Effect of Magnesite Addition and Mechanical Activation on the Synthesis of Fly Ash-Based Geopolymers

Alexander M. Kalinkin *, Elena V. Kalinkina, Alla G. Ivanova and Ekaterina A. Kruglyak

The Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences”, Tananaev Institute of Chemistry-Subdivision, Akademgorodok 26a, 184209 Apatity, Murmansk Region, Russia

* Correspondence: a.kalinkin@ksc.ru; Tel.: +7-81555-79523

Abstract: Ca/Mg carbonate minerals, such as calcite and dolomite, play an increasingly important role in the development of alkali-activated binders or geopolymers, which are regarded as promising sustainable cement materials. In contrast to studies on calcite and dolomite, the effect on geopolymer properties of the addition of natural magnesite (magnesium carbonate) to aluminosilicate raw materials has not been investigated. The aim of this study is to investigate the influence of mechanical activation (MA) and natural magnesite addition to fly ash (FA) on the compressive strength of geopolymers based on the natural magnesite–FA blend. Magnesite substitutes FA in amounts of up to 20 wt.%. Geopolymers were prepared using NaOH solution as an alkaline agent. XRD, FT-IR spectroscopy, thermogravimetry, SEM, and a dissolution test are used to investigate the geopolymerization process. The major reaction product was sodium-containing aluminosilicate hydrogel. Magnesite is found to transform, to a minor degree, to hydrotalcite. MA of the blend significantly improves geopolymer strength. For geopolymers based on (FA + magnesite) blends mechanically activated for 180 s, the strength is on average 8.0 ± 1.3, 3.0 ± 0.9, 1.5 ± 0.2, and 1.7 ± 0.5 times higher than that for the geopolymers based on the blends mechanically activated for 30 s at the age of 7, 28, 180, and 360 d, respectively. Although blending FA with magnesite does not increase geopolymer strength, for the mixtures containing 1%–10% magnesite, in general, the strength is either not reduced or it is reduced to a small degree compared to the geopolymers based on 100% FA. Using previously obtained data, for the first time, the effect of the addition of three Ca/Mg carbonate minerals to FA and MA on geopolymer performance is compared. Under similar conditions, geopolymer strength decreases in the order calcite > dolomite > magnesite. The main factors affecting the strength of geopolymers based on the mechanically activated blends of FA with magnesite including filler, dilution, and chemical effects are discussed.

Keywords: fly ash; natural magnesite; mechanical activation; geopolymers

1. Introduction

Synthesis of geopolymer materials based on coal fly ash (FA) and other man-made raw materials has been a subject of active research in past decades. Geopolymers are a subclass of alkaline-activated binders that are produced by the interaction of aluminosilicate raw materials with an alkaline agent (sodium hydroxide solutions and liquid glass). Geopolymer materials are considered a potential alternative to Portland cement and are promising for use as effective and environmentally sustainable cements and concretes in the construction industry [1,2]. Moreover, geopolymers are regarded as fire-resistant materials and as matrices for immobilizing heavy metals and radioactive waste [3–8].

Raw Class F FA is characterized by relatively low reactivity in geopolymer synthesis. To increase the reactivity of FA with respect to an alkaline agent and, consequently, to improve geopolymer performance, mechanical activation (MA) is a well-proven method. Here, the terms “MA” and “milling” refer to the same process of mechanical treatment of
a solid raw material in a mill. The effect of milling on FA reactivity and geopolymer strength has been studied by many researchers [8–21].

Another approach to improving geopolymer performance is to introduce various Ca/Mg-containing additives, including abundant and generally inexpensive carbonate minerals such as calcite CaCO$_3$ and dolomite CaMg(CO$_3$)$_2$. Lee and van Deventer [22] investigated the effects of inorganic salt contamination on the strength and durability of geopolymers based on a (90% FA + 10% kaolin) blend. The pastes were prepared using KOH solution and cured at ambient conditions. The addition of 1–2 wt.% laboratory-grade synthetic carbonates CaCO$_3$ or MgCO$_3$ (as opposed to chlorides) was favorable and resulted in an increase in compressive strength of up to 55% compared to the control sample (without a carbonate). The authors of the study suggested that a possible reason for the improvement of mechanical properties was the reduction of water content in the aluminosilicate gel due to the addition of a carbonate.

Over the past 20 years, improvements in the mechanical properties of alkali-activated materials through the addition of Ca/Mg carbonate minerals have been confirmed and further investigated in numerous studies. These studies were analyzed in a thorough review by Rakhimova [23]. The author of the review highlighted beneficial (i) filler, (ii) dilution, and (iii) chemical effects due to the addition of calcite or dolomite to low-calcium FA.

Unreacted carbonate particles can act as a fine filler, enhancing the packing density and thus improving compressive strength. Blending an aluminosilicate raw material with the carbonate to a certain degree (dilution) results in an increase in the alkali reagent/aluminosilicate ratio. This accelerates the geopolymerization reaction and increases the degree of reacted aluminosilicate, thereby strengthening the geopolymer matrix. As a result, it is possible to substitute increased amounts of FA with carbonate without degrading the mechanical properties of a geopolymer.

The chemical effect is related to the partial dissolution of Ca/Mg carbonates in an alkaline medium. Therefore, this effect depends on: (i) the nature of the carbonate; (ii) the nature, concentration, and dosage of the alkali reagent; (iii) the carbonate/aluminosilicate ratio in the geopolymer paste; (iv) the specific surface area of the solid components; and (v) the curing conditions. Despite the fact that both calcium and magnesium belong to the same group II of alkaline earth metals, their behavior within the alkali-activated binder is quite different [24]. Compared with magnesium, calcium plays a dominant role. The high availability of calcium leads to the development of high strength. Particularly, calcite is more effective than dolomite in improving the properties of geopolymer systems [25].

Calcium ions dissolved from carbonates in alkaline solutions can cause enhanced release of Si and Al ions from the aluminosilicate raw material [26] and a precipitation of secondary amorphous (e.g., C–A–S–H, N–C–S–H, and C–S–H gels [26,27]) and crystalline (e.g., Ca(OH)$_2$, pirssonite CaNa$_2$(CO$_3$)$_2$·2H$_2$O, and sodium carbonates [26–29]) phases, which influence binder performance. Nevertheless, magnesium is not an inert element in alkaline activation. Magnesium—inherently present in blast furnace slag (BFS) or externally added in the form of MgO—is regarded as a strength improving component of alkali-activated binders based on BFS [30–32]. The beneficial role of magnesium is reported to be explained, at least in part, by the formation of hydroaluminate Mg$_6$Al$_2$CO$_3$(OH)$_6$·4H$_2$O-like phases. It may be mentioned also that Sreenivasan et al. [33] showed that the Mg-rich and Ca-free mineral phlogopite K(Mg$_3$AlSi$_3$O$_io$(OH)$_2$: after thermal treatment has serious potential for use as an effective precursor for alkaline activation. In general, due to the complexity of geopolymerization reactions and the difficulties related to the separation and analysis of reaction products, the mechanisms underlying the chemical effect of Ca/Mg additives, including carbonate additives, have been studied only to a minor extent.

