



Use of Mine Tailings as Precast Construction Materials through Alkali Activation

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Abstract

A study of the application of mine tailings as precast construction materials through alkali activation has been carried out, focusing on efficiently activating mine tailings, reducing alkali consumption, decreasing curing time and improving compressive strength. Firstly, the effect of temperature on the alkali activation of mine tailings was studied. Secondly, the impact of additives, i.e., calcium hydroxide and aluminum oxide, on the compressive strength of samples was investigated. Thirdly, the impact of forming pressure on sample strength was studied. Test results showed that unconfined compressive strength (UCS) of 40 MPa was achieved with the geopolymerization products through optimization. Finally, to elucidate the geopolymerization mechanism of mine tailings, microscopic and spectroscopic techniques including SEM/EDX, XRD, and FTIR spectroscopy were used to investigate the microstructure and the elemental and phase composition of the geopolymerization products. The findings of the present work provide a practical method for applying mine tailings as precast construction materials through alkali activation.

Keywords Mine tailings · Alkali activation · Geopolymerization · Compressive strength · Durability

1 Introduction

In mining activity, after the valuable materials are extracted from ores, millions of tons of solid rejects, i.e., mine tailings, are stored in the tailings dam, which occupies a huge area of land and leads to high monetary, environmental and ecological costs. For example, the impoundment of mine tailings can result in serious environmental problems such as mine dust and tailings dam failure. On the other hand, the manufacture of general construction material results in a large amount of greenhouse gas emissions. Thus, there is great interest in the utilization of mine tailings, for which much energy is consumed during the comminution process, as construction materials using geopolymerization, a novel alkali-activation technique [1–6].

Geopolymerization is a process for obtaining a polymeric structure from aluminosilicate by dissolving aluminosilicate sources in a strong alkali (NaOH) solution at an elevated temperature. After curing at an elevated temperature for a specific time, the geopolymerization product shows greatly increased compressive strength. Therefore, the product can be used as construction materials such as bricks or road pavement material. This process provides a very promising method for the stabilization and recycling of mine tailings.

Various works have been carried out to study the impact of reaction temperature on geopolymerization. For example, some researchers have fabricated bricks through geopolymerization under ambient conditions or elevated temperature such as 60–90 °C [7, 8], while others have conducted geopolymerization at temperatures above 100 °C [2, 3].

It has been reported that, compared with monovalent cations such as Na⁺ and K⁺, multivalent cations, for example, Ca²⁺ and Mg²⁺, can help increase the strength of the geopolymerization product. The addition of a moderate amount of calcium-containing materials has a significant effect on the structure and properties of the geopolymer. Granizo et al. [9] claimed that the addition of calcium may initiate the formation of calcium silicate hydrate (C-S-H), which can improve the compressive strength of the geopolymer product. Yip et al. [10] also investigated the

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effects of the addition of calcite on a metakaolin-based geopolymer. The results indicated that the addition of a moderate amount of calcite had positive effects on the strength of the geopolymer product.

In the study of geopolymerization, successful cases with high compressive strength of the geopolymerization product are usually achieved with aluminosilicate minerals with a low Si/Al ratio, which is usually considered the most important parameter affecting the compressive strength of the geopolymer [11–13]. Many works have shown that an optimum Si/Al ratio should be in the range of 1–3.

To date, many studies have been carried out on the geopolymerization of clay minerals and fly ash [7, 8, 14, 15], with few works being focused on mine tailings [4]. Compared with other aluminosilicate sources, mine tailings have some disadvantages such as comparatively large particle size, low reactivity and high Si/Al ratio, which result in large consumption of alkali, long curing time, low compressive strength and weak resistance against water. All these problems hinder the application of the geopolymerization of mine tailings as construction materials. For example, it was reported [4] that the compressive strength of a product is less than 20 MPa after 7 days of curing when 15 M NaOH was already used.

It is therefore vital to focus on addressing the problems associated with conventional geopolymerization of mine tailings. In the present study, specific efforts will be made to increase the compressive strength—a key criterion for assessing a precast construction material—of mine tailings by increasing the activation temperature, adding $\text{Ca}(\text{OH})_2$ and reacted Al_2O_3 , and applying forming pressure to decrease the Si/Al ratio. The findings of the present study will demonstrate the effective treatment and utilization of mine tailings as precast construction material, saving the land required for tailings impoundment and reducing the demand for energy-intensive construction materials.

2 Materials and Methods

2.1 Materials

Research-grade sodium hydroxide (NaOH, >99%) and calcium hydroxide ($\text{Ca}(\text{OH})_2$, >95%) were obtained from Alfa Aesar. Aluminum oxide powder (Al_2O_3 , >98%) was from Sigma-Aldrich. Mine tailings samples, collected from the tailing dam of a copper mine in southern Tucson, were used as received without further processing. The major element composition of the mine tailings is shown in Table 1, and the mineral composition is listed in Table 2. The lab sieving test results, presented in Fig. 1, showed that the 80% passing size (P_{80}) of the tailings was approximately 240 μm .

Table 1 Major element composition of mine tailings

| Element | Weight % |
|---------|----------|
| O | 51.80 |
| Si | 31.60 |
| Al | 7.31 |
| Ca | 1.53 |
| Fe | 1.80 |
| S | 0.96 |
| K | 3.82 |
| Mg | 0.42 |
| Other | 0.76 |

2.2 Sample Preparation

Sodium hydroxide (NaOH) solutions were prepared by dissolving a specific amount of chemical pellets in tap water to prepare solutions at specific concentrations. The mass ratio of mine tailings to water was kept at 0.6. During experiments, sodium hydroxide solution was slowly added into a 500-ml reaction bottle with 140 g mine tailings being filled beforehand. The solid/liquid mixture was then stirred by a mixer for 3 min to make uniform slurry. The reaction bottle was sealed tightly, moved to an oven and cured at a specified temperature for a specified time. When the effect of additives such as calcium hydroxide and alumina was studied, a specific amount of additives was added into the reaction bottle with mine tailings before the alkali solution was added. After the alkali activation, the reaction bottle was removed from the oven and cooled down in a hood for approximately 40 min, during which mine tailings had already settle to the bottom of the reaction bottle. The supernatant was poured out of the bottle and collected for reuse. Activated mine tailings paste was taken out of the reaction bottle, stirred for 2 min and further filled into a cylindrical mold with an inner diameter of 3.2 cm and height of 6.4 cm. The tailings paste in the mold was gradually compressed manually by a hydraulic pump

Table 2 Mineral composition of mine tailings

| Element | Weight % |
|---------------|----------|
| Quartz | 28.66 |
| K-feldspar | 26.44 |
| Plagioclase | 31.65 |
| Muscovite | 4.03 |
| Biotite | 1.51 |
| Chlorite | 1.09 |
| Swelling clay | 2.39 |
| Kaolinite | 1.09 |
| Calcite | 1.78 |
| Pyrite | 0.61 |
| Anhydrite | 0.75 |

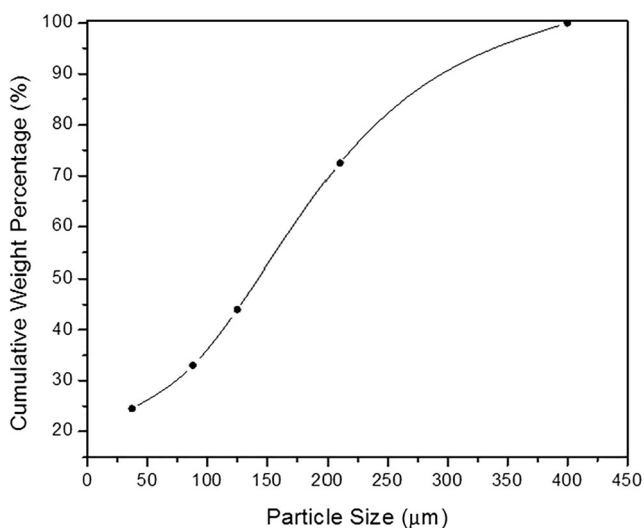


Fig. 1 Cumulative size distribution of mine tailings samples

press with specified pressure as needed. After the compression, the specimen was de-molded and cured in an oven at 90 °C for a specified time. Finally, the cured specimen was taken out of the oven, cooled in ambient conditions for 12 h and prepared for further compressive strength testing. Table 3 summarizes the tests conducted on the geopolymer samples under different conditions.

