

Article

Utilising Phosphogypsum and Biomass Fly Ash By-Products in Alkali-Activated Materials

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Abstract: Significant environmental issues are raised by the phosphogypsum (PG) waste that is being produced. In Lithuania, about 1,500,000 tons of PG waste is generated yearly, and about 300 Mt is generated yearly worldwide. A by-product of burning wood biomass in thermal power plants is biomass fly ash (BFA). By 2035, compared to 2008 levels, industrial biomass incineration for combined heat and power and, as a consequence, BFA, is expected to triple. This study revealed the possibility of using these difficult-to-utilise waste products, such as BFA and PG, in efficient alkali-activated materials (AAM). As the alkaline activator solution (AAS), less alkaline Na₂CO₃ solution and Na₂SiO₃ solution were used. The study compared the physical–mechanical properties of BFA-PG specimens mixed with water and the AAS. After 28 days of curing, the compressive strength of the BFA-PG-based, water-mixed samples increased from 3.02 to 6.38 MPa when the PG content was increased from 0 to 30 wt.%. In contrast, the compressive strength of the BFA-PG-based samples with AAS increased from 8.03 to 16.67 MPa when the PG content was increased from 0 to 30 wt.%. According to XRD analysis, gypsum crystallisation increased when the PG content in the BFA-PG-based samples with water increased. The presence of AAS in the BFA-PG-based samples significantly reduced gypsum crystallisation, but increased the crystallisation of the new phases kottenheimite and sodium aluminium silicate hydrate, which, due to the sodium ions' participation in the reactions, created denser reaction products and improved the mechanical properties. The outcome of this investigation aids in producing sustainable AAM and applying high volume of hardly usable waste materials, such as BFA and PG.

Keywords: phosphogypsum; alkali-activated materials; biomass fly ash; structure; compressive strength



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1. Introduction

The need for renewable energy sources based on biomass has increased, along with the pressure to protect the environment and provide sustainable energy sources. Ash generation nowadays is significantly increased by biomass [1,2]. Because of its biogenic characteristics, biomass fly ash (BFA) has become considered one of the most widely used wastes [3]. Primary solid biofuels account for around 9% of global energy production [4,5], and compared to 2008 levels, industrial biomass production is expected to increase threefold by 2035. During incineration, the biomass's organic components do not burn completely [6,7].

Nonetheless, a sustainable BFA management strategy is imperative, given the growing expense of BFA disposal and the rise in BFA amounts worldwide. As a result, some researchers have looked into the possibility of replacing concrete with BFA obtained from wood burning [8,9]. Research [10,11] has shown that BFA is applicable to the construction of roads.

Conversely, BFA's greater percentage of organic matter (20–25%) and pozzolanic nature [12] may negatively impact concrete's compressive strength and rheological behaviour [13,14]. Moreover, it has been noted that raising the BFA content impacts the

concrete's apparent density, water absorption [15], and the specimens' progressive deterioration of compressive strength. When BFA is used as an additional cementing material possessing hydraulic activity, it can be ground to enhance the mechanical characteristics of the concrete [16–20].

Phosphogypsum (PG) is calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). PG can broaden the basis for novel building materials [21]. PG is obtained as waste from the wet acid process to produce phosphoric acid from naturally occurring phosphate rock [22].

The composition of PG is complex, and the main factors influencing its use are fluoride, organic matter, residual phosphoric acid, and partially decomposed phosphate rock [23–27]. According to studies, the manufacturing of PG varies between 100 and 300 Mt. annually around the world [27,28]. When those PG by-products are disposed of improperly, they not only take up much space on land but also seriously harm the environment. There are particular distinctions between natural gypsum and PG [29]. For example, PG is noticeably less effective than natural gypsum when it comes to the cementing properties. PG also has a very low water solubility, which worsens as the temperature rises. Larger PG particles and lower impurity content are associated with a more regular crystalline form [23,30]. Pretreatment, such as calcining PG at a specific temperature of 170–200 °C [22,31–34], is required to enhance the binding features of the PG and prevent the creation of solid solutions containing phosphates and fluorides [23,35]. In addition, hemihydrate gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), which has hydraulic activity, is formed during dehydration. Certain studies have shown pre-treated PG to be a functional building material [29].

