



Article Effect of Activating Solution Modulus on the Synthesis of Sustainable Geopolymer Binders Using Spent Oil Bleaching Earths as Precursor

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Abstract:** The valorization of spent oil bleaching earths (SOBE) is crucial for the protection of the environment and the reuse of resources. In this research, alkali-activated binders were manufactured at room temperature using SOBE as a precursor by varying the mass ratio between the activating solutions of sodium silicate (Na₂SiO₃) and 6 M sodium hydroxide (NaOH) (activating solution modulus) (Na₂SiO₃/NaOH ratio = 1/1; 1/2; 1/3; 1/4) to investigate the influence on the technological properties of the materials. This process intends to evaluate the potential of SOBE, heat-treated at 550 °C (1 h), as a precursor of the reaction (source of aluminosilicates). Samples produced with higher amounts of sodium silicate developed a denser structure, with lower porosity and a higher amount of geopolymer gel. Maximum flexural (8.35 MPa) and compressive (28.4 MPa) strengths of samples cured at room temperature for 28 days were obtained with a Na₂SiO₃/NaOH mass ratio of 1/1. The study demonstrates that SOBE waste can be used as a precursor in the manufacture of geopolymer binders that show a good compromise between physical, mechanical and thermally insulating characteristics.

Keywords: spent bleaching earth; geopolymers; activating solution; activator modulus; compressive strength; microstructure

1. Introduction

Ordinary Portland cement (OPC) is the most widely used binding material in construction, being one of the materials with the highest production worldwide, with a production in 2016 of 4174 Mt, corresponding to a growth of 2.3% compared to 2015 [1]. The global cement industry is one of the main greenhouse-gas (GHG)-emitting contributors as it generates 800 kg CO₂ for each ton of Portland cement produced [2]. In order to meet environmental objectives, this industry is seeking alternative experimental ways to develop cements that require less energy to manufacture and emit less polluting gases into the atmosphere. Its contribution corresponds to about 8% of global CO₂ emissions (2.5 Gt/year), aggravating global warming and its consequences [3,4]. Alkali-activated binders, or geopolymers, constitute an environmentally friendlier alternative, since CO₂ emissions can be reduced by 20–50% in comparison to OPC [5–7]. Hardening occurs when reactive aluminosilicates come into contact with an alkaline solution (activator) [8,9]. In a strongly alkaline media, the reactive species of the solid precursor dissolve and then generate hydroxylated oligomers of the $Si(OH)_4^-$ and $Al(OH)_4^-$ types. During the polycondensation reaction, the tetrahedral units alternately join to form amorphous reticules that constitute the geopolymeric matrix [8,10]. Geopolymers have attracted considerable attention due to their compressive strength, low permeability, good chemical resistance and durability to acid and sulfate attack, as well as excellent thermal fire resistance [11–17].

Metakaolin, generated by thermal activation of kaolinite, is the benchmark precursor [18–21]. Other calcined clays have been tested [22,23], but all these sources are natural and non-renewable. Moreover, their activation requires a pre-calcination stage that is energy consuming and generates emissions. Several industrial wastes were then tested as candidates: fly ash, mainly from coal combustion but also from biomass burning; slags; waste glass; and spent zeolites, etc. [24–29].

The most commonly employed alkaline activators are sodium silicate (Na₂SiO₃) or potassium silicate (K₂SiO₃) and sodium hydroxide (NaOH) or potassium hydroxide (KOH) [30]. The hydroxide concentration, the silicate/hydroxide ratio and the alkaline cation employed (Na and/or K) are determinants in the geopolymerization process by determining the chemical reactions that take place [23,31–35]. Alkaline silicate hydrate is the activator with the highest activation potential compared to other activators, such as hydroxides, because it has dissolved silica particles that react in the geopolymerization process, resulting in alkaline-activated cements with better mechanical performance and durability [36]. Therefore, the geopolymerization process depends on many factors including the precursor and activator used, the solid/liquid ratio, the curing temperature and the aging time, which play a role in the mechanical and durability properties of the geopolymers [37–40]

