Thermal and microwave synthesis of silica fume-based solid activator for the one-part geopolymerization of fly ash

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Abstract
This paper tests the development of a silica fume-based material, capable to be used as a solid activator for the one-part geopolymerization of fly ash. Through a simple procedure, a mixture of silica fume, an amorphous and silicon-rich by-product, sodium hydroxide and water, is converted, after a low-temperature treatment, to a new powder product mainly containing sodium silicate (Na2SiO3). Two different treatment methods are tested for the synthesis of the solid activator: heat and microwave treatment. Microwave processing is more sustainable and more efficient than thermal treatment, since purer products are produced with less energy consumption. The use of these low embodied energy products, as the only solid activator of fly ash, leads to geopolymers with comparable mechanical performance to those prepared with commercial products revealing their potential successful addition in the geopolymer market.

Keywords Alkali activation · One-part geopolymer · Just-add water · Fly ash · Solid activator · Silica fume · Microwave treatment

Introduction
Geopolymers are the most promising cement replacers to meet the need for a more environmentally friendly construction sector that uses sustainable building materials (Zhang et al. 2020; Shehata et al. 2021). Traditional geopolymerization process is based on the activation of an aluminosilicate precursor using an alkaline sodium silicate solution (water glass) (Provis and Deventer 2014). More specifically, silica- and alumina-rich industrial wastes and by-products (e.g. fly ash and slags) (Zaharaki et al. 2016; Gnanadurai et al. 2021; Ren et al. 2021; Shahmansouri et al. 2021; Shrivas et al. 2022; Peng and Unluer 2022; Wu et al. 2022) are used as precursors, reducing the final geopolymer product’s energy footprint (Duxson et al. 2007; Turner and Collins 2013; Kioupis et al. 2018). Even so, despite the geopolymers’ characteristics (high strength, resistance to acid and heat), this technology has not been widely applied, due to issues caused by the activation solution. This high alkaline solution has two main drawbacks: it is very corrosive and causes handling issues, and its production process is based on high embodied energy materials such as alkali silicates (Alnahhal et al. 2021), minimizing the environmental benefits of geopolymer technology (Weil et al. 2009; Habert et al. 2011).

To overcome the first obstacle, the research community has focused, lately, on the development of solid activators, capable to substitute the alkaline solution (Luukkonen et al. 2018). More particularly, various reagents have been tested as single solid activators or as part of a mix of solid activators: Na2CO3 (Peng et al. 2015), NaAlO2 (Hajimohammadi et al. 2010), CaSO4 (García-Lodeiro et al. 2016), Na2SO4 (García-Lodeiro et al. 2016) and solid sodium silicates with various moduli (SiO2/Na2O molar ratio) (Nematollahi et al. 2015).

The most efficient, based on the mechanical properties of the final geopolymers, was found to be anhydrous sodium metasilicate Na2SiO3 (Nematollahi et al. 2015; Panitsa et al. 2021; Wang et al. 2021). However, alkali silicates have high embodied energy and high manufacturing cost as they need extreme conditions
for their production (Fawer et al. 1999). There are several different sodium silicate production methods. Sodium carbonate, \( \text{Na}_2 \text{CO}_3 \), and silica sand can be mixed and cured at 1000–1400 °C to produce sodium silicate, \( \text{Na}_2 \text{SiO}_3 \). Then, water is added to create the solution (water glass) (Lagaly et al. 2000). Sodium silicate can also be prepared directly by dissolving silica sand under pressure in a heated aqueous solution of sodium hydroxide, \( \text{NaOH} \) (Novotny et al. 1991).

An alternative method of producing sodium silicate compounds, using solid wastes and by-products, has been proposed (Alnahhal et al. 2021). Susan A. Bernal et al. prepared an alkaline solution by mixing silica fume or rice husk ash with aqueous NaOH, for the alkali activation of a metakaolin/slag binder mixture (Bernal et al. 2012). D. Kioupis et al. used waste glass to produce an alkaline solution for the geopolymerization of brick (Kioupis et al. 2020). Geopolymerization results showed the efficacy of those waste-based sodium silicate solutions. Moreover, Raffaele Vinai and Marios Soutsos have prepared a sodium silicate product that can be used as a solid activator in an alkali activation process (Vinai and Soutsos 2019).