In a recent study, we combined the positive effects of Ca/Mg carbonate addition to FA and MA. In other words, geopolymers were prepared using mechanically activated mixtures of FA with calcite [34] and dolomite [35]. MA of the mixtures was carried out in a planetary mill. Sodium hydroxide solution was used as an alkaline agent and curing
was carried out under normal conditions, namely at room temperature. It was shown that the addition of up to 10% calcite or dolomite to low calcium FA and the subsequent MA of the mixture significantly increased the compressive strength of the geopolymers, and a synergistic effect of the two factors was observed. The highest positive effect of carbonate additive was observed in the early period of curing. The strength of the geopolymer based on the (90% FA + 10% calcite) mixture at the age of 7 d was 8.0, 3.5, and 2.9 times higher than that of geopolymers based on 100% FA milled for 30, 180, and 400 s, respectively. At the age of 28 d, the corresponding strength was 2.5, 1.9, and 2.2 times higher. With increasing MA time (more than 400 s) and calcite content (more than 10%), the increase in geopolymer strength slows down significantly and the setting time and workability of the geopolymer paste decrease noticeably [34]. In line with the results of Yip et al. [25], the addition of calcite was preferable to the addition of dolomite. For the (FA + calcite) mixtures containing 1, 3, 5, and 10% carbonate mineral that was milled for 180 s, the compressive strength at the age of 7 d was 7.4, 11.2, 13.0, and 16.8 MPa, respectively. For the (FA + dolomite) mixtures, the corresponding strength was 4.8, 4.9, 4.7, and 11.2 MPa, respectively. With increasing curing time, the difference in strength of geopolymers containing calcite and dolomite additives decreases [35].

The product of geopolymerization of mechanically activated mixtures of FA with calcite and dolomite was an X-ray amorphous aluminosilicate hydrogel (N-A-S-H gel). For geopolymers based on the (90% FA + 10% calcite) mixture, partial transformation of calcite into vaterite (polymorphic variety of CaCO₃) and calcium hydroxide Ca(OH)₂ during alkaline activation was revealed. The positive synergistic effect of blending FA with calcite or dolomite and MA of the blends is most likely due to the following factors. Under the influence of MA, the reactivity of the components of the blend with respect to the alkaline agent increases significantly. The active surface centers of the particles of mechanically activated carbonate minerals, as well as the newly formed phases, presumably accelerate the formation of aluminosilicate hydrogel, the main cementitious phase of geopolymer binders [34,35].

Unlike the case of calcite and dolomite, the effect of adding natural magnesite (magnesium carbonate) to FA on the properties of geopolymers has not been studied. The purpose of this paper, following our previous studies [34,35], is to investigate, for the first time, the synthesis of geopolymers based on mechanically activated mixtures of low-calcium FA with natural magnesite MgCO₃ and to compare the influence of carbonate addition to FA on the mechanical strength of geopolymer composites in the calcite–dolomite–magnesite series. This study is important due to the need to improve the understanding of the influence of the nature of added Ca/Mg carbonate mineral on geopolymerization processes and geopolymer properties. Magnesite substituted FA in amounts of up to 20 wt.%. The geopolymer samples were characterized using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). To clarify the role of Mg in the synthesis of geopolymers, the dissolution of mechanically activated (FA + magnesite) mixtures in sodium hydroxide solutions was studied.

2. Materials and Methods

As noted above, one of the main objectives of this work was to compare the characteristics of geopolymers synthesized on the basis of (FA + carbonate) mixtures in the calcite–dolomite–magnesite series. In order to ensure the correctness of the comparison, the same FA was used in the experiments as had been used in previous works, in which calcite [34] and dolomite [35] were used as additives; moreover, the same conditions of MA and geopolymer synthesis were utilized.
2.1. Materials

Class F FA was collected from a thermal power plant situated in Apatity, Murmansk region, Russia. The major component of the FA was the glass phase, and the crystalline phases were α-quartz and mullite. For a detailed introduction to FA, go to reference [34]. Natural magnesite of SM-1 grade of the Satka group deposits produced by Magnesite Group LLC (Satka, Chelyabinsk Region, Russia) was used as a carbonate additive. Approximately 3% of quartz and minor amounts of dolomite, chlorite, talc, and pyrite were present in magnesite as impurities. XRD patterns of the FA and magnesite are shown in Figure 1. Magnesite was ground and sieved using a 300 μm mesh. The chemical compositions of the FA and magnesite are given in Table 1. The content of magnesite added to FA was 1, 3, 5, 10, and 20% relative to the mass of the (FA + magnesite) mixture. The appearance of the raw FA and raw magnesite is shown in Figure 2.

![Figure 1. The XRD patterns of the FA and natural magnesite. Phases marked are: Q—quartz SiO₂ (ICDD 00-046-1045), M—mullite 3Al₂O₃·2SiO₂ (ICDD 00-015-0776), G—magnesite MgCO₃ (ICDD 01-086-2348).](image)

| Table 1. Chemical composition of the FA and magnesite, wt.%. (n/a—not analyzed). |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                                | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO  | CaO | MgO | SO₃ | Na₂O | K₂O | C   | P₂O₅ | TiO₂ | LOI |
| FA                            | 56.26 | 18.39 | 8.58  | 0.69 | 2.14| 2.60| 0.18| 4.04 | 1.32| 0.88| 0.32 | 1.13 | 2.28 |
| Magnesite                     | 1.50 | n/a   | 0.36  | n/a  | 0.32| 46.20| 0.16| 0.07 | 0.03| n/a | n/a  | 0.02 | 50.47|
2.2. MA

MA of the (FA + magnesite) mixtures was performed in an AGO-2 laboratory planetary mill (Novic, Novosibirsk, Russia) in air at a centrifugal force of 40 g. Steel vials and steel balls 7–8 mm in diameter were used as the milling bodies (Figure 3). The details of MA are described in [34].

2.3. Preparation of Geopolymers

Synthesis of geopolymers was performed according to the procedure used in previous studies [34,35]. The milled (FA + magnesite) blends were mixed with 8.3 mol/L sodium hydroxide solution (~20 wt.% Na₂O) to prepare pastes of normal consistency from which 1.41 cm × 1.41 cm × 1.41 cm cubes were molded (Figure 4). The mass ratio of Na₂O (present in the NaOH solution) to the milled (FA + calcite) mixture in the paste was 0.06. Water
content was adjusted to ensure the same workability of pastes; thus, the water content varied. The water/solid (w/s) ratio was defined by taking into account the amount of water present in the sodium hydroxide solution. The compositions of the mixtures used for preparation of the pastes are shown in Table 2. Prepared specimens were cured at 22 ± 2 °C for 24 h. After demolding, the specimens were further cured to testing time in the same conditions used in the first 24 h. Compressive strength data were obtained from an average of 3 samples using a hydraulic press PGM-100MG4-A (SKB Stroypribor, Chelyabinsk, Russia).

