Research Article

The Effect of Activators on the Mechanical Properties and Microstructure of Alkali-Activated Nickel Slag

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1.Introduction

Industrial by-products and waste are produced during various industrial production processes, which mainly include blast furnace slag, granular phosphorous slag, fly ash, gangue, red mud, coal bottom ash, and nickel slag. From this list, nickel slag, which is the subject of discussion in this article, is industrially discharged during the production of nickel-iron alloy. Indeed, the rapid growth of the industry and the continuous improvement of industrialization levels in developing countries such as China have led to a rising demand for nickel. Elshkaki et al. [1] reported, for instance, that global demand is expected to increase by between 140% and 175% by 2025 and between 215% and 350% by 2050, with China producing approximately 110 million tons of nickel [2] in 2018. Generally speaking, the production of one ton of nickel results in several tons of the nickel slag [3]. Such a large amount of waste puts tremendous pressure on the environment and limited landfill resources. Finding suitable applications for this waste in order to mitigate the problems associated with environmental pollution is therefore of the utmost urgency.

Indeed, finding new sources for supplementary cementitious materials (SCMs) is becoming a matter of international concern, as supplies of traditional SCMs are becoming restricted, and the demand for SCMs to reduce CO2 emissions from concrete production is increasing [4–6]. Alkali-activated cementitious materials (AACMs), as a kind of geopolymer, are gradually becoming an alternative to cement due to their excellent mechanical properties and also constitute an answer to sulphate and chloride ion attacks on the materials [7–11].

Conventional two-part AACM cement is made by mixing a pozzolanic mineral admixture with alkali activator
solution and water. According to Zhang et al. [12], ground nickel slag can be used as a pozzolan active mineral admixture, which can be efficiently hydrated under alkali activation, thus becoming a substitute for cement. One of the main benefits of this alternative product is that it produces very little greenhouse gas when compared with ordinary Portland cement (OPC), which relies on the calcination of limestone and is responsible for generating about 5% of global greenhouse gas emissions [13]. It is worth noting here that an alkali activator is a substance that can provide an alkaline environment, dissolve silico-aluminum raw materials, and provide metal cations for reaction products. Hence, the type and concentration of alkali activators affect the properties and performance of the AACM. The most common alkali activators are NaOH, Na₂SiO₃, and Na₂CO₃ [14, 15].

Many studies (e.g., [16–19]) have shown that using an AACM as an alternative cement material has several advantages. For example, Rashad et al. [18] found that the average compressive strength of alkali-activated fly ash pastes can be as high as 52.4 MPa, with a standard deviation of 3.8. This compressive strength slightly exceeds the nominal compressive strength of an ordinary concrete of 50 MPa. Pan et al. [20] showed that the compressive strength of the alkali-slag-red mud cementitious material increases with age, and there is no decline in strength after a longer period. Sakulich et al. [21] also found that, after adding retarders (such as NaCl) to solve the problem caused by a too short setting time, an AACM could have tensile and compressive strengths equivalent to OPC mixing with fine aggregates.

At present, there are few studies that have explored the compressive strength of the nickel slag as an admixture for the AACM so that understanding regarding the optimal design of the AACM and its corresponding strength mechanism is limited. Zhang et al. [12] found that the compressive and flexural strength of alkali-activated nickel slag mortar is ranked from high to low so that the water glass group NaOH/Na₂CO₃ group NaOH group when the concentration of alkali activators is the same. However, their study focused on a two-part AACM whose activation process requires concentrated alkaline aqueous solution that is corrosive and sticky, making it difficult to handle, store, and transport, as well as hard on the user, and therefore limiting the promotion and application of alkali-activated cement [22]. On the other hand, one-part AACMs that are prepared by directly mixing a pozzolanic mineral admixture with solid alkali, as with the preparation of OPC, have been recognized to possess a wider potential application than a two-part AACM [22, 23]. This solid alkali activator was reported to help the AACM obtain early and ultimate strength, as well as excellent resistance to chemical attacks [20].

The limited studies on the mechanical performance of one-part AANS and the corresponding mechanisms have inspired us to undertake a comprehensive study on the influence of three solid alkali activators, Na₂SiO₃, NaOH, and Na₂SiO₃/Na₂CO₃, on the compressive strength of one-part AANS. A series of technologies including a scanning electron microscope (SEM), an energy-dispersive spectrometer (EDS), an X-ray diffractometer (XRD), Fourier transform-infrared (FT-IR) spectrum, and a mercury analyzer were used to explore the microstructure of one-part AANS, the composition of reaction products, and their pore structure. The results were then used to explore the mechanism behind variations in compressive strength for one-part AACM with different alkali activators. Finally, we suggest an optimal mixed design for the application of one-part AACM.

2. Materials and Methods

2.1. Materials. The raw materials for the test include nickel slag, cement, a solid alkali activator, standard sand, water, citric acid, and water reducer. The particle size of the undisturbed water-quenching nickel slag used in the test was about 3–4 mm. The Blaine surface area and specific gravity are 425 m²/kg and 3.02, respectively. Table 1 shows the chemical composition of the nickel slag. The SEM image and the crystal type are shown in Figures 1 and 2, respectively. Figure 1 shows that most of the particle shapes in the original nickel slag powder are similar to those in gravel. Figure 2 shows that there is no obvious peak in the spectrum of the original nickel slag powder, and a bulge is found between 10° and 40°, indicating that the main mineral phase of the nickel slag was a glassy phase.

