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Study on Properties of Slag Base Geopolymer Containing Portland Cement

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Abstract: To explore the application of slag-based polymers, a study was conducted on the physical and mechanical properties of alkali-activated slag-based polymers (AACS) containing silicate cement by partially substituting cement with slag. A comprehensive evaluation of AACS performance was carried out by testing the setting time, compressive/bending strength and shear bond strength, as well as using XRD and SEM microscopic testing methods. The results showed that the AACS material had a fast setting and hardening process. Within a certain range, the compressive strength increased with the increase of cement content and alkali concentration, and the setting time was shortened accordingly. The AACS material had high bending strength and shear bond strength, and even at the 10% cement content level, the bending strength could still be maintained above 8 MPa. According to the SEM experimental results, the micro-morphology of the new and old interface of the AACS material was compact, and the hydration products were fused with the old mortar substrate, exhibiting a good bonding state.

1. Introduction

In the context of energy conservation and emission reduction, alkali-activated cementitious materials are considered a potential substitute for traditional cement. These materials are produced by mixing industrial aluminosilicate waste materials (such as fly ash and slag) with alkali solutions [1]. Previous studies [2-4] have shown that alkali-activated cementitious materials have excellent properties such as early strength, high-temperature resistance, corrosion resistance, and frost resistance, making them suitable for applications such as fire-resistant and acid-resistant materials, foamed concrete, encapsulation of toxic pollutants, and road maintenance. Mohammad et al. [5] evaluated the mechanical and durability properties of alkali-activated slag (AAS) repair mortars and found that the slag polymer mortar exhibited high bond strength and the mortar activated by NaOH showed better resistance to chloride ion penetration. Wu Fang et al. [6] studied the effect of different roughness substrates on the bonding properties of alkali-activated slag mortar and found that the bonding mechanism of alkali-activated materials involves not only mechanical interlocking but also chemical bonding.

However, pure aluminosilicate waste materials require a large amount of alkali chemical reagents to achieve desired effects, which increases the cost of engineering applications [7]. In addition, the strength of pure polymer materials is relatively low compared to traditional cement mortar, limiting their engineering applications. Some studies have shown that adding silicate cement to the polymer can improve the development of strength defects in pure polymer and help to enhance the properties of alkali-activated cementitious materials [8]. Therefore, this study used silicate cement as an additive and Na_2SiO_3 and NaOH as activators to investigate the effects of different cement addition ratios, different types of alkalis, and different dosages on the setting time, compressive strength, flexural strength, and bonding properties of alkali-activated slag-based cementitious materials containing silicate cement (AACS). Shear tests were used to evaluate the bonding properties of AACS cementitious materials, and combined with microscopic testing methods to analyze hydration products and application effects, providing a theoretical basis for partially substituting slag for cement and expanding application scenarios.

2. Materials and methods

2.1. Raw materials

The cement used in this study was Zhuanpai ordinary Portland cement (P O 42.5) produced by Hebei Yanxin Building Materials Co., Ltd. The main chemical components of the cement and the S95 finely ground granulated blast furnace slag powder produced by Beijing Shougang Jiahua Building Materials Co., Ltd. are shown in Table 1. The high-quality silica fume provided by Beijing Dechang Weiye Construction Engineering Co., Ltd. was characterized according to the technical specifications in Table 2. Industrial grade sodium silicate produced by Tianjin Fuchen Chemical Reagents Factory was used as an alkali activator, and the white solid particles had a Na_2O: SiO_2 ratio of 1.03±0.03. The white solid particle NaOH (purity of 96%) was produced by Beijing Reagent Chemical Co., Ltd. The sand used in this study was ordinary river sand with a fineness modulus of 2.54. Tap water was used as the mixing water. A commercial repair material was selected as the reference material.

Table 1: Chemical composition of cement and blast furnace slag.

Materials	SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	K_2O	TiO_2	Na_2O	P_2O_5
Cement/%	21.28	4.76	59.6	3.25	3.03	2.70	0.98	0.35	0.22	0.16
Slag/%	33.41	14.23	38.5	9.23	2.09	0.37	0.39	0.79	0.34	0.03

Table 2: Technical indicators of silica fume.

