



Article

Structural Characterization of Geopolymers with the Addition of Eggshell Ash

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Abstract: It is well known that geopolymers are a new group of binder materials of alumosilicate origin. Geopolymers are made by the reaction of precursor aluminosilicate materials with alkaline activator solutions. The current research relates to a low-cost and eco-friendly procedure, suitable of being implemented in two easy steps. The first step is the production of a solid phase based on fly ash (Obrenovac, Serbia) and eggshell ash as waste materials rich in calcium. The second step is alkali activating the solid phase using an alkaline activator (a mixture of NaOH and Na₂SiO₃) and procedures in proper laboratory conditions. Four samples with different eggshell ash content were synthesized. The concentration of used NaOH was 12 mol dm⁻³. The structural properties of all investigated samples were analyzed by XRD (*X-ray diffraction*), DRIFT (*diffuse reflectance infrared Fourier transform*), SEM (*scanning electron microscopy*) and UV/Vis spectroscopy analysis. XRD determined the amorphous halo with the presence of quartz as the crystal phase in all of the investigated samples. These results were confirmed by DRIFT analysis. The morphology of the samples was determined by SEM analysis. UV/Vis showed that the material could be a potential adsorbent.

Keywords: alkali-activated; geopolymer; fly ash; eggshell ash; DRIFT; XRD; SEM; UV/Vis



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1. Introduction

On a global scale, the annual production of Portland cement is substantial, and it remains the most prevalent type of binder material utilized today. However, cement production is a highly energy-intensive process that necessitates significant consumption of natural resources. Additionally, the cement production process results in the release of substantial amounts of carbon dioxide into the atmosphere, contributing significantly to the issue of climate change [1]. As a result, there is a growing need for sustainable and environmentally friendly alternatives to Portland cement. Previous research has indicated that producing one ton of Portland cement generates an equivalent amount of carbon dioxide emissions, representing a substantial 6% of the overall greenhouse gas emissions from construction materials on a global scale [2]. Given the magnitude of this figure, it is clear that reducing the environmental impact of cement production is a critical challenge that requires immediate attention. Efforts are underway to develop more sustainable alternatives to Portland cement that can help mitigate the harmful environmental effects of this essential building material. The large amounts of emitted carbon dioxide and generated waste material are identified as two significant problems of Portland cement production. Therefore, it is evident that the reduction of Portland cement consumption will contribute to the decreasing of carbon dioxide emissions. The replacement of PC as a binder material with geopolymers effectively reduces PC consumption and, therefore, Sustainability **2023**, 15, 5419 2 of 13

CO₂ emission. A study of geopolymers extracted from different types of waste materials indicates that geopolymers are a superior replacement for regular polymers, especially considering the environmental impacts of solid wastes and the sustainability issues related to the use of natural materials and energy. In the latest period, there has been a higher recognition of dangerous solid waste production and its influence on human health and an increased center of attention on the ecological consequences of waste scrapping. This forces the industry to find alternate ways to reuse waste materials. One possibility for a solution is reusing the waste materials to make geopolymers as a substitute to building materials. Geopolymers represent an innovative group of porous ceramic materials characterized by low energy consumption during production for construction purposes; they are cheap and environmentally friendly with low emissions of CO₂.

Geopolymers can be developed by alkali activating waste materials such as fly ash (rich in alumina and silica) and eggshell ash (rich in CaO) [3,4]. Over the course of the past ten years, geopolymers have risen to become one of the most promising classes of inorganic materials. This is largely due to their demonstrated capacity to significantly reduce CO₂ emissions, which has made them a good option for environmentally conscious industries seeking to minimize their ecological impact [5]. These materials show excellent mechanical properties, thermal stability, resistance to strong acids and open flames, long-term durability, and recyclability, which makes them applicable in many fields.

