Mechanism of Alkali-Activated Copper-Nickel Slag Material

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A copper-nickel slag-based alkali-activated cementing material (CNSCM) for backfilling was prepared using copper-nickel slag as a raw material and sodium silicate (SS) as an activating agent. The effects of SS content (6%, 8%, and 10%) and curing humidity on the compressive strength of CNSCM were investigated using an electronic universal testing machine. Types of hydration products and microstructures were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy. The results indicated that by increasing the SS content, the compressive strength of the CNSCM exhibited an increasing trend, followed by a decreasing trend. The optimal content was 8%. Humidity was identified as another factor affecting compressive strength, which reached 17 MPa after curing for 28 d under standard conditions. A decrease in humidity could improve the compressive strength of the material. The main hydration reaction products of the CNSCM were C-S-H gel, Fe(OH)2 or Fe(OH)3 gel, and CaCO3.

1. Introduction

Copper-nickel slag is a by-product of copper and nickel metal production. In China, copper and nickel output generally exceeds 1 million tons annually. This production is accompanied by large amounts of copper-nickel slag discharge and accumulation and thus has become an urgent concern [1]. Production of 1 million tons of metallic copper and nickel by flash furnace smelting generally creates 6–16 tons of copper-nickel slag [2]. The annual storage of copper-nickel slag is currently about 5 million tons, and the cumulative storage exceeds 40 million tons. Secondary utilization of copper-nickel slag worldwide occurs in various forms, including extracting metals [3] and producing glass and ceramics [4]. In building materials, copper-nickel slag is mainly used as a raw material for correcting calcining cement clinker, mixing materials in concrete, and filling materials in mine and underground [5–8]. However, the comprehensive utilization ratio of the aforementioned copper-nickel slag only ranges from 15% to 25%; the rest still accumulates in the yard, occupying a large area of land and presenting significant environmental challenge.

A large number of studies have shown that copper-nickel slag generally contains SiO2, CaO, Fe2O3, and Al2O3, and many of them exist in the form of a glass phase. These products exhibit hydraulic potential and pozzolanic activity [9, 11–14]. Chen et al. examined the preparation of mine filling materials by using water-quenched nickel slag. The results indicated that the water-quenched nickel slag contained a glass phase and crystalline materials. When nickel slag was ground to a specific surface area of 540 m2/kg, a small amount of Na2SO4 and cement clinker could be used as activators to prepare cement-filled mining materials [4]. Microscopic analysis revealed the formation of ettringite and silicon (aluminum) gel containing Ca2+ and Mg2+ under the action activator. Gao demonstrated that incorporating an activator into the tailings produced cementitious filling and mining materials that could meet the requirements of mine cementing and filling [2]. Li illustrated that activated water-quenched nickel slag could serve as the main raw material to
obtain a cementing material that could replace cement in the production of mine filling [1]. Yang et al. used water-quenched nickel slag as a fine aggregate and a certain proportion of cementitious materials to prepare a cementing material with desirable characteristics, such as good water retention, good fluidity, and high hardening strength [3].

Tixier evaluated the effects of copper slag on the hydration of cement-based materials [6]. Ahmari assessed the feasibility of using copper mine tailings in the production of eco-friendly bricks based on geopolymerization [10]. Al-Jabri investigated the effects of using copper slag as a fine aggregate on the properties of cement mortars and concrete, and he found that up to 40%–50% (by weight of sand) of the copper slag could be used to replace fine aggregates to obtain a concrete with high strength and durability requirements [15]. Magallanes Rivera examined pastes of granulated blast-furnace slag (GBFS) and metakaolin (MK) at different GBFS/MK mass ratios and sodium silicate (SS) with different modulus as an activator to prepare samples, and then tested the compressive strength, as well as the structural and microstructural characteristics of the samples [16]. Onuaguluchi also studied the consistency, hardening, and toxic metal immobilization of concrete materials containing copper tailings as an additive [17]. Few studies have evaluated the effects of humidity on the mechanical properties and microscopic products of copper-nickel slag cementitious materials (CNSCMs) [18].