As the most common types of alkali activator used in the AACM, anhydrous Na₂SiO₃, NaOH, and Na₂CO₃ [14, 15] were used as alkali activators in this study and were all analytically pure. Their content was greater than or equal to 99%, greater than or equal to 96.0%, and greater than or equal to 99.8%, respectively. For example, in this paper, Na₂SiO₃ mass refers to Na₂O·SiO₂ powders (analytically pure), where the Na₂SiO₃ content is not less than 99% with a modulus = 1.

Sand was selected in accordance with China standard GB/T 17671-1999, which is equivalent to BS EN 197-1:2011. The maximum dry density, minimum dry density, specific gravity, and particle size d₅₀ are 1.75 g/cm³, 1.55 g/cm³, 2.63, and 0.17 mm, respectively. In the test, water used for mixing was distilled water. The retarder was anhydrous citric acid, and the water reducer was a lignin-based water-reducing agent. If the contents of Na₂SiO₃ exceeded 10%, the blended average tended to have poor workability due to the fast setting and hardening caused by the joint action of OH⁻ and the large number of active (SiO₄)⁴⁻ provided by Na₂SiO₃ [24]. Citric acid was therefore added to the mix.

Our trial and error tests also found that Na₂CO₃ could be added to the alkali activator Na₂SiO₃ to produce a high workability of the mixture and an expected compressive strength after the curing process, with an effect similar to citric acid. Thus, in our test, we designed three systems for the AACM: Na₂SiO₃, NaOH, and Na₂SiO₃/Na₂CO₃.

2.2. Sample Preparation. Table 2 shows the mix ratio of alkali-activated nickel slag mortar activated by the three alkali activators in this study. An OPC mortar group with ID
C was prepared for comparison. For all samples, the water/binder ratio was 0.35, and the binder/sand ratio was 1:2.

According to the design method for the proportions used in a geopolymer mix \(\frac{n(M_2O)}{n(Al_2O_3)} \approx 1.0 \pm 0.5\) used by researchers such as Li et al. [25], the range of the alkali activator content was determined first of all. The content of anhydrous Na\(_2\)SiO\(_3\) was set to 10%, 13%, and 15%. Then, the Na\(_2\)O content used for the other two alkali activators was the same as for the anhydrous Na\(_2\)SiO\(_3\) system.

Consequently, when the equivalent of Na\(_2\)O was set at 0.082 mol, the three systems activated by Na\(_2\)SiO\(_3\), NaOH, and Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\) were marked with a sample ID of NS10, NH6.56, and NS7.5-NC2.17, respectively. When the equivalent of Na\(_2\)O was set at 0.107 mol, the three systems activated by Na\(_2\)SiO\(_3\), NaOH, and Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\) were marked with a sample ID of NS13-N2-J1, NH8.5, and NS9.75-NC2.82, respectively. When the equivalent of Na\(_2\)O was set at 0.123 mol, the three systems activated by Na\(_2\)SiO\(_3\), NaOH, and Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\) were marked with a sample ID of NS15-N2-J4, NH9.84, and NS11.25-NC3.26, respectively. For the Na\(_2\)CO\(_3\)/Na\(_2\)SiO\(_3\) system, the content ratio of Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\) was set as 3.5.

Citric acid (2%) was mixed with the solid alkali activator and nickel slag during the ball milling operation for groups of NS13-N2-J1 and NS15-N2-J4. A water-reducing agent with a different content was also added to the mix to improve fluidity and workability.

Figure 3(a) shows the ball mill machine (Haoqiang Technology WZM-15 × 2 model) that was used to mix the original dried nickel slag with solid alkali activators. The ball mill tank volume was 15 L, and the inner diameter was 26 cm. The steel balls were 30 mm, 20 mm, and 10 mm in diameter, with a grading of 1:1:1 and a stacking density of 4,640 kg/m\(^3\). In order to maintain a high energy efficiency ratio when mortar with a high compressive strength is being prepared, the optimal ball mill design parameters were set as follows: the ball loading rate was 30%, and the ratio for the ball material was 15. The original nickel slag was milled at high speed for two hours and then mixed with a solid alkali activator for 0.5 hours. Mortar sample (cubic dimension) with a dimension of 50 mm × 50 mm × 50 mm was then prepared.

First of all, the requisite masses of dry cementitious materials and sand were prepared in the mixer depending on the proportions required. Then, distilled water with the admixture was added to the mixer to mix the cementitious materials and sand for 30 seconds at a low speed and another 30 seconds at a high speed. The cementitious material deposited at the bottom and on the wall of the mixer was then scraped out so that the mixture produced was uniform. This process took around 90 seconds. Afterwards, another 60 seconds of high-speed mixing was carried out. The fresh mortar was divided into two parts and then loaded into the steel mould. The steel mould with the mortar was then placed on the vibration table to achieve uniform vibration. The surplus part of the upper surface of the mould was then scraped off using a trowel.