Table 2. Composition of mixtures used for preparation of pastes.

| FA (wt.%) | Magnesite (wt.%) | w/s Ratio (30 s MA) | w/s Ratio (180 s MA) | w/s Ratio (400 s MA) |
|-----------|------------------|---------------------|----------------------|----------------------|
| 100       | 0                | 0.23                | 0.25                 | 0.28                 |
| 99        | 1                | 0.28                | 0.31                 | 0.31                 |
| 97        | 3                | 0.31                | 0.31                 | 0.31                 |
| 95        | 5                | 0.31                | 0.31                 | 0.31                 |
| 90        | 10               | 0.30                | 0.30                 | 0.31                 |
| 80        | 20               | 0.30                | 0.30                 | 0.31                 |

2.4. Dissolution Test

To evaluate the reactivity of FA and the effect of added magnesite on it, experiments on the dissolution of the mechanically activated FA and mechanically activated (90% FA + 10% magnesite) blends in NaOH solution were carried out. The concentration of NaOH solution was the same as it was in geopolymer synthesis (8.3 mol/L NaOH). A total of 1 g of solid raw material was added to 40 mL sodium hydroxide solution and stirred on a magnetic stirrer at room temperature (22 ± 2 °C) for 1, 5, and 24 h. The suspensions were then centrifuged, diluted (1:100), and analyzed on an ICPE-9000 inductively coupled plasma atomic emission spectrometer (Shimadzu, Kyoto, Japan) for silicon, aluminum, and magnesium content.

2.5. Characterization Methods

Powder XRD patterns were measured on a Shimadzu XRD-6000 (Shimadzu, Kyoto, Japan) instrument using Cu-Kα radiation. The XRD patterns were acquired at a step size
of 0.02° (2 theta) and the dwell time was 1 s. FT-IR spectra were recorded on a Nicolet 6700 FT-IR (Thermo Fisher Scientific, Waltham, MA, USA) spectrometer using potassium bromide tablets. Thermogravimetric (TG) analysis was performed on a NETZSCH STA 409 PC/PG (NETZSCH, Selb, Germany) instrument at a heating rate of 20 °C/min under an Ar atmosphere in platinum crucibles. The specific surface area of the powders was measured using the nitrogen BET method in a Flow-Sorb II 2300 instrument (Micromeritics Instruments, Norcross, GA, USA). SEM studies were performed using a LEO 420 (Carl Zeiss, Oberkochen, Germany) microscope operated at 10 kV after gold coating the fractured surface.

3. Results and Discussion

3.1. Effect of MA on the (FA + Magnesite) Blends

The specific surface area (SSA) of (FA + magnesite) blends increased with increasing duration of MA. For 30, 180, and 400 s of milling, the SSA was 3.3 ± 0.2, 4.8 ± 0.3, and 5.6 ± 0.3 m²/g, respectively, with mixture composition having only a slight effect on the SSA for each MA duration.

Figure 5 shows XRD patterns of the (90% FA + 10% magnesite) blends after MA for 30 s and 180 s. The hardness of magnesite (4.0–4.5 on the Mohs scale) is close to that of calcite (3.0) and dolomite (3.5–4.0) and markedly less than that of quartz (7.0) and mullite (6.3–7.5) [36,37]. Therefore, as in the case of mixtures of FA with calcite [34] and dolomite [35], the intensities of magnesite peaks in the XRD patterns of mechanically activated (FA + magnesite) blends were reduced under the influence of MA to a far greater extent than were the intensity of quartz and mullite peaks (compare curves 1 and 2 in Figure 5). A decrease in the intensity of magnesite peaks under the influence of MA indicates a noticeable structural disordering of the mineral and/or a decrease in the size of crystallites.

3.2. Mechanical Properties

Figure 6 represents the compressive strength of geopolymers measured after 7, 28, 180, and 360 d of curing.
Figure 6. Effect of magnesite content and MA time on the compressive strength of geopolymers cured for: (a) 7 d; (b) 28 d; (c) 180 d; (d) 360 d.

Increasing the MA time from 30 to 180 s, in line with the above data on the SSA of blends, markedly increased the strength of geopolymers prepared both using the unblended FA and (FA + magnesite) mixtures, especially in the early period of curing. For the geopolymers based on (FA + magnesite) blends mechanically activated for 180 s, the strength was on average 8.0 ± 1.5, 3.0 ± 0.9, 1.5 ± 0.2, and 1.7 ± 0.5 times higher than that for the geopolymers based on blends mechanically activated for 30 s at an age of 7, 28, 180, and 360 d, respectively. A further increase in MA time of up to 400 s, despite the increase in the SSA, either did not affect strength, or increased it to a minimal extent (Figure 6). This effect of “overgrinding” on compressive strength was also observed for geopolymers based on mechanically activated mixtures of FA with calcite [34] and dolomite [35]. A possible explanation for this is optimal particle size distribution, which is one of the key factors influencing geopolymer strength [9].

It should be noted that the addition of magnesite to FA did not improve the geopolymer strength for all the studied compositions and durations of MA. At the same time, for most geopolymers prepared using mixtures containing 1%-10% magnesite, the strength was actually not reduced or reduced to a small extent compared to the geopolymers based on 100% FA. The trend of strength reduction with the introduction of magnesite in the FA is clearly seen only for the geopolymers prepared using a (80% FA + 20% magnesite) blend cured for 28 d or more (Figure 6).

Figure 7 shows the compressive strength of geopolymers based on the (FA + magnesite) blends milled for 180 s, in comparison with the strength of similar geopolymers based on (FA + calcite) [34] and (FA + dolomite) [35] blends at the age of 7, 28, and 180 days. In
contrast to magnesite, increasing the dolomite and calcite content in the blends led to a gradual increase in strength. The most probable reason for the lack of strength increase as a result of magnesite addition is magnesite’s chemical composition, in which there is a prevalence of magnesium and almost no calcium (Table 1).

![Graphs showing the effect of calcite, dolomite, and magnesite content on the compressive strength of geopolymers.](image)

**Figure 7.** Effect of calcite, dolomite, and magnesite content on the compressive strength of geopolymers based on (FA + carbonate mineral) blends mechanically activated for 180 s and cured for: (a) 7 d; (b) 28 d; (c) 180 d. Data for calcite and dolomite are taken from [34] and [35], respectively.

For slight additions of magnesite (1%–3%), geopolymer strength decreased compared to the strength of a geopolymer based on 100% FA. With a further increase in magnesite content, strength increased and approached that of a geopolymer synthesized using 100% FA (Figure 7). The decrease in strength with modest additions of magnesite was also evident for geopolymers prepared using blends milled for 30 s and 400 s (Figure 6). The reason for the appearance of the minimum on the strength curves is not yet clear and requires further study.

As a representative example, Figure 8 shows the compressive strengths of geopolymers based on (90% FA + 10% carbonate) blends mechanically activated for 180 s, depending on the CaO/(CaO+MgO) content of the carbonate minerals, for 7, 28, and 180 d of curing. The data presented in Figure 8 confirm that calcium plays a highly important role in alkaline activation, and that its content in carbonate minerals is one of the key parameters affecting the performance of geopolymers based on (FA + carbonate) blends.
Figure 8. Effect of CaO/(CaO+MgO) content in carbonate minerals on the compressive strength of geopolymers based on (90% FA +10% carbonate) blends mechanically activated for 180 s and cured for 7, 28, and 180 days.