Spent oil bleaching earth (SOBE) is a waste product obtained in the refining process of edible crude oil. It is estimated that 120 million tons of oil are processed with bleaching earth worldwide, generating 2.5 million tons of spent bleaching earth as residue [41]. Moreover, the serious fire and contamination risks that arise during storage and disposal of spent bleaching earth require appropriate technical solutions. The current treatment of SOBE residue is not in line with the new circular economy policies promoted by the European Union, since in most cases it is disposed of in landfills [42]. New technologies that allow oil recovery and treatment of the earths, aiming to convert them into useful products are then needed [43]. Currently, studies are being carried out for its possible valorization as an adsorbent in wastewater treatment [43–46], fertilizer [47] and chicken feeding [48], as well as for its use as a raw material of different construction materials [49,50].

Oil bleaching earths are depleted bentonites, silica and alumina being the major constituents. They consist of 20–40 wt% residual oil, metallic impurities and other organic compounds [51]. Once the oil and organic compounds are removed, due to their composition they can be used as binders in the manufacture of geopolymers.

The manufacture of geopolymers at room temperature using SOBE as a precursor is challenging and constitutes the major novelty of this work. The effect of the modulus of the alkaline activator (mass ratio between sodium silicate and sodium hydroxide Na₂SiO₃/NaOH solutions) on the geopolymerization reaction was tested. Microstructural development and relevant properties of hardened samples were evaluated and discussed.

2. Materials and Methods

2.1. Raw Material

The spent oil bleaching earth (SOBE) residue was obtained from an olive oil production plant located in Vilches (Jaén, Spain). To dehydrate the residue received, it was dried in an oven at 105 °C. The sample had a moisture content of 6.66 wt%. It was then ground in a ball mill and sieved to a particle size of less than 100 μ m. A thermogravimetric analysis (TGA)-thermodifferential analysis (DTA) of the dry residue was carried out to determine the temperature of the heat treatment to which the residue should be subjected. DTA-TGA was carried out on a Mettler Toledo thermal analyser model TGA/DSC 1. About 10 mg of the OBE sample (with a particle size of <1 mm) was placed in an aluminium crucible with an air flow of 50 mL/min and a heating rate of 10 °C/min from 30 °C to 900 °C. The TGA-DTA analysis (Figure 1) indicated that combustion of the residue takes place between 180 and 550 °C. The combustion of the oil takes place in two stages. The mass loss of the residue between 100–415 °C (39.05 wt%), exothermic peak centered at 375 °C and the weight loss between 415–550 °C (16.8 wt%), as indicated by the more intense exothermic peak centred at 473 °C. At 550 °C combustion of the residue ends. Therefore, the calcination temperature of the OBE residue was 550 °C for one hour in a Carbolite 1200 F kiln with a heating rate of 10 °C/min and a one-hour dwell time.



Figure 1. TGA-DTA analysis of the spent oil bleaching earth (SOBE).

The determination of the chemical composition of the SOBE residue after calcination at 550 °C was determined by X-ray fluorescence (XRF), using a Zetium Malvern Panalytical apparatus (Netherlands). The residue was composed of a significant content of SiO₂ (68.4%) and Al₂O₃ (14.4%), which are elemental oxides for the development of the geopolymer structure (Table 1). The particle size of the calcined residue analysed with the Mastersize 2000 analyser from Malvern Instruments (Netherlands) was d(50) = 137 μ m and d(90) = 251 μ m.

Table 1. Chemical composition of SOBE after calcination at 550 °C.

Raw	Chemical Composition											
Material	SiO ₂	Al_2O_3	Fe ₂ O ₃	MgO	K ₂ O	CaO	TiO ₂	Na ₂ O	P_2O_5	SO_3	MnO	LOI
SOBE	68.35	14.43	3.21	2.05	0.90	0.35	0.33	0.18	0.09	0.04	0.01	9.96

LOI: Loss On Ignition.