The moulds containing the mortar were moved into a curing room where standard conditions (temperature 20 ± 2°C and relative humidity ≥ 95%) were maintained. The mould was then removed after 24 hours, and the mortar samples were placed in a standard curing room (temperature 20 ± 2°C and relative humidity ≥ 95%) for the amount of time stipulated in the design.

### 2.3. Measurement Methods

We determined the amount of water and the initial and final setting times required in the test methods for alkali-activated nickel slag cementitious materials with different alkali activators according to the appropriate test methods needed to achieve a standard cement consistency (GB/T 1346-2011, equivalent to ASTM C191-13) [26]. The fluidity of the mortar was measured according to the correct methods for determining the fluidity of cement mortar (GB/T 2419-2005, similar to EN196-3:2005) [27]. Our results show that the fluidity of each group was generally good and thus met the appropriate mixing requirements.

Table 1: The chemical composition of the nickel slag.

|   | SiO\(_2\) | Al\(_2\)O\(_3\) | CaO | Fe\(_2\)O\(_3\) | SO\(_3\) | TiO\(_2\) | MnO | MgO | K\(_2\)O | Others |
|---|----------|----------------|-----|---------------|---------|----------|------|-----|---------|--------|
|   | 22.26    | 18.97          | 33.90 | 2.87          | 2.49    | 0.77     | 2.87 | 7.81 | 0.43    | 7.63   |

Figure 1: SEM image of the nickel slag powder (magnification: 5000x).

Figure 2: XRD spectrum of the nickel slag powder.
After the test cube had been cured for one day, three days, seven days, and 28 days, the compressive strength of the mortar cube was measured using the compressive strength machine shown in Figure 3(b), according to China standard GB/T 17671-1999, which is equivalent to ASTM C109/C109M[26]. The loading rate was set at 2,400 ± 200 N/s, and the data showing the compressive strength of the mortar cube were recorded until the sample broke. It is worth noting that three replicates were measured in each group, and the average value of the strength of the three samples was taken as the representative result.

SEM images were also taken to reveal the microstructure of different alkali-activated nickel slag mortars and the effect of alkali activators on the morphology of hydrated products. The composition and content of the hydrated products were tested with XRD and FT-IR. A mercury porosimeter was used to measure the pore size distribution and the most probable pore size and porosity of the sample. All the testing methods noted above were conducted according to standard procedures so that these details are not included here.

3. Results and Discussion

3.1. Initial and Final Setting Times. Figure 4 shows the results of the initial and final setting times of the AANS activated by the three alkali activators with different contents. When the Na₂O equivalent was 0.082 mol, the initial setting time for the AANS was in the order of NS7.5-NC2.17 (Na₂SiO₃ + Na₂CO₃) > NS10 (Na₂SiO₃) > NH6.56 (NaOH). This can be explained by the fact that NaOH has the strongest alkalinity followed by Na₂SiO₃ and Na₂CO₃. When the Na₂O equivalent was the same, higher alkalinity tended to cause the rapid progress of the polycondensation reaction, resulting in a fast setting time for NH6.56. This result was consistent with Xin et al.’s [17] findings and confirmed that NaOH content plays a significant role in determining the setting and hardening of the AANS [28]. When the Na₂O equivalent was increased to 0.107 mol or 0.123 mol, the AACMs with the shortest initial setting or final setting time were still the AACMs prepared with NaOH. The AACMs prepared with Na₂SiO₃/Na₂CO₃ had the second shortest initial and final setting times.

We also observed that the initial setting time for NS11.25-NC3.26 (80 min) was 35 minutes less than for NS7.5-NC2.17 (45 min). This initial 45-minute setting time was consistent with the requirements of the Chinese National Standard for OPC [29]. The aforementioned shortened setting time caused by increasing the content of Na₂SiO₃ and Na₂CO₃ was attributed to a high concentration of Na⁺ in the blended system. An increasing amount of Na⁺ requires a
large amount of water to form hydrate, so the free water content of the entire system decreases rapidly. The dissolved silicon-oxygen tetrahedron monomer and aluminum-oxygen tetrahedron monomer could therefore quickly polymerize to produce a lower setting time [30]. Li et al. [31] also showed that the delay in the setting of an alkali-activated slag with Na₂CO₃ activation was due to the precipitation of calcite prior to C-A-S-H gel.

Unlike the NaOH and Na₂SiO₃/Na₂CO₃ systems, the increase in the content of Na₂SiO₃ delayed the initial and final setting times of the AACM. This was because when the amount of Na₂SiO₃ was increased, citric acid or a water-reducing agent was needed to improve fluidity and workability, as described in Section 2.1. H⁺ provided by citric acid reduced the alkalinity of the early hydration products, slowing down the hydration reaction and thus delaying the initial and final setting times. Consequently, for the three Na₂O equivalents (0.082, 0.107, and 0.123 mol), all the initial setting times of the Na₂SiO₃ samples exceeded the maximum value of 45 minutes for OPC required by the Chinese National Standard [29].