2.3 Uniaxial Compression Test

The compressive strength of reacted mine tailings samples was measured by the Verso Master loading machine at constant displacement rate of 0.4572 mm/min. Before each measurement, both ends of the specimens were polished by a piece of sandpaper to ensure that they were flat enough for the compression test. At a given experimental condition, a total of three measurements were taken and averaged.

2.4 Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy (SEM/EDS) Characterization

After the uniaxial compression test, the reacted mine tailings samples were characterized using an FEI INSPEC-S50/Thermo Fisher Noran 6 microscope. In the present work, samples were specifically studied for the morphology of fracture surface without being polished.

2.5 FTIR Characterization

A Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with the Smart iTR accessory was used to collect spectra in absorbance mode. The system was equipped with a KBr detector and a diamond ATR (attenuated total reflection) crystal with a 45° angle of incidence to ensure that signals were detected. The data collection time was 32 s, with

resolution of 4 cm⁻¹, and a range of 4000 cm⁻¹ to 525 cm⁻¹. Polished samples were used for FTIR characterization.

2.6 X-ray Diffraction (XRD) Characterization

XRD analyses were performed to investigate the microstructure and phase composition of raw materials and final products. Measurements were made using a Panalytical X'Pert Plus instrument equipped with a programmable incident beam slit and an X'Celerator detector. The X-ray radiation used was Cu Kα, λ = 1.5418 Å. The scan time and instrument parameters were identical for all samples.

3 Results and Discussion

3.1 Characterization of Original Copper Mine Tailings Samples

Before the geopolymerization study, copper mine tailings samples were characterized using inductively coupled plasma mass spectrometry (ICP-MS) and XRD analysis. The major element composition of mine tailings is shown as Table 1, and the mineral composition is listed as Table 2.

3.2 Effect of Activation Temperature

In the present work, mine tailings were activated with 10 M NaOH for 1 h at different temperatures in a sealed vessel, further molded at various forming pressures, and finally cured at 90 °C in an oven for 3 days. The compressive strength test results for the obtained samples are shown as Fig. 2. From the figure, one can see that when activation temperature is relatively low, for example, 90 °C and 120 °C, the compressive strength of samples is lower than 16 MPa and it does not change much with increasing forming pressure. When mine tailings are activated at 170 °C, the maximum compressive strength is as high as 25.65 MPa with 10 MPa forming pressure. Further increasing forming pressure will not increase the compressive strength of samples. When the activation temperature is 200 °C, increasing forming pressure increases the compressive strength of samples. However, the maximum compressive strength is 21.77 MPa even with 15 MPa forming pressure, and the value is lower than the optimum one obtained with an activation temperature of 170 °C.

When compared with some of the materials which have been applied for geopolymerization, such as clay minerals and fly ash, mine tailings usually show much less activity at a low reaction temperature, i.e., 60 °C–90 °C. It results in geopolymerization products with relatively weak mechanical strength compared with those obtained with 'active' geopolymerization sources. For example, the compressive strength of the geopolymerization product of mine tailings is

Table 3 Experimental condition of the prepared geopolymer and the tests conducted

| Sample label | No. | Activation temp (°C) | Activation time (min) | Ca(OH) ₂ (%) | Unreacted Al ₂ O ₃ (%) | Reacted Al ₂ O ₃ (%) | FP (MPa) | Curing time (days) |
|---------------------|-----|----------------------|-----------------------|-------------------------|--|--|----------|--------------------|
| 90–60–0-0-0-3-3 | 1 | 90 | 60 | – | – | – | 3 | 3 |
| 90–60–0-0-0-10-3 | 2 | 90 | 60 | – | – | – | 10 | 3 |
| 90–60–0-0-0-15-3 | 3 | 90 | 60 | – | – | – | 15 | 3 |
| 120–60–0-0-0-3-3 | 4 | 120 | 60 | – | – | – | 3 | 3 |
| 120–60–0-0-0-10-3 | 5 | 120 | 60 | – | – | – | 10 | 3 |
| 120–60–0-0-0-15-3 | 6 | 120 | 60 | – | – | – | 15 | 3 |
| 170–60–0-0-0-3-3 | 7 | 170 | 60 | – | – | – | 3 | 3 |
| 170–60–0-0-0-10-3 | 8 | 170 | 60 | – | – | – | 10 | 3 |
| 170–60–0-0-0-15-3 | 9 | 170 | 60 | – | – | – | 15 | 3 |
| 170–60–5-0-0-10-3 | 10 | 170 | 60 | 5 | – | – | 10 | 3 |
| 170–60–5-0.1–0-10-3 | 11 | 170 | 60 | 5 | 0.1 | – | 10 | 3 |
| 170–60–5-0.5–0-10-3 | 12 | 170 | 60 | 5 | 0.5 | – | 10 | 3 |
| 170–60–5-1-0-10-3 | 13 | 170 | 60 | 5 | 1 | – | 10 | 3 |
| 170–60–5-0-1-3-3 | 14 | 170 | 60 | 5 | – | 0.1 | 3 | 3 |
| 170–60–5-0-1-6-3 | 15 | 170 | 60 | 5 | – | 0.1 | 6 | 3 |
| 170–60–5-0-1-10-3 | 16 | 170 | 60 | 5 | – | 0.1 | 10 | 3 |
| 170–60–5-0-2-0-3 | 17 | 170 | 60 | 5 | – | 0.2 | 0 | 3 |
| 170–60–5-0-2-3-3 | 18 | 170 | 60 | 5 | – | 0.2 | 3 | 3 |
| 170–60–5-0-2-6-3 | 19 | 170 | 60 | 5 | – | 0.2 | 6 | 3 |
| 170–60–5-0-2-10-1 | 20 | 170 | 60 | 5 | – | 0.2 | 10 | 1 |
| 170–60–5-0-2-10-2 | 21 | 170 | 60 | 5 | – | 0.2 | 10 | 2 |
| 170–60–5-0-2-10-3 | 22 | 170 | 60 | 5 | – | 0.2 | 10 | 3 |
| 170–60–5-0-2-10-7 | 23 | 170 | 60 | 5 | – | 0.2 | 10 | 7 |
| 170–60–5-0-5-3-3 | 24 | 170 | 60 | 5 | – | 0.5 | 3 | 3 |
| 170–60–5-0-5-6-3 | 25 | 170 | 60 | 5 | – | 0.5 | 6 | 3 |
| 170–60–5-0-5-10-3 | 26 | 170 | 60 | 5 | – | 0.5 | 10 | 3 |
| 170–60–10-0-0-10-3 | 27 | 170 | 60 | 10 | – | – | 10 | 3 |
| 170–60–15-0-0-10-3 | 28 | 170 | 60 | 15 | – | – | 10 | 3 |
| 170–60–5-0-2-10-3 | 29 | 170 | 30 | 5 | – | 0.2 | 10 | 3 |
| 170–120–5-0-2-10-3 | 30 | 170 | 120 | 5 | – | 0.2 | 10 | 3 |
| 200–60–0-0-0-3-3 | 31 | 200 | 60 | – | – | – | 3 | 3 |
| 200–60–0-0-0-10-3 | 32 | 200 | 60 | – | – | – | 10 | 3 |
| 200–60–0-0-0-15-3 | 33 | 200 | 60 | – | – | – | 15 | 3 |

Note: Sample label is expressed as AT-At-Ca%-UR_Al%-R_Al%-FP-Ct, where AT: activation temperature; At: activation time; Ca%: addition of Ca(OH)₂; UR_Al%: addition of unreacted Al₂O₃; R_Al%: addition of reacted Al₂O₃; FP: forming pressure; Ct: curing time. For example, sample 170–60–5-0-2-10-3 was prepared by activating a mine tailings sample with 10 M NaOH at 170 °C for 60 min with the addition of 5% Ca(OH)₂ and 0.2% reacted Al₂O₃, further molding the paste with 10 MPa forming pressure, and finally curing it at 90 °C for 3 days. During the experiments, the NaOH concentration was fixed at 10 M, and the curing temperature was fixed at 90 °C. All of the additives were added by wt% of the mass of mine tailings. Some promising samples with which a high compressive strength was obtained were purposefully analyzed and studied using SEM/EDS, FTIR and XRD

usually less than 20 MPa; however, the compressive strength of the geopolymerization product of fly ash can be as high as 60 MPa [16–18]. The relative inertness of mine tailings may be due to the fact that the particle size of mine tailings is much larger than those of aluminosilicate minerals applied for geopolymerization. As shown in Fig. 1, the average particle size, P₈₀, of the tailings samples is approximately 240 μm, and

the value is much larger than that for clay minerals and fly ash, which is usually finer than 50 μm. Another reason for the low activity of mine tailings is due to their crystal structure, while fly ash, metakaolin and other clays minerals contain an amorphous phase. It is believed that an amorphous structure displays higher reactivity [3]. The activation of mine tailings at very high temperatures—as some researchers did by applying