The purpose of this study is to produce a waste-based sodium silicate solid substance from silica fume, with lower production energy requirements and embodied energy. Consequently, this substance will be able to totally substitute the commercial reagents with the same chemical formula. Silica fume is a by-product of silicon metal or ferrosilicon alloy production process, with a high amorphous silicon dioxide content (> 90%). The synthesis process includes the mixing of silica fume, \( \text{NaOH} \) and water. The created slurry is thermally treated at 150 °C to obtain a solid powder. Moreover, to simplify the production process and decrease the energy footprint of the waste-based final product, the use of microwave treatment was tested as well. Lastly, this new product is tested as a solid activator, for the geopolymerization of Greek fly ash, to investigate its reactivity and geopolymerization potential.

### Materials and methods

Silica fume from Sikafume® HR (\( \text{SiO}_2 \geq 90\% \) w/w) and commercial sodium hydroxide (CAS No. 1310–73-2, \( \text{NaOH} \geq 98.0\% \) w/w) was used. Commercial sodium metasilicate — \( \text{Na}_2 \text{SiO}_3 \) (CAS No. 6834–92-0), and sodium silicate — \( \text{Na}_2 \text{Si}_2 \text{O}_5 \) (CAS No. 6834–92-0), were also used as solid activators for comparison reasons. Fly ash was collected from Megalopolis power plant in Greece.

Its chemical composition was determined through X-ray fluorescence spectroscopy (XRF, Malvern Panalytical, Epsilon 1 Model) and is shown in Table 1. The raw materials’ particle size distribution was determined through Malvern Mastersizer Micro (Fig. 1). Fly ash was previously ground to a mean particle size \((d_{50})\) of approximately 20 μm, which is a typical fineness of fly ash when used in the construction industry.

For the synthesis of the silica fume-based activators (SFAs), specific amounts of silica fume, \( \text{NaOH} \) and water were mixed together to create a pulp. The amount of water that was added was the minimum needed to dilute completely the \( \text{NaOH} \) pearls. Then, the mixtures were treated appropriately, in order to obtain dry products in powder form.

![Fig. 1 Particle size distribution of fly ash (a) and silica fume (b)](image-url)
An investigation of several treatment parameters was carried out to determine their effect on the SFAs and optimize their synthesis process (Table 2). More particularly, treatment duration (0.5 h, 1 h, 2 h and 3 h), temperature (150 °C, 250 °C, 330 °C and 450 °C) and SiO$_2$/Na$_2$O molar ratio (1 and 2) were the three tested parameters during thermal treatment. An alternative treatment method was investigated as well, using a microwave oven for household use. The tested parameters during the microwave treatment were the treatment duration (2 min, 12 min and 20 min), the microwave power (120 W, 460 W and 700 W) and the SiO$_2$/Na$_2$O molar ratio (1 and 2). In both treatment methods, the minimum treatment duration was the least needed to get a dry product. More specifically, the temperature and duration range were selected in terms of the reactants pulp dehydration and the complete solubilization of NaOH reagent. The microwave power range was restricted by the microwave oven’s technical specifications. Concerning the SiO$_2$/Na$_2$O molar ratio, the value range was based on the serviceability of the produced sodium silicates in geopolymer technology; sodium silicates with SiO$_2$/Na$_2$O higher than 2 exhibit decreased water solubility and pH values (Nematollahi et al. 2015). The parameter range was also based on previous published studies (Vinai and Soutsos 2019).

The solubility of SFAs was determined by dilution of 1 g in 150 mL of water for 1 h under stirring, followed by filtration and weighing of the solid residue.

