RGNZ/MGPB

Mechanical activation and geopolymerisation of Taiwanese fly ash

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
DOI: 10.17794/rgn.2025.5.12

Original scientific paper

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Abstract

The use of raw fly ash in the production of cement and geopolymer products is limited due to its low reactivity. However, the reactivity of fly ash can be increased through a mechanical activation process, allowing for its wider use. This study focused on the mechanical activation and geopolymerisation of coal fly ash originating from Taiwan. The mechanical activation was carried out by grinding in a batch-stirred media mill for 1, 3 and 5 minutes. The fineness and specific surface area significantly increased after 1 minute, and then only slightly decreased with further milling. The lime absorbance test showed significant improvement in pozzolanic activity (130-140% increase) after mechanical activation. For geopolymer synthesis, a 10M NaOH solution was used as an alkali activator with a liquid/solid ratio of 0.35. The geopolymer containing 3-minute fly ash grind produced the highest 28-day compressive strengths (36.1 MPa). The structural characterisation of fly ash and geopolymer was carried out by Fourier Transform Infrared (FTIR) spectroscopy. Changes in the FTIR spectra of fly ashes indicated the formation of amorphous aluminosilicate gel, a new reactive product as a result of geopolymerisation. Based on the strength development of geopolymers, mechanical activation enhanced the reactivity of fly ash, resulting in rapid setting and higher strength development during the early stages of geopolymerisation. The results clearly showed that, after mechanical activation, fly ash became a more reactive raw material, offering greater application potential than its current uses in cement production, road construction, and soil stabilisation.

Keywords:

fly ash, geopolymer, mechanical activation, pozzolanic activity

1. Introduction

The cement industry is one of the main contributors to climate change, accounting for 5-8% of the annual global anthropogenic CO_2 emissions. Due to growing populations and economic development, resulting in increasing demand for housing and infrastructure, the global cement demand is still estimated to rise by 12-23% above 2020 levels by 2050 (**Cheng et al., 2023**). In their study, **Flower and Sanjayan (2007)** found that during the production of typical commercial concrete mixes, Portland cement is responsible for 74-81% of the total CO_2 emissions, followed by the production of coarse and fine aggregates. As the production of traditional Portland cement is getting increasingly unsustainable due to the high energy demand and the use of non-renewable raw materials, there is a pressing need to develop more environmentally friendly and sustainable construction materials.

Geopolymerisation of silica- and alumina-rich industrial by-products is one of the most heavily researched areas today, with significant progress being made in the field. The term "geopolymer" was first coined by Davidovits to describe the inorganic polymeric material, which is the product of the reaction between aluminosilicate-oxides with silicate under highly alkaline conditions (**Das and Rout, 2021; Xu and Van Deventer, 2000**). Geopolymers are considered synthetic analogues for natural zeolitic materials with similar hydrothermal conditions required for their synthesis (**van Jaarsveld et al., 1998; Xu and Van Deventer, 2000**). Contrary to zeolites' regular and highly crystalline structures, the much faster geopolymer reaction results in amorphous to semi-crystalline three-dimensional aluminosilicate materials (**Xu and Van Deventer, 2000**). The mechanism of the geopolymer reaction is still not fully understood to this day, however, the most proposed three main stages are: dissolution, transportation or orientation and reprecipitation/polycondensation (**Xu and Van Deventer, 2000; Das and Rout, 2021**). In simple terms, geopolymers are the product of the reaction of alumina- and silica-rich solids with alkaline solution. The alkaline solution can be sodium hydroxide (NaOH), potassium hy-

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Received: 30 April 2025. Accepted: 16 July 2025.
Available online: 21 October 2025

droxide (KOH), sodium silicate (Na_2SiO_3), potassium silicate (K_2SiO_3) solutions or various combinations (**Das and Rout, 2021**). The presence of these alkali salts/hydroxides is crucial in the geopolymerisation reaction, as they are needed for the dissolution of the silica and alumina (first stage of geopolymerisation), as well as for the catalysis of the condensation reaction (final stage). The geopolymer reaction begins with the dissolution of aluminosilicate solids, resulting in the formation of a gel layer on the surfaces of the particles. This gel then diffuses outwards, filling out the spaces between the particles through the precipitation of the gel and the dissolution of new solids. The aluminosilicate particles are bound together by the hardened gel phase which acts as a binder (**Xu and Van Deventer, 2000**). The geopolymerisation reaction takes place at temperatures lower than 100°C, making it an economically and environmentally more sustainable alternative to traditional concrete materials. Geopolymers also possess similar or superior mechanical and chemical properties, thermal resistance, fire and chemical resistance compared to traditional concretes (**Mucsi et al., 2015; Islam et al., 2025; Xu and Van Deventer, 2000**). Geopolymer technology was originally developed as the chemical activation of natural raw materials rich in Al_2O_3 and SiO_2 such as kaolin, metakaolin, silica fumes and calcined clay (**Farhan et al., 2020**). Geopolymerisation synthesis is also suitable for the high-rate utilisation of industrial by-products with high alumina and silica content, such as fly ash, ground granulated blast furnace slag (GGBS), red mud and mine tailings (**Ambrus and Mucsi, 2023; Nath et al., 2016; Kumar et al., 2010; Aziz et al., 2020; Kumar and Kumar, 2013; Mucsi et al., 2019; Manjarrez and Zhang, 2018; Moukannaa et al., 2018**). In conclusion, geopolymer technology greatly reduces the environmental impact of both traditional Portland cement-based concrete production and industrial by-products, helping the transition toward environmentally sustainable construction materials (**Ali et al., 2025; Liu et al., 2024; Islam et al., 2025**).

Among the above mentioned industrial by-products, fly ash is one of the most researched materials as a geopolymer precursor due to its easy availability, low cost and suitable chemical and mineralogical composition. Fly ash properties are highly dependent on the characteristics of the fired coal (e.g. origin, type, carbon content, particle size) and the combustion technology used (e.g. boiler configuration, temperature, gas cleaning equipment) (**Bhatt et al., 2019**). Fly ash has a high degree of pozzolanic reactivity due to its high SiO_2, Al_2O_3 and Fe_2O_3 content, which can cumulatively exceed 70%. The construction sector already applies fly ash as a cement substitute; however, its use is limited due to its relatively low pozzolanic activity compared to other cementitious materials, which can be detrimental to the quality of the produced concrete (**Hamada et al., 2024**). **Ali et al. (2025)** demonstrated the effectiveness of adding fly ash to concrete composites to counteract the detrimental effects of recycled coarse aggregate (RCA) on concrete quality. They found that substituting the cement with just the inactivated fly ash can improve the strength; however, this improvement in early strength development was lower than that of concretes containing mechanically and chemically activated fly ash. Adding either the mechanically or chemically activated fly ash further improved the properties of both fresh and hardened concrete. Their use enhanced the formation of C-S-H gel, resulting in a denser, stronger matrix. The best properties, including strength, permeability and density, were obtained by using chemically activated fly ash, as the highly alkaline environment accelerated the pozzolanic reaction and the formation of hydration products. Fly ash can also be used in combination with other waste materials, such as waste glass and GGBS, to produce foams with desirable properties (**Fóris and Mucsi, 2023; Liu et al., 2025**). Additionally, the low calcium content of fly ash was found to be particularly beneficial in terms of sulphate resistance as it reduces the formation of expansive products such as ettringite, which can be detrimental to the quality of geopolymers (**Islam et al., 2025**).