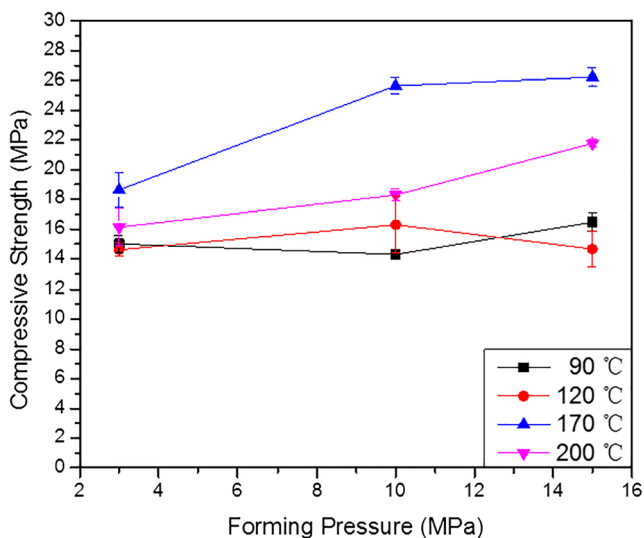


Fig. 2 Relationship between compressive strength, forming pressure and activation temperature

thermal treatment of mine tailings at 800 °C–900 °C for about 2 h to increase the reactivity by calcination—is not very economical because of the enormous thermal energy consumption. It is therefore interesting to study the applicability of geopolymerization at an elevated mild temperature, for example, 170 °C as used in the present study, to increase the reactivity of mine tailings and potentially the mechanical strength of the geopolymerization products.

Xu and van Deventer [1–3] studied the effect of temperature on geopolymerization by applying different types of aluminosilicate sources, and their results showed that a high curing temperature was beneficial for the release of Al from the crystal lattice. It was also reported that both the dissolution and condensation rates of geopolymerization increased at an optimum elevated curing temperature. This finding correlates well with the results obtained in the present work. As shown in Fig. 2, when the activation temperature is low, for example, less than 120 °C, increasing the activation temperature results in very little increase in the reactivity of the mine tailings during 1 h of reaction, and the compressive strength of the samples is still low, showing little dependence on temperature. When the activation temperature is high enough, for example, 170 °C, the mine tailings are successfully activated during this time frame, showing increased compressive strength. When the activation temperature is too high, above 200 °C, over-activation of mine tailings occurs in 1 h, resulting in reduced compressive strength. Indeed, during the experiment, when over-activation of mine tailings occurs, the paste becomes dark, sticky and very difficult to mold. Therefore, as shown in Fig. 2, mine tailings can be efficiently activated at 170 °C in 1 h with 10 M NaOH.

It is worth mentioning that one of the main goals of the present study is to reduce the alkali consumption, as alkali

consumption in a previously reported work was quite high [4]. For example, when the NaOH solution is 15 M, at which the highest compressive strength, i.e., ~20 MPa, is achieved, the calculated weight ratio of NaOH to mine tailings is about 1:3.5 at 27% water content [4]. In the present work, after mine tailings are activated at 170 °C for 0.5–1 h and further separated after sedimentation, about 80% alkali solution is recovered and reused at a similar 10 M alkali concentration. Because the weight of mine tailings (MT) is 140 g and the MT-to-water ratio is 0.6, the actually consumed NaOH (solid) is about 18.64 g for 140 g of mine tailings, resulting in a calculated weight ratio of NaOH to mining tailings of about 1:7.5. Therefore, the alkali consumption is successfully decreased using an alkali-activation strategy as applied in the present work. Again, further increasing the activation time (> 2 h) and temperature (200 °C) causes too over-activation of mine tailings to be activated, resulting in a sticky suspension with much less (<50%) alkali solution being recovered and reused, which inevitably increases the alkali consumption of the whole process. Therefore, in order to achieve high compressive strength and low alkali consumption, over-activation should be carefully avoided.

3.3 Effect of the Addition of $\text{Ca}(\text{OH})_2$

In the present work, $\text{Ca}(\text{OH})_2$ is intentionally added during the geopolymerization of mine tailings to study its impact on the compressive strength of the geopolymer.

Figure 3 shows the compressive strength test results for the samples, which are activated with 10 M NaOH and various amounts of $\text{Ca}(\text{OH})_2$ at 170 °C for 1 h, further molded under forming pressure of 10 MPa, and finally cured at 90 °C in an oven for 3 days. As shown by the figure, the compressive strength increases from 25.65 MPa to 30.09 MPa with the

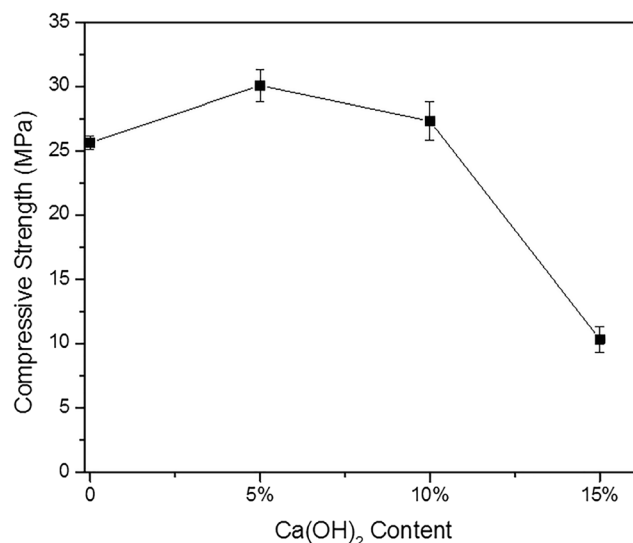


Fig. 3 The relationship between compressive strength and the addition of $\text{Ca}(\text{OH})_2$

addition of 5% $\text{Ca}(\text{OH})_2$. Further increasing the amount of $\text{Ca}(\text{OH})_2$ only reduces the compressive strength. Therefore, the maximum compressive strength is achieved with the addition of 5% $\text{Ca}(\text{OH})_2$.

One can see from Fig. 3 that increased compressive strength is obtained only with the addition of an optimum amount of Ca^{2+} . The addition of more $\text{Ca}(\text{OH})_2$ does not increase the compressive strength. This is because the high $[\text{OH}^-]$ from sodium hydroxide hinders the dissolution of $\text{Ca}(\text{OH})_2$. It has been observed during experiments that undissolved white $\text{Ca}(\text{OH})_2$ powder still exists in the paste when 15% $\text{Ca}(\text{OH})_2$ is added. This undissolved $\text{Ca}(\text{OH})_2$ powder hinders the condensation and further geopolymerization of dissolved $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedral, and then decreases the compressive strength of the geopolymer specimens. This result coincides well with the work by Yip et al. [10], who reported that less than 20% mineral additive increased the strength of a geopolymer, while more than 20% mineral additive only resulted in a decrease in reactive aluminosilicate content and a significant disruption of the geopolymer gel network.

3.4 Effect of the Addition of Al_2O_3

In the present work, as shown in Table 1 and Fig. 4, the Si/Al ratio of mine tailings is above 4, and the value is higher than the optimum Si/Al ratio. In order to decrease the Si/Al ratio, in the present work, Al_2O_3 is intentionally added during the geopolymerization of mine tailings to study the impact of Si/Al ratio on the compressive strength of geopolymer.

Figure 5 shows the compressive strength test results for the samples, which are mixed with various amounts of Al_2O_3

powders, activated with 10 M NaOH and 5% $\text{Ca}(\text{OH})_2$ at 170 °C for 1 h, further molded at 10 MPa forming pressure, and finally cured at 90 °C for 3 days. One can see from the figure that the compressive strength decreases with the addition of Al_2O_3 powders. For example, when mine tailings are activated together with 0.1% Al_2O_3 powders, the compressive strength decreases from 30.09 MPa to 26.39 MPa, and the value further decreases to 20.12 MPa when 0.5% Al_2O_3 is added.