In order to examine the SFA potential as solid activators in geopolymerization process, one-part fly ash geopolymers were prepared (Table 3). Solid activators (commercial and prepared) were dry mixed with fly ash for 3 min in a mortar mixer (Controls 65-L0005). Then, water was added in order

### Table 2: ID samples and the investigated parameters

| Mix ID       | SiO$_2$/Na$_2$O molar ratio | Treatment method | Temperature (°C) | Power (watt) | Treatment duration |
|--------------|-----------------------------|------------------|------------------|-------------|-------------------|
| 1SS_TT_330C_0.5 h | 1                           | Thermal          | 330              | -           | 0.5 h             |
| 1SS_TT_330C_1h   | 1                           | Thermal          | 330              | -           | 1 h               |
| 1SS_TT_330C_2h   | 1                           | Thermal          | 330              | -           | 2 h               |
| 1SS_TT_330C_3h   | 1                           | Thermal          | 330              | -           | 3 h               |
| 1SS_TT_150C_1h   | 1                           | Thermal          | 150              | -           | 1 h               |
| 1SS_TT_250C_1h   | 1                           | Thermal          | 250              | -           | 1 h               |
| 1SS_TT_450C_1h   | 1                           | Thermal          | 450              | -           | 1 h               |
| 2SS_TT_150C_1h   | 2                           | Thermal          | 330              | -           | 1 h               |
| 1SS_MT_L_12m    | 1                           | Microwave        | -                | 120         | 12 min            |
| 1SS_MT_M_12m    | 1                           | Microwave        | -                | 460         | 12 min            |
| 1SS_MT_H_12m    | 1                           | Microwave        | -                | 700         | 12 min            |
| 1SS_MT_M_2m     | 1                           | Microwave        | -                | 460         | 2 min             |
| 1SS_MT_M_20m    | 1                           | Microwave        | -                | 460         | 20 min            |
| 2SS_MT_M_2m     | 2                           | Microwave        | -                | 460         | 12 min            |

Abbreviations: 1SS, SiO$_2$/Na$_2$O molar ratio equal to 1; 2SS, SiO$_2$/Na$_2$O molar ratio equal to 2; TT, thermal treatment; MT, microwave treatment; 150°C-450°C, treatment temperature; 2m-3h, treatment duration in minutes or hours; L, M, H, microwave power (low, 120 W; medium, 460 W; high, 700 W)

### Table 3: Geopolymer mixtures prepared in this study [% wt.]

| Mix ID        | FA          | Activator | H$_2$O |
|---------------|-------------|-----------|--------|
|               | sol | 1SS_COM  | 2SS_COM | 3SS_COM | 1SS | 2SS | NH  |
| G2P           | 60.4| 14.8    | -       | -       | -    | -   | 9.8 | 14.9 |
| G1P_1SS_COM   | 61.3| -       | 15.3    | -       | -    | -   | -   | 23.4 |
| G1P_2SS_COM   | 63.1| -       | -       | 11.6    | -    | -   | 5.2 | 20   |
| G1P_1SS_TT_150C| 63.8| -       | -       | -       | 15.9 | -   | -   | 20.3 |
| G1P_2SS_TT_150C| 59.3| -       | -       | -       | -    | 10.9| 4.9 | 24.9 |
| G1P_1SS_MT_M  | 64.0| -       | -       | -       | -    | 16  | -   | 20   |
| G1P_2SS_MT_M  | 57.6| -       | -       | -       | -    | 10.6| 4.7 | 27.1 |