The mineralogy of calcined SOBE powdered sample was studied by X-ray Diffraction (XRD), using Empyrean X-ray powder diffraction equipment with a PIXcel-3D detector of PANalytical (Malvern, The Netherlands) (CuK α radiation, 0.15418 nm, 45 kV-40 mA, $2\theta = 10-60^{\circ}$, step size 0.013° and measurement time: 15 min). HighScore software was used to identify the crystalline phases. Calcined SOBE residue has a mineralogical composition consisting of montmorillonite (82.4 wt%) (PDF: 96-900-5020) and α -quartz (17.6 wt%) (PDF: 96-900-5020). Baseline deviation between 18–30° (2θ) indicates an amorphous fraction in the residue (Figure 2).



Figure 2. DRX of SOBE calcined at 550 °C.

The morphology of the SOBE precursor calcined at 550 °C was determined by scanning electron microscopy (SEM), using a JEOL SM 840 model (Akishima, Tokyo, Japan) assisted by energy dispersive X-ray spectroscopy (EDS). Prior to observation, the samples were carbon-coated using JEOL JFC 1100 sputter coating. The micrograph is shown in Figure 3. A heterogeneous distribution of particles of different sizes and shapes can be observed.



Figure 3. SEM micrograph of SOBE calcined at 550 °C.

2.2. Geopolymers Synthesis

The activating solutions were prepared previously. Sodium hydroxide solutions (6 M) were prepared by dissolving NaOH pellets (98% purity, Panreac) in distilled water. The NaOH solution was cooled prior to the addition of the sodium silicate activating solution with the appropriate Na₂SiO₃/NaOH mass ratio (1:1; 1:2; 1:3; and 1:4). The activating solution used was obtained by addition to the NaOH solution (6 M) of the appropriate amount of sodium silicate solution Panreac (29.2% SiO₂; 8.9% Na₂O; and 61.9% H₂O).

The geopolymers were prepared by mixing the SOBE-calcined raw material (200 g) and the alkaline activating solution in a planetary mixer Proeti for 90 s. The rotation speed of the blade on its axis was $140 \pm 5 \text{ min}^{-1}$ and the translation speed around the center of the container was $62.5 \pm 5 \text{ min}^{-1}$. The liquid/binder ratio was kept constant and equal to 1.4, the whole activating solution (including solids dissolved) was considered as the liquid phase and the SOBE precursor as the binder. Subsequently, the material adhering to

the vessel walls was removed with a spatula and mixed for another 30 s. The fresh pastes were poured into $60 \times 10 \times 10$ cm stainless steel moulds and subjected to 60 strokes on a Proeti punching table to remove air bubbles trapped in the paste and to achieve a higher compaction. The moulded pastes were cured at room temperature, and wrapped in cling film for 24 h. The cured pastes were then demoulded and stored at room temperature until the test ages of 7 and 28 days. The mixtures have been designated by SOBE-x:y where x:y is the mass ratio Na₂SiO₃:NaOH. The mix proportions of the synthesised geopolymers can be seen in Table 2.

Geopolymer	Water/Binder (Mass Ratio)	NaOH (g)	Na ₂ SiO ₃	Water (g)	Ms	Na+ (mol kg ⁻¹)	Si/Al (Molar Ratio)	Si/Na (Molar Ratio)
G-SOBE-1:1	0.71	27.54	140	112.5	1.27	6	5.22	2.75
G-SOBE-1:2	0.76	36.72	93.32	149.93	0.78	6	4.82	2.34
G-SOBE-1:3 G-SOBE-1:4	0.79 0.81	41.31 44.07	70.00 56.00	168.69 179.93	0.56 0.44	6 6	4.62 4.50	2.16 2.06

Table 2. Mix proportions for assessed samples.