Similarly to concrete, the characteristics of fly ash particle size have a significant effect on the setting behaviour, strength development and microstructure of geopolymers (**Kumar and Kumar, 2011**). Both **Zhang et al. (2012)** and **Gao et al. (2024)** found that the particle size characteristics, specific surface area, and mineral and chemical composition had a combined effect on the reactivity of the examined fly ashes. They concluded that while the surface area is not the main determining factor in terms of reactivity, it is important for the dissolution mechanism of fly ash, since the initial key reactions between the raw material and the alkaline solution occur on the surface of the particles. **Gao et al. (2024)** also noted the critical role of the optimal distribution of fine and coarse particles in the geopolymerisation process. The importance of fly ash fineness to geopolymer properties was also highlighted by **Das (2024)**. Particle size has a strong influence on the microstructural development of the geopolymer matrix, which is closely related to the development of mechanical properties. Using fine fly ash resulted in a more compact and homogenous matrix, implying the formation of more sodium aluminosilicate hydrate (N-A-S-H) gel. This is because the fine fly ash particles are more reactive and can be almost completely dissolved in the highly alkaline activator.

The reactivity of fly ash can be improved by thermal activation, mechanical activation and chemical activation (**Ali et al., 2025**). Mechanical activation is carried out by milling in high-energy mills, such as ball mill, planetary ball mill, vibratory mill and stirred media mill in both wet and dry modes (**Fu et al., 2008; Nath and Kumar, 2020; Ambrus and Mucsi, 2023; Marjanović et al., 2014; Temuujin et al., 2009; Kumar et al. 2017; Molnár et al.,**

2014; Yang et al., 2019). Mechanical activation reduces the particle size of fly ash and increases its specific surface area, thereby accelerating the precipitation and reaction rates, as well as increasing the dissolution rate of the SiO_2 and Al_2O_3 components. The reduced particle size enhances the formation of the N-A-S-H gel and other hydration products, resulting in a denser structure (**Debnath et al., 2022; Dong et al., 2025; Liu et al., 2024**). It was proven that geopolymers made from mechanically activated fly ash have higher mechanical strength and improved properties than those made from untreated fly ash (**Kumar and Kumar, 2011; Zhao et al., 2015; Chu et al., 2019; Mucsi et al., 2014a; Mucsi et al., 2014a; Somna et al., 2011**). The material properties and the grinding conditions (grinding media, grinding method, use of chemical additives) greatly influence the particle size distribution, the macroscopic and microscopic properties of the material (**Dong et al., 2025**).

Kumar and Kumar (2011) mechanically activated fly ash in a vibratory mill and investigated the effects on geopolymerisation at ambient (27°C) and elevated (60°C) temperatures. Mechanical activation was found to increase the reaction rate and decrease the reaction time. As the duration of mechanical activation increased, the compactness of the geopolymers also increased, which could be explained by the formation of a greater amount of aluminosilicate gel. A strong relationship was established between the geopolymer properties (setting time and compressive strength), and the reactivity and median particle size of fly ash.

Marjanović et al. (2014) studied the influence of mechanical activation on the properties of fly ash and the synthesised geopolymers. Four different Serbian fly ashes were ground in a planetary ball mill for 15, 30, 45 and 60 minutes. Based on the particle size distribution results, it was determined that 15 min was the optimum duration of mechanical activation ($x_{50} \sim 3$ μm), as the agglomeration of particles was observed with prolonged grinding times. The compressive strength of geopolymers made from raw fly ash was low (< 5 N/mm^2), then following mechanical activation, the strength of the geopolymers exceeded 50 N/mm^2. The improvement in strength can be attributed to the greater formation of geopolymer gel resulting from the increased availability of alumina through mechanical activation. Agglomeration during milling can be caused by irregular fragments adhering to particle surfaces and small particles bonding together via weak van der Waals forces. These phenomena can be inhibited by adding grinding aids such as triethanolamine (TAE), as presented by **Dong et al. (2025)**. TAE not only enhanced the fragmentation of large particles, but XRD analysis also implied that it decreased the interaction forces between particles.

Mucsi et al. (2015) carried out a comparative study on the mechanical activation of a landfilled brown coal fly ash in a ball mill, vibratory mill and stirred media mill. Based on the results, there was a strong correlation between the grinding conditions (mill type and residence time), the ground material characteristics (x_{50} and specific surface area (SSA)) and the resulting geopolymer properties. The finest fly ash product (x_{50} = 5.2 μm, SSA = 21116 cm^2/g) was achieved by using a stirred media mill, which also proved to be the most efficient grinding method in terms of grinding energy and kinetics. The increased SSA also resulted in a more than 10 times higher uniaxial compressive strength of the geopolymer, which can be attributed to the better solubility and the filler effect of the finer fly ash particles.

The objective of the present study is the mechanical activation (MA) in stirred media mill and geopolymerisation of Taiwanese coal combustion fly ash (FA). MA was systematically performed in a laboratory batch-stirred media mill in dry mode for different grinding periods. Particle size and geometric specific surface area (SSA) were determined to study the effect of mechanical activation. The pozzolanic activity of raw (RFA) and mechanically activated fly ash (MFA) was determined by the lime absorption method. The structures of the fly ashes and the synthesised geopolymers were monitored by Fourier Transform Infrared Spectroscopy (FTIR). Geopolymers (GP) were made from RFA and MFA, and their average 7- and 28-day compressive strength and apparent density were determined.

2. Materials and methods

The fly ash (RFA) used in this study was collected from the Linkou Power Plant, which is located in the Linkou District of New Taipei City, Taiwan (see **Figure 1**). The plant has three pulverised coal-fired units with ultra-supercritical (USC) steam boiler technology. Australian and Indonesian high-quality bituminous and subbituminous coal are used, preferably with low sulphur content, suitable for USC boilers.

The chemical composition of the RFA was determined by X-ray fluorescence analysis (XRF), the result of which is presented in **Table 1**. The total SiO_2, Al_2O_3 and Fe_2O_3 content is 81.46%, which exceeds the minimum 70% oxide content limit required for pozzolanic materials (**Hamada et al., 2024**) and can be classified as Class F based on the ASTM C618 classification (**Ambrus and Mucsi, 2023**). Loss on ignition (LoI) was measured at 950°C with a heating time of 90 minutes and a residence time of 60 minutes. Due to its properties, this fly ash is used in cement production, road construction and soil stabilisation. It is also used to replace cement by 10-25 wt%, based on the requirements of ASTM C618.

