One-part alkali activated slag using Ca(OH)$_2$ and Na$_2$CO$_3$ instead of NaOH as activator: more excellent compressive strength and microstructure

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Abstract

In this paper, sodium carbonate and calcium hydroxide instead of sodium hydroxide used as composite activators, and slag are applied to prepare one-part alkali-activated slag. Furthermore, the properties of the slag activated by sodium hydroxide are compared. The compressive strength, XRD, TGA, MIP, and SEM analysis of the two systems are performed. The results show that the one-part alkali-activated slag prepared from sodium carbonate and calcium hydroxide has a superior compressive strength against the slag activated by sodium hydroxide. It is also found that the hydration speed of the sodium hydroxide activated slag is faster, and thus the higher compressive strength of the one-part alkali-activated slag is not caused by the hydration speed. The hydration of one-part alkali-activated slag produces a certain amount of calcium carbonate, resulting in a lower porosity in comparison with the slag activated by sodium hydroxide, which may be the reason for the better compressive strength of one-part alkali-activated slag.

1. Introduction

Portland cement, as a traditional material in construction, is widely applied in the cementing of oil or gas wells and construction of infrastructure of cities, such as bridges or high-speed railways. The global yield of cement production was near 3.95 billion tons in 2018. The Portland cement is produced by a highly polluting industry, as a large amount of carbon dioxide (5%–7% of the total anthropogenic emission) and dust are released during the process, being very energy-consuming. The production of this cement in China has been the top in the world since 1985, and it holds over 50% of the global yield from 2007 to today [1]. In recent years, the issue of air pollution in China has become increasingly serious, and China assured the United Nations Framework Convention on Climate Change that the carbon emission of China will peak around 2030 [2, 3]. Therefore, China increased the cement production limit, providing excellent opportunities for the research, development, and commercialization of other binding materials as substitutes of cement. It is of considerable significance to reduce air pollution and ensure normal engineering construction by using industrial by-products such as alkali-activated slag, fly ash, waste glass, and metakaolin to develop cement substitute materials [4–6].

Slag can be obtained from a broad range of sources with low costs and has a high content of amorphous minerals, so it is often used as the raw materials for the alkali-activated materials [7, 8]. Sodium hydroxide and sodium silicate are commonly used as base activators, but due to their high cost and environmentally unfriendly production process, researchers are continually trying to use other types of base activators. Yang and Kim et al obtained the activated slag with favorable final strength using Ca(OH)$_2$ or CaO as the activator [9, 10]. However, the early-stage strength of this system was relatively low, and the 1-day strength was only about 3 MPa at a water-solid ratio of 0.4, which was due to the low alkalinity of the alkali-activated slag produced by Ca(OH)$_2$ or CaO in
the early stage. NaOH is one type of strong base, and NaOH-activated slag also showed much higher early strength [11, 12]. To decrease the cost of NaOH, Shaqour et al. replaced NaOH with the combination of Na2CO3 and Ca(OH)2 to activate natural clay, and found that the combination of these two chemicals functioned similarly in ensuring high compressive strength as using NaOH, while the cost-efficiency was highly increased [13]. The generation of NaOH by the combination of Na2CO3 and Ca(OH)2 (as shown in equation (1)) may be responsible for the high compressive strength.

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\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 = 2\text{NaOH} + \text{CaCO}_3
\]  

Currently, most researchers prepare the alkali-activated gel-based materials by the method involving two-part of non-Portland cement, during which the activator is first dissolved in water and then mixed with the precursor. In the process of two-part non-Portland cement production, it is necessary to dissolve alkali in water to prepare alkali solution. As the alkali solution (such as NaOH solution) has a strong corrosive effect, gloves, masks, and veils are required during operation, which is adverse to be produced and applied at large-scale [14]. Therefore, researchers are focusing on developing the one-part non-Portland cement method, i.e., first mixing the solids of activator and precursor, and then adding water into the solid gel materials [4, 14–20].