Fly ash is a byproduct of burning pulverized coal in electric power plants. It represents one of the most substantial forms of industrial waste produced on a worldwide scale due to the sheer volume of coal combustion that occurs in such facilities. As a result, fly ash has become a significant environmental concern, as it is imperative to find sustainable methods for disposing of or repurposing this waste material in a manner that minimizes its impact on the planet [6]. Geopolymers that are based on fly ash have been found to possess good mechanical properties. These include high compressive strength, low shrinkage, and remarkable resistance to chemical attacks. Furthermore, these materials have been identified as having the potential to serve as fire-resistant building materials within the construction industry [7]. Given their impressive combination of performance characteristics, fly ash-based geopolymers have become an increasingly good option for use in various applications where high performance and durability are essential [7].

Every day, a substantial quantity of waste materials in the form of eggshells are generated and ultimately disposed of in landfills [8]. Despite their potential for reuse or repurposing, these eggshells are frequently discarded as waste, contributing to the ever-growing environmental challenges of managing and reducing the volume of waste materials. However, innovative strategies are emerging to explore the potential of eggshells as a valuable resource that can be repurposed in various ways, including as a sustainable additive for the production of construction materials or as a source of calcium carbonate for use in the food industry [8]. Disposing of eggshells as waste material is a great challenge due to the possible attraction of pests causing health problems in humans [9]. During biodegradation, eggshells in landfills generate smell and provoke microbial development [10]. Eggshell ash can be used in developing geopolymers and can be a fragmentary replacement for cement. Due to the existence of CaO₂, the eggshell ash has the properties of cement [8]. Hamada et al. have shown that the insertion of eggshell ash develops the durability of concrete by reducing water adsorption. Additionally, this type of concrete has a high resistance on the sulfates and acids in the environment [11]. On the other side, fly ash as a by-product of industrial processes in the thermal power plant has pozzolanic properties and can be used as a substitute component in the production of cement. Al₂O₃ and SiO₂, presented in fly ash, are essential minerals for the process of polymerization. Abundant amounts of eggshell and fly ash enable this kind of waste material to replace cement in concrete [12]. Mineral structure and chemical-physical properties of fly ash have an effect on the quality of the concrete. Based on the results from the work of Shekhawat et al., it was concluded that eggshell ash can contribute to developing the mechanical strength of fly-ash-based geopolymers with the use of CaO present in eggshell ash [12].

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Bearing in mind that fly ash and eggshell are produced yearly in high quantities, it is evident that their usage in construction would significantly reduce the amount of waste in landfills [12]. Since the cement and food industries produce significant amounts of pollution, there is a growing need to address this problem [3]. This problem can be solved by producing a geopolymer from waste materials. This paper aims to synthesize geopolymers from waste materials (fly ash and eggshell ash) and to monitor the influence of Ca on geopolymerization.

Overall, the incorporation of waste materials, such as fly ash, eggshell ash, wood ash, lathe scraps, into reinforced concrete beams, shows promise as a way to improve the performance of geopolymers while also promoting sustainability in the construction industry [13]. Organic wastes such as coconut fibers and rubber tree shells can be used as additives in cement to improve its strength, crack resistance, and elasticity. These materials can be compared to eggshells in their ability to enhance the properties of cement [14,15]. One way to manage waste materials is through the implementation of circular economy principles, where waste materials are seen as resources rather than liabilities. This approach involves designing products and processes that minimize waste generation and promote the reuse and recycling of materials. Another way to manage waste materials in a sustainable manner is through the development of innovative technologies that can convert waste materials into valuable resources. For example, waste materials such as fly ash, slag, and industrial wastewater can be used as raw materials for the synthesis of inorganic polymers, such as geopolymers. Geopolymers have excellent mechanical properties and can be used as building materials or environmental remediation agents. Further research and development in this area will be important to fully understand the potential of waste materials as construction materials and optimize their use in geopolymers.

In conclusion, waste materials are a significant challenge for society, but also present an opportunity for innovation and sustainable development. Through proper management and innovative technologies, waste materials can be transformed into valuable resources and contribute to a more sustainable future.