In the present study, the effects of oxide components of copper-nickel slag are analyzed. This study aims to investigate the relationship between alkali dosage, curing humidity, curing age, strength, and microstructure of cementitious materials, which can meet engineering requirements and solve the comprehensive management of copper-nickel slag. The development and use of copper-nickel slag is expected to provide scientific reference for future research.

2. Experiments

2.1. Materials. The copper-nickel slag used in this study was sourced from the Xinjiang copper-nickel mine in Northwest China. The particle features and size were analyzed by X-ray fluorescence (XRF) emission spectroscopy (Figure 1). The chemical composition of the copper-nickel slag is listed in Table 1. The raw materials were used to synthesize cementing materials based on copper-nickel slag, including copper-nickel slag and SS (modulus = 3.0, Be° = 37.6).

The copper-nickel slag belongs to acid slag, on the basis of the basicity coefficient of copper-nickel, as determined using formula (1) [19]. The formula indicates that the activity coefficient and mass coefficient can be used to reflect the ratio of the active component to the inactive component of the copper-nickel slag. The results of formulas (2) and (3) show that the activity of the copper-nickel slag is relatively low. Thus, most studies regard copper-nickel slag as an inert material added to cement calcination or concrete as a fine aggregate. However, in the current study, copper-nickel slag is mixed as an activator and used to stimulate its potential activity as a brand-new iron-rich cementitious material.

\[ M_b = \frac{w(\text{CaO} + \text{MgO})}{w(\text{SiO}_2 + \text{Al}_2\text{O}_3)} = \frac{1.253 + 6.212}{30.68 + 1.473} = 0.232 < 1.0. \]  

(1)

Activity coefficient:

\[ M_a = \frac{w(\text{Al}_2\text{O}_3)}{w(\text{SiO}_2)} = 0.048 < 0.12. \]  

(2)

Mass coefficient:

\[ K_k = \frac{w(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)}{w(\text{SiO}_2 + \text{MnO} + \text{TiO}_2)} = \frac{1.253 + 6.212 + 1.473}{30.68} = 0.291 < 1.0. \]  

(3)

Figure 2 presents the X-ray diffraction (XRD) patterns of the copper-nickel slag, a crystalline material mainly consisting of forsterite (2FeO-SiO₂) and fayalite (2MgO-SiO₂).

2.2. Methods. External blending was conducted to mix different amounts of SS into the dried copper-nickel slag. The water-solid ratio (WSR) of the system was 0.17. The samples in Experiment 1 were prepared in accordance with proportions listed in Table 2. Each group consisted of 3 specimens with 4 different treatment durations: 3, 7, 14, and 28 d. The copper-nickel slag was subjected to planetary ball milling. SS was dissolved in water and poured into a slurry mixer, together with copper-nickel slag powder. The materials were stirred and poured into a cement mold (20 mm × 20 mm × 20 mm), which was placed on a cement mortar shaking table. The materials were compacted and molded using a vibration tamper. They were then placed in a curing box and steam-cured at 25°C ± 1°C, with relative humidity equal to 95% ± 1%. The samples were demolded, with a curing time of 24 h, and placed in a standard curing box. Strength and microscopic tests, such as mineral analysis, were performed by infrared spectroscopy and scanning electron microscopy.

2.3. Tests. X-ray fluorescence: the oxide composition of the raw test material was analyzed using a German Bruker SRS3400 XRF emission spectrometer; the emission target was a Cu target. Compressive strength: unconfined compression strength tests were performed on cured cylindrical samples by using an electronic universal testing machine with a capacity of 100 kN (22.48 kip) and a constant strain rate of 0.5%/min (ASTM C39/C39M). During testing, a considerably thin layer of lubricant coating was applied to the two ends of each sample to minimize friction, as well as subsequent shear stress development of the loading frame.
X-ray diffraction: the phase composition of the sample was analyzed using a German Model D500 XRD spectrometer. The emission target was a Cu target, with a scan range (2θ) from 5° to 80°. The scan rate was 2°/min, with a step size of 0.02. The tube voltage was 40kV, and the tube current was 30mA.