On the other hand, the PG that has been pre-treated shows a delayed setting time when compared to natural gypsum [36,37], but it also exhibits increased residual strength when exposed to higher temperatures [38]. Products with cementitious qualities are produced by combining ground granulated blast furnace slag (GGBFS), lime waste, and pre-treated PG (as a source of CaSO_4). These products feature improved hydration, rheological characteristics, and the resilience in the presence of sulphates [39] while maintaining the same mechanical qualities as those created using ordinary Portland cement (OPC) [31]. Although the mentioned studies demonstrate that using pre-treated PG with different slags is feasible, little research has been done on using BFA with pre-treated PG [40]. Given the anticipated increase in this waste, it is imperative to look into possible applications for it as a building material [41]. Research [9] has investigated the viability of substituting class F fly ash with high calcium biomass wood ash in manufacturing a geopolymer mortar.

Evaluating the engineering qualities of mortar specimens involved substituting BFA for FA at three different replacement ratios: 10, 20, and 30% by binder mass [9]. The study concluded that the only geopolymer samples that contained 10% biomass wood ash showed superior qualities to the control mortar. These findings answer questions about biomass wood ash waste management and indicate many opportunities to conduct more research into the application of these wastes in the manufacturing of alkali-activated materials. Conversely, in the earlier research, geopolymer mortars were made by substituting or adding BFA at a maximum of 30%, and the findings of these investigations demonstrated suitable engineering qualities up to 10% or 20% substitution ratios of BFA. Thus, it remains significant and challenging to attain sufficient engineering properties by utilising a significant quantity of BFA debris as waste material. The high amount of organic matter affects the samples containing BFA waste in terms of longevity, mechanical performance, and higher absorption of water [23,31]. The durability and mechanical characteristics of the samples that included biomass bottom ash (BBA) were examined in the study [42] using various processing techniques, such as crushing, burning, and eliminating light particles. Using these methods, the researchers were able to measure how much the organic matter content of each material affected the longevity and mechanical characteristics of samples. Therefore, this study prepared geopolymer samples with three replacement ratios using untreated and treated BBA at 10, 30, and 50% by binder mass. In contrast to previous investigations, an alkaline activator, created by combining potassium hydroxide and Na_2SiO_3 solutions,

was used to activate the geopolymer binder. The outcomes showed that samples produced using BFA that had been processed had better longevity and mechanical characteristics.

From observation of the literature, it can be seen that both BFA and PG wastes have the potential to be used in the creation of new building materials [19,43,44]. The results of our earlier study [45] demonstrate that using BFA alone, without any additives, causes the specimens' strength development to be low. Thus, achieving acceptable technical qualities using a large BFA volume remains significant and problematic. The high organic matter content of the BFA influences the specimens' mechanical performance, water absorption capacity, and durability [46]. The study's findings showed that pre-treated BFA enhanced the mechanical and longevity properties of the samples.

It can be seen that when PGs are improperly disposed of, they take up much space on land and seriously harm the environment. Therefore, using PG as a calcium ion source in AAM and a component to ensure early BFA-based sample strength could effectively utilise both BFA and PG waste products [47–49]. In this study, water-mixed and alkali-activated paste samples were prepared with five proportions of calcined PG (10%, 20%, 30%, 50% and 70% by mass of binder) substituted for milled BFA.

The pure PG and pure BFA samples were investigated in the same way. This research was intended to investigate the effects of replacing different quantities of BFA with treated by calcination PG in the sample to assess the potential benefits of calcined PG in enhancing the physical and mechanical properties, structure development and mineralogical efficiency of the BFA-PG paste. This study has created a new binder, almost 100% from waste, with great potential to supplement existing traditional binders. Constructors often need materials that are light enough, but also have sufficient strength. There is still a need for products with high strength-to-density ratios and the presented research brings new insights to the development of such materials. The created composite can be used as a non-structural material in multistored construction and as a structural material for low-rise construction. This research includes the investigation of the density, mechanical properties, and structure of hardened paste. Furthermore, the products resulting from the hydration of BFA-PG pastes have been studied using thermogravimetry–differential thermal analysis (TG-DTA), scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques.

2. Materials and Methods

2.1. Materials

The BFA used in this research was sourced from a biomass power plant, where it was produced from pine tree wood chips. Table 1 details the chemical composition of the BFA. It can be observed that the primary oxides in the BFA are CaO (31.50%) and SiO₂ (22.91%). The BFA also contains alkalis in the form of K₂O (4.00%) and Na₂O (0.26%), along with a significant proportion of MgO (3.57%). Prior to its application, the BFA was milled to improve its reactivity. The milled BFA features a bulk density of 570 kg/m³, a true density 1852 kg/m³, a specific surface area of 835 m²/kg, and an average particle size of 11.83 µm.