2. Materials and Methods

2.1. Preparation of Samples

Fly ash and eggshell ash, as a solid precursor, were used as starting materials in the synthesis of geopolymer. Fly ash represents a waste material from the Obrenovac thermal power plant. Eggshells were slow thermally treated to 550 °C and kept at that temperature for 1 h in order to remove organic compounds. The shells were, subsequently, crushed and pulverized in a vibratory cup mill (Fritsch, Pittsboro, Germany) for 1 min. Geopolymer synthesis is a polymerization reaction that occurs with the help of alkaline-activated solution and waste materials, fly ash, and eggshell ash, mixed in precisely defined ratios. An alkaline activator was used with a mixture of Na_2SiO_3 and NaOH in the ratio of 1.6 for the synthesis of geopolymer samples. The ratio of the solid to liquid phase was 0.85. The concentration of used NaOH was 12 mol·dm⁻³.

The mixture ratios of the starting material of the prepared geopolymer samples are shown in Table 1.

Table	1.	Solid	s ratio	in	gec	pol	ymer	samp	les.
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Sample	Fly Ash (%)	Eggshell Ash (%)
GP7	100	0
GP9	70	30
GP11	30	70
GP13	0	100

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Four samples were synthesized with an increased amount of eggshell ash. The first sample, GP7, contained no eggshell ash while the last sample, GP13, contained 100% eggshell ash.

2.2. Methods

In this work, to achieve physico-chemical characterization, two analytical methods were employed: XRD and DRIFT. The morphology of the synthesized materials was also investigated using SEM analysis.

2.2.1. X-ray Powder Diffraction (XRPD)

XRD analysis was conducted at room temperature by using an Ultima IV Rigaku diffractometer, Rigaku Tokyo, Japan, equipped with CuK α 1,2 radiation for phase analysis of the obtained powders. The next parameters used for XRD analysis: D/TeX Ultra high-speed detector; 2θ range- 5– 80° ; continuous scan mode: a scanning step size -0.02° ; a scan rate of 10° /min. A Si-monocrystalline sample carrier was used. To evaluate the material's phase identification, PDXL2 (Ver. 2.8.4.0) software was used [16]. Using the ICDD database, all obtained powders were identified [17]. For phase identification, analysis selected ICDD cards were used: 01-081-2027-calcite, 01-076-0739-trone, 01-072-0185-sodium silicate, 00-046-1045-quartz. Raw fly ash and raw eggshell ash were identified by using the ICDD data base; selected ICDD cards were used: 01-086-2237-quartz, 00-015-0776-mullite, 00-009-0466-albite, and 01-083-4602-monophase calcite.

2.2.2. Diffuse Reflectance Infrared Fourier Transform (DRIFT)

For the DRIFT analysis, the samples were first dusted and then evenly dispersed in anhydrous potassium bromide (KBr) pellets. The spectra were acquired at room temperature using a Perkin Elmer Spectrum Quant instrument, Beaconsfield, UK. The spectral data were collected within the range of 4000 to $500~\rm cm^{-1}$, allowing for a comprehensive analysis of the samples.

2.2.3. Ultraviolet-Visible Spectroscopy (UV/Vis) Analysis

To investigate the potential adsorption capabilities of the samples, UV/Vis spectroscopic analysis was employed. Similar to the DRIFT method, the samples were dusted prior to being mounted on a UV-2600 carrier provided by Shimadzu Corporation, Kyoto, Japan. This technique allowed for a thorough examination of the absorbance properties of the synthesized materials, providing valuable insight into their potential adsorption characteristics.

2.2.4. Scanning Electron Microscope Spectroscopy

The microstructure analysis was performed on a Au-coated surface of the samples using a Japan Electron Optics Laboratory (Akishima, Japan) electron microscope (JEOL JSM) 6390 LV at 15 kV, Oxford Instruments X-MaxN (Oxford, UK).

3. Results and Discussion

Physico-chemical properties of all prepared samples were examined by XRD, DRIFT, and SEM analysis.