Abbreviations: G, geopolymer sample; 1P, one-part; 2P, two-part; sol, sodium silicate solution; 1SS_COM, Na$_2$SiO$_3$ anhydrous commercial product; 2SS_COM, Na$_2$Si$_2$O$_5$ commercial product; NH, NaOH; 1SS, SFA with SiO$_2$/Na$_2$O molar ratio equal to 1; 2SS, SFA with SiO$_2$/Na$_2$O molar ratio equal to 2; TT, thermal treatment; MT, microwave treatment; 150°C, treatment temperature (150 °C); M, microwave power (medium, 460 W)
to reach the desired workability of the paste and to obtain homogenous slurry. At that moment, slurry was casted into cubic moulds (50 × 50 × 50 mm) and compacted mildly. The specimens were kept at room temperature for 2 h before cured at 70 °C for 48 h. Finally, compressive strength testing was carried out on the 7th day after casting of the specimens, using a uniaxial testing press from Matest, E181N model, with load rate value 1.5 KN/s, according to ASTM C109. The treatment duration for the thermally treated SFAs used for the geopolymer preparation reached 1 h and for the microwave treated 2 min.

A two-part geopolymer (2P) was also prepared as a reference sample, using a sodium silicate solution as activator (SiO2 = 27.6–28.4% wt. and Na2O = 8.5–8.8% wt.). The 2P synthesis parameters were previously optimized and kept constant in all one-part geopolymers (1P). The method of optimization was reported elsewhere (Panagiotopoulou et al. 2015; Kioupis et al. 2018). The optimized synthesis parameters, for the geopolymerization of the fly ash used in this study, are Si/Al = 2.18 and Na/Al = 1. In case of the 2SS activators, further addition of NaOH is required in the raw mixture, in order to obtain the same synthesis parameters.

Raw materials and products were characterized appropriately by applying three analytical techniques. The mineralogical characterization was carried out by X-ray diffraction (XRD), using a Bruker D8 ADVANCE x-ray diffractometer employing CuKa radiation. The measuring conditions were 2θ range 10–70°, step size 0.1°/s (0.02 s for Topas analysis), and the data were evaluated using Diffrac Eva v3.1 software. The evaluation of activators’ crystallinity was performed through TOPAS software. Prior to the measurement, a known amount (9.9% w/w) of zincate (commercial reagent, CAS No 1314–13-2) was added as a spike. FTIR measurements were conducted on a Fourier Transform IR spectrophotometer (Jasco 4200 Type A). The FTIR spectra were obtained within a wavenumber range from 400 to 4000 cm−1 and resolution of 4 cm−1, using the KBr technique. Lastly, the final geopolymers were examined applying scanning electron microscopy (SEM) on a SEM-EDAX/FEI Quanta 200 equipped with a low vacuum secondary electron (LFD) detector.

Results and discussion

Synthesis and characterization of the SFAs

Figures 2 and 3 present the XRD patterns of the SFAs products with SiO2/Na2O ratio equal to 1 and 2, respectively, after thermal and microwave treatment.

The silica fume pattern presents a broad hump around 2θ = 21° which is indicative of amorphous silicon oxide. In the case of products with a molar ratio of SiO2/Na2O = 1, regardless of the treatment method or the applied parameters, silica fume was converted successfully to the crystalline phase of Na2SiO3, similarly to the commercial product 1SS(COM) (Figs. 2a, 3a). In the case of thermally treated samples, traces of natrite, Na2CO3, and thermonatrite, Na2CO3·H2O (<4% w/w), are also present in the final products, because of the sodium hydroxide carbonation. However, carbonation did not occur in the microwave treated samples since no carbonates were detected in their XRD patterns. This is most probably due to the limited air exposure of these samples as the treatment lasts less than 20 min.

1 The overall amount of Si involved in the geopolymerization process expressed as the Si/Al molar ratio.

2 The alkalinity of the activators expressed as sodium to aluminium molar ratio Na/Al.
Moreover, SFAs with a ratio of \( \text{SiO}_2/\text{Na}_2\text{O} = 2 \) (Figs. 2b, 3b) show high amorphousness like the commercial product 2SS_COM. A displacement of the amorphous peak of silica fume at higher diffraction angles (2θ ≈ 29°) is observed for both products prepared with \( \text{SiO}_2/\text{Na}_2\text{O} = 2 \) (2SS_TT_330C_1h and 2SS_MT_M_2m). This is a sign of atoms’ reorganization and the formation of new amorphous phases. Table 4 presents the % w/w mineral composition of the solid activators as it was obtained from the quantitative XRD analysis along with their solubility in water.