3.2. The Effect of Alkali Activators on Compressive Strength

3.2.1. The Influence of Alkali Activator Content. Figure 5 shows that the compressive strength of a mortar cube increases as the curing age increases, regardless of types and content of the alkali activator. During the first three days, the increasing rate of compressive strength was relatively large, and then the rate of increase gradually decreased. This development in strength was similar to that of OPC. The highest 28-day compressive strength values of alkali-activated nickel slag mortars with Na₂SiO₃ (Figure 5(a)), NaOH (Figure 5(b)), and Na₂SiO₃/Na₂CO₃ (Figure 5(c)) were 83.93 MPa, 81.10 MPa, and 96.02 MPa, respectively. Thus, the alkali-activated nickel slag mortar with a composite alkali activator of Na₂SiO₃/Na₂CO₃ (11.25% Na₂SiO₃ and 3.26% Na₂CO₃) possessed the largest 28-day compressive strength, while the alkali activator of Na₂SiO₃ had a similar compressive strength to that of NaOH.

Interestingly, regardless of the alkali activator used, the compressive strength of alkali-activated nickel slag mortar generally increased fast with an initial increase in the content of the alkali activator and stabilized with a further increase in the alkali activator content when the same curing age was reached. For example, Figure 5(b) shows that, at 28 days, the alkali-activated nickel slag mortar excited by NH₈.52 (i.e., the content of NaOH was 8.52%) had a 12% higher strength than the one excited by NH₆.56 (i.e., the content of NaOH was 6.56%) when the content of NaOH increased by 1.96% (from 6.56% to 8.52%), while with a further 1.32% increase in NaOH (from 8.52% to 9.84%), the alkali-activated nickel slag mortar only had a further 3% increase in terms of strength. This result was expected as more raw nickel slag materials could be dissolved for polymerization with an increase in NaOH content, which could impact both the rate of decomposition of the raw materials and the ensuing polymerization rate [32]. However, when NaOH is too high, the excessive gel generated on the raw material becomes a barrier to further polymerization.

3.2.2. The Influence of the Alkali Activator Type. Figure 6 shows the influence of different types of the alkali activator on the compressive strength of the alkali-activated nickel slag mortar cube. Regardless of the type of the alkali activator, the compressive strength of the Na₂O equivalent increased as the curing age increased. The compressive strength increased fast and then stabilized with an increase in the curing age. For example, in Figure 6(a), when the Na₂O equivalent was 0.082 mol and its curing age was three days, the compressive strength was between 52.7% and 65.1% of its compressive strength at 28 days. At a curing age of seven days, the compressive strength was between 82.3% and 88.9% of the compressive strength at 28 days.

As seen in Figure 6(a), when the Na₂O equivalent was 0.082 mol, at a curing age of one day, the compressive strength of NH₆.56 (i.e., with the content of NaOH at 6.56%)
was higher than that of NS10 (i.e., the content of Na2SiO3 was 10%). In contrast, at a curing age of between three and 28 days, the compressive strength of NH6.56 (i.e., when the content of NaOH was 6.56%) became lower than that of NS10 (i.e., the content of Na2SiO3 was 10%). Such a contrast was caused by the change of alkalinity and the products. At one day, a higher alkalinity proved to be favorable to the disintegration of raw materials causing the generation of more gels. When Na2O was equivalent between NaOH, Na2SiO3, and Na2CO3, the order of alkalinity was NaOH > Na2SiO3 > Na2CO3. Therefore, at one day, the compressive strength of NH6.56 (i.e., when the content of NaOH was 6.56%) was higher. Later, as the curing age increased, anhydrous Na2SiO3 gradually dissolved, which not only provided OH\(^-\) for the reaction process but also (SiO\(_4\))\(^{4-}\) [24], which worked together to increase the compressive strength of the Na2SiO3 system and surpassed that of the NaOH system. The lower alkalinity of the Na2SiO3/Na2CO3 system prevented partial Na2SiO3 from entering the geopolymer network, which impeded the development of

Figure 5: The influence of different contents of alkali activators, Na2SiO3 (a), NaOH (b), and Na2SiO3/Na2CO3 (c), on the compressive strength of the alkali-activated nickel-slag mortar cube.
compressive strength. Therefore, the Na$_2$SiO$_3$/Na$_2$CO$_3$ system always had the lowest compressive strength when the Na$_2$O equivalent was 0.082 mol.

Interestingly, there was a change in the order of compressive strength as the content increased. As we can see in Figures 6(b) and 6(c), when the Na$_2$O equivalent was 0.107 mol, the Na$_2$SiO$_3$/Na$_2$CO$_3$ system always had the highest compressive strength. On the one hand, the content increased the alkalinity of the solution, while on the other hand, CO$_3^{2-}$ reacted preferentially with Ca$^{2+}$ to form CaCO$_3$ and aluminosilicate. The consumption of Ca$^{2+}$ sped up the dissolution of the gelling material and increased the fluidity of the material as well as the porosity. Because of the presence of sodium carbonate and higher alkalinity, the dissolution of anhydrous Na$_2$SiO$_3$ was enhanced at an early age, and the dual role of Na$_2$SiO$_3$/Na$_2$CO$_3$ in the hydration process made the compressive strength of the mortar of the Na$_2$SiO$_3$/Na$_2$CO$_3$ system higher than that of the other two systems.