According to the XRD results, quartz forms up to 52.0% of the BFA, dicalcium silicate up to 19.7%, portlandite up to 15.0%, lime up to 9.20%, and calcite up to 3.80% (Figure 1).

The chemical composition of the PG is presented in Table 1. The PG is formed from the reaction between sulphuric acid and natural apatite. With an insignificant quantity of SiO₂ (2.13%), the two main oxides in the PG are SO₃ (48.4%) and CaO (39.5%). Compared to the BFA, the PG has 1.25 times more calcium. Before utilisation, the PG underwent a calcination process for 24 h at 200 °C, then ground it into powder using a ball mill for 48 h. The PG serves as a part of the hydraulic binder, contributing to the early strength of the sample. The processed PG has a mean particle size of 15.23 µm, a specific surface area of 359 m²/kg, a bulk density of 719 kg/m³, and a true density of 2237 kg/m³.

The calcination process alters the main component of PG from CaSO₄·2H₂O to CaSO₄·0.5H₂O.

According to the XRD analysis (Figure 2), the unprocessed PG consists of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and some silicates. After calcination, the PG comprises anhydrite (CaSO_4) and hemihydrate gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$).

Table 1. Chemical compositions of the BFA and PG.

Compound Formula	BFA (wt%)	PG (wt%)	Compound Formula	BFA (wt%)	PG (wt%)
SiO_2	22.9	2.13	Y_2O_3	0.02	0.03
Al_2O_3	2.63	0.11	SrO	0.09	0.26
CaO	31.5	39.5	Na_2O	0.26	—
MgO	3.57	0.11	Cr_2O_3	0.02	—
SO_3	0.88	48.4	NiO	0.01	—
P_2O_5	2.71	1.09	Rb_2O	0.02	—
K_2O	4.00	0.05	BaO	0.17	—
ZnO	0.10	0.01	CeO_2	—	0.19
TiO_2	0.21	0.03	Nd_2O_3	—	0.07
MnO	2.07	0.01	Nb_2O_5	—	0.002
Fe_2O_3	2.32	0.01	F	—	1.41
CuO	0.02	0.01	LOI *	26.5	6.578

* Loss on ignition. The sum of PG is not equal to 100.

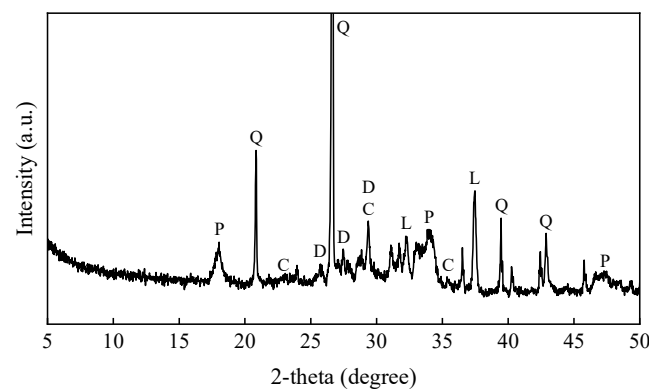


Figure 1. XRD curve of the BFA (D—dicalcium silicate, P—portlandite, Q—quartz, L—lime, C—calcite).