3.1. X-ray Diffraction Analysis (XRD)

In order to monitor phase changes in the synthesized samples, the XRD method was used. Mineral composition of the tested samples shows that calcite $CaCO_3$ is one of the main components in all four samples. Figure 1a–f show the results of the analysis of all synthesized samples, G7, G9, G11, G13, respectively. Sample GP7 consists of sodium carbonate salt, also called throne in mineralogy; as well, sodium silicate and quartz were identified as the accompanying phases shown in Figure 1c. The most intense quartz peak occurs at a theta angle of about 27° and the most intense throne peak occurs at about 35°

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 2θ . Figure 1d also contains sodium carbonate, as well as quartz, and differs from GP7 in the content of calcite, which shows an intense peak at an angle about 30° 2θ . It is noticeable according to results that samples GP7 and GP9 have some higher background in a range from about 5– 45° 2θ than in GP11 and GP13, which indicates a slightly higher proportion of amorphous phase in semi-crystalline geopolymer matrix.

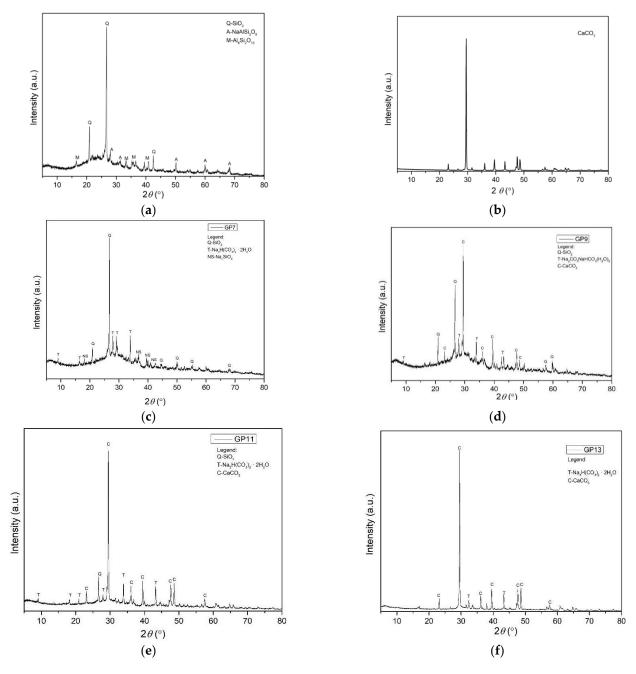


Figure 1. XRPD patterns of synthesized samples: (a) raw fly ash, (b) raw eggshell ash, (c) GP7, (d) GP9, (e) GP11, and (f) GP13.

X-ray diffraction analysis of the initial crushed eggshell sample showed the presence of monophase calcite. In the case of the sample of fly ash used as a starting material for the synthesis of geopolymers, the results of XRD showed the existence of quartz, mullite, and albite. In addition, a slightly higher background was observed in the range of $10\text{--}40^\circ$ 2θ , indicating the presence of amorphous phases. These amorphous phases are often attributed to the contribution of organic matter and coal dust generated during the

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combustion process. Samples GP9 (Figure 1d) and GP11 (Figure 1e) have a very similar mineral composition while sample GP13 (Figure 1f) consists predominantly of calcite, which in this sample is almost monophasic. Based on the obtained results, it is noticeable that in samples GP11 and GP13, there are peaks that are narrower, distinctly defined and sharp, which indicates a good constituent ordering of the identified phases. Based on the results, samples GP7 and GP9 reveal some higher background, indicating an amorphous matrix with a semi-crystalline structural order of crystalline phases, which represents the obtained geopolymer structure.

3.2. Diffuse Reflectance Infrared Fourier Transform (DRIFT)

The structural characteristics of alkali-activated materials were determined by using DRIFT analysis. Bertaux et al. [18] observed that the fine powder structure of the sample provide good and uniform diffusion of infrared light into the samples. The DRIFT spectra of the analyzed samples are shown in Figures 2 and 3. Figure 2 shows the spectra of raw pure materials.

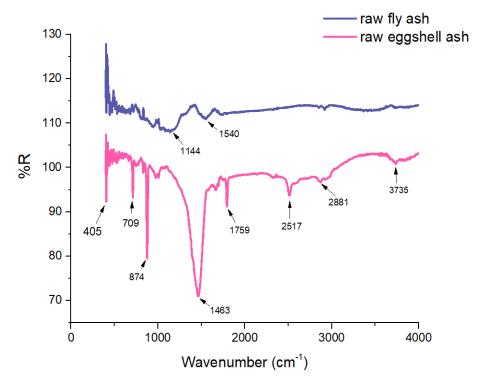


Figure 2. DRIFT spectrum of raw samples.