Loss on ignition (%)	Chloride (%)	Silicon dioxide (%)	Specific surface area(m^2/kg)	The ratio of water demand (%)	Activity index (%)
2.56	0.032	94.42	2.09×10^4	110	103

2.2. Mix Proportions

Considering the comparison and the effect of the activating agent, two types of activating agents, NaOH and Na_2SiO_3, were used. The addition of Na_2SiO_3 (based on the binder material) was set at 2%, 3%, and 4%, and the addition of NaOH (based on the binder material) was set at 1%, 1.5%, and 2%. The cement was added as an admixture and was set at 50%, 30%, and 10% (based on the binder material). The water-binder ratio was designed to be 0.5. The specific mix proportions are shown in Table 3.

Table 3: Test mix proportion.

Number	Cement(g)	Slag(g)	Silica fume (g)	Sand(g)	NaOH(g)	Na_2SiO_3 (g)
P0	100	-	-	200	-	-
50P-2S	50	42	8	200	-	2
50P-3S	50	42	8	200	-	3
50P-4S	50	42	8	200	-	4
50P-1H	50	42	8	200	1	-
50P-1.5H	50	42	8	200	1.5	-
50P-2H	50	42	8	200	2	-
30P-2S	30	62	8	200	-	2
30P-3S	30	62	8	200	-	3
30P-4S	30	62	8	200	-	4
30P-1H	30	62	8	200	1	-
30P-1.5H	30	62	8	200	1.5	-
30P-2H	30	62	8	200	2	-
10P-2S	10	82	8	200	-	2
10P-3S	10	82	8	200	-	3
10P-4S	10	82	8	200	-	4
10P-1H	10	82	8	200	1	-
10P-1.5H	10	82	8	200	1.5	-
10P-2H	10	82	8	200	2	-

Note: P0 represents the ordinary Portland cement mortar. 50P-2S and 30P-1H represent the experimental groups with 50% cement content and 2% sodium silicate content, and 30% cement content and 1% sodium hydroxide content, respectively. The others are similar.

2.3. Test method

2.3.1. Preparation and physical-mechanical property testing of AACS binders

The required amounts of Na_2SiO_3 or NaOH and water were weighed, NaOH solution and Na_2SiO_3 solution were prepared 2 hours in advance and cooled at room temperature for later use. The alkali-activated slag-silicate cement mortar was prepared using the same mixing method as the cement mortar. The mixing water was replaced with the prepared alkali solution. The consistency of the mortar was determined according to GB/T 1346-2011 "Test methods for water demand, setting time and soundness of cement". The compressive and flexural strength of the specimens were determined according to the methods specified in JTG E30-2005 "Standard test methods for highway engineering cement and concrete".

2.3.2. Measurement of Bonding Performance of AACS Cementitious Materials

The shear bond strength was determined according to ASTM C882. Half-block specimens were first prepared and cured for 28 days as the substrate. Different repair mortars were then poured and joined together to form a complete structure, which was further cured for 28 days before being loaded and tested according to the method shown in Figure 1.

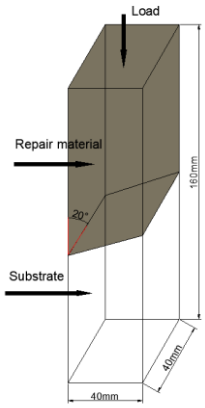


Figure 1: Schematic diagram of shear bond strength loading.

2.3.3. Microscopic Performance Testing

The microscopic morphology of the specimens was observed using a JEOL JMS 6500F field emission scanning electron microscope produced by JEOL Ltd. of Japan, and the sample phase analysis was performed using an XRD-7000 X-ray diffractometer produced by Shimadzu Corporation of Japan.

3. Results and Discussion

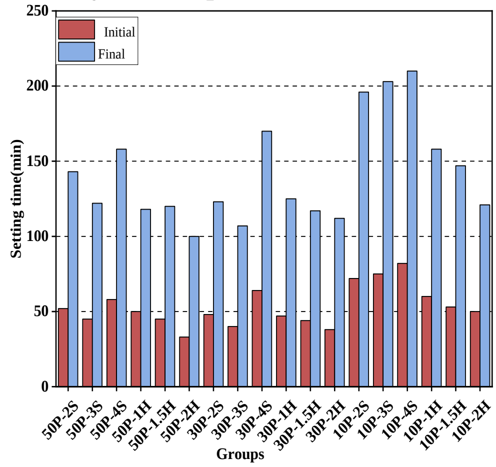
3.1. Setting Time and Strength Development of AACS Binders

As shown in Figure 2(a), the setting time of the mortar shortened with the increase of alkali and cement content. This is because the addition of alkali promotes the polymerization reaction of slag: the OH^- in alkali rapidly dissolves SiO_2 and Al_2O_3 in slag and then re-aggregates to form C-S-H and C-A-H, resulting in early strength development. In addition to its own hydration that forms strength, the addition of cement accelerates the polymerization process due to the heat of hydration, further promoting the setting and hardening of the system.