The lower strength of geopolymers based on the (FA + magnesite) blends was likely also due to their high w/s ratio equal to 0.28–0.31 (Table 2) in comparison with that of the mixtures of FA with calcite and dolomite, which was 0.23–0.26 [34,35]. It is also necessary to take into consideration that carbonates are microfillers in the geopolymer composite. Hence, differences in mechanical properties of geopolymers also depend on differences in the surface properties of carbonates that determine the strength of their connection with the geopolymer matrix (filler effect). This issue is beyond the scope of this article and needs further investigation.

Thus, for the studied Ca/Mg carbonates, the strength of the corresponding composite geopolymers decreased in the order CaCO$_3$ (calcite) > CaMg(CO$_3$)$_2$ (dolomite) > MgCO$_3$ (magnesite). In terms of strength improvement, the favorable effect of carbonate addition to FA was observed only for the first two minerals.

3.3. Dissolution Experiments

The dominant step in geopolymerization is the formation of sodium-containing aluminosilicate hydrogel (N–A–S–H gel). In turn, the rate of geopolymer gel formation is determined by the rate of dissolution of silicon and aluminum from raw materials into alkaline solution. In geopolymer compositions, due to the high values of the raw material/alkali solution ratio, as well as the overlapping processes of dissolution, gel formation, and its polycondensation, it is impracticable to analyze the change in Si and Al concentrations in the liquid phase over time. In this regard, experiments on the dissolution of aluminosilicates in alkaline solutions at relatively low solid/solution ratios provide useful information for an enhanced understanding of geopolymer reactions [38,39]. The dissolution test results for 100% FA and a (90% FA + 10% magnesite) blend milled for 30 s and 180 s are presented in Table 3 and Figure 9.
Table 3. Concentrations of SiO$_2$ and Al$_2$O$_3$ after dissolution of the mechanically activated FA and (90% FA + 10% magnesite) blend in sodium hydroxide solution. $^1$.

| Raw Material          | MA Time, s | Dissolution Time, h | SiO$_2$, mg·L$^{-1}$ | Al$_2$O$_3$, mg·L$^{-1}$ |
|-----------------------|------------|---------------------|----------------------|--------------------------|
| FA                    | 30         | 1                   | 1.75                 | 1.08                     |
|                       | 30         | 5                   | 3.34                 | 1.68                     |
|                       | 30         | 24                  | 8.90                 | 4.16                     |
|                       | 180        | 1                   | 3.98                 | 1.18                     |
|                       | 180        | 5                   | 7.12                 | 2.29                     |
|                       | 180        | 24                  | 23.53                | 6.82                     |
| 90% FA + 10% magnesite| 30         | 1                   | 1.41                 | 0.813                    |
|                       | 30         | 5                   | 2.22                 | 1.06                     |
|                       | 30         | 24                  | 3.96                 | 1.57                     |
|                       | 180        | 1                   | 1.60                 | 0.246                    |
|                       | 180        | 5                   | 4.41                 | 0.832                    |
|                       | 180        | 24                  | 11.44                | 3.48                     |

$^1$ The concentration of MgO in all solutions was less than 0.1 mg·L$^{-1}$.

Table 3 and Figure 9 show the following trends. Firstly, in line with geopolymer strength (Figure 6), the increase in MA time from 30 to 180 s led to a significant increase in Si and Al concentration in the alkaline solution (Table 3). Secondly, there was almost synchronous dissolution of silicon and aluminum from both 100% FA and its mixture with magnesite (Figure 9). The calculated correlation coefficient of Si and Al leaching for 30 s MA was 0.96, while that for 180 s MA was 0.95. This probably indicates that silicon and aluminum are extracted from FA into the alkaline solution in a linked form [38]. Third, as a result of adding magnesite to FA, the extent of leaching both Si and Al decreased significantly (actually, by half, in most experiments). The reason for this decrease may be: 1) precipitation of magnesium hydroaluminosilicates and 2) the formation of colloidal particles of aluminosilicate composition and their coagulation with subsequent separation from the liquid phase during centrifugation. Interestingly, a significant decrease in the dissolution of silicon and aluminum was not accompanied by a comparable decrease in the strength of the corresponding geopolymers (Figure 6). Hence, the decrease in Si and Al concentration in the case of the (FA + magnesite) blends (Figure 9) might occur under the influence of a second factor, namely, as a result of coagulation.

Figure 9. Silicon and aluminum dissolution from the FA and (90% FA + 10% magnesite) blend mechanically activated for: (a) 30 s; (b) 180 s.
It should be noted that the concentration of MgO in all solutions was negligible—less than 0.1 mg·L$^{-1}$. As shown below (see Section 3.5), magnesium was released from the blend during alkaline dissolution and then precipitated, forming new solid phases.

3.4. TG Analysis

As an example, Figure 10 represents the TG data of geopolymers prepared using the (90% FA + 10% magnesite) blend mechanically activated for 30 s and 180 s after curing for 28 d. Increasing the MA time of the mixture of FA with magnesite led to an increase in weight loss upon heating the geopolymer.

![Figure 10](image_url)

**Figure 10.** Thermogravimetric (TG) curves of the geopolymers based on the (90% FA + 10% magnesite) blend milled for: 1—30 s, 2—180 s. Curing time was 28 d. The shaded area corresponds to the removal of water tightly bound with the geopolymer gel.

Differential thermogravimetric (DTG) curves for these samples are shown in Figure 11. The most intensive peak in the DTG curve for both samples with a maximum in the region of 100–120 °C corresponds to a removal of adsorbed and weakly bound water. The minute peaks in the 200–450 °C region appear to be due to the removal of tightly bound water. The second intensive peak on the DTG curve in the region of 450–650 °C corresponds to the decomposition of carbonate groups of magnesite. For the geopolymer based on the blend milled for 180 s, this peak corresponds to a low temperature compared to the peak of a geopolymer synthesized using the blend milled for 30 s.
Figure 11. Differential thermogravimetric (DTG) curves of the geopolymers based on the (90% FA + 10% magnesite) blend milled for: 1—30 s, 2—180 s. Curing time was 28 d.

In order to clarify the effect of MA time on the decomposition of magnesite during heating, experiments on MA of 100% magnesite in the same regime as MA of the (FA + magnesite) mixtures were performed. Figure 12 shows DTG curves of the raw magnesite and magnesite milled for 30 s and 180 s.

The DTG peak corresponding to the maximum rate of CO$_2$ release from magnesite shifted to the region of lower temperatures with increasing MA time. The shift of the peak for magnesite (Figure 12) and geopolymer (Figure 11) can be explained by an increase in the degree of structural disorder of magnesite with increasing MA time. Increasing milling time led to an accumulation of excess energy in the mineral and, consequently, to a decrease in thermal stability.
For geopolymers based on a mechanically activated (90% FA + 10% magnesite) blend (Figure 11), the DTG peak of magnesite decomposition corresponds to a temperature which is 70–100 °C lower than that for the mechanically activated 100% magnesite (Figure 12). This can be explained as follows. As noted above, the hardness of the minerals present in FA is markedly higher than that of magnesite. The hardness of the glass phase present in FA in the form of microspheres is 5.0–6.0 according to the Mohs scale [40], which is also higher than that of magnesite (4.0–4.5). Thus, during MA of the (FA + magnesite) blend, the intensity of mechanical impact on the carbonate mineral was higher than during MA of 100% magnesite. The structural disorder of magnesite during MA of the (FA + magnesite) blend was caused not only by the impact of milling bodies (balls), but also by the hard components of FA. As a result, the thermal stability of magnesite in the former case was reduced compared to its thermal stability in the latter.