Observing the spectra of raw samples of fly ash and eggshell ash, a significant difference in spectra is observed; the spectrum of eggshell ash shows intense peaks compared to the spectrum of fly ash. Intense peaks at $405~\rm cm^{-1}$ and $709~\rm cm^{-1}$ belong to C-O vibrations, which can be associated with the in-plane deformation and out-plane deformation modes, respectively, in the presence of calcium carbonate [19]. Intense peaks at $1759~\rm cm^{-1}$ and $874~\rm cm^{-1}$ are associated with the presence of calcium carbonate. The peak at $1463~\rm cm^{-1}$ belongs to C-O vibrations from $\rm CO_3^{2-}$. A broad band centered at $1540~\rm cm^{-1}$ at the raw fly ash DRIFT spectrum correspond to asymmetric stretching and a peak at $1144~\rm cm^{-1}$ is assigned to symmetric stretching vibrations of Si-O-Si and Si-O-Al [20,21].

The results of the DRIFT analysis of geopolymers GP7, GP9, GP11, and GP13 samples were compared and presented in Figure 3. The wider peak at $3500~\rm cm^{-1}$, which occurs in all four samples, belongs to the stretching vibrations –OH (hydrogen bond) and bending vibrations of $\rm H_2O$ molecule adsorbed between the interlayer structure of the samples. The presence of organic matter with significantly reduced absorption was observed in all synthetized samples on the band $2978~\rm cm^{-1}$ [22].

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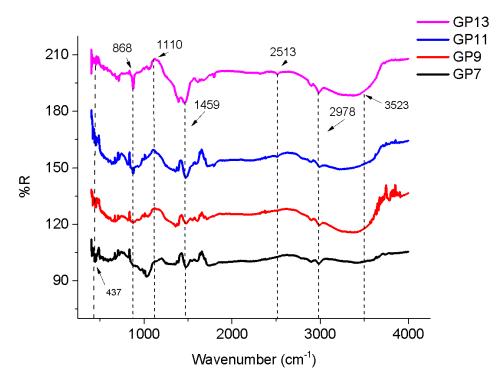


Figure 3. DRIFT spectrum of synthesized samples GP7, GP9, GP11, and GP13.

The DRIFT spectra of all the samples examined in this study, from GP7 to GP13, have shown a prominent peak at a wavelength of $1110~\rm cm^{-1}$, which is associated with the Si-O-Si asymmetric stretch vibrations, known as the "fingerprint" polymerization. Furthermore, the DRIFT spectra have indicated the presence of an additional peak at a wavelength of $1459~\rm cm^{-1}$, which is attributed to the asymmetrical stretching of $\rm CO_3^{-2}$ bands. This was confirmed by a sharp peak observed at approximately $868~\rm cm^{-1}$, which is characteristic of these vibrations. The XRD technique also confirmed the existence of $\rm CaCO_3$ in the GP13 sample. Additionally, the samples displayed a band at $2513~\rm cm^{-1}$ that corresponds to the vibration of carbonate [23]. According to the literature, the signal appearing at $437~\rm cm^{-1}$ is of the bending vibration of Si-O [24]. It is noteworthy that both the XRD and DRIFT analyses have confirmed the expected results, i.e., the highest concentration of calcium was found in the GP13 sample.

3.3. UV/Vis Analysis

The absorbance of the synthesized samples was measured using a UV-2600 instrument manufactured by Shimadzu Corporation, in the wavelength range from 250 to 1000 nm, with barium sulfate serving as a reference sample. The analysis of the obtained UV/Vis spectra determined that the examined materials containing fly ash in their structure show significant absorption at a wavelength of 260 nm.