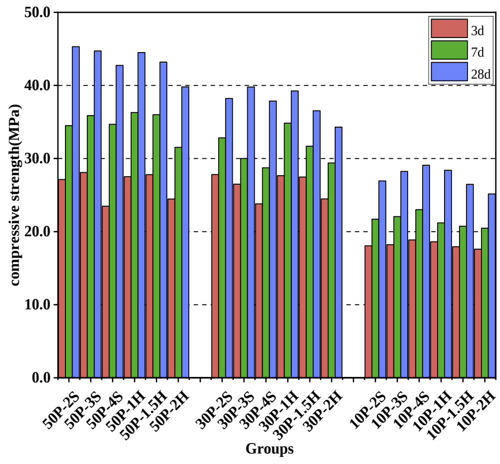
The compressive strength of the AACS binder is shown in Figure 2(b). The strength decreases as the cement content decreases, and within a certain range, the strength increases with the increase of alkali content. This indicates that both the addition of cement and alkali are beneficial to the strength development of the AACS binder. The 28-day compressive strength of the 30P-2S, 30P-3S, 10P-2S, and 10P-3S groups were 38.22, 39.79, 26.94, and 28.24 MPa, respectively. From the perspective of alkali concentration, within a certain range, the strength of the AACS binder increases with the increase of alkali concentration, but the strength decreases when the alkali concentration is too high. This is because a low-concentration alkali solution can promote the dissolution and re-aggregation of silicon and aluminum monomers in slag, and the hydration products of the system accumulate rapidly. Under high concentration OH^- state, the concentration of Si^{4+} and Al^{3+} ions rapidly increases, and due to the ion effect, the increased ion concentration hinders the precipitation of Ca^{2+}, thereby delaying the strength development of the system. This result is consistent with the experimental results of A. Palomo et al. [8], but whether the hydration of the system continues in the later stage needs further exploration.

The flexural strength of the AACS binder behaves similarly to the compressive strength, as shown in Figure 2(c). The addition of cement and alkali in the appropriate range can enhance the flexural strength of the binder. Unlike compressive strength, the difference in flexural strength between binders with different cement content levels is not significant. The 28-day flexural strengths of the

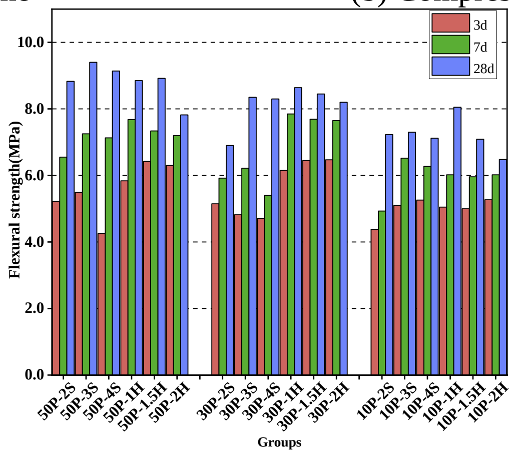
10P-1H, 30P-1H, and 50P-3S groups were 8.05 MPa, 8.64 MPa, and 9.4 MPa, respectively, indicating that the hydration products of the activated slag have better bonding performance than those of ordinary cement hydration products.



(a) Setting time



(b) Compressive strength



(c) Flexural strength

Figure 2: The setting time and strength of different combinations of AACS materials.

3.2. XRD

XRD testing was carried out on the 30P-1H, 30P-2S, and 50P-3S experimental groups after 28 days of curing. The X-ray diffraction spectrum is shown in Figure 3. The results showed that the crystal phases of the different combinations of experimental groups were similar, mainly including SiO_2, $CaCO_3$, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, and small amounts of $KAlSi_3O_8$, $Ca(OH)_2$, $CaMg(CO_3)_2$, etc.