Fourier transform infrared: the Fourier transform infrared (FTIR) spectra were analyzed using the KBr pellet method (1mg sample per 100mg KBr) on a spectrometer, with 32 scans per sample collected from 4000 to 400 cm⁻¹ at a 4 cm⁻¹ resolution.

Scanning electron microscopy: the microstructure of the cured mortar was examined by scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. Chemical elemental analyses were also performed by energy-dispersive X-ray spectroscopy and SEM. The samples were fractured to expose the fresh surface before mounting them on aluminum stubs by using carbon paint. The samples were then sputter-coated with gold and palladium for SEM examination.

3. Results

3.1. CNSCMs Modified by SS

3.1.1. Effect of SS Dosage on Compressive Strength. The experiment aimed to investigate the activity of CNSCMs with different SS contents and different curing times. In the experiment, 6%, 8%, and 10% SS contents were used as activators, and the compressive strengths of the materials with curing times of 3, 7, 14, and 28 d were tested. The effects of activator content on the compressive strengths of CNSCMs cured for different durations are presented in Figure 3. The SS content was markedly influenced by the properties of CNSCMs. When dosage was set to 6%, the strength after curing for 3 d was relatively low, reaching only 2.1 MPa. With an increase in the curing time, the mechanical strength of the CNSCMs improved, and the compressive strength after curing for 28 d reached about 10.6 MPa. These results showed that in the early stages of curing, SS acted more as a binder; thus, the compressive strength was higher than that at a low dosage. Moreover, alkali activation and pozzolanic reaction are insufficient when the content is relatively low. When the SS content reached 8%, the compressive strength evidently changed; the mechanical strength after curing for 3 d was only 5.4 MPa, but the strength of the
samples cured for 28 d reached the maximum (17 MPa). These results indicated that the dosage of 8% facilitates the dissolution of ions. The compressive strength of each age slightly decreased relative to that with a dosage of 8%, whereas the SS content increased to 10%, and the decline rate was about 23.5% at 28 d, with 13.1 MPa. The reason is that as curing time increases, the excessive alkali negatively affects the mechanical strength owing to excessive free OH\(^{-}\) remaining in the samples, thereby weakening the structure of pastes [20]. Overall, the compressive strength of the CNSCMs tended to increase and then decreased with an increase in SS content. Therefore, copper-nickel slag is not only an inert admixture in concrete but also exhibits pozzolanic activity. To eliminate the self-solidification effect of SS, inactive quartz sand was finely ground to the same size as that of the copper-nickel slag, and samples were prepared by adding 8% SS. After 3 d, the samples did not solidify and could not be demolded.

3.1.2. XRD Analysis. The XRD results of CNSCMs with different SS contents and cured for 28 d are presented in Figure 4. Fayalite and forsterite, the main mineral components of the copper-nickel slag, did not participate in the hydration reaction during the alkali-activated process because of their stable chemical properties. Thus, the location and intensity of their diffraction peaks did not change. Compared with the XRD pattern of the copper-nickel slag, the XRD pattern of the CNSCMs showed two diffraction peaks (2\(\theta\) = 29° and 2\(\theta\) = 37°). According to previous studies [21–27], these two peaks belong to C-S-H gel and Fe(OH)\(_2\) or Fe(OH)\(_3\) gel, respectively. These two substances were the new products of the copper-nickel slag during alkali activation. This finding indicated that with SS as an activator, the iron phase in the copper-nickel slag was activated and reacted with OH\(^{-}\) in the solution. However, the intensity of the C-S-H gel diffraction peak was low because C-S-H is an amorphous gel and has poor crystallinity. Together, these gel-like substances strengthened the system.