For geopolymers based on the mechanically activated (FA + calcite) [34] and (FA + dolomite) [35] blends, a correlation was observed between compressive strength and the proportion of water tightly bound to the geopolymer gel, determined by weight loss in the temperature range of 120–500 °C. Weight loss during heating at a temperature >500 °C was associated mainly with the removal of CO₂ as a result of the decomposition of carbonate groups [34]. Since magnesite is less thermally stable than calcite, when heating the geopolymers synthesized using (FA + magnesite) blends, carbon dioxide release started according to the DTG data at a low temperature (about 450 °C; see Figure 11). Taking into account the DTG data (Figure 11), it is reasonable to assume that removal of water tightly bound with N–A–S–H gel occurs in the range of 120–450 °C (shaded area in Figure 10). Weight loss in this temperature region for the geopolymers based on (90% FA + 10% magnesite) blends milled for 30 and 180 s was 3.44% and 4.23%, respectively. The higher content of tightly bound water for the geopolymer prepared using a (90% FA + 10% magnesite) blend milled for 180 s in comparison to that milled for 30 s is consistent with geopolymer strength (Figure 6 b). It should be taken into account that the indicated contents of tightly bound water are approximate, because a part of the water present in the gel structure is likely removed at temperatures above 450 °C due to dehydroxylation as a result of condensation of the silanol and aluminol groups of the geopolymer gel [41] simultaneously with the decomposition of magnesite.

3.5. XRD and FT-IR Spectroscopy Analysis

Figure 5 (curves 3 and 4) shows XRD patterns of geopolymers synthesized using the (90% FA + 10% magnesite) blend mechanically activated for 180 s and cured for 7 and 180 d. The formation of N–A–S–H gel is evidenced by the appearance of a halo in the 2θ = 25–35° region [18]. It is noteworthy that the intensity of magnesite peaks in the XRD patterns of geopolymers decreased slightly compared to that of the blend from which the geopolymer was prepared (curve 2 in Figure 5). This indicates a partial transformation of magnesite into another amorphous and/or poorly crystalline phase(s). The formation of new crystalline phases was also possible, but in amounts that would not allow their detection by XRD, even in the case of geopolymers at the age of 180 days (Figure 5, curve 4). The formation of new phases according to XRD data (not shown) was not detected for all of the studied geopolymers.

For a clear understanding of the chemical processes occurring during geopolymerization, the (80% FA + 20% magnesite) blend milled for 180 s was leached with NaOH solution, as described in Section 2.4. The leaching time was 24 h. The solid residue was filtered and washed with distilled water before analysis. Figure 13 presents XRD patterns of the blend before and after leaching. In the XRD pattern of the leach residue (Figure 13, curve 2) compared to that of the blend (Figure 13; curve 1), the intensities of magnesite peaks decreased drastically. In addition, peaks of new compounds—hydrotalcite Mg₆Al₂CO₃(OH)₁₆·4H₂O (ICDD 00-041-1428) and brucite Mg(OH)₂ (ICDD 01-071-5972)—appeared. This indicates the high reactivity of natural magnesite with respect to alkali
solution and the possible formation of minute amounts of hydrotalcite and brucite (not determined by XRD) during geopolymerization of the (FA + magnesite) blends.

Figure 13. The XRD patterns of the (80% FA + 20% magnesite) blend mechanically activated for 180 s: 1—before leaching; 2—after leaching with NaOH solution. Phases marked are: Q—quartz SiO₂ (ICDD 00-046-1045), M—mullite 3Al₂O₃·2SiO₂ (ICDD 00-015-0776), G—magnesite MgCO₃ (ICDD 01-086-2348), B—brucite Mg(OH)₂ (ICCD 01-071-5972), H—hydrotalcite Mg₆Al₂CO₃(OH)₁₆·₄H₂O (ICCD 00-041-1428).

Figure 14 shows the FT-IR spectrum of the (90% FA + 10% magnesite) blend, milled for 180 s, as well as the spectra of a geopolymer synthesized using this blend at the age of 7 d and 28 d.

Figure 14. The FT-IR spectra: 1—the (90% FA + 10% magnesite) blend milled for 180 s, 2 and 3—the geopolymer synthesized using this blend after 7 and 28 d of curing, respectively.
The main absorption band at 1081 cm$^{-1}$ in the spectrum of the (90% FA + 10% magnesite) blend (Figure 14; curve 1) is due to asymmetric stretching Si-O-T (T = Si or Al) vibrations of the FA components. The peaks at 1456, 887, and 748 cm$^{-1}$ correspond to magnesite. Other peaks in the 800–600 cm$^{-1}$ region are associated with the presence of quartz and mullite in the FA [42–45]. The broad band at 3432 cm$^{-1}$ (stretching O-H vibrations) in the spectra of the blends is due to adsorption of H$_2$O from air by the (FA + magnesite) blend during MA. In the FT-IR spectra of the geopolymers at the age of 7 and 28 days (Figure 14; curves 2 and 3) compared to the spectrum of the unreacted mixture (Figure 14; curve 1), the band of asymmetric stretching vibrations Si–O–T (T = Si or Al) is shifted to the region of low wave numbers. There is also an increase in the intensity of the O–H stretching vibration band at 3700–3100 cm$^{-1}$ and the H–O–H bending vibration band at 1641 cm$^{-1}$. These changes indicate the formation of N–A–S–H gel and are close to the corresponding changes in the FT-IR spectra of geopolymers based on the blends of FA with calcite and dolomite [34,35].

Most interesting, in our opinion, is the appearance of a shoulder at 1412 cm$^{-1}$ in the IR spectra of geopolymers at the main peak of magnesite corresponding to the asymmetric stretching vibrations of the carbonate group (Figure 14, curves 2 and 3). This change is pronounced in the spectra of the geopolymers based on the mechanically activated blend containing 1% magnesite (Figure 15). This change can be explained by the increase noted above in the magnesite reactivity with respect to NaOH solution due to a decrease in the magnesite proportion in the mixture with the FA.

![Figure 15](image-url)

**Figure 15.** The FT-IR spectra: 1—the (99% FA + 1% magnesite) blend milled for 180 s; 2 and 3—the geopolymer synthesized using this blend after 7 and 28 d of curing, respectively.