The early compressive strength of the mortar of NS13-N2-J1 (i.e., when the content of Na$_2$SiO$_3$ was 13%) was the lowest. This was due to the mixture of citric acid in NS13-N2-J1, which reduced the alkalinity of the system and was not conducive to the progress of the polycondensation reaction, leading to a lower compressive strength at an early stage than that of NH8.52. As the curing age increased, the effect of citric acid gradually weakened, and the compressive strength of the NS13-N2-J1 mortar was close to, or slightly higher than, that of NH8.52.

In accordance with the development of compressive strength described above (Figures 5 and 6), when the equivalent of Na$_2$O was 0.123 mol, the compressive strength

![Graphs showing compressive strength development over age](https://via.placeholder.com/150)

**Figure 6:** When $n$(Na$_2$O) = 0.082 mol (a), $n$(Na$_2$O) = 0.107 mol (b), and $n$(Na$_2$O) = 0.123 mol (c), the compressive strength of an alkali-activated nickel slag mortar is excited by different types of the alkali activator.
of Na$_2$SiO$_3$/Na$_2$CO$_3$ at 28 days was the highest, with a slightly higher increase of 1.4% than that of the equivalent of Na$_2$O when it was 0.107 mol. Therefore, when the content of Na$_2$O was 0.107 mol (i.e., the content of Na$_2$SiO$_3$ was 9.75% and the content of Na$_2$CO$_3$ was 2.82%), the compressive strength of the Na$_2$SiO$_3$/Na$_2$CO$_3$ sample became almost optimal. A further increase of Na$_2$O beyond 0.107 mol proved not to be economical, however. In this study, the compressive strength at 28 days was 32.4% higher than that of OPC.

3.3. Microstructural Analysis. To further understand the impact of alkali activators on the development of compressive strength, the results of a microstructural analysis are presented in this section. As shown in Section 3.2, when the content of Na$_2$O reached 0.107 mol, an optimal compressive strength was also produced. The samples with Na$_2$O equivalents of 0.107 mol were therefore chosen in order to conduct a microstructural analysis on the types and content of the hydrated products, the pore size distribution, and the porosity of AACMs.

3.4. SEM-EDS Analysis. Figures 7–9 show the representative SEM images of the reaction products of AACMs activated by Na$_2$SiO$_3$, NaOH, and Na$_2$SiO$_3$/Na$_2$CO$_3$ at various curing ages.

The results show that, at a curing age of one day, there were many unhydrated nickel slag particles of different sizes, with some appearing as clusters in the Na$_2$SiO$_3$ system. The particles and clusters are not closely combined, and a large number of long, wide cracks can be observed. In the NaOH system, however, a large number of nickel slag particles and flocculated materials are closely combined, though several cracks and large pores still exist. In the Na$_2$SiO$_3$/Na$_2$CO$_3$ system, a large amount of hydrated gel encapsulates the unhydrated nickel slag particles, with their close combination leading to shorter cracks.

When the curing age was three days, more nickel slag particles participated in the hydration reaction, and denser reaction products were formed in all the systems. Thus, the reaction products of the three systems are all connected in one piece. It is worth noting here, however, that there are still unhydrated nickel slag particles. With further curing, the microstructure of the three systems becomes more compact. This hydration development contributes to a quick increase in the compressive strength of the systems, as shown in Figures 5 and 6. Compared with the NaOH and Na$_2$SiO$_3$ systems, the Na$_2$SiO$_3$/Na$_2$CO$_3$ system appears smoother and more interconnected as the curing age increases. This is consistent with the results given in Figure 10 which shows that the Na$_2$SiO$_3$/Na$_2$CO$_3$ system has a denser microstructure with smaller pores than the other two systems. Thus, the Na$_2$SiO$_3$/Na$_2$CO$_3$ system also has a higher compressive strength when compared with the other two systems, as shown in Section 3.2 (Figure 5).

The reaction products of the three systems were then analyzed by EDS. The mass ratio analysis of elements in the reaction products of the NH8.52 and NS9.75-NC2.82 systems at each curing age is shown in Figures 11 and 12; their corresponding SEM images are shown in Figures 8 and 9 (where the zones marked A represent the gel areas for EDS analysis). The results of the mass ratio analysis of the reaction products of the NH8.52 and NS13-N2-J1 groups were generally consistent, so only the results for the NS9.75-NC2.82 system are shown and analyzed here.

Figure 11 shows that the mass ratio of Ca/Si decreased considerably as the curing age increased from one to three days. In the following three to seven days, the mass ratio of Ca/Si continued to decrease but at a more moderate rate. Afterwards, the mass ratio of Ca/Si tended to be constant with a stable value of 1.686. The mass ratio of Ca/(Si + Al) decreased dramatically between one and three days, with the ratio value fluctuating between 0.85 and 0.86. As the curing age increased, the mass ratio of (Na + Ca)/(Si + Al) fluctuated between one and three days and then increased significantly between three and seven days. Finally, the mass ratio converged to 1.35 at a curing age of 28 days.