Concerning the SFAs with a molar ratio of \( \text{SiO}_2/\text{Na}_2\text{O} = 1 \), it is obvious that products with higher crystallinity, compared with the commercial ones, were prepared. In addition, heat treatment is more efficient for the preparation of high crystalline samples (62–81%), compared with the microwave treatment (50–70%). Sodium silicate \( \text{Na}_2\text{SiO}_3 \) is

### Table 4: Mineral composition and water solubility of the solid activators

| Sample ID | \( \text{Na}_2\text{SiO}_3 \) (%) | \( \text{Na}_2\text{CO}_3 \) (%) | \( \text{Na}_2\text{CO}_3*\text{H}_2\text{O} \) (%) | Amorphous (%) | Normalized solubility (%) |
|-----------|---------------------------------|---------------------------------|---------------------------------------------|--------------|----------------------------|
| Commercial |                                |                                 |                                             |              |                            |
| 1SS_COM   | 50.90                           | -                               | 49.10                                       | 99.10        |                            |
| 2SS_COM   | 0.00                            | -                               | 100.00                                      | 99.20        |                            |
| Thermal treated |                      |                                 |                                             |              |                            |
| 1SS_TT_330C_0.5h | 66.71 | 3.65                            | 1.14                                        | 28.49        | 98.00                      |
| 1SS_TT_330C_1h  | 77.35 | 1.91                            | 1.75                                        | 18.98        | 95.81                      |
| 1SS_TT_330C_2h  | 71.04 | 2.67                            | 0.43                                        | 25.85        | 96.09                      |
| 1SS_TT_330C_3h  | 72.29 | 0.16                            | 0.16                                        | 25.98        | 96.73                      |
| 1SS_TT_150C_1h  | 58.97 | 2.24                            | 0.64                                        | 38.15        | 97.22                      |
| 1SS_TT_250C_1h  | 69.48 | 3.20                            | 0.43                                        | 26.89        | 96.89                      |
| 1SS_TT_450C_1h  | 80.91 | 1.91                            | 0.01                                        | 17.17        | 96.58                      |
| 2SS_TT_330C_1h  | 1.76  | 0.00                            | 0.00                                        | 98.24        | 76.40                      |
| Microwave treated |                  |                                 |                                             |              |                            |
| 1SS_MT_M_2min  | 56.10 | -                               | 43.90                                       | 97.63        |                            |
| 1SS_MT_H_2min  | 52.60 | -                               | 43.00                                       | 98.83        |                            |
| 1SS_MT_L_12min | 50.30 | -                               | 49.70                                       | 97.92        |                            |
| 1SS_MT_M_12min | 69.90 | -                               | 30.10                                       | 97.32        |                            |
| 1SS_MT_H_12min | 66.70 | -                               | 33.30                                       | 97.76        |                            |
| 1SS_MT_M_20min | 64.30 | -                               | 35.70                                       | 98.37        |                            |
| 2SS_MT_M_2min  | 0.00  | -                               | 100.00                                      | 95.52        |                            |
| SF         | -                               | -                               | 100.00                                      | 7.93         |                            |

*Normalized solubility refers to the SFAs soluble part excluding the soluble crystalline carbonate phases.

**Fig. 3** XRD patterns of SFAs prepared through microwave treatment with ratio \( \text{SiO}_2/\text{Na}_2\text{O} = 1 \) and 2
the main crystalline phase, and in some cases the only one, which characterizes the SFAs composition.

The increase of the temperature from 150 to 450 °C increases the content of crystalline Na₂SiO₃ by 27%, in the thermally treated samples (Fig. 4a). In a similar manner, the crystalline content of Na₂SiO₃ in the microwave treated samples was enhanced by 28% when the power of the microwave source altered from 120 to 460 W (Fig. 4b). In both cases, further increase of temperature or power did not yield any remarkable change of the crystalline content.