As shown in Fig. 5, the addition of Al_2O_3 powder does not increase the compressive strength of the geopolymerization product of mine tailings at all, even though Al_2O_3 powder is added for the purpose of increasing Si/Al ratio and therefore compressive strength. The decrease in sample strength is due to the fact that, comparatively, Al_2O_3 powder is more ‘inert’ than mine tailings. It is noticed that after 1 h of activation with alkali at 170 °C, there is still a large amount of white unreacted Al_2O_3 powder in the paste. This ‘inert’ unreacted Al_2O_3 powder will hinder the formation of a geopolymer network during the curing process, resulting in reduced compressive strength. In order to address the problem, another method of adding Al_2O_3 was applied by first reacting Al_2O_3 powder with 10 M NaOH at 200 °C for 1 h and then adding the activated Al_2O_3 to the mine tailings for further activation.

Figure 6 shows the compressive strength test results for the samples, which are mixed with various amounts of reacted Al_2O_3 , activated with 10 M NaOH and 5% $\text{Ca}(\text{OH})_2$ at 170 °C for 1 h, further molded at different forming pressures, and finally cured at 90 °C for 3 days. In this case, Al_2O_3 powder is reacted with 10 M NaOH at 200 °C for 1 h, and then the reaction product is mixed with mine tailings. Figure 6 shows that when a specific amount of reacted Al_2O_3 is added, the compressive strength increases with the increase in

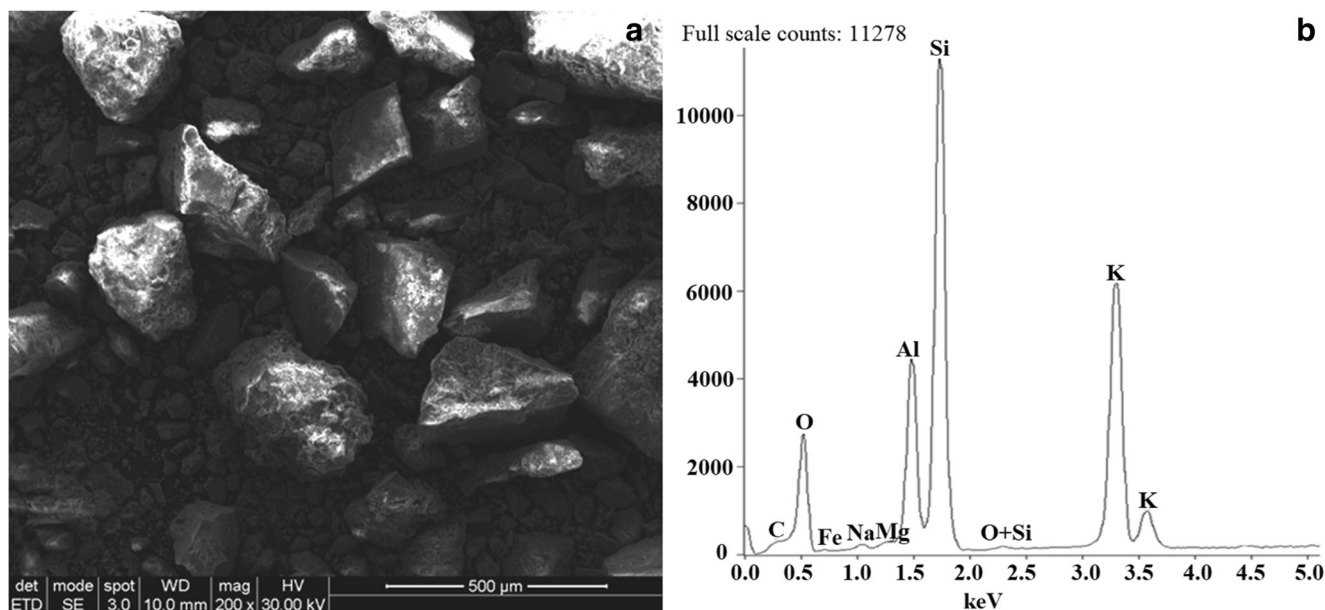


Fig. 4 SEM/EDS analysis of mine tailings: (a) SEM image of mine tailings as received; (b) EDS analysis of Fig. 4a

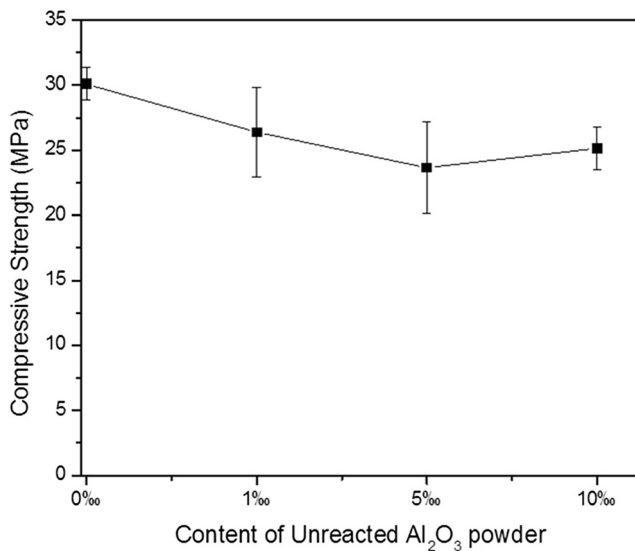


Fig. 5 The relationship between compressive strength and the addition of Al₂O₃ powder

forming pressure. For example, for the case of 0.2% (weight ratio to mine tailings) reacted Al₂O₃ being added, the compressive strength reaches 40.65 MPa at 10 MPa forming pressure. Figure 6 also shows that, in general, when the forming pressure is fixed, the highest compressive strength is achieved with the addition of 0.2% reacted Al₂O₃. Increasing the addition of reacted Al₂O₃ does not increase compressive strength further.

Geopolymerization can be briefly described as two steps. Firstly, an aluminosilicate source reacts with NaOH, releases free [SiO₄] and [AlO₄] tetrahedral units and produces geopolymeric precursors. Secondly, the polymeric precursors link to each other by sharing oxygen atoms, condense and further form a geopolymer. It is also reported that the rate of dissolution of Al from the natural aluminosilicate sources is

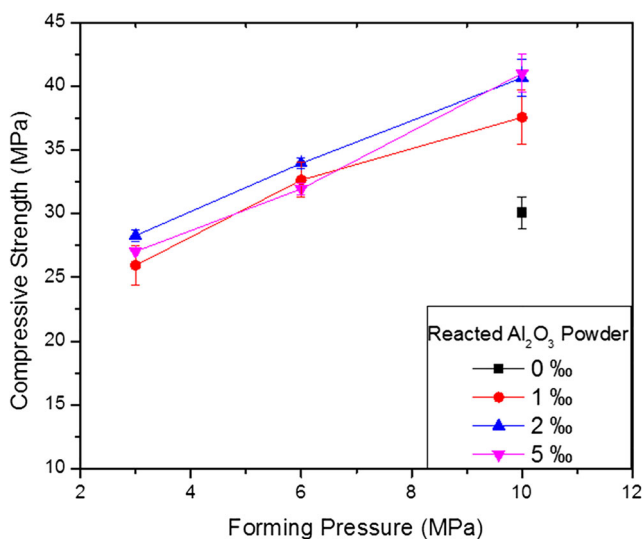


Fig. 6 The relationships between compressive strength, the addition of reacted Al₂O₃ and forming pressure

usually low, and the amount is not sufficient to produce enough geopolymeric precursors for further geopolymerization condensation, resulting in relatively low compressive strength [1–3]. The problem can be partially addressed by activating mine tailings at an elevated temperature and increasing the Al dissolution rate. However, it is also evident that increasing the activation temperature will increase the dissolution rate of Si. Because the Si/Al ratio in mine tailings is comparatively high, an excess of Si geopolymeric precursors in the paste would not be beneficial for the geopolymerization process, because excessive Si geopolymeric precursors may readily form sodium silicate, which has low compressive strength. Therefore, it is also important to increase the amount of Al geopolymeric precursors. As shown in Fig. 6, the addition of reacted Al₂O₃ can successfully increase the compressive strength. This result is in line with findings reported by mixing mine tailings with aluminosilicate sources with a low Si/Al ratio, such as kaolinite and fly ash.