Figure 12 shows the mass ratio variations of the AACM activated by Na$_2$SiO$_3$/Na$_2$CO$_3$. When compared with Figure 10, we can see that the changing trend of the Ca/Si mass ratio and Ca/(Si + Al) mass ratio is similar to that of NaOH. Both decrease rapidly at first and then reach a stable value. The mass ratio change of (Na + Ca)/(Si + Al) is different from the NaOH group at an early curing age. As the curing age increases, the mass ratio of (Na + Ca)/(Si + Al) increases continually until it reaches 1.234, beginning at a high rate of increase and ending with a negligible rate of increase.

The fact that the mass ratios of Ca/Si, Ca/(Si + Al), and (Na + Ca)/(Si + Al) in cementitious materials stabilize at a curing age of 28 days leads us to conclude that most reaction products are formed at 28 days. This observation indicates that the SEM images of 28-d samples (Figures 7–9) are representative of the microstructure of the final reaction products and can thus be used for the compressive strength analysis carried out in Section 3.2.

3.5. XRD Analysis. Figure 13 shows the XRD spectra of the reaction products of an alkali-activated nickel slag activated by different types of alkali activators at different curing ages when the Na$_2$O equivalent was 0.107 mol. The product spectra of Na$_2$SiO$_3$-activated nickel slags were generally the same as those of Na$_2$SiO$_3$/Na$_2$CO$_3$-activated nickel slags, indicating that the reaction products of the two are also similar. Here, we only present the representative XRD spectra of alkali-activated nickel slags activated by Na$_2$SiO$_3$/Na$_2$CO$_3$.

As we can see in Figure 13(c), the alkali-activated nickel slag powder prepared with Na$_2$SiO$_3$/Na$_2$CO$_3$ had a large diffusion peak in a range between 20° and 40°, indicating that there were a large number of amorphous substances. The main crystal phases were spinel, Na$_2$SiO$_3$, and Na$_2$CO$_3$. When the curing age was one day, the diffraction peak of anhydrous Na$_2$SiO$_3$ in the reaction products disappeared, indicating that a large amount of anhydrous Na$_2$SiO$_3$ was hydrated.
Figure 7: SEM images of NS13-N2-J1 (magnification: 5000x) at one day (a); three days (b); seven days (c); 28 days (d).

Figure 8: SEM images of NH8.52 (magnification: 5000x) at one day (a); three days (b); seven days (c); 28 days (d).
The new diffraction peaks generated were CaCO$_3$, tobermorite, calcium silicate hydrate, gehlenite, gmelinite, and stilbite. When the curing age was three days, the diffraction peaks listed above were intensified, and new diffraction peaks of pillar zeolite appeared. When the curing age was seven days, the diffraction peaks noted above continued to be intensified, with new crystals of orthorhombic zeolite ($2\theta = 26.70$) being formed. By 28 days, no new crystalline phase substances were formed, but all the diffraction peaks noted above were intensified.

If we compare Figure 13(b) with Figures 13(a) and 13(c), we can see that the polymer product activated by NaOH is different from the other two. Figure 13(b) shows that there is a hump in the range between 20° and 40°, with the main crystal phases being spinel and Na$_2$CO$_3$, which were produced by the carbonization of NaOH. Compared with the original powder of a nickel slag, most of the diffraction peaks of Na$_2$CO$_3$ in the hydrated products disappeared after one day's hydration, and new diffraction peaks appeared, namely, tobermorite, CaCO$_3$, calcium silicate hydrate, epistilbite, gehlenite, and gmelinite.

As the curing age increased, no new diffraction peaks appeared in the reaction products, indicating that no new substances were formed. However, the intensity of the diffraction peaks of gmelinite was significantly enhanced. The intensity of the diffraction peaks of tobermorite, calcium silicate hydrate, and CaCO$_3$ was also enhanced, indicating that hydration was continuously increasing. Although the reaction products were slightly different from those of the other two groups, all the hydration levels increased as expected.

Figure 13 also shows that the alkali-activated nickel slags activated by the three alkali activators all produced reaction products mainly composed of Ca, Si, Ca, Si, Al; and Na, Ca, Si, Al. The different degrees of hydration at different ages indicate that hydration increases in line with the curing age.

3.6 FT-IR Analysis. Figure 14 represents the FT-IR spectra of an alkali-activated nickel slag activated by different alkali activators when the Na$_2$O equivalent was 0.107 mol. The results show that the infrared spectra of the alkali-activated nickel slags activated by the three alkali activators were similar, indicating that the reaction products of the three AACMs were also similar. Here, we only present the FT-IR spectra of Na$_2$SiO$_3$/Na$_2$CO$_3$-activated nickel slags that are representative of all FT-IR spectra (Figure 14(c)).