The thermogravimetry (TG) curves of the specimens are presented in Figure 5. On the TG curve for the CNSCM, one slight step of weight loss is observed. The relative weight loss at temperatures in the 50°C–112°C range was attributed to the loss of free water and loosely bound water; in the 112°C–453°C range, the weight loss was ascribed to the loss of structural water that was present in the form of –OH sites in the geopolymer gel. For the CNSCM, in the 105°C–500°C region (221°F–932°F), the amounts of water loss of the C-S-H gel were 3.2%, 3.2%, and 4.8%. In the 112°C–453°C region, the higher the SS dosage, the greater the water loss. This finding indicated that the amount of C-S-H gel in the CNSCM increased with an increase in SS dosage. The TG curves for both 6% and 8% SS contents diverged from the TG curve for 10% SS content. Low CaO content (3.253%, Table 1) was detected in the copper-nickel slag. Thus, the C-S-H formed with an increase in the SS content could have a reduced Ca/Si ratio, with Ca/Si possibly containing a small amount of amorphous sol gel [28]. Consequently, the CNSCMs exhibited reduced compressive strength and increased mass loss when the SS content was 10%.

3.1.3. FTIR Analysis. Figure 6 presents the copper-nickel slag FTIR and the cementitious material with different SS contents and a curing time of 28 d. The absorption peak of the copper-nickel slag samples at 438 cm\(^{-1}\) corresponded to the bending vibration of the Si-O-Al bond in the [SiO\(_4\)]\(^4\)\(^{-}\) group in fayalite and forsterite. This finding indicated that the Si-O-Al bond in the copper-nickel slag gradually depolymerized and participated in the hydration reaction under the effect of SS. Two absorption peaks at 1752 and 3412 cm\(^{-1}\) represent the bending vibration of combined
3.1.4. Microstructural Analysis. SEM images of CNSCMs with different SS contents for 28 d are presented in Figure 7. In Figure 7(a), the microstructure of the copper-nickel slag is relatively compact, and a large number of granular crystal structures are found on most of the grey basement surface. All crystals were confirmed to be fayalite and forsterite. Si and Fe are the two major constituents of the copper-nickel slag, which may be attributed to the Fe-containing minerals being more brittle and easier to mill. Most dense structures of fayalite and forsterite were not broken (Figure 7(b)), indicating that the reaction of copper-nickel slag with alkali was insufficient at low OH\(^-\) content. Owing to the dense structure of the surface, the entry of ions such as OH\(^-\) to the structure was hampered, causing its collapse. A large number of loose structures revealed that the fayalite and forsterite were broken with an increase in the SS content (Figures 7(c) and 7(d)); simultaneously, gel-like substances appeared on the surface of the particles. These substances wrapped and adhered loose particles to increase the strength of the specimens. As observed, when the dosage was set to 10%, the loose structure was more mechanically stacked after being destroyed. More loose structures and a considerably large amount of gel-like substances were found when the dosage was set to 8%, indicating that 8% SS content contributed to the formation of gel-like substances.

3.2. CNSCMs Modified under Different Curing Humidities

3.2.1. Effect of Curing Humidity on Compressive Strength. When SS was used to modify the copper-nickel slag, although the compressive strength of the CNSCM was relatively high, the actual environmental requirements (dry and moisture-less atmosphere) were not met. We also observed that the specimen exhibited a loose internal structure and high porosity, suggesting that the activity of the sediment was so limited that it could not effectively improve the strength of the specimen. Therefore, Experiment 2 aimed to investigate the effect of curing humidity on the activity of copper-nickel slag. The samples in Experiment 2 were prepared in accordance with the composition listed in Table 3.