The findings shown in Figure 4 indicate that sample GP13, which was synthesized solely from eggshell ash, exhibits an extremely low absorbance value of approximately 0.85. This observation can be attributed to the formation of a highly crystalline and dense structure as a result of the eggshell activation reaction. The low absorbance value can be correlated with the structural properties of GP13, as revealed by XRD analysis (Figure 1f), indicating a high degree of structural order with a negligible proportion of the amorphous phase. Sample GP7, which is synthesized only from fly ash, shows a slightly higher absorbance value of about 1.1. This result can also be attributed to the structural order of the synthesized material, as evidenced by the presence of an amorphous matrix in the XRD sample (Figure 1c), which can be related to a higher background in the diffractogram of the GP7 sample (Figure 1d,e). Sample GP11, which consists of 30% wt. fly ash and 70% wt. eggshell ash, shows an absorption value of approximately 1.2. On the other hand, sample

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GP9, which contains 70% fly ash and 30% eggshell ash, shows the highest absorption value of about 1.4. It is interesting that in these two samples, the XRD diffractograms show a slightly higher background, as shown in Figure 1d,e, which suggests a higher presence of an amorphous geopolymeric matrix with semi-crystalline residual phases.

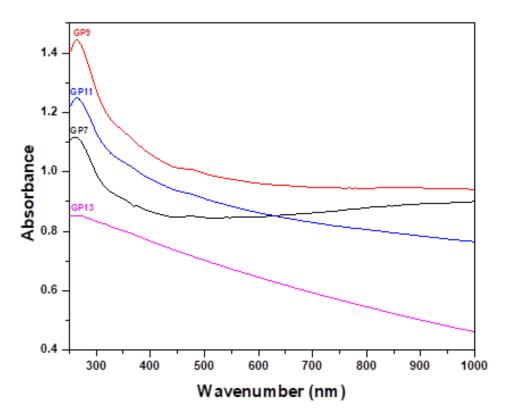


Figure 4. UV/Vis spectra of all samples.

3.4. Scanning Electron Microscope Analysis (SEM)

In Figure 5, there are scanning electron microscopy (SEM) micrographs that depict the raw samples of both fly ash and eggshell ash, and samples that have varying amounts of eggshell ash. The magnification used for these micrographs was 400×. Upon observation of the images presented in Figure 5a through Figure 5f, a noticeable change in the structure of the geopolymer can be observed with an increase in the quantity of eggshell ash. It can be observed that as the content of eggshell ash is increased, there is a distinct appearance of needle-shaped structures that were not present in lower concentrations. This suggests that the introduction of additional eggshell ash has an impact on the overall structure of the geopolymer. Under SEM analysis, a sample of raw fly ash (Figure 5a) was observed to exhibit the characteristic morphology of fly ash, with the majority of the particles appearing as small spherical shapes. SEM analysis was performed to observe the differences in the structure of eggshell ash, Figure 5b, after geopolymerization. A noticeable structural contrast exists between eggshell ash before and after geopolymerization. Following the process of geopolymerization, there is a distinct emergence of a needle-shaped structure that is characteristic and can be easily observed. However, this distinct structure is not present in the raw eggshell ash material prior to undergoing geopolymerization.

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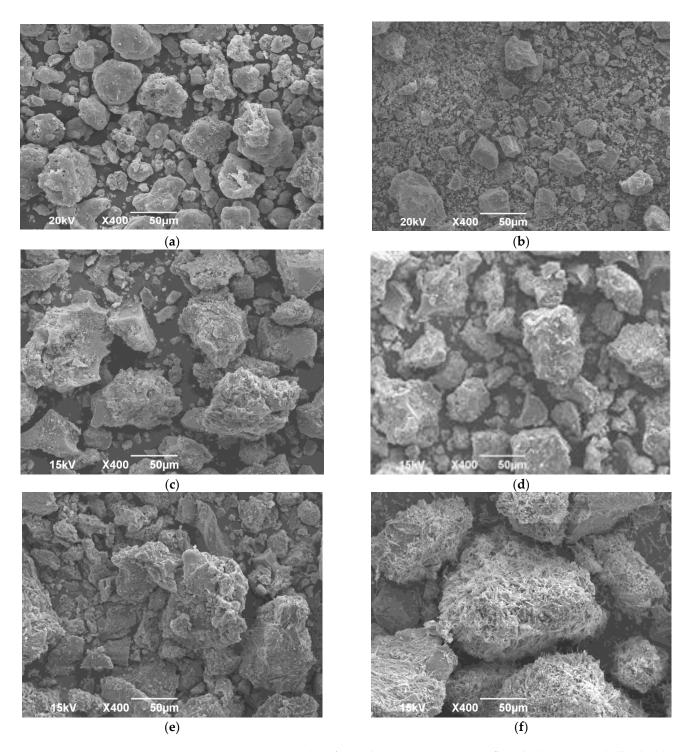