The absorption peaks corresponding to the wave numbers of 3,460 cm$^{-1}$ and 1,640 cm$^{-1}$ appear to be due to the asymmetric stretching and bending vibrations of the Si-O-H bond, respectively. The absorption peak areas at wave numbers of 3,460 cm$^{-1}$ and 1,640 cm$^{-1}$ of the reaction products are larger than those of original nickel slag powder. As the curing age increases, the band area also gradually
increases. This indicates that, as the curing age increases, the Si-O-H bond strength and the number of reaction products also increase, as does the content of bound water molecules.

The absorption peak corresponding to a wave number of 1,430 cm\(^{-1}\) is caused by the symmetrical stretching vibration of the C-O bond [33], which indicates that carbonate is present in the nickel slag and the reaction products. According to the XRD spectrum, carbonates are CaCO\(_3\) and Na\(_2\)CO\(_3\). With an increase in the curing age, the band area around a wave number of 1,430 cm\(^{-1}\) also gradually increases, indicating that the number of C-O bonds and the carbonate content also increase.

The absorption peak corresponding to the wave number of 960 cm\(^{-1}\) appears because of the asymmetric stretching vibration of the Si-O-Si (Al) bond [33], which represents the absorption peak of the Si-Al component in the original nickel slag powder. According to the literature [34] on the subject, the characteristic peak of the asymmetric stretching vibration of the TOT (T = Si or Al) bond in the C-(A)-SH gel, the main reaction product of cement and the AACM of a

Figure 10: The pore size distribution of alkali-activated nickel slags activated by different types of the alkali activator. (a) NS13-N2-J1. (b) NH8.52. (c) NS9.75-NC2.82.
slag, is located near the wave number 970 cm\(^{-1}\); the characteristic infrared absorption peak of wave number 996 cm\(^{-1}\) is attributed to the asymmetrical stretching vibration of the T-O-T (T=Si or Al) bond in the aluminosilicate mineral. Compared with the spectra of the original nickel slag, the characteristic infrared absorption peaks of the Si-O-Si (Al) bonds move towards a larger wave number than those of the reaction products. In the original nickel slag powder, the asymmetrical stretching vibration peak of the Si-O-Si (Al) bond was located at 960 cm\(^{-1}\). When the curing age was one day, the asymmetrical stretching vibration peak of the Si-O-Si (Al) bond moved to 986 cm\(^{-1}\), and as the curing age increased, the peak moved towards a larger wave number. At 28 days, this peak was located at 1,000 cm\(^{-1}\). In addition, the peak area of the Si-O-Si (Al) bond also increased, indicating that the degree of polymerization and content of aluminosilicate were both increasing. The observations noted above are consistent with existing studies such as [35].

The absorption peak corresponding to a wave number of about 675 cm\(^{-1}\) is due to the symmetrical tensile vibration of the Si-O-Si and Al-O-Si bonds [33]. The characteristic absorption peaks around 670 cm\(^{-1}\) are observed in the hydration attributed to the formation of new amorphous zeolite phases during the geopolymerization process.

The infrared absorption band near the wave number of 990 cm\(^{-1}\) is caused by the asymmetrical stretching vibration of the T-O-T bond in the aluminosilicate mineral, which is a characteristic of aluminosilicate gels. Figure 14 shows that, with the increase of the curing age, the characteristic peaks of the aluminosilicate gel in the nickel slag geopolymer activated by the three alkali activators gradually move towards a larger wave number, and their band areas also increase. Such a change in the FT-IR spectra is consistent with the results shown in Section 3.2, where the compressive strength of polymers increased as the curing age increased.

Figures 14(a)–14(c) show that the aluminosilicate gel characteristic peaks of the Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\)-activated nickel slag geopolymer have the largest wave number and band area, indicating that the aluminosilicate gel in this geopolymer has the highest degree of polymerization and the largest content. This corresponds with the finding that the compressive strength of the Na\(_2\)SiO\(_3\)/Na\(_2\)CO\(_3\)-activated nickel slag geopolymer is higher than the other two groups. The results of the FT-IR analysis are thus consistent with the compressive strength results outlined in Section 3.2, and the microstructure characteristics outlined in Section 3.3.1.

3.7. Pore Structure Analysis. The literature [35] indicates that pores in concrete can generally be divided into four categories: harmless pores (<20 nm), less-harmful pores (20–50 nm), harmful pores (50–200 nm), and more-harmful pores (>200 nm). Figure 10 shows the distribution of pore-size polymers activated by three alkali activators at different curing ages. The results show that the pores are small, i.e., the harmless pores dominate, indicating that a large number of gel substances were generated to fill in the sample volume. The percentages of harmless pores increased as the curing age increased. For example, at a one-day curing age, harmless pores accounted for more than 80% in the NS9.75-NC2.82 group, about 70% in the NH8.52 group, and 53.73% in the NS13-N2-J1 group. In the ensuing period, the distribution of harmless pores in the NS13-N2-J1 group increased significantly and, at 28 days, was 51.4% higher than at one day.
Figure 10 also shows that the NS9.75-NC2.82 group had a better pore size distribution than the other two groups. This was reflected by the fact that the harmless pores accounted for more than 90% of all the pores in the NS9.75-NC2.82 group, while they accounted for around 80% of all pores in the NS13-N2-J1 and NH8.52 groups. Figure 15 also shows that the porosity of the harmless pores in the NS9.75-NC2.82 group was higher than the other two groups. The pores in the Na2SiO3/Na2CO3 system, which were smaller than in the NaOH and Na2SiO3 systems, verified that the...
compressive strength of the alkali-activated nickel slags activated with Na$_2$SiO$_3$/Na$_2$CO$_3$ was the highest, as shown in Figures 5 and 6 (Sections 3.2.1 and 3.2.2).