Figure 8 shows the relationship between compressive strength and different levels of humidity for different curing periods. In the experiment, 8% SS was used as the activator, and the test piece after demolding was cured with humidity levels of 40%, 70%, and 95%, and the compressive strengths of the samples cured for 3, 7, 14, and 28 d were evaluated. As indicated in Figure 7, curing humidity played an important role in the increase in compressive strength. The mechanical strength of the specimens varied when humidity was reduced. The compressive strength of the CNSCM was relatively low under standard curing conditions (17 MPa) when the curing period was 28 d. The reason is that the humidity in the cement standard curing box was relatively high, allowing water vapor to penetrate the specimens through the internal pores. This process reduces the alkalinity of the system, preventing the copper-nickel slag from exhibiting high potential activity. Under curing conditions with 70% humidity, the compressive
strength of the samples after curing for 3d was 80% that of the sample cured for 28d. This finding indicated that hydration products easily formed and enhanced the compressive strength under curing conditions with 70% humidity. Subsequently, with an increase in the curing period, the strength slightly increased. The specimen placed in the air (cured with 40% humidity) maintained a significant increase in mechanical strength. The samples cured for 3d showed strength similar to that achieved under standard curing conditions, whereas those cured for 7d achieved strength equal to 15 MPa. The strength of the samples cured for 28d exceeded that of the samples cured with 70% humidity, reaching about 21 MPa, with the compressive strength increasing to 73.8%. The pH-dependent solubility of Si is considered one of the most important thermodynamic factors influencing slag activation. Higher alkalinity (and consequently higher amounts of OH\(^{-}\) ions) results in increased dissociation of Si, along with the liberation of Ca, and thus increases the potential to form larger amounts of strength imparting reaction products at early ages.

3.2.2. XRD Analysis. The XRD results for the CNSCMs cured for 28d with different levels of humidity are presented in Figure 9. The location and intensity of fayalite and forsterite diffraction peaks did not change, implying that these substances did not participate in the hydration reaction during the alkali-activated process. The diffraction peak intensities at \(2\theta = 29^\circ\) and \(2\theta = 37^\circ\) were the highest in N6. This result indicates that the alkali-activated reaction was the most sufficient under curing conditions with 40% humidity, generating more C-S-H gel and Fe(OH)\(_2\) or Fe(OH)\(_3\) gel, and increasing the compressive strength of the samples. Calcium carbonate

**Figure 7:** SEM micrographs of CNSCMs with different SS contents and curing time of 28d. (a) Copper-nickel slag, (b) 6%, (c) 8%, and (d) 10%.

**Table 3:** Mix proportions of Experiment 2.

| Number | SS (%) | CNS | WSR | Curing humidity (%) |
|--------|--------|-----|-----|---------------------|
| N4     | 8      | 250 | 0.17| 95                  |
| N5     | 8      | 250 | 0.17| 70                  |
| N6     | 8      | 250 | 0.17| 40                  |

SS, sodium silicate; CNS, copper-nickel slag; WSR, water-solid ratio.
crystals (CaCO3) were simultaneously detected in the N5 and N6 samples, which confirmed that C-S-H gel in the CNSCM reacts with carbon dioxide in the atmosphere when the humidity is lower, improving the strength of the specimen. The reason is that the large amount of water vapor in the curing box prevents the gel from coming into contact with carbon dioxide in the air. Moreover, the lower the curing humidity, the greater the chance of contact with carbon dioxide, the greater the production of calcium carbonate, and the higher the diffraction peak strength of calcium carbonate.

3.2.3. Microstructural Analysis. SEM images of the copper-nickel slag and CNSCMs cured under different levels of humidity for 28 d are presented in Figure 10. The energy-dispersive spectroscopy (EDS) micrograph of the CNSCMs cured for 28 d was examined to analyze the morphology of the reaction products. The elemental concentration is provided in Table 4.

Figures 10(a) and 10(b) show that the CNSCMs destroyed most of the original fayalite dense structure, generating a substance similar to gel materials compared with the copper-nickel slag. EDS analysis of point A showed that these flocculent materials included Ca and Fe elements. These flocculent materials bound some inert components together, substantially improving the compressive strength of the material. A large number of needle-like or tube-like products were generated and filled in the pores of the products, rendering the structures denser (Figures 10(c) and 10(d)). These observations, combined with FTIR analysis, indicated that the needle bar product was Na2CO3.

4. Discussion

Copper-nickel slag is difficult to activate because fayalite and forsterite belong to the inert ingredients of copper-nickel slag. However, copper-nickel slag also exhibits pozzolanic activity because of rapid cooling during water quenching. Crystals do not fully exude; parts of these maintain the form of a glass phase, and the main components of these substances contain SiO2, CaO, Al2O3, and MgO. When added to an activator, these materials react with it to generate a zeolite-like product that reflects the gelling properties.