Figure 5. SEM micrographs of samples containing (**a**) raw fly ash, (**b**) raw eggshell ash, (**c**) GP7, (**d**) GP9, (**e**) GP11, and (**f**) GP14. Magnification $400 \times$.

Figure 5e,f show that the addition of the eggshell resulted in a needle-shaped structure, which was not observed in samples containing 0 and 30 wt% of eggshell. Agglomerates of needle particles represent a part of irregularly shaped particles originating from water glass, NaOH, and $CaCO_3$. It can be concluded that the structure is mostly non-uniform, with the presence of differences in shape and size. The microstructures of the geopolymers made by the utilization of diverse concentrations of waste material are various. Figure 6c shows the microstructure of the sample containing no eggshell ash under a magnification of 2500x. Upon observation, it is evident that the structure of the sample in question closely

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resembles that of foam, which can suggest an incomplete process of geopolymerization. Furthermore, the sample that does not contain any eggshell ash exhibits a more fragile structure in comparison to the other samples.

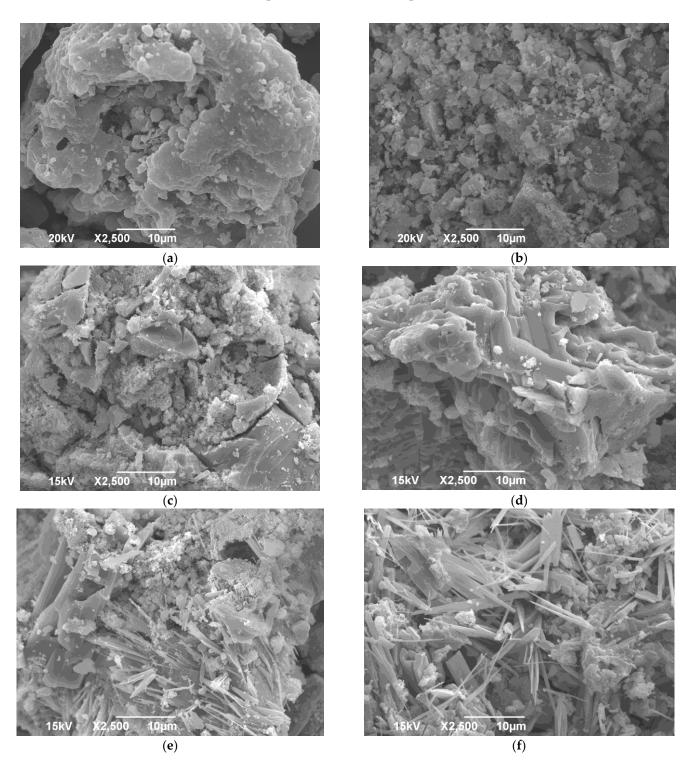


Figure 6. SEM micrographs of samples containing (**a**) raw fly ash, (**b**) raw eggshell ash, (**c**) GP7, (**d**) GP9, (**e**) GP11, and (**f**) GP13. Magnification 2500×.

Upon conducting SEM analysis, it can be observed that there are structural differences between the samples of raw materials and the synthesized geopolymers. Specifically, the raw eggshell ash sample exhibits a more compact structure in comparison to the raw fly ash

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sample. As Figure 6d shows, the structure of the sample containing 30 wt% of eggshell is more compact, with a larger fraction of grouped particles than that of the sample containing no eggshell (Figure 6c). The layered gel porous structure of the sample containing 70 wt% is shown in Figure 6e. There are also some single particles and needle-like structures. Based on SEM micrographs, the number of needle structures increases with the increase of eggshell (CaCO $_3$) concentration. The surface changes resulting from the polymerization process of waste materials can be observed in the SEM micrographs. The resulting structure is complex and inhomogeneous, composed of independent or agglomerated particles with multiple interconnected pores.