The particle size distribution and geometric specific surface area (SSA) were measured using a HORIBA LA-950V2 laser particle size analyser in wet mode. Distilled water was the dispersing media and Na-pyrophosphate was the dispersing agent for the measurements. The particle size of RFA is between 0.20 and 200 μm,

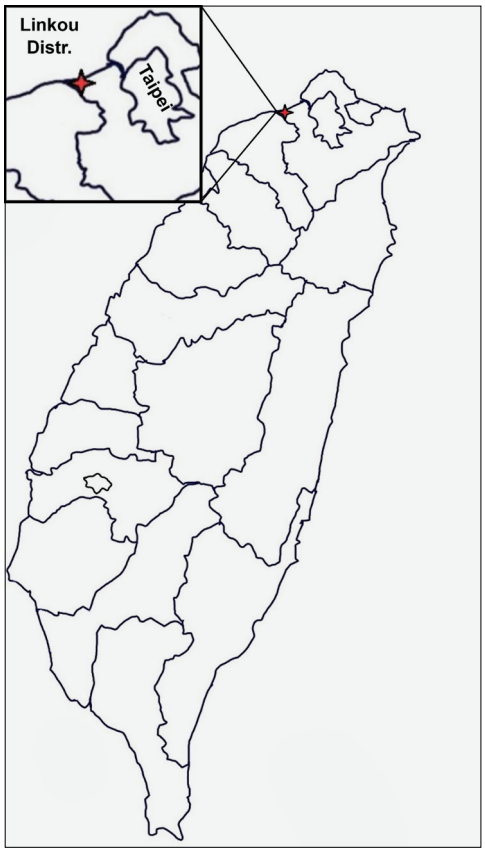

Figure 1. Location of Linkou Power Plant in Taiwan

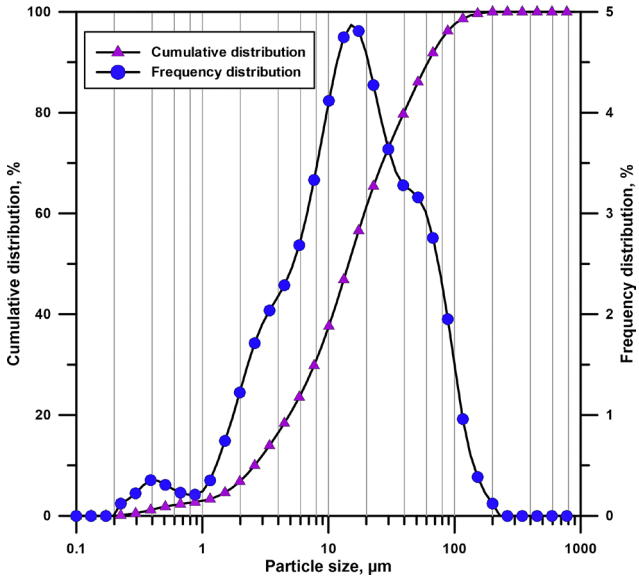

Figure 2. Cumulative and frequency distribution curves of particle size of RFA

with two main peaks located at around 0.40 and 15 μm on the frequency distribution curve (see **Figure 2**). The characteristic particle sizes of the RFA are the following: x_{10} = 2.60 μm, x_{50} = 14.44 μm, x_{80} = 39.69 μm, and the SSA was calculated to be 4736 cm^2/g.

The particle density was determined by the pycnometer method using isopropyl alcohol. The particle density of RFA was 2.42 g/cm^3.

The mechanical activation of the RFA was carried out by dry grinding in a laboratory batch-stirred media mill at a peripheral speed of 6 m/s. The lining of the mill and the grinding discs are made of a high-wear resistant Al_2O_3 material. The mill is also equipped with a water-cooling system to prevent the lining from overheating during milling. The used grinding media were SiLibeads ZY-type ceramic beads with a diameter of 0.8-1.0 mm and specific weight of 6 kg/l. The beads are made of yttrium stabilised zirconium oxide, making them highly resistant to wear and tear, ensuring low contamination of the milled product. Two batches of grinding beads were used in rotation. For each milling round, the media filling and the material filling ratios were constant at 0.7 and 0.8, respectively. The milling was carried out for 1, 3, and 5 minutes. The grinding media and the milled product were separated using a 500 μm sieve. While the degree of wear and breakage of the grinding media was negligible, emptying the mill and sieving resulted in a loss of beads. To ensure consistency, the mass of the grinding media batch was measured before each grinding session and supplemented accordingly.

The FTIR spectra of the fly ash samples and the geopolymer matrices were measured using a JASCO FT/IR 4220 spectrometer equipped with a diamond ATR accessory. The spectra data were collected in the range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1} and baseline corrected.

The method described in the standard MSZ 4706–2:1998 "Complements for cement. Natural pozzolanic complements (trass) for cement." was used to study the effect of mechanical activation on the pozzolanic activity of fly ash. For the test, 100 ml of saturated lime solution was added to 2 g of material then sealed and shaken. The solution was shaken every day. Titration was performed every other day by taking 50 ml of the solution, to which methylene orange indicator was added and then 0.05 mol/L HCl solution was slowly added to the lime solution until the colour of indicator changed. Following the titration, 50 ml of fresh lime solution was added to the base solutions. The measurement took 30 days in total. Using the HCl solution loss, the lime uptake per 1 g of material can be determined.

NaOH solution with a molarity of 10 M was used for geopolymer synthesis. The liquid/solid ratio was kept at a constant 0.35 for all geopolymer mixtures. The solid and liquid components were mixed manually, then the pastes were cast into a polyvinyl chloride mould divided into 20×20×20 mm cubes. The specimens were manually compacted by gently dropping the mould at least 10 times to remove air bubbles. The geopolymers were stored hermetically sealed in the mould at room temperature for six days. Once removed from the mould, the hardened specimens were stored in separate Ziploc bags for each mixture at room temperature until the day of the compressive strength measurements.

Table 1. Chemical composition (weight %) of the Taiwanese FA

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO	P_2O_5	Na_2O	K_2O	LoI
wt%	50.96	23.89	6.61	8.38	1.48	1.21	1.49	0.72	0.88	2.29

The uniaxial compressive strength (UCS) measurements were carried out 7 and 28 days after preparation using a SZF-1 type hydraulic compression-testing machine with a maximum load capacity of 25 kN. For each age, the average USC values of three cube specimens (see **Figure 3**) are given. Prior to the UCS tests, the size and mass of the specimens were measured to determine their specimen density.