Treatment duration effect on Na₂SiO₃ crystalline content of SFAs was not so pronounced in relation to the temperature or power effect. In particular, a treatment duration increase, from 0.5 to 1 h, in thermally treated samples led to a 14% increase of the crystalline Na₂SiO₃ (Fig. 4a). Similarly, an alteration of treatment duration, from 2 to 12 min, in microwave treated samples led to a 20% increase in the crystalline content (Fig. 4b). Higher treatment duration, for both treatment methods, did not favour higher crystalline contents.

Concerning the effect of SiO₂/Na₂O molar ratio, products with SiO₂/Na₂O = 1 obtained a high crystalline content (> 50%), while those prepared with SiO₂/Na₂O = 2 are almost totally amorphous, following the structure of the commercial sodium silicates (1SS_COM and 2SS_COM).

Table 4 also presents the normalized solubility of the activators, calculated by excluding the carbonates’ content. Results showed that commercial sodium silicates 1SS_COM and 2SS_COM are totally soluble in water. Silica fume, the raw material of the SFAs, is almost entirely insoluble in water, since it contains more than 90% SiO₂ (7.9%). Moreover, all SFAs with a molar ratio of SiO₂/Na₂O = 1, regardless the way they have been treated, are highly soluble in water (> 95%), similarly to the commercial product 1SS_COM, indicating that their amorphous phase consists of highly soluble compounds and, of course, the successful conversion of silica fume to new products. As concerns SFAs with a molar ratio of SiO₂/Na₂O = 2, the 2SS_TT_330C_1h sample exhibited a lower water solubility (76.4%), indicating lower conversion yield. On the contrary, the sample 2SS_MT_M_2min showed a high solubility, close to 95%, which may be attributed to higher conversion of silica to soluble silicate compounds.

Figure 5a presents the FTIR spectra of the SFAs (SiO₂/Na₂O = 1) prepared in this study. For comparison, the spectrum of the commercial sodium silicate (1SS_COM) as well as that of silica fume is presented in the same figure. Silica fume exhibits the typical vibrations of Si–O bonds. In particular, the absorption peaks at 1100 and 804 cm⁻¹ are assigned to asymmetric and symmetric stretching vibrations of Si–O–Si bonds, while that at 470 cm⁻¹ is attributed to the bending vibrations of O–Si–O bonds. The band at 1630 cm⁻¹ is related to the −OH bending vibrations, and it indicates the existence of absorbed water. Concerning the 1SS_COM, the absorption peaks at 1036, 967, 885, 711, 590 and 515 cm⁻¹ are attributed to varied IR vibrations of Si–O–T (T: Si or Na) and O–Si–O bonds on the structure of sodium silicates (Table 5). Furthermore, the band at 1450 cm⁻¹ is assigned to the vibrations of carbonate ions, and it is linked to the presence of sodium carbonate phase. It is obvious that irrespective the processing conditions, the reactants have successfully been transformed to sodium silicates. In particular, all the SFAs exhibit identical infrared spectra to that of the commercial product (Fig. 5). Furthermore, the characteristic broad peak of silica fume is not detected in the spectra of the activators, indicating the total conversion of silica fume to sodium silicates. The formation of the sodium silicate structure is majorly indicated by the shift of the Si–O–Si band at 1100 cm⁻¹ to lower wavenumbers through the enrichment of Si–O–T bonds by Na: “trident” absorption at 1040, 970 and 880 cm⁻¹. These results are in accordance with solubility rates of 1SSs (Table 4).

Figure 5b presents the FTIR spectra of the 2SS activators (SiO₂/Na₂O = 2), prepared in this study, along with the spectra of the commercial sodium silicate (2SS_COM) and silica.
fume. The 2SS_COM exhibits absorption peaks at 1005 and 880 cm$^{-1}$ which are assigned to the asymmetric and symmetric stretching vibrations of Si–O–Na bonds, respectively (Table 5). In addition, the band at 755 cm$^{-1}$ could be linked to the stretching of O–Si–O bonds. The spectrum of 2SS_COM is relatively featureless revealing the amorphous nature of this material, in accordance with the XRD analysis. As in the case of 1SS_COM, the band at 1450 cm$^{-1}$ is related to the presence of sodium carbonate phases.