From the data shown in Figure 15, it is clearly seen that the shoulder present in the magnesite peak at 1445 cm$^{-1}$ in the geopolymer spectrum at the age of 7 d (curve 2) was transformed into a peak at 1393 cm$^{-1}$ for the geopolymer at the age of 28 d (curve 3). As noted above, hydrotalcite Mg$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O was found to form as a product of the alkaline activation of BFS, which contains a significant amount of magnesium (8–9% MgO) [30]. In the IR spectrum of this mineral, there is an intense band in the 1400–1360 cm$^{-1}$ region corresponding to the vibrations of the CO$_3^{2-}$ group [46]. Apparently, the alkaline activation of the (FA + magnesite) blend also produces a minute amount of hydrotalcite. This is indicated by (i) the appearance of a peak at 1393 cm$^{-1}$ in the IR spectrum of a geopolymer prepared using the (99% FA + 1% magnesite) blend (Figure 15; curve 3) and (ii) the XRD data on the leaching residue (Figure 13; curve 3).
As mentioned above, according to XRD data (Figure 13; curve 2), one of the products of leaching the (FA + magnesite) blend with NaOH solution was magnesium hydroxide (brucite). In the IR spectrum of brucite, there is a characteristic OH stretching vibration band at 3698 cm\(^{-1}\) [47]. Since this band is absent in the spectra of geopolymers (Figures 14 and 15), the formation of brucite during geopolymerization of the (FA + magnesite) blends is unlikely, taking into account the significantly lower alkali content in the geopolymer paste compared with that in the suspension during leaching.

The data obtained suggest the following implications of magnesite addition to the FA on the strength of composite geopolymers. As in the case of composite geopolymers based on mixtures of FA with calcite and dolomite, the above-mentioned filler and dilution effects appeared upon the introduction of magnesite into FA. Most likely, for this reason, when the content of magnesite in the mixtures was 10% or less, in general, there was no significant reduction in strength compared to that in the geopolymers synthesized using 100% FA (Figure 6). For the geopolymers prepared using a (80% FA + 20% magnesite) blend, reduced strength was observed for all curing times, except for geopolymers at the age of 7 d. In the early periods of curing (7 d), the dilution effect probably prevailed for geopolymers based on this blend. An increased ratio of alkaline agent to FA led to an accelerated initial formation of the geopolymer gel in comparison with the geopolymers based on blends with low magnesite content. This provided a relatively high strength of geopolymer based on the (80% FA + 20% magnesite) blend compared to that of other geopolymers at the age of 7 days (Figure 6 a). At later curing times, the lack of FA in the blend was supposed beginning to have an effect. As a result, in comparison with the blends with less magnesite content, the degree of geopolymer gel decreased and the strength decreased.

The formation of hydrotalcite can be considered a manifestation of a chemical effect when magnesite is introduced into FA (Figures 13–15). The influence of hydrotalcite on the properties of the studied geopolymers, due to the slight degree of its formation, is likely to be minor. To reveal the role of this mineral in the geopolymerization of (FA + magnesite) blends, additional studies are needed.

### 3.6. Microstructural Studies

Figure 16 shows SEM images of geopolymers at 28 d of age prepared from a (90% FA + 10% magnesite) blend mechanically activated for 30 and 180 s and exhibiting compressive strengths of 1.9 and 9.0 MPa, respectively. The increased strength of the geopolymer synthesized using the blend milled for 180 s is consistent with its less porous and more homogeneous microstructure (Figure 16c) compared to the similar geopolymer prepared from the blend mechanically activated for 30 s (Figure 16a).

Magnified SEM images (Figure 16b,d) clearly show that, for the geopolymer based on the blend mechanically activated for 30 s (Figure 16b), a large proportion of spherical particles of unreacted FA is present in the sample structure. Unreacted FA particles are loosely bound to the geopolymer matrix and may even leave cavities when the specimen is tested for compressive strength, as marked in Figure 16b. This negatively affects the physical and mechanical properties of geopolymers, since voids around unreacted particles can be potential centers of microcrack initiation and pathways for microcrack propagation.
Figure 16. SEM images of the geopolymer synthesized using a (90% FA + 10% magnesite) blend mechanically activated for: (a,b) 30 s; (c,d) 180 s. Curing time was 28 d. In Figure 16b,d, unreacted FA spherical particles are marked with yellow crosses.

4. Conclusions

The research objects in this study were geopolymers prepared using mechanically activated mixtures of FA with natural magnesite. Magnesite replaced the FA in amounts of 1, 3, 5, 10, and 20 wt.%. MA of the (FA + magnesite) blends was carried out in a laboratory planetary mill. Sodium hydroxide solution was used as an alkaline agent and curing was at room temperature. The geopolymers were tested for compressive strength after curing for 7, 28, 180, and 360 d. FT-IR spectroscopy, XRD, TGA, and SEM were used to characterize the geopolymer samples. The leaching of Si, Al, and magnesium from mechanically activated (FA + magnesite) mixtures in NaOH solution was studied.

The following major conclusions are derived from the present study:

1. Experiments on leaching of the mechanically activated (FA + magnesite) blend with NaOH solution showed that the dissolution of silicon and aluminum occurred synchronously. This indicates that Si and Al were extracted from the FA into the alkaline solution in a linked form. The addition of magnesite to the FA led to a significant decrease in the concentration of both Si and Al in the solution. The reason for this decrease might be the formation of aluminosilicate gel, which was accelerated under the influence of magnesite. The increase in the MA time of the (FA + magnesite) blend from 30 to 180 s was accompanied by a marked increase in the degree of Si and Al
transition into NaOH solution. This is explained by the increased reactivity of blend components with respect to sodium hydroxide solution.

2. In agreement with dissolution experiments, as well as with the results of FT-IR spectroscopy, TG analysis and SEM, increasing the MA time of the mixture of FA and magnesite from 30 to 180 s on average increased the strength of geopolymers by a factor of $8.0 \pm 1.5, 3.0 \pm 0.9, 1.5 \pm 0.2$, and $1.7 \pm 0.5$ after curing for 7, 28, 180, and 360 d, respectively. A further increase in the MA time to 400 s, despite the increase in the specific surface area, either did not change the strength, or increased it to a slight extent, which can be explained by the effect of “overgrinding”.

3. For the studied calcium and magnesium carbonates, the strength of the corresponding composite geopolymers decreased in the series CaCO$_3$ (calcite) $>$ CaMg(CO$_3$)$_2$: (dolomite) $>$ MgCO$_3$ (magnesite). In contrast to calcite and dolomite, the addition of magnesite to the FA did not improve the strength of the composite geopolymer. The most probable reason for the lack of strength increase as a result of magnesite addition is magnesite’s chemical composition, in which magnesium dominates among the metals, while calcium is practically absent. A decrease in the strength of geopolymers based on the blends of FA with magnesite is also due to these blends’ higher water demand compared to the demands of blends of FA with calcite and dolomite.

4. Although the addition of magnesite to FA did not improve the geopolymer performance, for most blends containing 1%-10% magnesite, their strength either did not decrease or it decreased to a minimal extent compared to geopolymers based on 100% FA. This can probably be explained by filler and dilution effects. Alkaline activation of the (FA + magnesite) blend according to FT-IR spectroscopy data apparently resulted in the formation of hydrotalcite in minute amounts, which was not determined by XRD in the geopolymers. To elucidate the influence of hydrotalcite on the properties of composite geopolymers, additional studies are needed.

5. In this work, a planetary mill was used as the mechanical activator. Future research should aim to obtain similar results using other types of mills (e.g., vibratory and attrition mills), which are currently used in industry for large-scale production. A study on the effect of adding magnesite to other raw materials used to prepare alkali activated binders, such as BFS, is also of interest.