As an activator, water glass has two functions. The first is to provide the required SiO2 in the early stages of polymerization and act as a binder. The other is to provide a highly alkaline environment for polymerization reaction, facilitating the depolymerization of silicate from copper-nickel slag into [SiO4]4− and [AlO4]5− groups. After the polycondensation reaction, zeolite-like materials with a high degree of polymerization are reformed. When the SS content is low, a small amount of OH− is left in the solution, hence the low pH of the solution. In this study, most of the raw materials could not participate in the reaction. The internal depolymerization of the copper-nickel slag occurs slowly, reducing the formation speed of high-polymerization macromolecules. Consequently, the strength of the sample fails to increase. Microscopic tests such as electron microscopy also show that dense fayalite and forsterite were not destroyed in a low-alkalinity environment, and a large number of active materials were still not activated. However, the strength at 6% was higher than the latter from the results of the compressive strength test, which was attributed to SS acting more as a binder in the structure. Although the dosage of the activator is considerably high, the surplus Na2SiO3 forms Na2SiO3·5H2O during the curing process. However, Na2SiO3·5H2O does not participate in the hydration reaction during curing, adversely affecting the strength of the material.

To meet actual environmental requirements, the samples were cured at reduced levels of humidity in this study. The compressive strength of the CNSCMs was higher mainly because the water in the CNSCMs evaporate into...
the environment, causing the original alkali concentration in the material to rise. Such a high-alkali environment is more conducive to the precipitation of SiO$_2$, Al$_2$O$_3$, and CaO. Therefore, large amounts of SiO$_2$, Al$_2$O$_3$, and CaO in the copper-nickel slag were dissolved to form more zeolite-like materials such as C-S-H gel. Second, owing to the presence of much weaker chemical bonds such as Ca-O and Mg-O in the glass network than those of Si-O and Al-O, OH$^-$ could have replaced the reaction with Ca$^{2+}$ and Mg$^{2+}$. Such replacement would destroy the network structure of the glass dominated by oxygen-silicon tetrahedra and oxygen-aluminum tetrahedra. With respect to the production process, a large number of iron phase reacts with OH$^-$ in the system to form Fe(OH)$_2$ or Fe(OH)$_3$ gel, with a small amount of C-S-H gel, because of the high content of Fe$_2$O$_3$ in the copper-nickel slag. These gel-like substances are wrapped on the surface of the structure destroyed by the activator and serve as filling agents, speeding up the increase in compressive strength. The XRD, FTIR, and SEM test results indicate that another reason for the higher compressive strength of the test samples cured with lower humidity is that the hydration products of the active SiO$_2$, Al$_2$O$_3$, and CaO in the copper-nickel slag with SS react with CO$_2$ in the air to form a carbonate crystal filled with tiny pores, increasing the density of the original structure.

5. Conclusions

The development of compressive strength, pore structure, water permeability, and microstructure of a copper-nickel slag-based alkali-activated cementing material are analyzed in this study. The conclusions are summarized as follows:

(1) The significant factors affecting the compressive strength of the copper-nickel slag-based alkali-activated cementing material were Na$_2$SiO$_3$ concentration and curing humidity. With respect to the curing duration, NaOH concentration slightly affected compressive strength. When the Na$_2$SiO$_3$ concentration was low, the compressive strength was relatively high because of the binder. By contrast, when the dosage was too high, the compressive strength decreased, owing to the excessive alkali that negatively affected the mechanical strength of the

Table 4: Composition of CNSCM by SEM-EDS.

| Point | C   | O   | Na  | Al  | Mg  | Ca  | Si   | Fe   |
|-------|-----|-----|-----|-----|-----|-----|------|------|
| A     | 10.29 | 47.44 | 4.94 | 1.39 | 2.12 | 0.93 | 12.73 | 19.12 |
material. The optimum content was 8%, with the compressive strength of 17 MPa and a curing period of 28 d.

(2) To enhance the properties of the composites, CNSCMs with the same amount of SS were cured under three different levels of humidity (40%, 70%, and 95%). Under the standard curing humidity, the strength of the CNSCM was relatively low. The compressive strength was higher under curing conditions with 40% and 70% humidity.