2.3. Characterisation of Geopolymers

Degree of reaction was used in addition to characterisation techniques to dissolve the aluminosilicate gels formed [52]. For determination, 1 g of ground and sieved geopolymer (100 μ m) was attacked with a 250 mL solution of HCl (1:20) for 3 h. The solution was then filtered, and the insoluble residue was washed with deionized water and dried to constant weight and calcined at 1000 °C (3 h). The degree of reaction is calculated according to Equation (1):

$$Degree of reaction = (1 - calcined mass) \times 100$$
(1)

The flexural strength of the geopolymers (5 samples for each series) at 7 and 28 days was determined with an MTS Insight 5 machine (Eden Prairie, MN, USA) of 5 kN capacity with a displacement speed of 0.2 mm/min according to UNE-EN 1015-11:2020 [53]. The results shown are the average of 5 repeated samples. The flexural strength is determined according to Equation (2):

$$\sigma_{\rm F} = 1.5 \frac{Fl}{bd^2} \tag{2}$$

where *F* is the load (N); *l* is the distance between the axes of the support rollers (mm); *b* is the width of the specimen (mm); and *d* is the thickness of the specimen (mm).

The compressive strength of the geopolymers was measured with a MST 8101 (100 kN) (Eden Prairie, MN, USA) universal testing machine at 7 and 28 days with a displacement of 2.0 mm/min according to UNE-EN105-11:2020 [53]. The results shown are an average of five samples. The compressive strength is given by Equation (3):

$$F_{\rm C} = \frac{F}{S} \tag{3}$$

with *F* the force (N); *S* the area of the specimen face under load; and σ_c the compressive strength (MPa).

σ

The bulk density (φa) of the geopolymers at 28 days was calculated according to UNE-EN 1015-10:2020 [54]. The real density (φr) was measured using a picnometer employing gasoline and fine crushed samples with particle size less than 63 µm.

The total porosity (P_T) was calculated according to the following Equation (4):

$$PT = \left(1 - \frac{\varphi a}{\varphi r}\right) * 100 \tag{4}$$

Water absorption (W_a) was carried out by immersing the dry samples in water at room temperature for 24 h and comparing the wet mass (m_h) with the dry mass (m_d) according to Equation (5):

$$Wa = \frac{(\mathrm{mh} - \mathrm{ms})}{\mathrm{md}} * 100 \tag{5}$$

The thermal conductivity of the geopolymers after 28 days of curing was determined at 20 °C according to ISO 8302:1991 [55] using a FOX 50 heat-flow meter (TA Instruments, New Castle, DE, USA).

The samples were analysed using a Vertex 70 Bruker (Billerica, Massachusetts, United States) Fourier transform infrared spectrophotometer (FTIR). Infrared scans were carried out in the wavenumber range from 400 to 4000 cm⁻¹, with a resolution of 4 cm⁻¹, and 100 cycles were performed to record the spectrum. Mineralogical analysis and micrograph images of the geopolymers were performed by XRD and SEM-EDS, respectively, using the same conditions as for the raw material. Quantitative phase analysis (QPA), not accounting for the amorphous phase, was assessed using the Rietveld method. The Rietveld data-analyses-recorded XRD patterns were evaluated using the GSAS software package and its graphical interface EXPGUI [56,57]. Those parameters were refined: scale factors, zeropoint, 10 coefficients of the shifted Chebyshev function to fit the background, unit cell parameters. The profile was modelled using the Thompson-Cox-Hasting formulation of the pseudo-Voigt function [58], and two Lorentzian terms (LX and LY), one Gaussian term (Gw, which is angle independent), peak correction for asymmetry, as well as sample displacement effects, were refined. The starting atomic parameters for the refined phases (i.e., montmorillonite and quartz) were taken from the literature [59,60].