3.5 Effect of Forming Pressure

Previous works have shown that the compressive strength of a geopolymer increases with the concentration of NaOH, and geopolymerization is usually efficient when the concentration of NaOH is above 10 M. However, a high alkali dosage no doubt increases the cost of applying mine tailings as construction material. In addition, it results in a large amount of unreacted NaOH trapped in the geopolymerization product. When the sample comes in contact with water, the residual alkali will dissolve in the water, resulting in an increase in solution pH and a decrease in the compressive strength of the geopolymerization product. To mitigate this problem, a forming pressure is applied on geopolymerization products before curing to remove the unreacted NaOH, which will be reused for the activation of the mine tailings. Therefore, the strategy of applying forming pressure not only will reduce the consumption of alkali, but will also increase the resistance of the geopolymerization product against water. In the present work, three different forming pressures are applied on geopolymerization products before curing to study the effect of forming pressure on the final compressive strength.

As shown in Fig. 6, the compressive strength increases with an increase in forming pressure. At forming pressure of 10 MPa, the compressive strength reaches as high as 40.65 MPa, which is about 10 MPa higher than that obtained with no forming pressure applied. Figure 6 clearly shows that applying forming pressure is beneficial for increasing the strength of geopolymerization products of mine tailings.

3.6 Effect of Activation Time

Figure 7 shows the compressive strength test results for the samples, which are mixed with 0.2% activated Al₂O₃

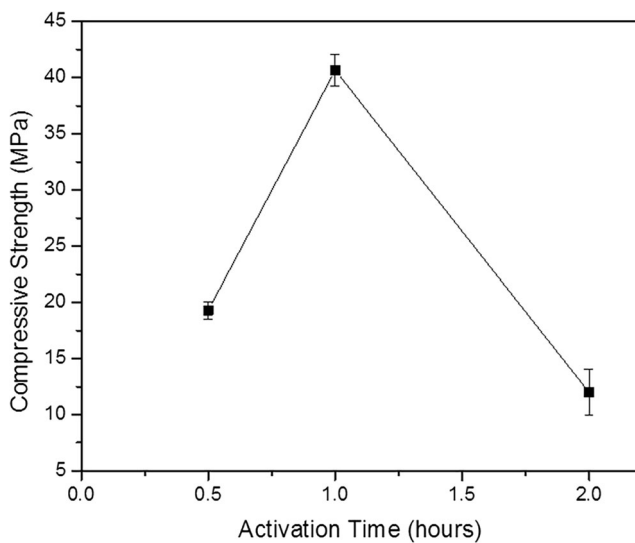


Fig. 7 The relationship between compressive strength and activation time

beforehand, activated with 10 M NaOH and 5% Ca(OH)₂ at 170 °C for different times, further molded at 10 MPa forming pressure, and finally cured at 90 °C for 3 days. When the activation time is 0.5 h, the compressive strength is as low as 19.30 MPa. The value increases to 40.65 MPa when activation time is increased to 1 h. Further increasing the activation time to 2 h only reduces the compressive strength to 12.00 MPa.

As mentioned before, the geopolymerization process usually occurs in two steps. In the first step, an aluminosilicate source reacts with NaOH, releases free [SiO₄] and [AlO₄] tetrahedral units and produces geopolymeric precursors. Increasing activation time will increase the amount of free geopolymeric precursors in the paste, and the change is beneficial for the second step of the geopolymerization condensation process. As shown in Fig. 7, when activation time is increased from 0.5 h to 1 h, the compressive strength increases from 19.30 MPa to 40.65 MPa.

However, when activation time is too long, too many Si geopolymeric precursors are produced in the paste due to the high Si/Al ratio of mine tailings and the high dissolution rate of Si [19]. The change is not beneficial for the geopolymerization process, because excessive Si geopolymeric precursors can readily form sodium silicate, whose compressive strength is usually low. As shown in Fig. 7, when activation time is increased from 1 h to 2 h, the compressive strength decreases from 40.65 MPa to 12.00 MPa. Therefore, the optimum activation time at this temperature is 1 h.

3.7 Effect of Curing Time

Figure 8 shows the compressive strength test results for the samples, which are mixed with 0.2% activated Al₂O₃ beforehand, activated with 10 M NaOH and 5% Ca(OH)₂ at 170 °C

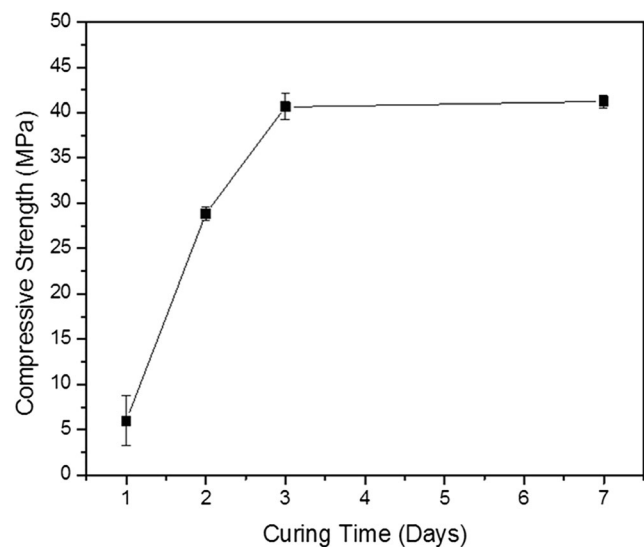


Fig. 8 The relationship between compressive strength and curing time

for 1 h, further molded at 10 MPa forming pressure, and finally cured at 90 °C for various numbers of days. The results show that compressive strength increases with the increase in curing time to 3 days. For example, when curing time is 1 day, compressive strength is as low as about 6 MPa. The value increases to 31.2 MPa at a curing time of 2 days. Compressive strength further increases to 40.65 MPa when the curing time is increased to 3 days. Further increases in curing time do not result in a further increase in compressive strength.

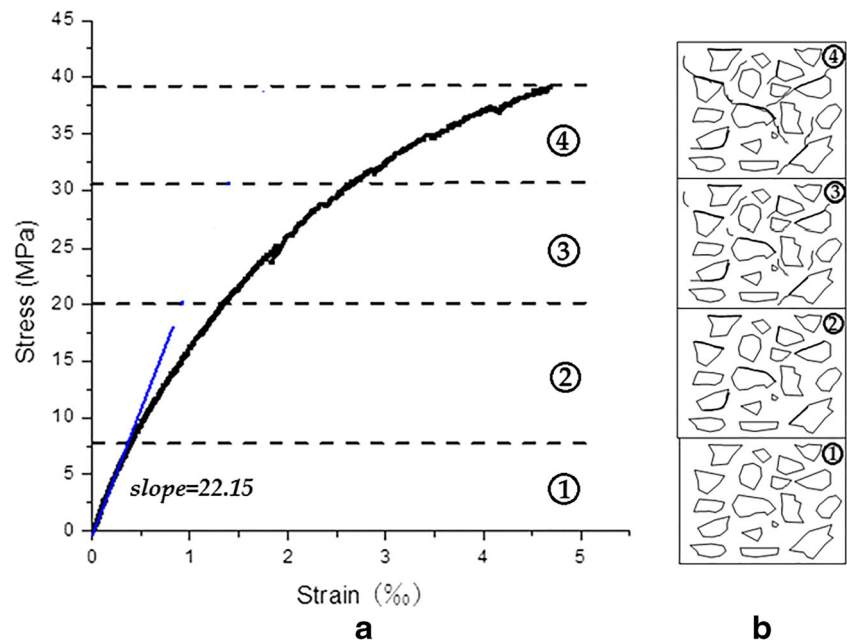
In general, an adequate curing time is required to obtain the advanced mechanical and durability performance. However, prolonged curing at high temperature also has adverse impacts on the strength of geopolymer. It is because a prolonged curing process at an elevated temperature could result in the dehydration of geopolymer and subsequent cracking, which will destroy the structure of geopolymer and thus reduce the compressive strength [20].

One can see from Fig. 8 that the compressive strength of the mine tailings samples reaches a plateau after a 3-day curing time. Because the time applied for conventional geopolymerization of mine tailings is usually greater than 7 days [4], a shorter curing time, as achieved in the present work, has the advantage of greatly reducing the operational cost.