Therefore, in this paper, one-part non-Portland cement was prepared using Na2CO3, Ca(OH)2, and slag, where the three were uniformly mixed dry, and then the appropriate amount of water and the dry mixture was directly mixed, to prepare and form the one-part alkali-activated slag. The difference between the strength of the combined Na2CO3-Ca(OH)2 activated slag, and the equivalent NaOH activated slag were compared and studied. Furthermore, the strength variation law of the combined Na2CO3-Ca(OH)2 activated slag was discussed at 50, 70 and 90 °C on 1d, 3d, 7d, and 28d. Characterization of slag microstructures was performed using x-ray diffractometry (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and mercury intrusion porosimeter (MIP).

2. Experimental materials and methods

2.1. Materials and sample preparation

The slag selected in this study was slag S95, obtained from Shandong Kangjing Material Technology Co., Ltd. The particle size distribution is shown in figure 1, and the chemical composition is listed in table 1. NaOH, Ca(OH)2, and Na2CO3 were purchased from Shandong You suo Chemical Technology Co., Ltd.

Table 2 shows the formulas for the preparation of the slag slurry, activated by sodium hydroxide (NS) and that activated by sodium carbonate and calcium hydroxide (CCS). In the first formula, the mass ratio of sodium hydroxide to slag was 6%. In the following formula, the dosage of Na2CO3 and Ca(OH)2 was calculated based on the already defined mass ratio of 6% of NaOH and slag generated by the complete reaction of the two and the binder/water mass ratio of the two formulas was 1:0.46.

According to the standards of the American Petroleum Institute (API), the alkali-activated slag slurry was prepared using a corrugated mixer. The NS sample was prepared by first dissolving NaOH in water and then mixing with slag after the sodium hydroxide solution was cooled. The mixture was first stirred in the mixer at a lower speed of 4000 rpm for 15 s and then at a high speed of 12000 rpm for 35 s. In the preparation of the CCS
sample, Na₂CO₃, Ca(OH)₂, and slag was dry-mixed for 5 min, followed by mixing with water. The mixture stirred similarly to NS to obtain the CCS sample. The as-prepared NS and CCS samples were poured into a 51 × 51 × 51 mm mold and cured in a water bath at various temperatures, respectively.

2.2. Experimental measurement
To accurately test the compressive strength of the samples, the samples with the same formula, the same curing time and temperature were tested three times, and then the test results were averaged. The crushed samples were soaked in acetone for 3 days, followed by a drying process at 50 °C, vacuum conditions for 24 h. The bulk product was used for SEM and mercury penetration analysis and ground into powder for XRD and TGA analysis.

The effects of activator type and curing time on the hydration product were analyzed quantitatively using a Bruker D8 Advance x-ray diffractometer with a 2θ range of 5°–80°. The change of the hydration product was analyzed qualitatively and quantitatively by TGA (NETZS 209F3) with a testing temperature range of 30 °C–1000 °C, a sample weight of 20 mg, and a heating rate of 10 °C min⁻¹. The obtained pore volume and size distribution of the sample was measured by MIP (AutoPore IV 9500) with a pressure range of 0.0007–414 MPa. The characterizations of the microstructures were performed on an ultra-high-resolution field emission SEM (FE-SEM, ZEISS MERLIN).

3. Results and discussion
3.1. Comparison of compressive strength between two types of sample
This section discusses the strength of the alkali-activated slag samples obtained by two activation methods with a curing time of 1 and 3 days. Figure 2 shows that the compressive strength of NS and CCS gradually increased with curing time, while the compressive strength of sample CCS was higher than that of the NS sample. Due to the same W/b ratio for both NS and CCS, the difference in strength should not be induced by the W/b ratio. Also, the content of NaOH produced by the reaction between sodium carbonate and calcium hydroxide in CCS was the same as that of NS. Moreover, it took a particular time for sodium carbonate in CCS to react with calcium hydroxide to form sodium hydroxide. In contrast, sodium hydroxide in NS was directly dissolved in slurry water, so the alkali concentration in the early NS was higher than that in CCS. Consequently, the higher strength of CCS than NS was not caused by the activator concentration.
3.2. Effect of curing temperature on strength evolution

In this section, the compressive strength evolution of CCS at curing temperatures of 50, 70, and 90 °C were tested for 1, 3, 7, and 28 days (figure 3). It can be seen from the figure that the curing temperature had some influence on the CCS sample. But the influence of temperature on the compressive strength is less obvious than the curing time. With the extension of curing time, the compressive strength of the CCS sample gradually increased, which exceeded 30 MPa after 28 days.