3. Results and Discussion

3.1. *Reaction Degree*

The reaction degree of the geopolymers after 28 days curing as a function of the activation solution modulus, $Na_2SiO_3/NaOH$ mass ratio, is presented in Table 3. HCl extraction dissolves sodium aluminosilicate, calcium aluminosilicate and carbonate phases [61]. The reaction degree tends to increase in samples prepared with higher $Na_2SiO_3/NaOH$ mass ratios, indicating the formation of a greater amount of N-A-S-H geopolymer gel.

Table 3. Reaction degree of the samples.

Sample	G-SOBE-1:1	G-SOBE-1:2	G-SOBE-1:3	G-SOBE-1:4
Reaction degree (%)	52.5	47.3	45.7	43.5

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the raw material (SOBE) and geopolymers after 28 days curing are shown in Figure 4. A broad band centered at 1035 cm^{-1} , corresponding to the Si-O-Si groups, is observed in the raw material, together with a weak shoulder centered at 940 cm⁻¹, related to the vibration of the Al-OH bond of the bentonite [62]. The bands centered at 800 and 459 cm^{-1} are attributed to the stretching vibration of the Si-O bond [63,64]. Two bands are observed in the high-frequency region. A band centered at 3630 cm⁻¹ associated with the Al-OH functional group [62] and the absorption bands located at 3400 cm^{-1} and 1617 cm^{-1} , assigned to the stretching vibration and bending vibrations, respectively, are characteristic of the -OH groups of adsorbed water [65]. The geopolymers present similar patterns to the SOBE precursor, apart from the disappearance of the Al-OH functional group centered at 3630 cm⁻¹ and of the Si-OH functional group centered at 459 cm⁻¹. This may indicate that the montmorillonite layer reacts with the alkaline medium, giving rise to a geopolymeric gel [66] according to XRD data. The broad band between 1200 cm⁻¹ and 900 cm^{-1} is associated with the asymmetric Si-O-Si vibration and the symmetric Al-O-Si bending vibration [67]. It can be observed that the Si-O-T (T:Si or Al) stretching vibration, centered on the precursor at 1035 cm⁻¹, shifted to lower frequencies in the geopolymers

 $(1004-994 \text{ cm}^{-1})$. This change also indicates that the geopolymerization reaction has taken place due to the activation of the amorphous phase of the SOBE residue with the formation of N-A-S-H aluminosilicate gel, which means the condensation of Si-O tetrahedra as well as SiO₄ and AlO₄ in the geopolymer [40,68-70]. The band shift at lower frequencies may be due to an increase in the content of non-bridging oxygens, as well as to an increase in the amount of tetrahedral aluminum in the gel structure [27,71]. In all geopolymers, centered shoulders are also observed at 930 cm^{-1} , which can be assigned to the formation of an Al-rich gel. Initially an aluminum-rich gel is formed, and with the progress of the reaction, when the aluminum is depleted the formation of a Si-rich gel begins [72]. The intensity of the band is also attributable to the amount of Si-O or Al-O in a tetrahedral configuration. The intensity decreases with a decreasing Na₂SiO₃/NaOH molar ratio of the activating solution [73]. Geopolymers synthesized using a $Na_2SiO_3/NaOH = 1/1$ mass ratio (Ms = 1.27) show a more intense band, suggesting greater disorder in the formed gel [68,74]. These results are consistent with the differences in compressive strength, discussed below. The bands centered at 3300-3200 cm⁻¹ and 1635 cm⁻¹ indicate the presence of water molecules adsorbed on the surface or trapped in the large cavities of the polymeric network [75]. The intensity of such bands enhances when the Na₂SiO₃/NaOH mass ratio increases, probably due to a higher dissolution of the SOBE precursor, leading to the formation of more hydrated compounds according to the reaction degree data. The absorption bands around 1450 cm^{-1} and $866-870 \text{ cm}^{-1}$ are typical of the C-O bond stretching of the CO3 vibrational groups that are present in the inorganic carbonates found in all the spectra of geopolymer samples due to the formation of sodium carbonate [76].