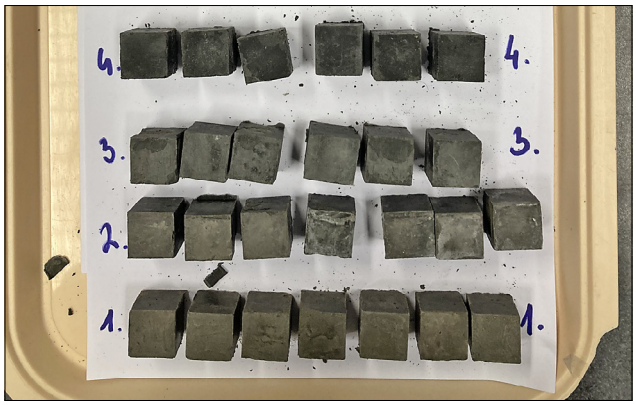

Figure 3. Prepared GP specimens

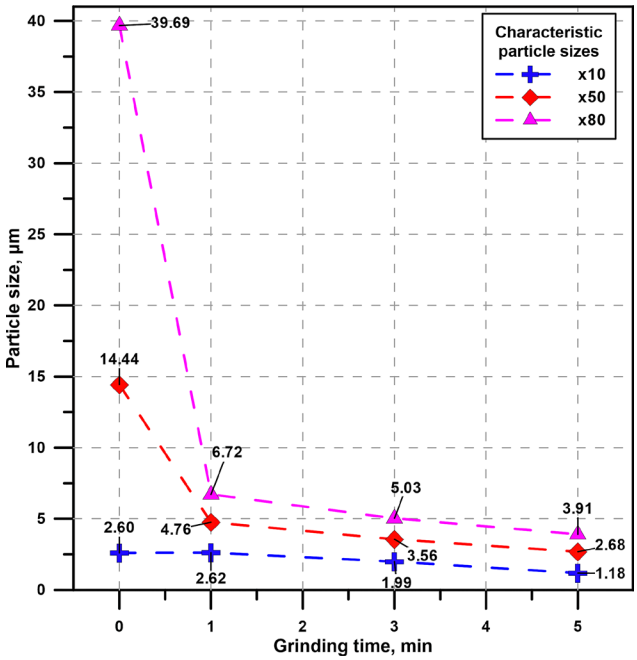

Figure 4. Characteristic particle sizes as a function of grinding time

3. Results and discussion

3.1. Particle size and specific surface area

The effect of mechanical activation in the stirred media mill on the characteristic particle sizes (x_{10}, x_{50} and x_{80}) are shown in **Figure 4**. There is technically no deviation in the x_{10} value following 1 min of mechanical activation; however, with prolonged grinding the size reduction is higher. Contrary to the x_{10}, the initial x_{50} and x_{80} values decreased considerably (by 67% and 83%), but the decrease was less with further grinding, only 22-25%. These observations correlate well with the findings of **Kumar and Kumar (2011)**, **Fu et al. (2008)** and **Nath and Kumar (2020)**, who also found that the increase in fly ash fineness is more prominent in the initial stages of grinding, which slows down in later stages.

The change in the frequency distribution after mechanical activation in the stirred media mill can be well observed in **Figure 5**. As a result of 1 minute of grinding, the first mode of the RFA frequency curve below 1 µm disappeared and became monomodal, with the second mode of ~11 µm shifting to a higher frequency at a smaller particle size range from 1 to 20 µm. On the MFA3 curve, the submicron particles reappear between ~0.2-1 µm and the sharpest peak shifts to a smaller particle size with a slightly increased frequency. This indicates a higher degree of fragmentation of coarse particles and deagglomeration. This process with higher grinding time further intensified as the mode associated with the ultrafine particle fraction became more prominent, also in good correlation with the significant increase in geometric SSA (see **Figure 6**).

In general, the geometric SSA increased exponentially with prolonged grinding time (see **Figure 6**). The

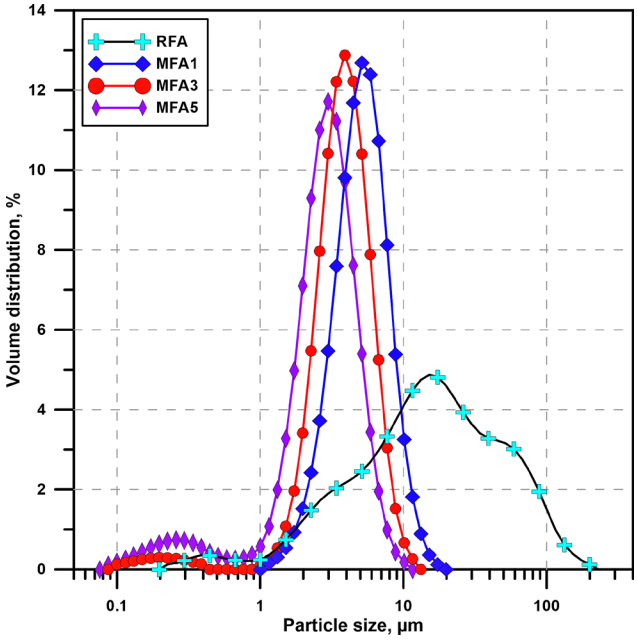

Figure 5. Frequency curves of the RFA and MFA samples

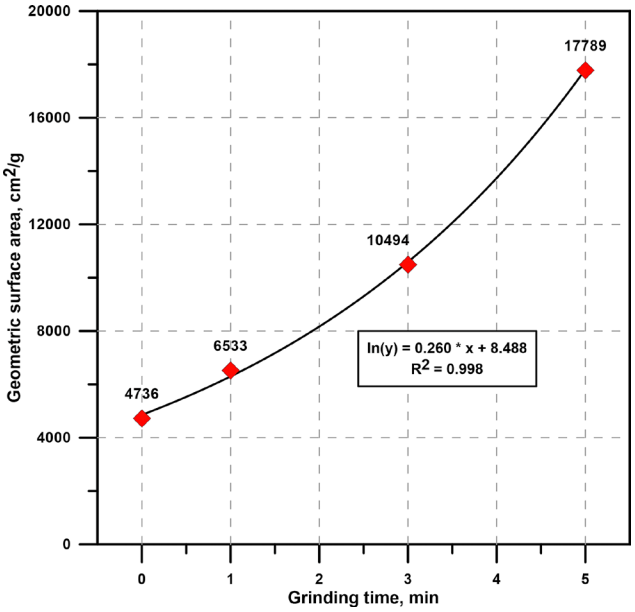

Figure 6. Geometric surface area as a function of grinding time

sharp increase in the geometric SSA between 1 and 3 minutes of grinding suggests the formation of ultrafine particles, as evidenced by the reappearance of the first mode and the slight shift toward finer particle size on the frequency curve. The highest SSA was obtained after 5 minutes of mechanical activation, resulting in a 70% increase compared to MFA3. The geometric SSA increased almost 4 times from 4736 cm^2/g to 17789 cm^2/g after 5 minutes of grinding compared to the RFA.

3.2. Pozzolanic activity

Pozzolanic reaction is defined as the interaction between the amorphous silica and alumina content of materials and the calcium hydroxide ($Ca(OH)_2$) formed during cement hydration, which promotes the formation of additional cementitious compounds (**Hamada et al., 2024**). The pozzolanic activity of fly ash is much lower than traditional natural pozzolanic materials (i.e. trass) and other "manufactured" pozzolanic materials like silica fume, as the pozzolanic reaction takes place extremely slowly on the glassy outer shell of fly ash particles (**Opoczky, 2001**). The mechanical activation of fly ash by fine grinding breaks the particle's vitreous outer layer (surface activation) and liberates the inner part with a high glassy phase, thereby increasing the proportion of the glassy phase participating in the pozzolanic reaction, resulting in a stronger geopolymer (**Opoczky, 2001; Mucsi et al., 2015; Gao et al., 2024**). The pozzolanic activity of fly ash can be enhanced by increasing its surface area, as this improves the reactivity with $Ca(OH)_2$ in the cement paste, leading to improved concrete strength and durability (**Hamada et al., 2024**).