(3) The XRD, FTIR, and SEM/EDS results indicated that the reaction products in the CNSCM were mainly C-S-H gel and Fe(OH)$_2$ or Fe(OH)$_3$ gel. The increase in the compressive strength increase under lower curing humidity was attributed to the reaction of C-S-H gel with CO$_2$ in the air to generate CaCO$_3$. This bar-like substance filled the gaps inside the structure.

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

Conflicts of Interest
There are no conflicts of interest in this publication.

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References
[1] K. Q. Li, Y. Y. Zhang, P. Zhao, and L. Feng, “Activating of nickel slag and preparing of cementitious materials for backfilling,” Advanced Materials Research, vol. 936, pp. 1624–1629, 2014, in Chinese.
[2] S. J. Gao, W. Ni, K. Q. Li et al., “Preparation and hydrated mechanism of mine filling material of water-granulated secondary nickel slag,” Journal of the Chinese Ceramic Society, vol. 41, no. 5, in Chinese, 2013.
[3] Z. Q. Yang, Q. Gao, Y. Q. Wang et al., “Experimental study on new filling cementing material using water-hardening nickel slag tailings of Jinchuan mine,” Chinese Journal of Geotechnical Engineering, vol. 36, no. 8, pp. 1498–1506, 2014, in Chinese.
[4] J. Chen, W. Ni, and J. W. Zhang, “Preparation of cemented whole tailings backfilling materials by using iron and steel slag as major row materials of the cementing agent,” Modern Mining, vol. 30, no. 11, pp. 171–174, 2014, in Chinese.
[5] K. S. Al-Jabri, M. Hisada, S. K. Al-Oraimi, and A. H. Al-Saidy, “Copper slag as sand replacement for high performance concrete,” Cement and Concrete Composites, vol. 31, no. 7, pp. 483–488, 2009.
[6] R. Tixier, R. Devaguptapu, and B. Mobasher, “The effect of copper slag on the hydration and mechanical properties of cementitious mixtures,” Cement and Concrete Research, vol. 27, no. 10, pp. 1569–1580, 1997.
[7] K. S. Al-Jabri, M. Hisada, A. H. Al-Saidy, and S. K. Al-Oraimi, “Performance of high strength concrete made with copper slag as a fine aggregate,” Construction and Building Materials, vol. 23, no. 6, pp. 2132–2140, 2009.
[8] W. Wu, W. Zhang, and G. Ma, “Mechanical properties of copper slag reinforced concrete under dynamic compression,” Construction and Building Materials, vol. 24, no. 6, pp. 910–917, 2010.
[9] C. Cartwright, F. Rajahpouri, and A. Radlinskna, “Shrinkage characteristics of alkali-activated slag cements,” Journal of Materials in Civil Engineering, vol. 27, no. 7, Article ID B4014007, 2015.
[10] S. Ahmari and L. Zhang, “Production of eco-friendly bricks from copper mine tailings through geopolymerization,” Construction and Building Materials, vol. 29, no. 4, pp. 323–331, 2012.
[11] G. Puerta-Falla, A. Kumar, L. Gomez-Zamorano, M. Bauchy, N. Neithalath, and G. Sant, “The influence of filler type and surface area on the hydration rates of calcium aluminate cement,” Construction and Building Materials, vol. 96, pp. 657–665, 2015.
[12] B. Gorai, R. K. Jana, and Premchand, “Characteristics and utilisation of copper slag—a review,” Resources, Conservation and Recycling, vol. 39, no. 4, pp. 299–313, 2003.
[13] S. R. Mirhosseini, M. Fadaee, R. Tabatabaei, and M. J. Fadaee, “Mechanical properties of concrete with Sarcheshmeh mineral complex copper slag as a part of cementitious materials,” Construction and Building Materials, vol. 134, pp. 44–49, 2017.
[14] S.-j. Liu, Q.-q. Hu, F.-q. Zhao, and X.-m. Chu, “Utilization of steel slag, iron tailings and fly ash as aggregates to prepare a polymer-modified waterproof mortar with a core-shell styrene-acrylic copolymer as the modifier,” Construction and Building Materials, vol. 72, no. 2, pp. 15–22, 2014.
[15] K. S. Al-Jabri, A. H. Al-Saidy, and R. Taha, “Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete,” Construction and Building Materials, vol. 25, no. 2, pp. 933–938, 2011.
[16] R. X. Magallanesrivera, “Alkali-activated slag-metakaolin pastes: strength, structural, and microstructural characterization,” Journal of Sustainable Cement-Based Materials, vol. 2, no. 2, pp. 111–127, 2013.
[17] O. Onuaguluchi, O. Eren, O. Burciaga-Diaz, and J. I. Escalante-Garcia, “Copper tailings as a potential additive in concrete: consistency, strength and toxic metal immobilization properties,” Indian Journal of Engineering & Materials Sciences, vol. 19, no. 2, pp. 79–86, 2012.
[18] L. Wang, Y. Wei, G. Lv, L. Liao, and D. Zhang, “Experimental studies on chemical activation of cementitious materials from smelting slag of copper and nickel mine,” Materials, vol. 12, no. 2, pp. 303–314, 2019.
[19] K. S. Al-Jabri, M. Hisada, A. H. Al-Saidy, and S. K. Al-Oraimi, “Performance of high strength concrete made with copper slag as a fine aggregate,” Journal of the Chinese Ceramic Society, vol. 37, no. 7, pp. 1074–1078, 2009, in Chinese.
[20] M. Sofi, J. S. J. van Deventer, P. A. Mendis, and G. C. Lukey, “Engineering properties of inorganic polymer concretes
[22] D. Ravikumar and N. Neithalath, “Effects of activator characteristics on the reaction product formation in slag binders activated using alkali silicate powder and NaOH,” *Cement and Concrete Composites*, vol. 34, no. 7, pp. 809–818, 2012.