4. Conclusions

The subject of this paper is the influence of Ca on the synthesis of geopolymers. The first part of the paper presents the preparation of the starting materials for the synthesis of alkali-activated material. In the work of Ivanović et al., colleagues examined the "Effect of alkaline activator concentration and aging time on the structure of geopolymers based on metakaolin". Samples with a higher NaOH content in the alkaline activator give better physico-chemical and mechanical characteristics. Using an alkaline activator with a concentration higher than 12 M NaOH results in a strong exothermic reaction, and for this reason, an alkaline activator with a concentration of 12 M NaOH was used for the synthesis in this work [25]. The influence of the physico-chemical structure on the synthesis of natural inorganic materials and the influence on radioactivity was investigated by Nenadović et al. [26–28]. In the research, Ivanović et al., in 2018, it was confirmed that natural radioactivity decreases with geopolymer synthesis during alkaline activation [28]. For future research, the plan is to examine the effect of adding eggshell ash on radioactivity.

Physico-chemical characterization of the obtained samples was performed by utilization of the following methods: XRD, DRIFT, UV/Vis, and SEM.

XRD analysis is a powerful tool for characterizing the structure and mineralogy of geopolymers. By providing information on the degree of crystallinity, phase composition, and amorphous content, XRD analysis also helps to optimize the synthesis and performance of geopolymers for various applications, such as construction materials. XRD analysis was employed to define the mineralogical structure of the synthesized geopolymers. The results showed that the main crystalline phase was quartz, followed by throne and calcite. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy is a commonly used technique for analyzing the chemical properties of materials, including geopolymers. DRIFT analysis determined the existence of quartz and was certified by XRD analysis. A wide vibration with a maximum at 3500 cm⁻¹ was observed, which is attributed to vibrations of stretching and deformation of water molecules (O-H). The wave number at 1000 cm⁻¹ was detected and matched the Si-O stretching vibration. Overall, SEM analysis is a powerful tool for studying the properties of materials. By providing high-resolution images and elemental analysis, SEM can help researchers understand the morphology and composition of scanned materials, and how it can be used in various applications. SEM analysis confirmed the change in phase composition as well as XRD analysis. Thanks to the microscopic observation, several different morphologies of the samples were observed: some are elongated, rounded, and angular; porous; and crystal needles appear. Based on the literature data, cementitious materials for the production of which fly ash and eggshell ash are used show better performance than ordinary cement in terms of water penetration, fire resistance, and influence the minimization of carbon dioxide production (CO_2) , and we assume that our tested material is the same [29]. The internal structure, pore distribution, and composition of the modified sample size changed with the increasing amount of eggshell ash. The morphology and SEM results showed that the eggshell ash was well-bonded to the silica- and aluminum-rich fly ash. Geopolymers formed from fly ash and eggshell ash exhibit an amorphous structure. UV/Vis spectroscopy provides valuable information on the optical properties, such as the absorbance of geopolymers. Based on the UV/Vis analysis, it can be assumed that the synthesized samples can be

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used as potential adsorbents, which could be confirmed by further research. Owing to the increased amount of calcium carbonate, they can be recommended for use in construction as green and durable materials.

Overall, geopolymers rich in calcium are a promising class of inorganic polymers that have unique properties and a wide range of applications.

Author Contributions: M.I. and S.K. conceptualized the research, designed and prepared theresearch plan, synthesized the samples and wrote and revised the manuscript. D.B. and M.N. wrote part of the manuscript and analyzed obtained results. M.M.M. contributed to the analysis and discussion of the XRD results. M.I., together with S.K., completed the DRIFT analysis. S.K. also contributed to the analysis and discussion of the UV/Vis. L.K. and V.B.P. contributed to the interpretation of the SEM results. All the authors contributed to the literature research, data analysis and the preparation of the manuscript. All authors have read and agreed to the published version of the manuscript.

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