It is evident from the lime absorption test results (see **Figure 7**) that by grinding in the stirred media mill, the pozzolanic activity of the fly ash was significantly improved. The initial 40.2 mg/g FA total lime uptake of the untreated fly ash was raised to between 93.3-96.4 mg/g FA, the highest lime absorption achieved by the 3-minute grinding. This improvement can be attributed to the increase in surface area and the breakdown of the vitreous outer layer of the fly ash. Initially, the dissolution of the active components of the raw material by the alkali activator occurs on the particle surface, during which the vitreous outer layer is gradually destroyed. However, this process is relatively slow, which inhibits the depolymerisation-condensation polymerisation reaction of FA (**Liu et al., 2025**). To enhance the reactivity of FA, it is necessary to destroy the glassy structure of the particles, as described in detail through the geopolymerisation process by **Liu et al. (2025)**. Mechanical grinding destroys the vitreous outer layer of the FA, exposing the inner alumina and silica compounds that participate in geopolymer or cementitious reactions. Thus, the higher absorption of lime by MFAs is due to the increased availability of these compounds, as well as the increased surface area of the active sites compared to RFA.

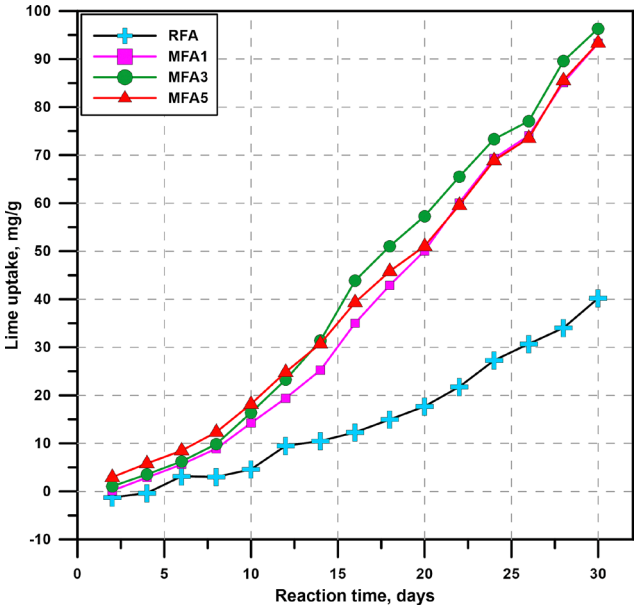

Figure 7. Lime uptake of the RFA and MFAs

3.3. Compressive strength and specimen density

The average UCS results presented in **Figure 8** show that the mechanical activation of the RFA significantly enhanced the compressive strength of the MFA-based geopolymers. Compared to the RFA-based geopolymer (RFAGP), the increase in the 7-day compressive strength was more than 200% even after only 1 minute of milling (MFA1GP). The rate of improvement is much lower for the 28-day UCS values but still ranges from 53-91%. Overgrinding resulted in a decrease of USC. The MFA1GP and MFA5GP specimens yielded similar compressive strength results at both ages. The geopolymer

made from the MFA3 achieved the highest compressive strength at both ages, reaching maximum strengths of 26.2 MPa and 36.1 MPa at 7 and 28 days of age, respectively. **Mucsi et al. (2015)** found that after increasing the fineness of FA by grinding in a high-energy mill, the solubility of SiO_2 and Al_2O_3 in the NaOH solution can be enhanced, resulting in a higher amount of GP gel. They also suggest that the <1 μm unreacted size fraction can act as a filler, playing a role in improving the geopolymer strength.

For RFAGP, the compressive strength improved by 361% between 7 and 28 days, indicating a prolonged strength development and longer setting time (**Nath and Kumar, 2020**). Meanwhile, the rate of strength development during this period is much lower in the case of MFA-geopolymers, suggesting that the majority of the geopolymerisation of FA occurs in the earlier stages of geopolymer formation and slows down over time. These differences in strength development demonstrate the enhancing effects of mechanical activation on the reactivity of FA, resulting in the more rapid dissolution of FA, leading to faster setting and higher strength development at the earlier stages (**Temuujin et al., 2009**).

The specimen density values at 7 and 28 days ranged from 1.874-1.917 g/cm^3 and 1.803-1.932 g/cm^3, respectively. The particle size reduction did not cause a substantial change in the specimen density of the geopolymers. The MFA3GP had the highest specimen density at both ages, but the increase is considerably lower, only 2%, compared to the UCS values.

As a result of the rapid setting caused by mechanical activation, the workability of the fresh geopolymer paste deteriorated as the grinding time increased. This resulted in difficulties during the moulding and the compaction of the specimens. The morphology and fineness of fly ash are important factors in terms of its use in the production of ordinary Portland cement concretes. The spherical FA particles and the wide size distribution contribute to lower water demand and better workability, as well as higher packing density of the concrete, resulting in higher strength. During grinding, this spherical morphology of FA is destroyed and the range of sphere sizes is reduced, which could also be the cause of the lower workability of the fresh concrete (**Temuujin et al., 2009; Felekoğlu et al., 2009**). Raising the fly ash content can also affect the fluidity of fly ash-slag geopolymer foam concrete, which increases due to the low surface tension of the spheroidal glassy microstructure of the raw fly ash particles. With mechanical activation, this structure is damaged, leading to reduced surface tension and increased cohesion between particles, resulting in the decreased flow of the slurry (**Liu et al., 2025**). In conclusion, the decrease in UCS and specimen density between MFA3GP and MFA5GP can be partially explained by the inadequate compaction of the specimens caused by the combined effects of rapid setting and poor workability of the geopolymer paste.

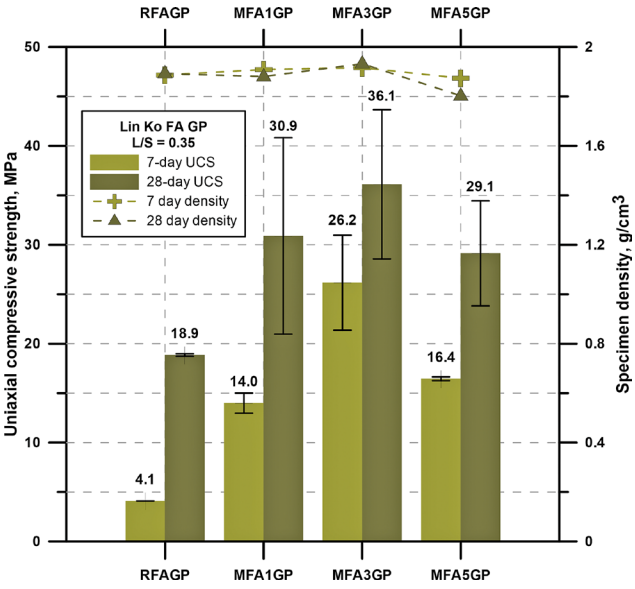

Figure 8. Compressive strength and specimen density of Taiwanese fly ash-geopolymers