The spectra of the prepared 2SSs show clear differences in relation to that of the commercial product (2SS_COM). The thermally treated product (2SS_TT_150C_1h) exhibits a displacement of the wide absorption peak (1000 cm$^{-1}$) to higher wavenumbers (1050 cm$^{-1}$), while the band at 880 cm$^{-1}$ is almost undetectable. This observation indicates the partial transformation of the silica fume to silicate compounds since a lower portion of Si–O–Na bonds has been formed in the final product. This speculation is in good accordance with the solubility of the products since 2SS_TT_150C_1h sample shows a reduced solubility in water indicating that unreacted silica is still present in the product. The spectrum of the microwave treated sample (2SS_MT_M_2m) is quite similar with the spectrum of the thermally treated sample.

Table 5 FTIR band assignments

| Frequencies (cm$^{-1}$) | Assignments |
|-------------------------|-------------|
| 1630                    | –OH bending vibrations (H$_2$O) |
| 1450                    | O–C–O stretching vibrations |
| 1100                    | Si–O–Si asymmetric stretching vibrations |
| 800                     | Si–O–Si symmetric stretching vibrations (inter-tetrahedral Si–O–Si) |
| 475                     | O–Si–O bending vibrations |
| 590                     | In-plane Si–O–Si stretching mode coupled with O–Si–O and Si–O–Si bending modes |
| 1035                    | Si–O–Na asymmetric stretching vibrations |
| 970                     | Si–O–Si asymmetric stretching vibrations |
| 880                     | Si–O–Na symmetric stretching vibrations |
| 710                     | Si–O–Si symmetric stretching vibration |
| 520                     | Si–O–Na asymmetric stretching vibrations |
| 1005                    | Si–O–Na symmetric stretching vibrations |
| 750                     | O–Si–O stretching |

Fig. 5 FTIR spectra of a SFAs with molar ratio SiO$_2$/Na$_2$O = 1 and b SFAs with molar ratio SiO$_2$/Na$_2$O = 2 along with those of commercial sodium silicate, silica fume
Synthesis and characterization of geopolymers

In order to evaluate the potential of the prepared samples, they were applied as activators for the geopolymerization of fly ash.

The SFAs were selected in terms of the lowest energy consumption during their preparation. Therefore, the xSS_TT_150C_1h and xSS_MT_M_2m samples ($x = \text{SiO}_2/\text{Na}_2\text{O} = 1$ or 2) were used for the synthesis of geopolymers (Table 4). For comparison reasons, one- and two-part geopolymers were also prepared, using the commercial products. It is worth mentioning that the SFAs required quantities were calculated according to the assumption that they are totally consisted of sodium silicate phases.

An initial evaluation step of the successful production of building materials concerns the mechanical properties’ measurement. In Fig. 6, the uniaxial compressive strength of the prepared geopolymers is presented (average of three specimens). The geopolymer synthesis through the traditional liquid activator (G2P) achieves a compressive strength of 62.3 MPa. The replacement of the activation solution with commercial solid activators was successful, as expected (Panitsa et al. 2021), since products with identical mechanical strength were obtained irrespectively of the SiO$_2$/Na$_2$O ratio of the activator (Fig. 6). The further replacement of the solid commercial activators by the SFAs showed promising results. More particularly, the geopolymers incorporating the 1SS_TT_150C or 1SS_MT_M_2m activators achieved the 90 to 95% of the compressive strength of the reference synthesis (G2P). The fact that the thermally treated activator achieves slightly lower mechanical strengths can be attributed to the presence of carbonate phases which lowers the reactivity of the material.