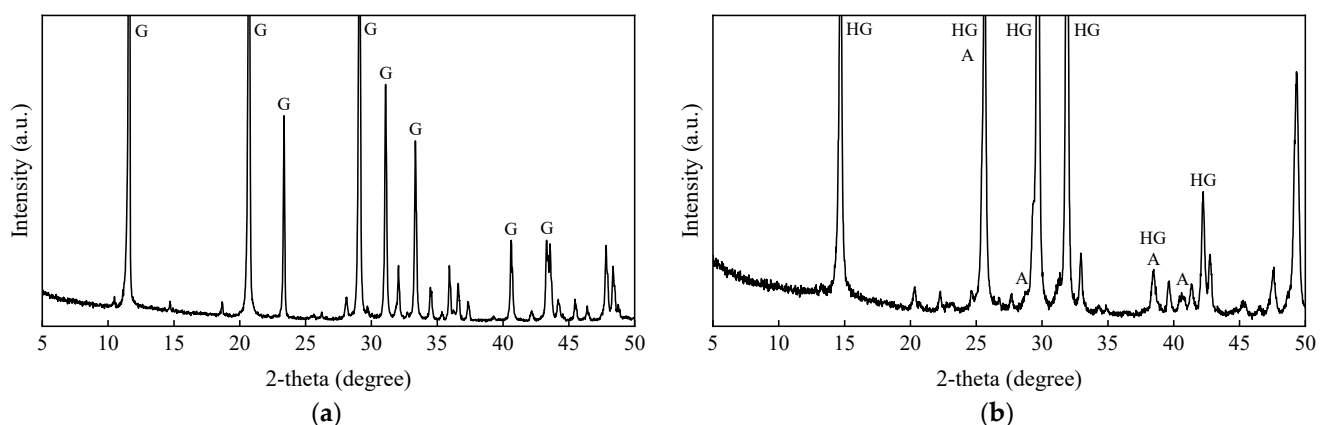


Figure 2. XRD curves of the (a) untreated PG and (b) calcined PG (A—anhydrite, HG—hemihydrate gypsum, G—gypsum).

Two components were used as an alkaline activator solution (AAS): Na_2CO_3 and sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$, $\text{H}_2\text{Na}_2\text{O}_4\text{Si}$) solution. Na_2CO_3 solution was prepared dissolving Na_2CO_3 crystalline powder with water. The density of the Na_2SiO_3 solution was 1388 kg/m^3 , its concentration was constant at 50 wt%, and the molar ratio of SiO_2 to

Na₂O was 3.2. Na₂SiO₃ has a boiling point of 100 °C. H₃BO₃ (purity 99.5%) was employed in the activation reaction as a retarder. H₃BO₃ was used in a solid state.

2.2. Paste Composition and Design

Water-mixed BFA-PG samples and alkali-activated BFA-PG samples have been manufactured in compliance with the compositions presented in Tables 2 and 3 to investigate how the water and alkali activators affect the samples' physical–mechanical properties and structure development. The impact of the partial BFA replacement by PG in the compositions was evaluated. Both the pure BFA and the PG samples were created to interpret the results thoroughly. The water–solid ratio of all the water-mixed samples was constant at 0.52.

Table 2. Composition of water-mixed pastes (wt%).

Sample	B100-P0	B90-P10	B80-P20	B70-P30	B50-P50	B30-P70	B0-P100
BFA	100	90	80	70	50	30	0
PG	0	10	20	30	50	70	100

Table 3. Composition of alkali-activated material pastes.

Sample	Binder Content		Na ₂ CO ₃ Solution Concentration	Na ₂ CO ₃ /Na ₂ SiO ₃ Solute Ratio
	BFA (wt%)	PG (wt%)	(wt%)	
B100-P0-A	100	0	15	0.90
B90-P10-A	90	10	15	0.90
B80-P20-A	80	20	15	0.90
B70-P30-A	70	30	15	0.90
B50-P50-A	50	50	15	0.90
B30-P70-A	30	70	15	0.90
B0-P100-A	0	100	15	0.90

The concentration of the Na₂CO₃ solution and Na₂SiO₃ solution was constant at 15 wt% and 50 wt%, respectively. Therefore, the ratio between Na₂CO₃/Na₂SiO₃ for the AAS preparation was chosen based on previous research [45,50] and kept constant at 0.90. Every composition had the same water–binder ratio of 0.52. All the water used in the compositions consists of extra water and the water in the Na₂CO₃–Na₂SiO₃ solution.

After mixing, the freshly prepared pastes were poured into 160 × 40 × 40 mm moulds. These were then compacted on a vibrating table for 20 s. The moulds filled with the paste were maintained in ambient conditions, with a relative humidity (RH) of 35 ± 5% and a temperature of 20 ± 2 °C, for 48 h. After this period, the pastes were removed from the moulds and stored under the same environmental conditions until they were tested.

2.3. Test Methods

The samples' bulk density and compressive strength, cured at ambient conditions for 2, 7, and 28 days, were estimated using the standard procedure [51].

Using a Pundit 7 device, the ultrasonic pulse velocity (UPV) method was used to assess the structure formation of the prepared specimens. The specimens were positioned between a transmitter and receiver running at 54 kHz ultrasonic transducers. The transducers were squeezed toward the specimens at two opposite positions, and petroleum jelly was applied to ensure proper contact between the transducers and the specimen [33]. The ultrasonic pulse velocity (UPV) was calculated using Equation (1):

$$UPV = \frac{l}{\tau} \cdot 10^6 \quad (1)$$

where l is the distance between the cylindrical heads of the transducers and τ is the time of pulse pervasion.