[23] P. D. Silva, K. Sagoe-Crenstil, and V. Sirivivathanon, “Kinetics of geopolymerization: role of Al₂O₃ and SiO₂,” *Cement and Concrete Research*, vol. 37, no. 4, pp. 512–518, 2007.

[24] D. Krizan and B. Zivanovic, “Effects of dosage and modulus of water glass on early hydration of alkali-slag cements,” *Cement and Concrete Research*, vol. 32, no. 8, pp. 1181–1188, 2002.

[25] H. Z. Lian, Z. L. Zhang, and Y. H. Wang, “Rapid evaluation on activity of pozzolanic materials,” *Journal of Building Materials*, vol. 4, no. 3, pp. 299–304, 2001, in Chinese.

[26] Y. F. Hou, D. M. Wang, Q. Li et al., “Effect of water glass performance on fly ash-based geopolymers,” *Journal of the Chinese Ceramic Society*, vol. 36, no. 1, pp. 61–64, 2008, in Chinese.

[27] J. Chang, Y. F. Fang, and Y. Li, “Effects of calcium to silicon ratios on accelerating carbonation of calcium silicate hydrate,” *Journal of the Chinese Ceramic Society*, vol. 42, no. 11, pp. 1377–1382, 2014, in Chinese.

[28] K. Garbev, P. Stemmermann, L. Black, C. Breen, J. Yarwood, and B. Gasharova, “Structural features of C-S-H(I) and its carbonation in air–A Raman spectroscopic study. Part I: fresh phases,” *Journal of the American Ceramic Society*, vol. 90, no. 3, pp. 900–907, 2007.

[29] H. Peng, “Study on comprehensive utilization of Nalanda furnace slag,” *Metal Mine*, vol. 34, no. 3, pp. 58–61, 2004, in Chinese.

[30] A. M. Kalinkin, S. Kumar, B. I. Gurevich et al., “Geopolymerization behavior of Cu-Ni slag mechanically activated in air and in CO₂ atmosphere,” *International Journal of Mineral Processing*, vol. 112–113, no. 24, pp. 101–106, 2012.