Concerning the geopolymer synthesis with 2SSs activators, the prepared geopolymers exhibit remarkably lower compressive strength in comparison to the G2P. Both G1P_2SS_TT_150C and G1P_2SS_MT_M_2m have much lower compressive strength than geopolymers with the commercial activators. These results are in accordance with the characterization analysis (solubility studies and FTIR) of these SFAs showing that silica fume has totally transformed in sodium silicate compounds.

Figure 7 presents backscattered images of the geopolymers and EDS analysis of selected points. The geopolymers present the typical microstructure of fly ash-based geopolymers, exhibiting a heterogenous structure consisting of a dense matrix and unreacted fly ash material. In particular, the fly ash cenospheres are partially or totally dissolved, depending on the progress of geopolymerization reaction.

Comparing the geopolymer materials, it can be seen that the products prepared with SFAs of SiO$_2$/Na$_2$O = 1, G1P_1SS_TT_150C (Fig. 7b) and G1P_1SS_MT_M (Fig. 7c), exhibit similar microstructure with that prepared with the commercial activator (G1P_1SS_COM) (Fig. 7a). Furthermore, the stoichiometry of the geopolymer matrix obtained by EDS analysis is almost identical for the aforementioned samples and close to Si:Al:Na ~ 21:10:9.

The G1P_2SS_COM (Fig. 7d) sample presents comparable microstructure to G1P_1SS_COM (Fig. 7a), while the prepared aluminosilicate gel contains a slightly higher amount of sodium (Si:Al:Na ~ 20:9:11). The sample prepared with thermally treated SFA (Fig. 7e and f) shows a completely different morphology. The structure seems to be
Fig. 7  Backscattered micrographs of the prepared geopolymer samples: a G1P_1SS_COM, b G1P_1SS_TT_150C, c G1P_1SS_MT_M, d G1P_2SS_COM, e and f G1P_2SS_TT_150C along with their EDX analysis (the areas of analysis is marked with red signs in micrographs)
porous with large openings (> 200 μm), while it lacks cohesiveness revealing that a low portion of aluminosilicate gel has been formed. This observation confirms the findings of the alkali silicate preparation experiments that showed an extremely low conversion yield of silica fume to silicates when SiO₂/Na₂O equaled to 2. The sample’s stoichiometry by EDS analysis was calculated to Si:Al:Na ≈ 8:3:26 indicating that the unreacted sodium of waste-based activator has covered superficially the fly ash material.

Conclusions

This study concerns the synthesis of silica fume-based solid activators for fly ash geopolymerization. To reduce the energy requirement and simplify the synthesis procedure, microwave treatment was also applied, in addition to thermal treatment. Their potential of the activators was evaluated on the basis of the compressive strength of the relative geopolymers.

Results showed that:

- Silica fume was successfully converted to a solid activator, rich in sodium silicate Na₂SiO₃, capable to solo-activate the aluminosilicate raw material. Prepared geopolymers showed the same mechanical strength to the reference ones that reached 60 MPa.
- Solid activators based on silica fume were obtained through a simple process where silica fume was mixed with NaOH and water to create a pulp. The pulp was then treated appropriately (thermal/microwave treatment) to deliver a new powder product.
- Microwave processing is more sustainable and more efficient than thermal treatment, since purer products are produced with less energy consumption.
- XRD and FTIR results revealed the conversion of silica fume to a new product with a high sodium silicate content (> 50%). More particularly, solid activators with a molar ratio SiO₂/Na₂O = 1 are highly water-soluble materials (> 95%) and reactive enough to participate successfully in the geopolymerization process.

The next step of this research will be the life cycle analysis (LCA) and life cycle cost analysis (LCCA) of the produced alkali silicates in order to quantify the benefits from their application in geopolymer technology.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Olga Andriana Panitsa and Dimitrios Kioupis. The first draft of the manuscript was written by Olga Andriana Panitsa and Dimitrios Kioupis, and all authors commented on previous versions of the manuscript. Prof. Glikeria Kakali supervised the research work, reviewed and edited the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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