3.3. Mineralogy of Geopolymer Binders

Figure 5 shows XRD spectra of the precursor and geopolymer binders. Patterns are similar, being montmorillonite and quartz, the crystalline phases having been detected. The partial dissolution of montmorillonite upon geopolymerization, revealed by the FTIR analyses and confirmed by QPA results (Table 4) [77], and the increase in the amorphous phase are the most relevant observations. However, the fraction of montmorillonite that dissolves is small for all the activator modules used, as observed by other authors [78]. Quartz peaks remain almost unchanged, indicating its non-reactive character. The analysis confirms the low dissolution of the crystalline phases by the activating solutions. The amorphous hump at 18–30° (2θ) in the SOBE precursor becomes more prominent and slightly shifts to 20–35° (2θ) with the geopolymerization progress [79].



Figure 4. FTIR of SOBE and geopolymer binders.





Figure 5. XRD of raw material and geopolymer cements as function of $Na_2SiO_2/NaOH$ mass ratio of activating solution.

	Phase Composition (wt%)					
Sample	Montmorillonite	α-Quartz				
Raw material	82.4 ± 0.2	17.6 ± 0.3				
G-SOBE-1:1	81.8 ± 0.2	18.2 ± 0.2				
G-SOBE-1:2	81.3 ± 0.2	18.7 ± 0.3				
G-SOBE-1:3	81.7 ± 0.2	18.3 ± 0.5				
G-SOBE-1:4	80.5 ± 0.2	19.5 ± 0.3				

Table 4. Quantitative crystalline phase composition as derived from the Rietveld refinements *.

* There were 3578 total observations for each refinement. The agreement factors of all the refinements were: $\chi^2 \le 4.92$; $R_{wp} \le 5.57\%$; and $R_p \le 4.20\%$.

3.4. Bulk Density, Total Porosity and Water Absorption of Geopolymer Binders

The values of bulk density, total porosity and water absorption of the geopolymers are shown in Figure 6. As expected, bulk density and total porosity or water absorption values followed an opposite tendency when the Na₂SiO₃/NaOH mass ratio of the activator changed. G-SOBE-1:1 specimens have a bulk density of 1828 kg/m³, total porosity of 20.7% and water absorption of 4.35%. As the Na₂SiO₃/NaOH mass ratio decreases, density decreases while total porosity and water absorption increases: G-SOBE-1:4 geopolymers show density = 1453 kg/m^3 , total porosity = 37.9% and water absorption = 14.9%. Samples prepared with lower Na₂SiO₃/NaOH mass ratios have more water (see Table 2). The water/binder ratio increases from 0.71 in G-SOBE-1:1 to 0.81 in G-SOBE-1:4 specimens; the removal of water will generate porosity [80]. Inadequate amounts of binder precursor and alkali solution results in less efficient dissolution of the precursor, with consequent creation of pores in the geopolymer matrix and the formation of a less homogeneous structure [81]. The ultimate removal of excess water upon drying will also create porosity. A decrease in the Si/Al molar ratio tends to generate less dense structures as a consequence of slower geopolymerization, according to the degree of reaction data [82]. So, we have physical and chemical/reactive contributions to the observed tendencies.



Figure 6. Bulk density, total porosity and water absorption of geopolymers after 28 days of curing as functions of the $Na_2SiO_3/NaOH$ mass ratio.

3.5. Compressive and Flexural Strength of Geopolymer Binders

Figure 7 shows the compressive strength of samples cured for 7 and 28 days. Values ranged from 10.1 to 17.9 MPa (7 days) and 15.7 to 28.9 MPa (28 days). An increase in the Na₂SiO₃/NaOH mass ratio enhances resistance, in direct relationship with higher compactness. Figure 8 shows a linear correlation between compressive strength and bulk density. The enhancement of soluble Si, by using an activator with a higher modulus, extends the geopolymerization process and the formation of the N-A-S-H aluminosilicate gel responsible for the consolidation of the geopolymer matrix and the development of mechanical strength [83–87].