3.4. FTIR spectroscopy

The FTIR spectra of RFA and the three MFAs are presented in **Figure 9**. The high-intensity broad band at ~1054 cm^{-1}, present in the spectra of both RFA and MFAs, is attributed to the asymmetric stretching vibrations of T – O – Si (T = Al or Si). This band is characteristic of fly ashes and is the result of the combined vibrations of the quartz, mullite and vitreous components. The presence of quartz also contributes to the band at 698 cm^{-1} and the double band at 795-777 cm^{-1} (**Marjanović et al., 2014**). The intensity of the double peak increases as the grinding time increases. These bands are characteristic of the bending vibrations of Si–O–Si bonds of quartz, and the higher intensity can be explained by the breakdown of the covalent bond in the silicate network of fly ash (**Ambrus and Mucsi, 2023; Djobo et al., 2016**). The peak at 556 cm^{-1} is related to the symmetric stretching vibration of Si – O – Si and Al – O – Si (**Panias et al., 2007**). Milling weakens the bonds within the particles, making them more reactive with alkali activators during geopolymerisation (**Debnath et al., 2022**). In general, the spectra of fly ash were not significantly altered by mechanical activation, although the prominent peaks shifted to higher intensities, which is the result of higher infrared absorbance due to higher specific surface area (**Mucsi et al., 2015; Debnath et al., 2022**). However, it shows remarkable differences in the band sharpening observed in the silicate mineral region (around 1200–1000 cm^{-1}), which provides insight into the concentration and structural order of the silicate mineral. According to **Hamada et al. (2024)**, the increase in peak intensity is due to the disintegration of larger particles into finer particles, as well as the breakdown of molecular bonds. The observed sharpening of the band indicates an increase in the concentration of

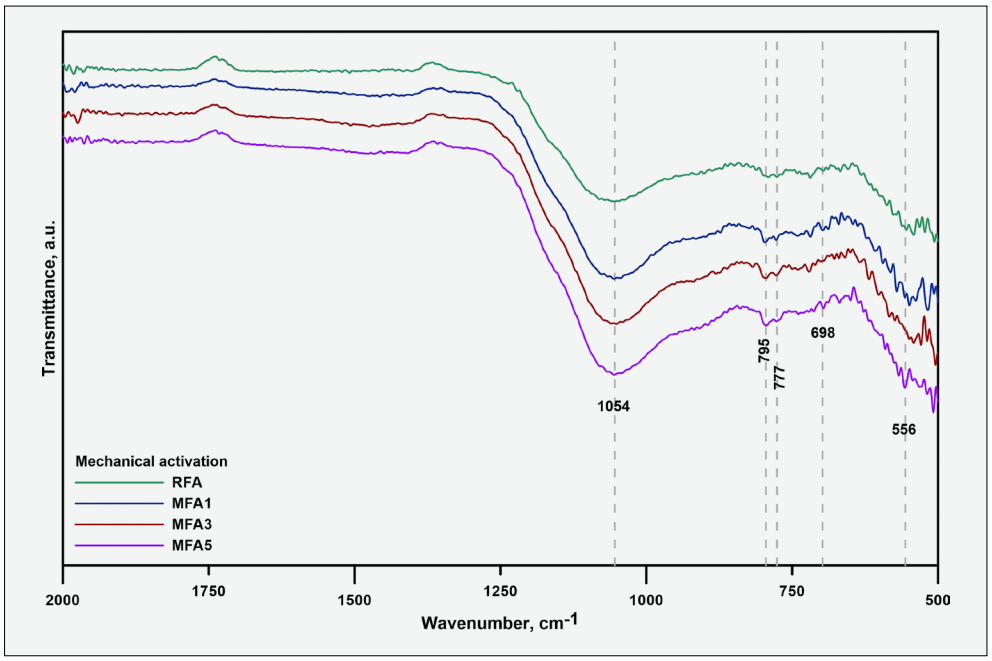

Figure 9. FTIR spectra of the RFA and MFAs

reactive material and silica content (SiO_2), both of which can be attributed to grinding activity.

Several new peaks and bands appeared as a result of the geopolymerisation of fly ash as can be seen in **Figure 10a**. The most prominent change can be observed in the peak attributed to the asymmetric stretching vibrations of Si – O – T (T = Al or Si) bonds. The main band at ~1050 cm^{-1} on the spectra of fly ashes shifts to a lower wavenumber at ~970 cm^{-1} with higher intensity, resulting in a sharp peak on the spectra of fly ash geopolymers. This prominent shift signifies structural reorganisation and the formation of new reaction products, namely, the amorphous aluminosilicate gel. This can be the result of the dissolution of the amorphous phase of fly ash in the strong alkaline activating solution (**Kumar et al., 2017; Panias et al., 2007**). The series of small bands located between ~795 and 690 cm^{-1} is associated with the presence of quartz (**Marjanović et al., 2014**), the change in intensity is similar to those located in the spectra of the fly ashes. A broad band with a peak located at 3300 cm^{-1} and a low-intensity peak at ~1650 cm^{-1} appear in the spectra of both the RFA and MFA geopolymers. These peaks are attributed to the stretching vibrations of O–H bonds of adsorbed water and the bending vibrations of H – O – H bonds of water molecules enclosed within the aluminosilicate structure, respectively (**Kumar et al., 2015; Kumar et al., 2017**). **Panias et al. (2007)** found a correlation between the intensity of the water-related peaks and the compressive strength of geopolymers. A higher intensity of these peaks indicates a greater degree of water adsorption, as can be seen on the RFAGP spectrum (**Kumar et al., 2015; Kumar and Kumar, 2011**), which also had the lowest 7-day UCS. However, the intensity of both bands significantly decreased for MFA3GP, which had the highest 7-day UCS. The band appearing at ~1400 cm^{-1} in every spectrum, is characteristic of the stretching vibrations of C = O, indicative of carbonate groups (i.e. Na_2CO_3) in the structure which is the product of the atmospheric carbonation of NaOH aqueous phase. The highest and lowest intensities of this band were detected for RFAGP and MFA3GP, respectively, indicating a higher degree of carbonation due to the unreacted alkali in the geopolymer matrix containing untreated fly ash (**Kumar et al., 2015; Panias et al., 2007**).

On the spectra collected after prolonged curing of geopolymers (see **Figure 10b**), considerable change can be observed in the bands related to the structural water content (3700-3000 cm^{-1} and 1650 cm^{-1}). Both of these peaks appeared at a higher intensity for MFA3GP, for RFAGP, these peaks shifted to a significantly lower intensity after 28 days. The peak attributed to the C=O bond also shifted towards lower intensity, indicating a lower rate of carbonisation. This decrease could be due to the increased involvement of fly ash in the hydration reaction over a longer curing period. This inhibits the carbonisation process due to the reduced availability of free alkali (**Liu et al., 2024**). This correlates well with the change observed in Si – O – T (T = Al or Si) peak at 970 cm^{-1} in the geopolymer spectra, which became much sharper over time, indicating greater polymerisation (**Kumar and Kumar, 2011**. The peak at 970 cm^{-1} on the spectrum of MFA3GP shifted to the highest intensity which also had the highest 28-day UCS.