3.8 Stress–Strain Curve of the Geopolymerization Product

The stress–strain behavior of the geopolymerization product was also studied in the present work by attaching strain gauges on opposite faces and at mid-height during the compressive strength measurement. Figure 9 shows the stress–strain behavior of the optimum sample no. 29. From the figure, one can see

Fig. 9 The stress–strain behavior of a geopolymer specimen made of mine tailings. (a) The stress–strain curve; (b) the schematic cracking modes during different breakage sections



that the stress–strain behavior of the geopolymerization product is very similar to that of typical concrete. That is, the stress–strain curve also consists of four sections: (1) When the stress is below 20% of ultimate strength, the transition zone cracks remain stable. The stress–strain plot is linear and the dynamic modulus, as obtained from the slope of the fitting line, is 22.15 GPa, the value of which is comparable to that of concrete. (2) At 20% and 50% of ultimate strength, the transition zone micro-cracks begin to increase in length, width and number. The stress–strain plot becomes nonlinear. (3) At 50% to 75% of the ultimate strength, cracks begin to form in the matrix, further propagate and increase in the matrix, causing the stress–strain plot to become horizontal. (4) At 75% to 80% of the ultimate stress, the stress reaches a critical stress level for spontaneous crack growth under a sustained stress. Cracks propagate rapidly in both the matrix and the transition zone. Failure occurs when the cracks join together and become continuous.

3.9 SEM/EDS Analysis

SEM/EDS analysis of the samples prepared with different forming pressure was carried out to clarify the mechanism involved in applying forming pressure for increasing compressive strength, and the results are shown in Fig. 10. By comparing Fig. 10a and d, one can clearly see that after applying 10 MPa forming pressure, the structure of the geopolymerization product becomes rigid, with many fewer cracks, which is beneficial for high rigidity and thus for high compressive strength. This finding correlates well with Fig. 6.

In addition, Fig. 10 shows that the amount of Na and the Si/Al ratio decrease with the increase in forming pressure. For

example, Fig. 10c shows that when no forming pressure is applied, both the amount of Na and the Si/Al ratio are very high. As mentioned before, neither of these properties is beneficial for increasing the strength of geopolymerization product. In addition, the fact that both Na and O show very high peaks on the spectrum suggests that there is still a salient amount of unreacted NaOH present inside the mine tailings geopolymer. On the other hand, as shown in Fig. 10f, when 10 MPa forming pressure is applied, the peaks of Na and O are greatly depressed in the spectrum, suggesting that redundant NaOH is squeezed out. In addition, the Si/Al ratio becomes much smaller.

Element mapping analysis has been conducted on a polished cross section for the geopolymer specimens synthesized with different forming pressure, and the results obtained with the elements, i.e., Si, K, Al, Ca and Na, are shown in Fig. 11. For the element mapping of Si, several spots with very high intensity of Si are observed, with no other elements being detected at the same position. As also shown by the mineral composition of mine tailings listed in Table 2, it suggests that these Si-rich spots stand for quartz (SiO_2). For those spots with lower Si intensity, elements such as K, Al and Na can be detected at the same position. It suggests that these spots represent K-feldspar and plagioclase particles. Because mine tailings themselves are a low-calcium source, as shown in Table 1, and calcium was added in the form of $\text{Ca}(\text{OH})_2$, the element mapping of Ca generally delineates the distribution of the geopolymer product after activation. Figure 11 shows that the boundary of element distribution becomes increasingly sharp with increased forming pressure, especially for the case of Ca. It also shows that the distribution of geopolymer product becomes homogeneous and condensed with forming

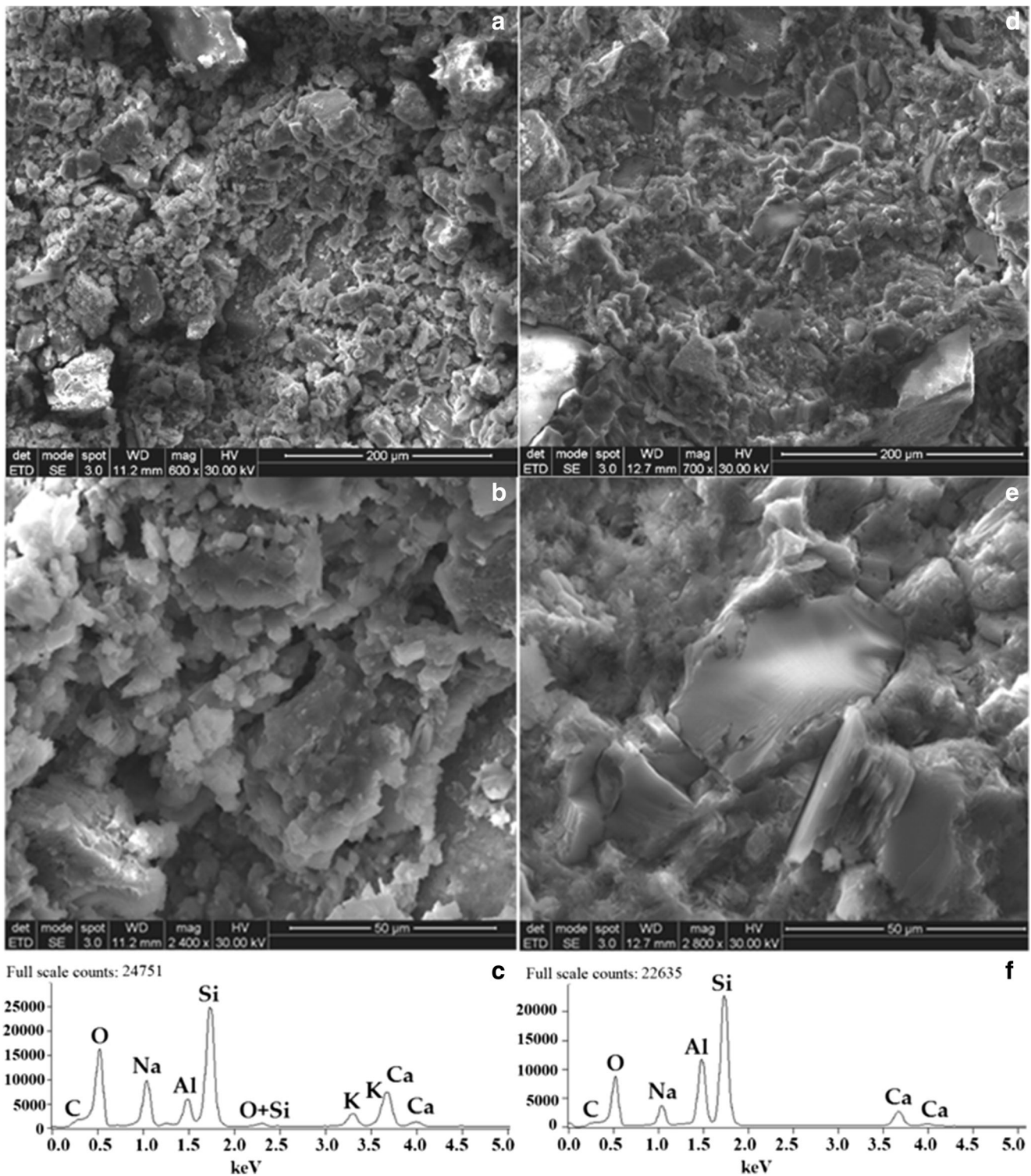


Fig. 10 SEM/EDS analysis of the geopolymerization product of mine tailings. (a) SEM image of mine tailings geopolymer without applying forming pressure; (b) higher magnification of Fig. 10a; (c) EDS analysis

of Fig. 10a; (d) SEM image of mine tailings geopolymer with 10 MPa forming pressure; (e) higher magnification of Fig. 10d; (f) EDS analysis of Fig. 10d

pressure being applied. Element mapping analysis also shows that mine tailings are still the main components of the final products after geopolymerization, and these particles are bound together with the geopolymer, which is the reaction

product of mine tailings with alkali activator and additives. Therefore, applying forming pressure does not change the mechanical properties of these mine tailing particles. However, it affects the geopolymer—the ‘binder’—instead.