Author Contributions: Conceptualization, A.M.K. and E.V.K.; methodology, A.M.K., E.V.K., A.G.I. and E.A.K.; investigation, A.M.K., E.V.K., A.G.I. and E.A.K.; writing—original draft preparation, A.M.K.; writing—review and editing, E.V.K., A.G.I. and E.A.K.; visualization, A.G.I. and E.A.K. All authors have read and agreed to the published version of the manuscript.

Funding: The reported study was funded by RFBR, project number 20-03-00486.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge V.V. Semushin for his help in the SEM studies.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Davidovits, J. Geopolymers: ceramic-like inorganic polymers. J. Ceram. Sci. Technol. 2017, 8, 335–349. https://doi.org/10.4416/JCST2017-00038.
2. Provis, J.L. Alkali-activated materials. Cem. Concr. Res. 2018, 114, 40–48. https://doi.org/10.1016/j.cemconres.2017.02.009.
3. Mehta, A.; Siddique, R. An Overview of geopolymers derived from industrial by-products. Constr. Build. Mater. 2016, 127, 183–198. https://doi.org/10.1016/j.conbuildmat.2016.09.136.
4. Tang, Z.; Li, W.; Hu, Y.; Zhou, J.L.; Tam, V.W.Y. Review on designs and properties of multifunctional alkali-activated materials (AAMs). Constr. Build. Mater. 2019, 200, 474–489. https://doi.org/10.1016/j.conbuildmat.2018.12.157.
5. Luukkonen, T.; Heponiemi, A.; Runtti, H.; Pesonen, J.; Yliniemi, J.; Lassi, U. Application of alkali-activated materials for water and wastewater treatment: A review. Rev. Environ. Sci. Biol. 2019, 18, 271–297. https://doi.org/10.1007/s11157-019-09494-0.
6. Dogan-Saglamtimore, N.; Bilgil, A.; Ertürk, S.; Bozkurt, V.; Süzgeç, E.; Akan, A.G.; Nas, P.; Çetin, H.; Szechynska-Hebda, M.; Hebda, M. Eco-geopolymers: Physico-mechanical features, radiation absorption properties, and mathematical model. *Polymers* **2022**, *14*, 262. https://doi.org/10.3390/polym14020262.

7. Oglat, A.A.; Shalbi, S.M. An alternative radiation shielding material based on barium-sulphate (BaSO4)-modified fly ash geopolymers. *Gels* **2022**, *8*, 227. https://doi.org/10.3390/gels8040227.

8. Ranjarb, N.; Kuenzel, C.; Spangenberg, J.; Mehrali, M. Hardening evolution of geopolymers from setting to equilibrium: A review. *Cem. Concr. Compos.* **2020**, *114*, 103729. https://doi.org/10.1016/j.cemconcomp.2020.103729.

9. Muci, G.; Kumar, S.; Csoke, B.; Kumar, R.; Molnar, Z.; Racz, A.; Mádai, F.; Debreczeni, A. Control of geopolymer properties by grinding of land filled fly ash. *Int. J. Min. Proc.* **2015**, *143*, 50–58. https://doi.org/10.1016/j.minpro.2015.08.010.

10. Kumar, R.; Kumar, S.; Mehrrota, S.P. Towards sustainable solutions for fly ash through mechanical activation. *Resource. Conserv. Recyc.* **2007**, *52*, 157–179. https://doi.org/10.1016/j.resconrec.2007.06.007.

11. Kumar, S.; Kumar, R. Mechanical activation of fly ash: Effect on reaction, structure and properties of resulting geopolymer. *Ceram. Int.* **2011**, *37*, 533–541. https://doi.org/10.1016/j.ceramint.2010.09.038.

12. Cristelino, N.; Tavares, P.; Lucas, E.; Miranda, T.; Oliveira, D. Quantitative and qualitative assessment of the amorphous phase of a Class F fly ash dissolved during alkali activation reactions—Effect of mechanical activation, solution concentration and temperature. *Compos. Part. B Eng.* **2016**, *103*, 1–14. https://doi.org/10.1016/j.compositesb.2016.08.001.

13. Kumar, R.; Kumar, S.; Alex, T.C.; Singla, R. Mapping of calorimetric response for the geopolymerisation of mechanically activated fly ash. *J. Therm. Anal. Calorim.* **2019**, *136*, 1117–1133. https://doi.org/10.1007/s10973-018-7736-3.

14. Kumar, S.; Kumar, R.; Alex, T.C.; Bandopadhyay, A.; Mehrrota, S.P. Influence of reactivity of fly ash on geopolymerisation. *Adv. Appl. Ceram.* **2007**, *106*, 120–127. https://doi.org/10.1179/17437607X159293.

15. Matsukau, M.; Yokoyama, K.; Okura, K.; Murayama, N.; Ueda, M.; Naito, M. Synthesis of geopolymers from mechanically activated coal fly ash and improvement of their mechanical properties. *Minerals* **2019**, *9*, 791. https://doi.org/10.3390/min9120791.

16. Temuujin, J.; Williams, R.P.; van Riessen, A. Effect of mechanical activation of fly ash on the properties of geopolymers cured at ambient temperature. *J. Mater. Process Technol.* **2009**, *209*, 5276–5280. https://doi.org/10.1016/j.jmatprot.2009.03.016.

17. Chu, Y.-S.; Davaab, B.; Kim, D.-S.; Seo, S.-K.; Kim, Y.; Ruescher, C.; Temuujin, J. Reactivity of fly ashes milled in different milling devices. *Rev. Adv. Mater. Sci.* **2019**, *58*, 179–188. https://doi.org/10.1515/rams-2019-0028.

18. Kumar, S.; Muci, G.; Kristály, F.; Pekker, P. Mechanical activation of fly ash and its influence on micro and nano-structural behaviour of resulting geopolymers. *Adv. Powder Technol.* **2017**, *28*, 805–813. https://doi.org/10.1016/j.apt.2016.11.027.

19. Marjanovic, N.; Komljenovic, M.; Basacrevic, Z.; Nikolic, V. Improving reactivity of fly ash and properties of ensuing geopolymerisation methods through mechanical activation. *Constr. Build. Mater.* **2014**, *57*, 151–162. https://doi.org/10.1016/j.conbuildmat.2014.01.095.

20. Kato, K.; Xin, Y.; Hitomi, T.; Shirai, T. Surface modification of fly ash by mechano-chemical treatment. *Ceram. Int.* **2019**, *45*, 849–853. https://doi.org/10.1016/j.ceramint.2018.09.025.

21. Fernández-Jiménez, A.; Garcia-Lodeiro, I.; Maltseva, O.; Palomo, A. Mechanical-chemical activation of coal fly ashes: An effective way for recycling and make cementitious materials. *Frontier. Mater.* **2019**, *6*, 51. https://doi.org/10.3389/fmats.2019.00051.

22. Lee, W.; van Deventer, J. The effects of inorganic salt contamination on the strength and durability of geopolymers. *Colloids Surf. A Physicochem. Eng. Asp.* **2002**, *211*, 115–126. https://doi.org/10.1016/S0927-7757(02)00239-X.

23. Rakhimova, N. Calcium and/or magnesium carbonate and carbonate-bearing rocks in the development of alkali-activated cements—a review. *Constr. Build. Mater.* **2022**, *325*, 126742. https://doi.org/10.1016/j.conbuildmat.2022.126742.