As the cement content increased from 30% to 50%, the height of the characteristic peak of quartz (SiO_2) near $2\theta=27°$ decreased, and the amount of the aluminosilicate gel phase increased, indicating that increasing the cement content is conducive to promoting the hydration reaction of SiO_2 in the slag. As the alkali concentration and cement content increased, the intensity of the SiO_2 characteristic peak weakened, indicating that both alkali and cement content can promote the depolymerization of SiO_2, thereby accelerating the formation of the internal gel network.

Compared with the 30P-1H group, the XRD spectrum of the 30P-2S group was significantly flatter, with fewer characteristic peaks and weaker intensity, indicating that there were fewer hydration products in the system and a lower degree of hydration reaction. This shows that the alkali concentration has a significant influence on the hydration degree of the slag. Within a certain range, the higher the alkali concentration, the more complete the hydration reaction of the slag. Therefore, the presence of cement and alkali is conducive to the hydration reaction of the slag-geopolymer cement composite system, thereby enhancing the development of system strength.

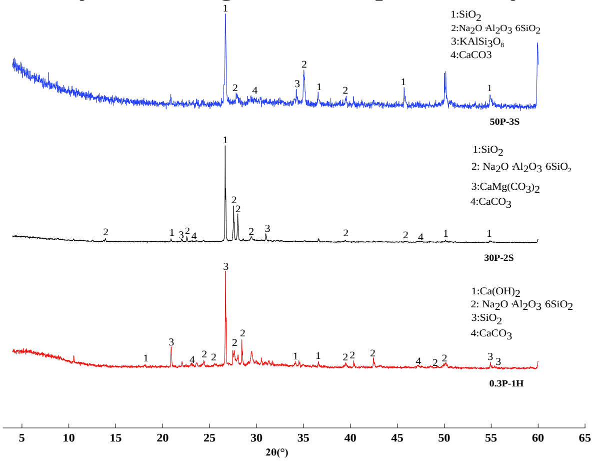


Figure 3: XRD patterns of AACS materials.

3.3. Shear bond strength of AACS repair materials

To compare different cement contents and ensure sample representativeness, we selected four groups of materials: 50P-3S, 30P-1H, 10P-4S, and ordinary cement mortar P0. Figure 4 shows the results of the shear bond strength test for different bonding materials. Specifically, the 50P-3S group exhibited a shear bond strength of 34.6 MPa, an improvement of 14.4% compared to ordinary cement repair mortar P0, while the 30P-1H group showed a shear bond strength of 33.85 MPa, an increase of 11.9% compared to P0. Except for the 10P-4S group, alkali-activated cementitious materials exhibited higher bond strength than ordinary cement mortar.

Figure 5 shows the microstructure of the interface between the repair materials and the old mortar substrate. As seen in Figure 5(a), there were obvious gaps between the ordinary cement repair mortar P0 and the old substrate, resulting in lower bond strength. In contrast, for the 50P-3S and 30P-1H groups, the cracks at the bond interface were small or non-existent, indicating good adhesion between the two surfaces. Macroscopic test results confirmed the higher shear bond strength of the two repair mortar specimens. Shi et al. [9]demonstrated through a tensile strength test that alkali-activated binders have better bonding properties than ordinary Portland cement, as the abundant Si^{4+} and Al^{3+} ions in the alkali-activated system can react with the $Ca(OH)_2$ on the substrate surface to improve the interfacial strength.