Figure 7. Compressive strength of samples cured for 7 and 28 days.



Figure 8. Relationship between bulk density and compressive strength of geopolymers cured for 28 days.

The flexural strength values of the samples are shown in Figure 9. Between distinct formulations the changes follow the same trend in mechanical resistance after 28 days curing. However, differences after 7 days are minor, and sample G-SOBE-1:4 shows the maximum value (2.2 MPa). Progress with curing age is now more expressive, and resistance after 28 curing days is three to four times higher than at 7 days. Interestingly, it was observed that flexural strength values are only about three times lower than corresponding compressive resistances in samples cured for 28 days.



Figure 9. Flexural strength of samples cured for 7 and 28 days.

3.6. Thermal Conductivity

The geopolymers showed thermal conductivity values in the range 0.30–0.41 W/mK (Figure 10), being lower in samples less dense (the ones prepared with a lower Na₂SiO₃/NaOH mass ratio). As expected, there is an inverse relationship between thermal conductivity and porosity [88]. In general, geopolymers exhibit lower thermal conductivity values than Portland cement (1.5 W/mK) [89,90], due to the existence of pores in the microstructure [91,92].



Figure 10. Thermal conductivity of samples cured for 28 days.

3.7. Microstructure of Geopolymer Binders

SEM micrographs at different magnifications of geopolymer binders cured for 28 days are shown in Figures 11 and 12. At low magnification ($220 \times$, Figure 11) a homogeneous, dense and compact morphology can be observed in all samples. In any case, non-homogeneously distributed pores and some microcracks are visible. As expected from the density/porosity values, G-SOBE-1:1 samples seem more compact.

As the $Na_2SiO_3/NaOH$ mass ratio decreases, more pores formed due to water evaporation during curing [93] are observed, possibly due to an increase in the water/binder ratio (Table 2).

At higher magnification $(2000 \times, Figure 12)$, sodium aluminosilicate gel with a spongy and globular morphology is visible in all samples. Its elemental chemical composition reveals the dominance of silicon, aluminum and sodium (zone 1 EDS analysis), as expected. In addition, unreacted SOBE particles with angular shapes are also visible. EDS analysis (zone 2) shows an abundance of silicon and aluminum, and smaller quantities of potassium, iron and magnesium. It can be observed that as the amount of sodium silicate decreases the geopolymers contain more unreacted SOBE particles and possess a higher porosity.



Figure 11. SEM micrographs (220× magnification) of geopolymers cured for 28 days. (**a**) G-SOBE-1:1; (**b**) G-SOBE-1:2; (**c**) G-SOBE-1:3; and (**d**) G-SOBE-1:4.



Figure 12. SEM/EDS micrographs (2000× magnification) of geopolymers cured for 28 days. (**a**) G-SOBE-1:1; (**b**) G-SOBE-1:2; (**c**) G-SOBE-1:3; and (**d**) G-SOBE-1:4.

4. Conclusions

Spent oil bleaching earths (SOBE), generated in the oil bleaching process, were used as a precursor of geopolymer binders prepared with activating solutions with distinct Na₂SiO₃/NaOH mass ratios. Physical, mechanical and thermal properties changed with the mentioned activator modulus. Flexural and compressive strengths, bulk density and thermal conductivity increase when the Na₂SiO₃/NaOH mass ratio increases, while total porosity and water absorption decrease. Maximal flexural (8.4 MPa) and compressive (28.8 MPa) strength values were obtained in samples cured for 28 days at room temperature. The enrichment of soluble Si with the use of a higher amount of sodium silicate in the activator enhances the geopolymerization rate and extends it, generating higher compact and homogeneous microstructures due to the formation of a higher amount of threedimensional aluminosilicate hydrate [N-A-S-H] gel.

This work proved, for the first time, that SOBE can be used as a raw material of geopolymer binders, requiring pre-calcination at just 550 °C and sieving pre-treatment. This alternative contributes to the implementation of circular economy actions in this crucial activity.

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