3.5. *Relationship between compressive strength, SSA, x_{50} and lime absorption*

The 7-day and 28-day compressive strengths as a function of SSA, median particle size (x_{50}) and lime uptake are presented in **Figure 11**. The relationship between these parameters was examined based on the best

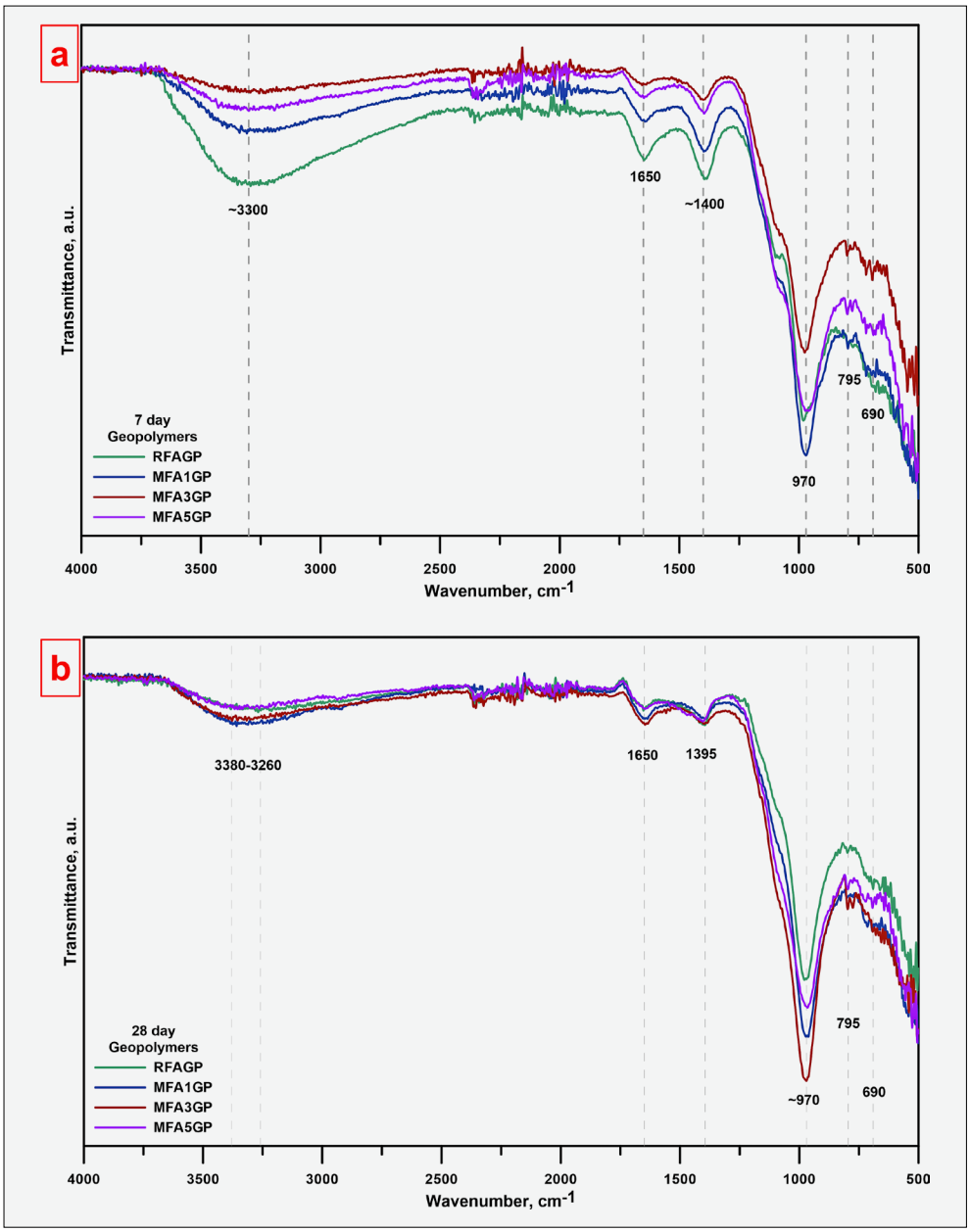

Figure 10. FTIR spectra of GPs at the age of (a) 7 days and (b) 28 days

fit function to the points. The weakest correlation was found with the SSA of the FA. Higher coefficient of determination fit was observed between the 7-day UCS and the SSA (R^2 = 0.513), indicating that the SSA may have a bigger influence – although weak – on the earlier stages of strength development, as a higher SSA can enhance the dissolution rate of FA in the initial stages of geopolymerisation (**Zhang et al., 2012**). Stronger correlation was found between the UCS and the x_{50}, and between the UCS and the amount of lime absorbed, both of which follow an exponential trend. **Gao et al (2024)** observed a similarly strong relation between the compressive strength of geopolymers and the median particle size of FA. The authors, along with **Kumar and Kumar (2011)**, suggest that x_{50} more accurately characterises the particle size distribution when the reactivity of FA is considered.

4. Conclusions

The following conclusions can be drawn from the experimental results presented above:

- Mechanical activation had a significant effect on the reactivity of the investigated Taiwanese fly ash. The pozzolanic activity of MFAs, determined by lime uptake test, increased by 130-140% compared to the RFA.
- However, overgrinding resulted in a smaller increase in the pozzolanic activity of FA, which also affected the compressive strength of the geopolymer.