24. Lloyd, R.R.; Provis, J.L.; van Deventer, J.S.J. Microscopy and microanalysis of inorganic polymer cements. 2: The gel binder. *J. Mater. Sci.* **2009**, *44*, 620–631. https://doi.org/10.1085/jms-008-3078-z.

25. Yip, C.K.; Provis, J.L.; Lukey, G.C.; van Deventer, J.S. Carbonate mineral addition to metakaolin-based geopolymers. *Cem. Concr. Compos.* **2008**, *30*, 979–985. https://doi.org/10.1016/j.cemconcomp.2008.07.004.

26. Cwirzen, A.; Provis, J.L.; Penttala, V.; Habermehl-Cwirzen, K. The effect of limestone on sodium hydroxide-activated metakaolin-based geopolymers. *Constr. Build. Mater.* **2014**, *66*, 53–62. https://doi.org/10.1016/j.conbuildmat.2014.05.022.

27. Ortega-Zavala, D.E.; Santana-Carrillo, J.L.; Buriacâ-Díaz, O.; Escalante-García, J.I. An initial study on alkali activated limestone binders. *Cem. Concr. Res.* **2019**, *120*, 267–278. https://doi.org/10.1016/j.cemconres.2019.04.002.

28. Firdous, R.; Hirsch, T.; Klimm, D.; Lothenbach, B.; Stephan, D. Reaction of calcium carbonate minerals in sodium silicate solution and its role in alkali-activated systems. *Miner. Eng.* **2021**, *165*, 106849. https://doi.org/10.1016/j.mineng.2021.106849.

29. Cousture, A.; Renault, N.; Gallias, J.L.; Ndiaye, K. Study of a binder based on alkaline activated limestone. *Constr. Build. Mater.* **2021**, *311*, 125323. https://doi.org/10.1016/j.conbuildmat.2021.125323.

30. Ben Haha, M.; Lothenbach, B.; Le Sauv, G.; Winnefeld, F. Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag—Part I: Effect of MgO. *Cem. Concr. Res.* **2011**, *41*, 955–963. https://doi.org/10.1016/j.cemconres.2011.05.002.

31. Jin, F.; Gu, K.; Al-Tabbaa, A. Strength and drying shrinkage of reactive MgO modified alkali-activated slag paste. *Constr. Build. Mater.* **2014**, *51*, 395–404. https://doi.org/10.1016/j.conbuildmat.2013.10.081.

32. Shen, W.G.; Wang, Y.H.; Zhang, T.; Zhou, M.K.; Li, J.S.; Cui, X.Y. Magnesia modification of alkali-activated slag fly ash cement. *J. Wakan Univ. Technol. Mater. Sci. Ed.* **2011**, *26*, 121–125. https://doi.org/10.7159/si11595-011-0182-8.
33. Sreenivasan, H.; Kinnunen, P.; Heikkinen, E.P.; Illikainen, M. Thermally treated phlogopite as magnesium-rich precursor for alkali activation purpose. *Miner. Eng.* 2017, 113, 47–54. https://doi.org/10.1016/j.mineng.2017.08.003.

34. Kalinkin, A.M.; Gurevich, B.I.; Myshenkov, M.S.; Chislov, M.V.; Kalinkina, E.V.; Zvereva, I.A.; Cherkezova-Zheleva, Z.; Paneva, D.; Petkova, V. Synthesis of fly ash-based geopolymers: Effect of calcite addition and mechanical activation. *Minerals* 2020, 10, 827. https://doi.org/10.3390/min10090827.

35. Kalinkin, A.M.; Gurevich, B.I.; Kalinkina, E.V.; Chislov, M.V. and Zvereva, I.A. Geopolymers Based on Mechanically Activated Fly Ash Blended with Dolomite. *Minerals* 2021, 11, 700. https://doi.org/10.3390/min1070700.

36. Lide, D.R. (Ed.). *CRC Handbook of Chemistry and Physics*, 89th ed.; Taylor and Francis Group: Oxfordshire, UK; CRC Press: Boca Raton, FL, USA, 2008; p. 2736.

37. Schumann, W. *Handbook of Rocks, Minerals, and Gemstones*; Houghton Mifflin Company: New York, NY, USA, 1993; p. 380.

38. Xu, H.; Van Deventer, J.S.J. The geopolymerisation of alumino-silicate minerals. *Int. J. Miner. Process* 2000, 59, 247–266. https://doi.org/10.1016/S0301-7516(99)00074-5.

39. Rattanasak, U.; Chindaprasirt, P. Influence of NaOH solution on the synthesis of fly ash geopolymer. *Miner. Eng.* 2009, 22, 1073–1078. https://doi.org/10.1016/j.mineng.2009.03.022.

40. Emelyanova, V.; Dosumova, B.; Dzhatkanbaeva, U.; Shakiyev, E.; Kurokava, H.; Kairbekov, Z.; Muhitova, D.; Shakiyeva, T.; Mylykbaeva, Z. The microspheric catalysts of sodium sulphite low-temperature oxidation by oxygen in water solutions. *Chem. Bull. Kaz. Nat. Univ.* 2013, 71, 27–35. https://doi.org/10.15328/chemb_2013_327-35.

41. Duxson, P.; Lukey, G.C.; van Deventer, J.S.J. Physical evolution of Na-geopolymer derived from metakaolin up to 1000 °C. *J. Mater. Sci.* 2007, 42, 3044–3054. https://doi.org/10.1007/s10853-006-0535-4.

42. Lee, W.K.W.; Van Deventer, J.S.J. Use of infrared spectroscopy to study geopolymerization of heterogeneous amorphous aluminosilicates. *Langmuir* 2003, 19, 8726–8734. https://doi.org/10.1021/la026127e.

43. Fernández-Jiménez, A.; Palomo, A. Mid-infrared spectroscopic studies of alkali-activated fly ash structure. *Microporous Mesoporous Mater.* 2005, 86, 207–214. https://doi.org/10.1016/j.micromeso.2005.05.057.

44. Álvarez-Ayuso, E.; Querol, X.; Plana, F.; Alastuey, A.; Moreno, N.; Izquierdo, M.; Font, O.; Moreno, T.; Diez, S.; Vázquez, E.; et al. Environmental, physical and structural characterisation of geopolymer matrices synthesised from coal (co-)combustion fly ashes. *J. Hazard. Mater.* 2008, 154, 175–183. https://doi.org/10.1016/j.jhazmat.2007.10.008.

45. White, W.B. The carbonate minerals. In *The Infrared Spectra of Minerals*; Farmer, W.C., Ed.; Mineralogical Society: London, UK, 1974; pp. 227–284.

46. Kloprogge, J.T.; Frost, R.L. Fourier Transform Infrared and Raman spectroscopic study of the local structure of Mg, Ni and Co—hydrotalcites. *J. Solid State Chem.* 1999, 146, 506–515. https://doi.org/10.1006/jssc.1999.8413.

47. Ryskin, Y.I. The vibrations of protons in minerals: Hydroxyl, water and ammonium. In *The Infrared Spectra of Minerals*; Farmer, W.C., Ed.; Mineralogical Society: London, UK, 1974; pp. 137–181.