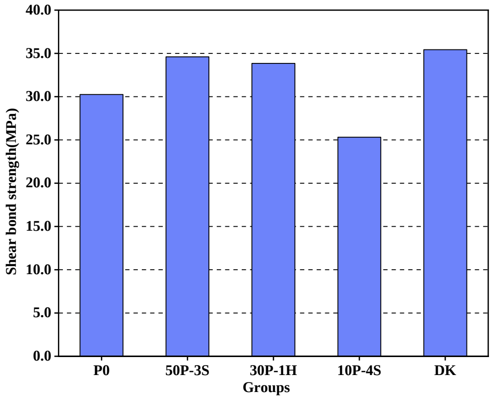
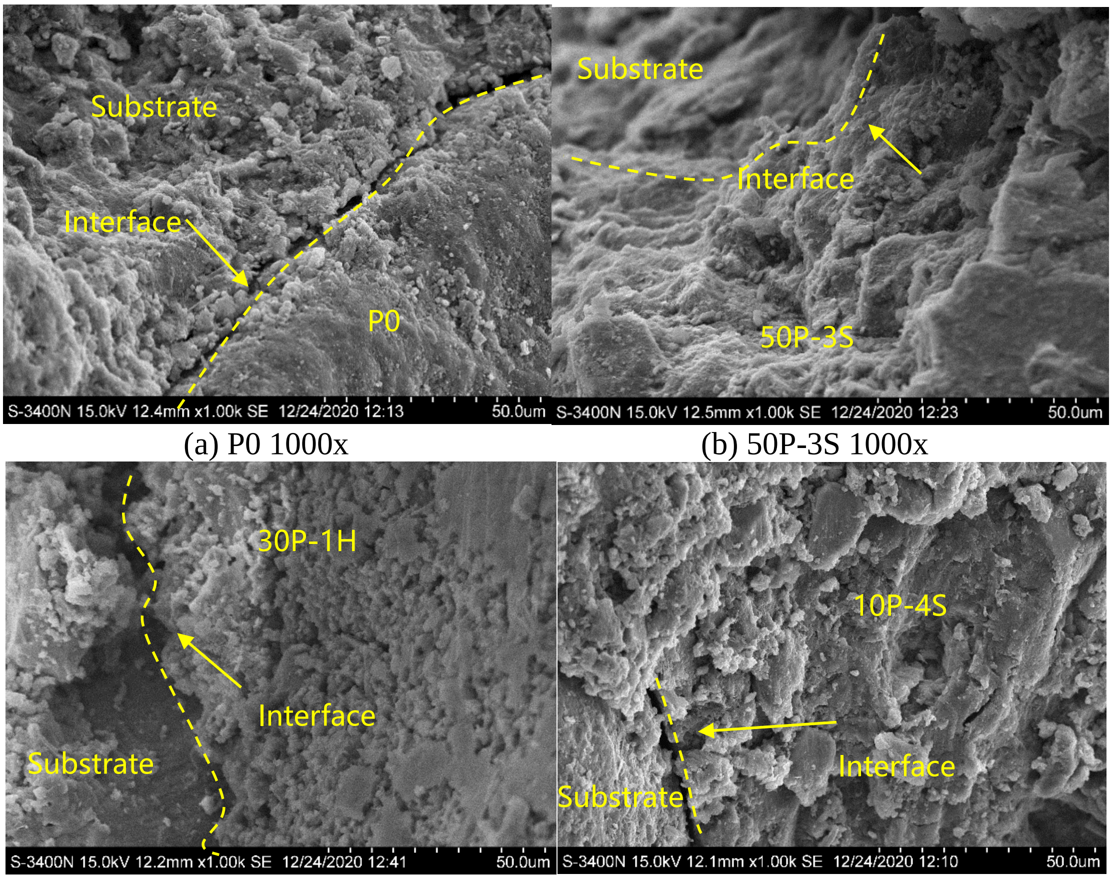


Figure 4: Shear bond strength of specimens.



(a) P0 1000x (b) 50P-3S 1000x

(c) 30P-1H 1000x (d) 10P-4S 1000x

Figure 5: Micromorphology of bonding interface of different repair materials.

4. Conclusion

We investigated the physical and mechanical properties of alkali-activated slag cement (AACS) and arrived at the following conclusions:

(1) AACS has fast-setting and hardening properties. Based on XRD analysis, within a certain range, the compressive strength of AACS increases with increasing cement content and alkali concentration, while the setting time is shortened accordingly.

(2) Compared with ordinary cement mortar, AACS has excellent bonding properties, as evidenced by high flexural and shear bonding strength. The difference in flexural strength of the cementitious material under different cement content levels is not significant. The flexural strength of AACS with 10% cement content is still above 8 MPa, indicating that the hydration products of alkali-activated slag and ordinary cement have better bonding properties.

(3) Alkali concentration affects the formation of hydration products in AACS, and the microstructure gap between AACS and old mortar interface is small, with the hydration products and old substrate interlaced and fused, resulting in good bonding status.

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