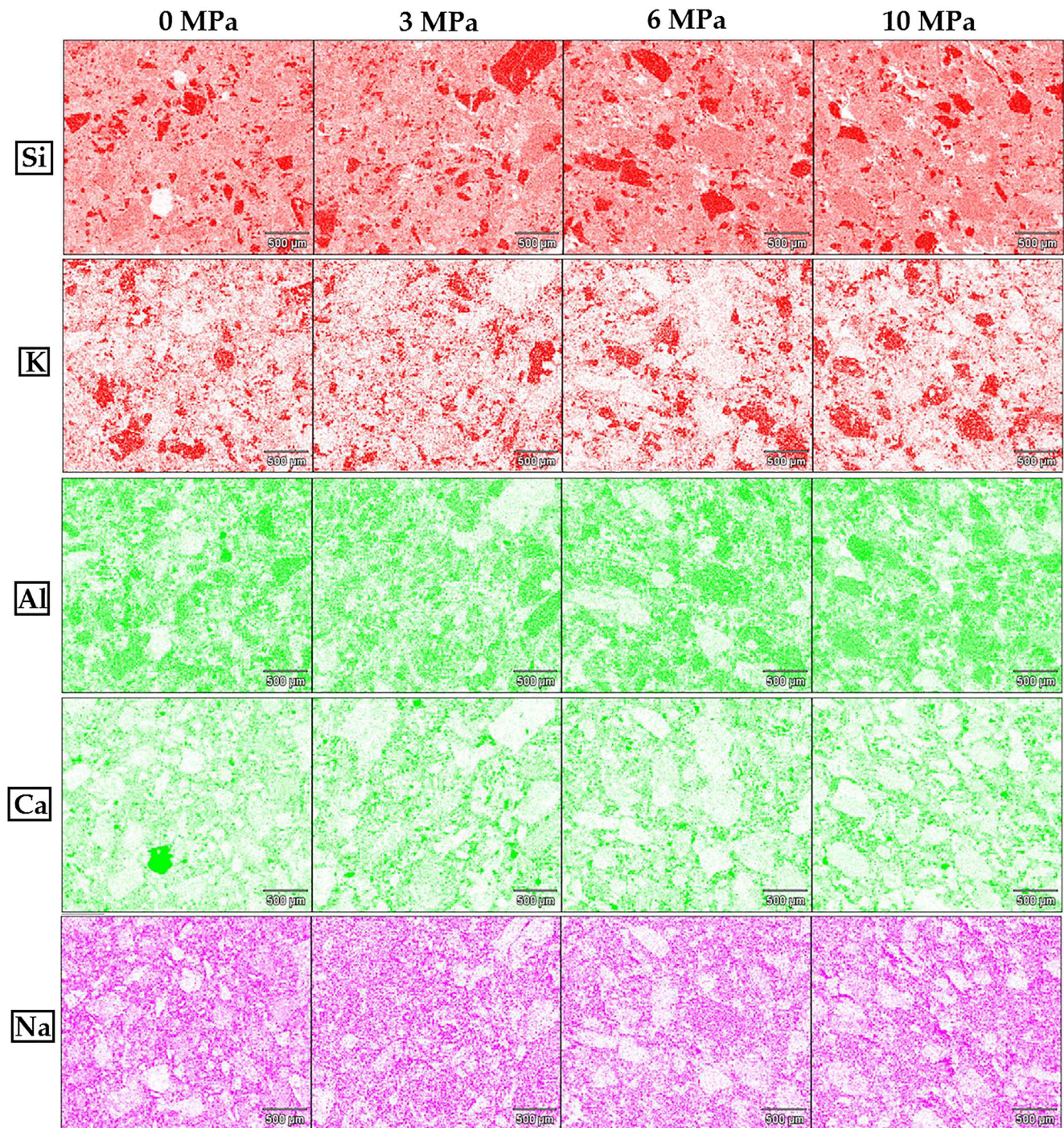


Fig. 11 SEM/EDS element mapping of geopolymers specimens prepared with different forming pressure

It is also worth noting that the compressive strength and density do not change further when forming pressure exceeds 10 MPa. In addition, a high density of construction material will adversely increase the self-weight of a building, which restricts the height of the building [21]. Therefore, a forming pressure above 10 MPa was not further studied in the present work.

In summary, the SEM/EDS analysis results as shown in Figs. 10 and 11 suggest that applying forming

pressure not only yields products that are compact by reducing voids, but decreases both Na and the Si/Al ratio. Both factors account for the high compressive strength achieved by applying forming pressure. Therefore, the application of forming pressure is beneficial for the geopolymerization process of mine tailings, and this finding agrees well with the UCS test results, as shown in Fig. 6.

3.10 FTIR Analysis

Figure 12 shows the FTIR spectra of mine tailings (MT) and geopolymer specimens prepared under different conditions, respectively. During the preparation of the geopolymer specimens, mine tailings are activated with 10 M NaOH at 170 °C for 1 h, further molded at 10 MPa forming pressure, and finally cured at 90 °C for 3 days. Some FTIR characteristic peaks related to aluminosilicates are summarized from the literature and listed in Table 4. For the mine tailings powder, the strong band at 950 cm^{-1} corresponds to the asymmetric stretching of Si–O–Si and Al–O–Si bonds in an aluminosilicate framework. In general, the band at 950 cm^{-1} shifts towards a lower wave number after geopolymerization, suggesting that a change in the microstructure of the mine tailings takes place, and new aluminosilicate geopolymers are produced. For example, as shown in Fig. 12, when mine tailings were activated by only NaOH, the band at 950 cm^{-1} shifts by 4 cm^{-1} to 946 cm^{-1} , which is attributed to the fact that after the geopolymerization of silicates with NaOH, the silicon-rich species take up Na^+ in their structures [22]. When mine tailings are activated with the addition of $\text{Ca}(\text{OH})_2$, the band at 950 cm^{-1} shifts by 8 cm^{-1} to 942 cm^{-1} , which suggests that the silicon-rich species take up Ca^{2+} in their structures after geopolymerization. Further, when the mine tailings are activated with the addition of reacted Al_2O_3 , the band at 950 cm^{-1} shifts by 12 cm^{-1} to 938 cm^{-1} , suggesting that the silicon-rich species take up Al^{3+} in their structures after geopolymerization.

The band with a peak at 874 cm^{-1} is attributed to the Si–O stretching and OH bending of the Si–OH group [26]. The peak

exists in all the three spectra obtained with no Al_2O_3 being added. However, for the sample no. 29, the peak at 874 cm^{-1} disappears, and this is because of the addition of reacted Al_2O_3 , which decreases the Si/Al ratio, producing a cross-linking aluminosilicate geopolymer framework and reducing the band of the Si–OH group.

The band with a peak at 776 cm^{-1} is due to the symmetric stretching of the Si–O–Si group. Similar to the findings obtained for the band at 950 cm^{-1} , the band shifts towards a lower wave number after geopolymerization, suggesting a change in the microstructure of the mine tailings and the production of new aluminosilicate geopolymers. For example, as shown in Fig. 12, when mine tailings are activated by only NaOH, the band at 776 cm^{-1} shifts by 4 cm^{-1} to 772 cm^{-1} , which is also attributed to the silicon-rich species taking up Na^+ in their structures. When mine tailings are activated with the addition of $\text{Ca}(\text{OH})_2$, the band at 776 cm^{-1} shifts by 8 cm^{-1} to 768 cm^{-1} , suggesting that silicon-rich species take up Ca^{2+} in their structures after geopolymerization. Further, when mine tailings are activated with the addition of reacted Al_2O_3 , the band at 776 cm^{-1} shifts by 12 cm^{-1} to 764 cm^{-1} , suggesting that the silicon-rich species take up Al^{3+} in their structures after geopolymerization.

