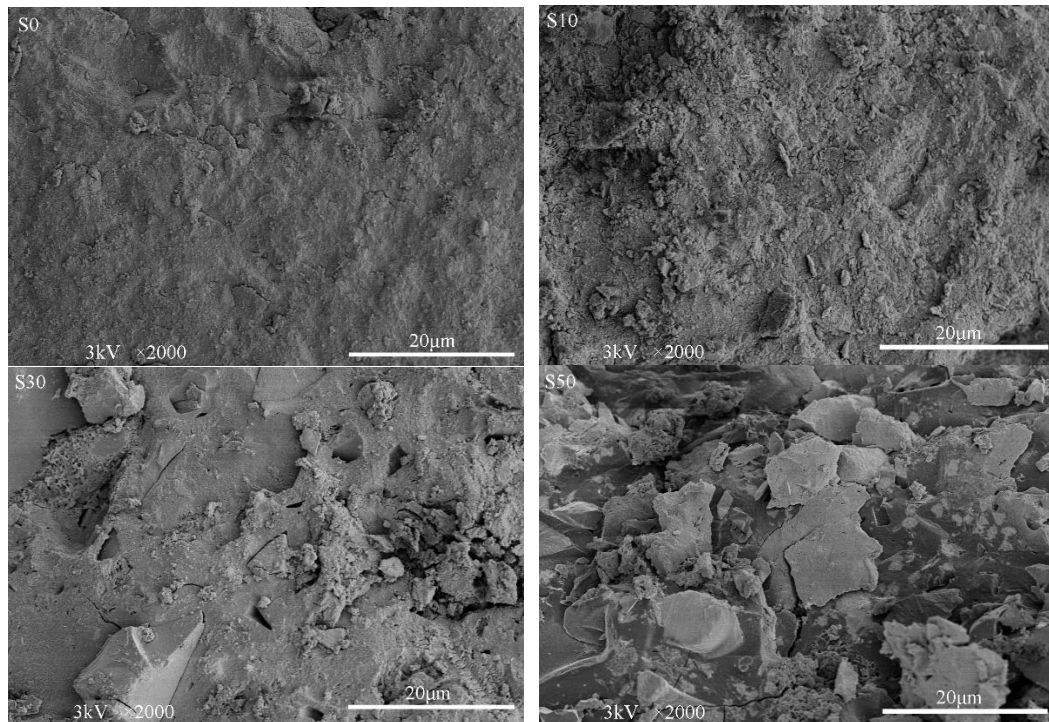

Figure 4. Thermogravimetric analysis of S0, S30, and S50 specimens (40°C～600°C).

3.4. SEM analysis

Figure 5 displays the SEM patterns of specimens with the slag content of 0%, 30% and 50% separately. It can be seen from the figure that there are significant differences in the microstructure of geopolymer specimens. Besides, the amount of gelatinous and flocculent products significantly increases with the increase in slag content. As the slag content increases, a large amount of CaO is introduced into the mixture. Ca in the slag promotes the exchange with sodium ions. The products are therefore transformed from N-A-S-H gels into C-A-S-H gels, and the original three-dimensional disordered structure is retained [18]. Some CaO reacts with the depolymerized SiO_4 and AlO_4 tetrahedrons to form C-S-H gels while some Ca replaces Na to form C-S-H and C-A-S-H gels. The geopolymerization process is necessarily the polycondensation of SiO_4 and AlO_4 tetrahedrons. Na^+ and Ca^{2+} are used to balance the charges. The hydration products of slag-containing coal gangue geopolymers are mainly C-(A)-S-H and N-A-S-H gels. The two kinds of gels, which are highly compatible, jointly constitute the network-like

disordered structure of polymers. The high strength development of geopolymers cementitious materials is attributed to the stable, cross-linked and three-dimensional structure of aluminosilicate polymers. As the figure shows, the disordered network structure is enhanced with the increase in slag content, which is consistent with the strength analysis results.

Figure 5. SEM analysis of the CGG specimens of slag contents 0%, 10%, 30%, and 50%.

4. Conclusions

The paper studies the impact of slag content on the strength of coal gangue geopolymers and explores the geopolymerization mechanisms by using XRD, TG-DTG, and SEM. The concrete conclusions are as follows:

(1) Coal gangue can be used to prepare geopolymers. As the slag content increases, the compressive strength of coal gangue geopolymers increases. Compared with P.O 42.5 pure cement specimens, coal gangue geopolymers can obtain higher early strength. Besides, the rise in slag content tends to bring a more substantial increase in the compressive strength.

(2) With the rise in slag content, the amount of calcium-containing zeolite phases and the surface roughness of coal gangue geopolymers increase accordingly. The addition of Ca leads the C-(A)-S-H and N-A-S-H gels to interweave with each other and jointly constitute the network-like disordered structure of polymers.

(3) The XRD, TG-DTG and SEM results are consistent with the strength analysis results. Slag can significantly improve the compressive strength of coal gangue geopolymers and generate compatible products when added as a calcium source.

Acknowledgments

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