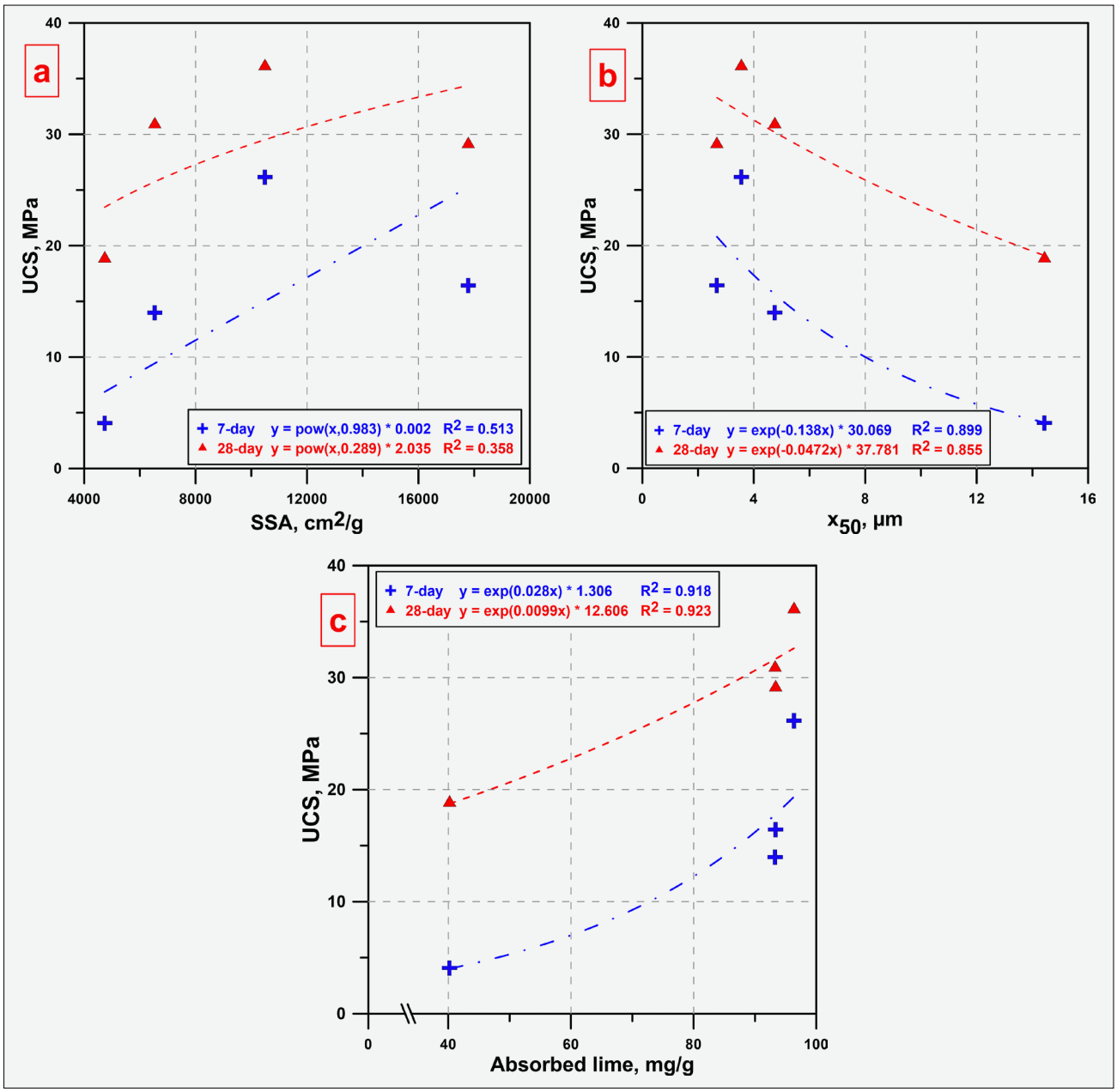

Figure 11. UCS as a function of (a) SSA, (b) x_{50} and (c) absorbed lime

- Optimal fineness was found to be at 3 min residence time mechanical activation where median particle size and specific surface area were 3.56 µm and 10494 cm^2/g, respectively.
- A strong correlation was found between the lime uptake results of the ground fly ash and the resulting geopolymer compressive strength. The MFA3 had the highest total lime uptake (96.4 mg/g FA), from which the geopolymers with the highest compressive strength (36.1 MPa at the age of 28 days) were produced.
- FTIR results show that after mechanical activation, the prominent peaks on the spectrum of RFA shifted to higher intensities, which is the result of higher infra-absorbance due to higher specific surface area as well as the breakdown of molecular bonds. The shift of the main peak at ~1054 cm^{-1} in the FA spectra shifted to lower wavenumbers after geopolymerisation, indicating structural reorganisation and formation of new reaction products (amorphous aluminosilicate gel).
- In order to better support the results of FTIR measurements and understand the structural changes that occur as a result of milling and geopolymerisation, XRD and SEM measurements are necessary.
- Overall, it can be concluded that the mechanical activation of Taiwanese fly ash can significantly enhance its pozzolanic activity, decreasing reliance on traditional cement manufacturing processes and helping to lower CO_2 emissions. Therefore, it pro-

vides an environmentally friendly alternative to traditional materials and helps to reduce the global environmental impact.

Acknowledgement

The authors would like to thank Dr. Ferenc Móricz associate professor for the XRF measurement and Dr. Ákos Debreczeni associate professor for conducting the compressive strength tests.

Funding

This study was carried out within the framework of project no. 2019-2.1.7-ERA-NET-2022-00051 entitled "Foamed Geopolymer Made by Additive Manufacturing for the Construction Technology Applications" with support from the National Research, Development and Innovation Fund of the Ministry of Culture and Innovation and Hungarian Organizations, in the financing of the ERA-NET COFUND/EJP COFUND Programme with co-funding from the European Union Horizon 2020 research and innovation programme.

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SAŽETAK

Mehanička aktivacija i geopolimerizacija letećega pepela s Tajvana

Uporaba sirovoga letećeg pepela u proizvodnji cementa i geopolimernih proizvoda ograničena je zbog njegove niske reaktivnosti. Međutim, reaktivnost letećega pepela može se povećati postupkom mehaničke aktivacije, čime se omogućuje njegova šira primjena. Ovo istraživanje usmjereno je na mehaničku aktivaciju i geopolimerizaciju letećega pepela dobivenoga iz ugljena s Tajvana. Mehanička aktivacija provedena je mljevenjem u mlinu s miješanim medijem u trajanju od 1, 3 i 5 minuta. Finoća i specifična površina znatno su se povećale već nakon 1 minute, a s daljnjim mljevenjem tek su se neznatno mijenjale. Test apsorpcije vapna pokazao je znatno poboljšanje pucolanske aktivnosti (povećanje od 130 do 140 %) nakon mehaničke aktivacije. Za sintezu geopolimera korištena je otopina natrijeva hidroksida (NaOH) koncentracije 10M kao alkalni aktivator, s omjerom tekućina / čvrsta faza od 0,35. Geopolimer koji je sadržavao pepeo mljeven 3 minute postigao je najveću tlačnu čvrstoću nakon 28 dana (36,1 MPa). Strukturna karakterizacija letećega pepela i geopolimera provedena je Fourierovom transformacijskom infracrvenom (FTIR) spektroskopijom. Promjene u FTIR spektrima letećih pepela upućivale su na to da se geopolimerizacijom stvara novi reaktivni produkt amorfni alumosilikatni gel. Na temelju snage razvoja geopolimera mehanička aktivacija povećala je reaktivnost letećega pepela, što je dovelo do brzoga vezivanja i većega razvoja čvrstoće u ranim fazama geopolimerizacije. Rezultati jasno pokazuju da je nakon mehaničke aktivacije leteći pepeo postao reaktivnija sirovina nudeći veći potencijal primjene nego što je to slučaj u njegovoj trenutačnoj upotrebi u proizvodnji cementa, izgradnji cesta i stabilizaciji tla.

Ključne riječi:
leteći pepeo, geopolimer, mehanička aktivacija, pucolanska aktivnost

Author's contribution

Fanni Dolgos (department engineer): data curation, investigation, visualization, writing – original draft and writing – review & editing. **Roland Szabó** (research fellow): conceptualization, investigation, methodology, supervision, writing – review & editing. **Wei-Ting Lin** (professor): resources and writing – review & editing. **Gábor Mucsi** (professor): conceptualization, methodology, resources, supervision and writing – review & editing.
All authors have read and agreed to the published version of the manuscript.