The band with a peak at 720 cm^{-1} is attributed to the symmetric stretching of Si–O–Si and Al–O–Si bonds in an aluminosilicate framework [27]. For the starting mine tailings source, the band does not exist, while the band appears in all three samples after geopolymerization with alkali, suggesting that some new aluminosilicate geopolymer is induced. Therefore, the peak at $\sim 720 \text{ cm}^{-1}$ is a specific ‘fingerprint’ of the geopolymer matrix indicating that the polymeric

Fig. 12 FTIR spectra of MT and geopolymer specimens activated (a) with NaOH only, (b) with 5% $\text{Ca}(\text{OH})_2$ being added, (c) with 5% $\text{Ca}(\text{OH})_2$ and 0.2% reacted Al_2O_3 being added

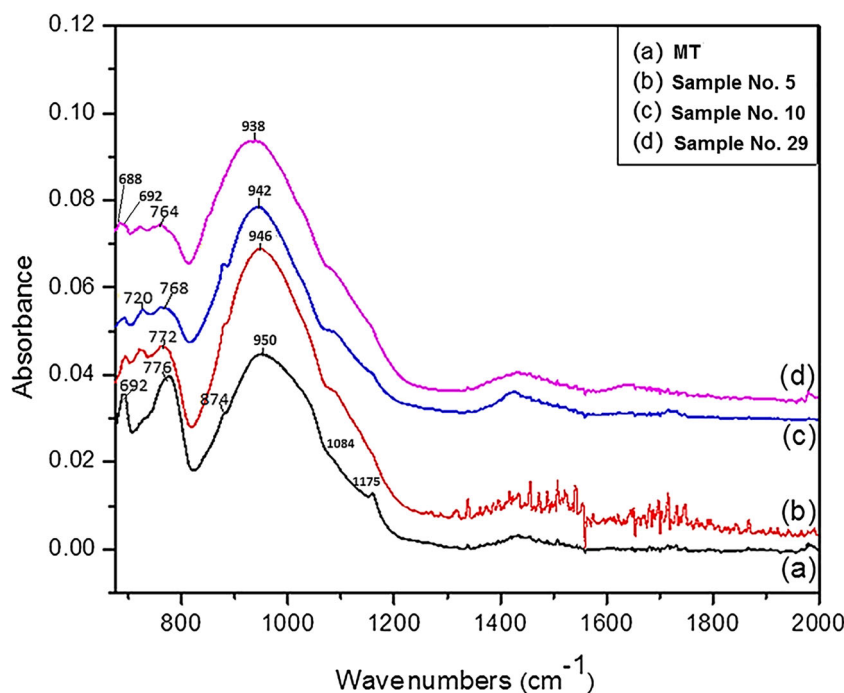


Table 4 FTIR characteristic bands and their corresponding species as listed in references

| Assignment | Wave number (cm ⁻¹) | Characteristic bands | Ref. |
|-----------------------|---------------------------------|-------------------------------------|----------|
| (Si–O–Si and Al–O–Si) | 950~1200 | Asymmetric stretching | [23, 24] |
| (Si–O–Si and Al–O–Si) | 1080 | Asymmetric stretching | [24] |
| (Si–O–Si and Al–O–Si) | 1074 | Asymmetric stretching | [25] |
| (Si–OH) | 882 | Si–O stretching, OH bending (Si–OH) | [26] |
| (Si–O–Si) | 798 | Symmetric stretching | [26] |
| (Si–O–Si and Al–O–Si) | 727 | Symmetric stretching | [27] |
| (Si–O–Si) | 694 | Symmetric stretching | [28] |

precursors, [SiO₄] and [AlO₄] tetrahedral, have formed a cross-linking aluminosilicate framework, further condensed and finally formed geopolymers.

Quartz is present in the original mine tailings, as shown in Table 2, and it introduces a series of bands located at 692, 776, 1084 and 1175 cm⁻¹ in the spectrum [29]. The decrease in the peaks at 692 and 1175 cm⁻¹ and the shifting of the peak at 776 cm⁻¹ to a lower wave number after geopolymerization, as shown in Fig. 12, demonstrate that quartz is closely involved during all the geopolymerization processes in mine tailings.

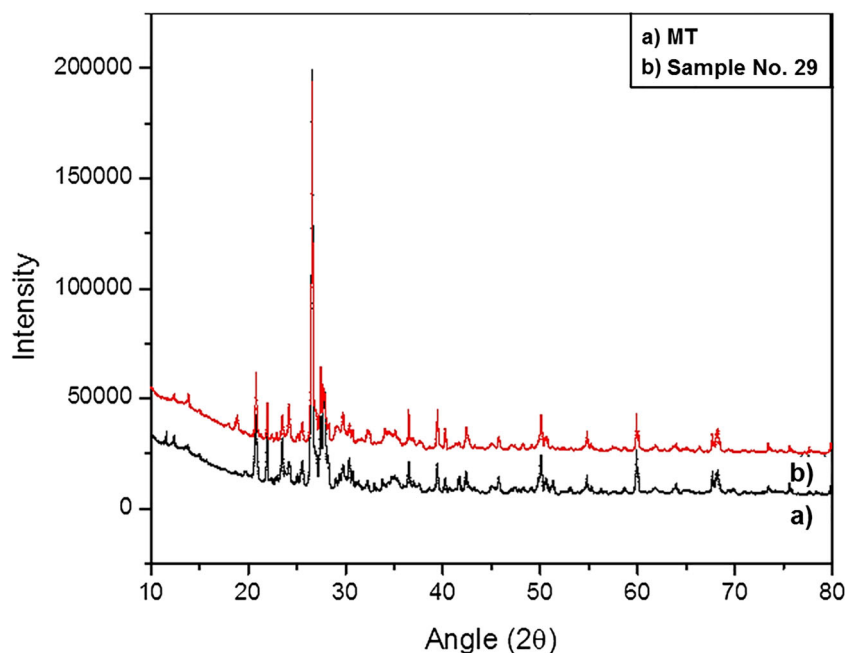
It is worth noting that the band at 688 cm⁻¹, which is due to the asymmetric stretching vibrations generated by the Al–O bonds in the AlO₄ groups [30], does not exist in any of the three spectra obtained without the addition of reacted Al₂O₃. However, for sample no. 29, the peak at 688 cm⁻¹ appears in the spectrum because of the addition of reacted Al₂O₃.

3.11 XRD Analysis

Figure 13 shows the XRD patterns of the original mine tailings powder and the geopolymer specimen no. 29. The major

components of mine tailings are crystalline material, quartz, albite with approximate composition (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈, orthoclase with approximate composition KAlSi₃O₈ and gypsum, which is consistent with the composition shown in Table 2. After geopolymerization, one can see that the intensity of quartz decreases, but the patterns are still crystalline, and most of the peaks are similar with that of mine tailings. This can be explained by the fact that the mine tailing particles were only partially reacted, as shown in SEM micrographs and element mapping of Figs. 10 and 11. Another change in the XRD pattern is that two new peaks can be found for the geopolymer specimen. One is around 18.8°, which is identified as sodium aluminum silicate hydrate. Another newly formed phase is zeolite 5A, Ca₅Na₂Al₁₂Si₁₂O₄₈, with Si/Al ~ 1, which can be found at 13.8°. Both of the new phases are low-silica zeolites widely observed in hydroxide-activated geopolymer synthesis [31]. The last difference between the patterns is that the peak corresponding to gypsum disappears after geopolymerization, meaning that the Ca²⁺ in gypsum took part in the geopolymerization process.

Fig. 13 XRD patterns of original mine tailings powder and the geopolymer specimen synthesized under optimum conditions



4 Conclusions

The present study has focused on addressing the problems associated with conventional geopolymerization of mine tailings, such as large consumption of alkali, low compressive strength and long curing time. In order to decrease the Si/Al ratio and increase the reactivity and compressive strength of mine tailings, specific efforts have been tried by increasing activation temperature, adding $\text{Ca}(\text{OH})_2$ and reacted Al_2O_3 , and applying forming pressure. Experiment results show that the compressive strength in the geopolymerization production of mine tailings increases substantially. For example, unconfined compressive strength (UCS) of 40 MPa can be achieved with the geopolymerization samples after mine tailings are activated by NaOH at 170 °C for 1 h with the addition of $\text{Ca}(\text{OH})_2$ and alkali activated Al_2O_3 , further compressed with 10 MPa forming pressure, and finally cured at 90 °C for 3 days. The stress–strain behavior of the geopolymerization specimen is similar to that of concrete, and the dynamic modulus is 22.15 GPa. The SEM/EDS analysis results suggest that applying forming pressure will not only make products compact by reducing voids, but decrease both Na and the Si/Al ratio. Both reasons account for a high compressive strength as achieved with a forming pressure being applied. The results obtained with FTIR and XRD analyses showed that the microstructure of mine tailings changes and new geopolymers are produced after geopolymerization. The findings of the present work provide a practical method for applying mine tailings as precast construction materials such as bricks and tiles through alkali activation.

5 Future Work

This manuscript was focused on solving the technical problems of using mine tailings as precast construction material to achieve products with high compressive strength. Future work will include (1) further optimization of working conditions, for example, activation time between 1 h and 2 h; (2) the long-term stability of products; and (3) both economic and ecological evaluations.

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Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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