From the analysis of the pore structure given above, the harmless pores in all the groups of polymers increased, with porosity decreasing, indicating that the compressive strength of polymers activated by alkali activators increases continuously in line with the curing age. The pore structure of the NS9.75-NC2.82 system had the lowest porosity and the smallest pore size. This indicates that the microstructure of the NS9.75-NC2.82 system was the densest and, therefore, that it had the highest compressive strength in one-part AANS prepared with the three alkali activators.

3.8. Optimal Design for the Application of One-Part AANS. Based on the above analysis and the discussion of the initial and final setting times, compressive strength, and microstructure, we found that the reaction degree of the AACM depended on the composition of activators, governing both the kinetics of formation and the intrinsic characteristics of the reaction products [28]. The results of our comprehensive testing show that, after reaching a certain critical value, increasing the content of alkali activators only results in a slight increase in compressive strength. For the purpose of economy, out of the three contents (0.082mol, 0.107mol, and 0.123mol) in this study, the Na$_2$O equivalent of 0.107mol seems to be the optimal choice. For the Na$_2$O equivalent, one-part AANS activated by Na$_2$SiO$_3$/Na$_2$CO$_3$ achieved higher compressive strength than if it was activated by Na$_2$SiO$_3$ and NaOH. This compressive strength was also much higher than that of OPC (at a 28-day curing age, it was 32.4% higher in our study). The analysis of microstructures, hydration components, and pore structure accords well with the results for strength. The addition of Na$_2$SiO$_3$/Na$_2$CO$_3$ to the AACM with an Na$_2$O equivalent of 0.107 mol is therefore recommended for potential engineering applications.

A detailed optimal design for the application of one-part AANS is thus proposed as follows: the water binder ratio is around 0.35; the binder sand ratio is 1:2; the mill ball loading rate is 30%; and the ball material ratio is 15. The original nickel slag can be milled at high speed for two hours and then mixed with a solid alkali activator for another 0.5 hour of milling at low speed. The Na$_2$O equivalent is

Figure 14: FT-IR spectrum of the alkali-activated nickel slags when the Na$_2$O equivalent was 0.107 mol. (a) NS13-N2-J1. (b) NH8.52. (c) NS9.75-NC2.82.
0.107 mol when the content of Na$_2$SiO$_3$ and Na$_2$CO$_3$ is 9.85% and 2.82%, respectively.

As other mechanical properties such as tensile strength are also important in cementitious materials, a further study should be carried out in the future to evaluate and optimize the tensile strength of one-part AANS with Na$_2$SiO$_3$/Na$_2$CO$_3$.

### 4. Conclusions

This study has explored the effects of the different types and contents of the alkali activator on the setting time and compressive strength of one-part AANS. Based on the findings, an optimal design for the application of one-part AANS has been suggested above.

When the Na$_2$O equivalent was 0.082 mol, the initial setting time of an AANS activated by anhydrous Na$_2$SiO$_3$/Na$_2$CO$_3$ was the longest, while an AANS activated by NaOH had the shortest initial setting time. When the Na$_2$O equivalent was increased to 0.107 mol or 0.123 mol, the AACM with the shortest time was still the one prepared with NaOH, and the initial and final setting times were both shorter for the AANS activated by anhydrous Na$_2$SiO$_3$/Na$_2$CO$_3$, while the initial and final setting times were both prolonged for AACM activated by anhydrous Na$_2$SiO$_3$.
Activated by different types and contents of alkali activators, the development pattern for compressive strength was similar to that of OPC. The compressive strength growth rate of one-part AANS decreased as the curing age increased. With an increase in content, the compressive strength of the AANS activated by anhydrous Na$_2$SiO$_3$ fluctuated. The compressive strength of AANS activated by NaOH and Na$_2$SiO$_3$/Na$_2$CO$_3$ increased with the increasing content of the alkali activators and then reached stability. When the content of Na$_2$O was 0.107 mol, the compressive strength of the Na$_2$SiO$_3$/Na$_2$CO$_3$ sample reached its optimum and was also more economical.

With an increase in the curing age, the microstructures of the three groups of one-part AANS gradually became denser, and the degree of hydration increased. The characteristic peaks of the aluminosilicate gels gradually moved in the direction of a large wave number, and the band area also increased. Harmless pores increased and porosity decreased as the curing age increased, supporting the fact that compressive strength increases with an increase in the curing age.

An optimal design for the practical engineering application of one-part AANS has therefore been suggested. A future study might focus on the evaluation and optimization of the tensile strength of one-part AANS with Na$_2$SiO$_3$/Na$_2$CO$_3$.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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