3.3. XRD

Since the compressive strength of CCS higher than that obtained for NS at the curing time of 3 days, their hydration products were analyzed and compared by XRD (figure 4). As can be seen, when the curing time was 3d, there was a significant formation of calcium carbonate in the hydration products of CCS, while no formation of calcium carbonate in NS hydration products could be observed. Because the diffraction peaks of C-A-S-H and calcium carbonate overlapped, it is difficult to analyze the difference of C-A-S-H content in the hydration products of the samples NS and CCS separately, but the sum of C-A-S-H and calcium carbonate in the hydration products...
products of CCS far exceeded NS. By XRD analysis, only calcium carbonate was generated in CCS, and the reason for the higher compressive strength of CCS sample than the NS sample cannot be directly determined from these results.

3.4. TGA
In XRD analysis, the diffraction peaks of C-A-S-H and calcium carbonate overlapped, so it was hard to accurately judge the difference between C-A-S-H in hydration products of sample NS and CCS. Therefore, TGA analysis was carried out for the two samples when the curing time was 3 days, as shown in figure 5. It can be seen, that the content of C-A-S-H in the hydration products of NS samples was higher than that of CCS samples, which may be caused by the fact that the concentration of alkali-activator sodium hydroxide in the NS samples was higher in the early hydration stage than that of CCS samples, and the hydration degree of NS samples was higher. The results above indicate that the higher CCS strength than NS was not obtained due to the faster hydration rate of CCS in comparison with NS. Furthermore, more calcium carbonate was generated in the hydration products of CCS but was not formed in NS.

Figure 6 presents the TGA results of CCS cured at 50 °C for 1, 3, 7, and 28 d. The contents of C-A-S-H and calcium carbonate in the hydration product constantly increased with curing time, suggesting the continuing
increase of the hydration level of CCS, which may be the reason why the strength of CCS increased with the curing time.

3.5. MIP
The pore distribution of cement paste has a significant influence on the compressive strength of the samples [13]. In order to study the difference of pore distribution between NS sample and CCS sample, MIP was used to test the porosity distribution samples with a curing time of 3 days (figure 7). As can be seen, the porosity of CCS was much lower than that observed in the case of NS. Moreover, the proportion of medium and small pores in the CCS sample was higher, which may be the main reason for the higher strength of sample CCS than the NS one [21, 22]. The decreased porosity of CCS could be attributed to the filling by calcium carbonate, formed in the reaction between sodium carbonate and calcium hydroxide [21].

3.6. SEM
The SEM micrographs of CCS and NS cured for three days (figure 8) showed similar microstructures of CCS and NS with the main hydration product of C-A-S-H, while CCS had a denser morphology. This could be attributed to the low content of calcium carbonate dispersing in other hydration products. But calcium carbonate is not observed in the sample CCS.

4. Conclusions
In this paper, based on the principle that \( \text{Na}_2\text{CO}_3 \) reacts with \( \text{Ca(OH)}_2 \) to form \( \text{NaOH} \), one-part non-Portland cement was prepared by using the activator mentioned above and slag, as the three materials were dry-mixed...
first and then directly mixed with water, forming the one-part alkali-activated slag. The as-prepared slag system was compared with that activated by NaOH. Through the characterizations, including compressive strength tests, XRD, TGA, MIP, and SEM. The following conclusions were drawn:

1. The one-part alkali-activated slag prepared from Na$_2$CO$_3$ and Ca(OH)$_2$ exhibited better compressive strength. Its compressive strength was 60% higher than that activated by NaOH.

2. The TGA results show that the NS sample produced more C-A-S-H, indicating that it was hydrated faster, so the hydration rate did not cause the excellent compressive strength performance of the CCS system.

3. According to MIP and SEM analysis, the CCS sample was denser, its porosity was much smaller than that of the NS sample, and CCS samples had more small pores, which may lead to the higher compressive strength of CCS sample.

4. The XRD and TGA results confirmed the formation of calcium carbonate in the hydration product of CCS, while it was not observed in the case of the NS sample. The formation of calcium carbonate may be the reason for the observed difference in porosity between CCS samples and NS samples.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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