A high multichannel performance sequential Wavelength Dispersive X-ray Fluorescence (WD-XRF) spectrometer (AXI-OS-MAX, Panalytical, Eindhoven, The Netherlands) was used to analyse the BFA and PG powders. For 1440 s, the WD-XRF system was in use. “Omnian” software was used for the quantitative analysis, and correlating standards were employed for a standard-less analysis. A SmartLab (Rigaku, Tokyo, Japan) X-ray diffractometer was used to measure the XRD patterns of the studied BFA, PG, and AAM pastes using an X-ray tube with a 9-kW rotating Cu anode. The measurements were performed using Bragg–Brentano geometry with a graphite monochromator on the diffracted beam and a step-scan mode with a step size of 0.02° (in 2θ scale) and a counting time of 1 s per step. The measurements were conducted in the 2θ range of $5\text{--}50^\circ$. Phase identification was performed using the PDXL (Ver. 2.8, Rigaku) software package and the ICDD powder diffraction database PDF4+ (2021 release). The Reference Intensity Ratio (RIR) method was employed to determine the mineral content. Using a Linseis STA PT-1600 thermal analytical device (Selb, Germany), the TG/DTA lines of the starting materials and the AAM pastes were recorded up to 1000°C (at a rate of $10^\circ\text{C}/\text{min}$); the specimens weighed (50 ± 5) mg and the heating environment was the air.

The SEM EVO 50 EP (resolution 1.5 nm, Zeiss, Oberkochen, Germany) was used to evaluate the characteristics of the AAM pastes of different compositions.

3. Results

3.1. Density

In the initial seven days of curing, the density of the water-mixed specimens declined swiftly, by about 9.6–16.7%, then continued to decrease slowly until reaching 28 days, where it was reduced by 13.0–19.9%, as shown in Figure 3a. The findings indicate that specimen B0-P100, consisting solely of PG, possessed the highest density at any curing time. On the other hand, the specimen B100-P0, which contained only BFA, has the lowest density. An observed trend is that increasing the PG content led to a higher density in the paste. That is primarily because PG's the density was higher than the BFA's [32].

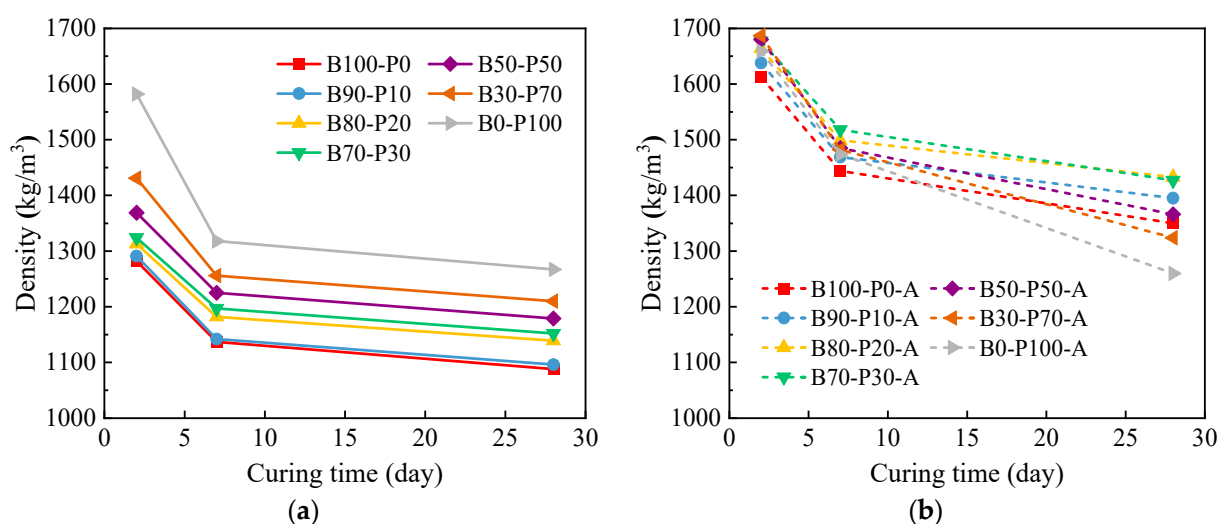


Figure 3. Density of BFA-PG specimens cured during 28 days: (a) with water; and (b) with AAS.

The density of the samples activated with AAS generally shows the different tendencies as in the compositions mixed with water. It can be noticed that the density of the sample with AAS, compared to the same composition mixed with water, is higher. Apparently, that results from the higher density of the AAS solution. Raising the amount of PG, the density of the samples increases. As shown in Figure 3b, the density mainly decreases until seven days of curing (9.5–12.2%). During the 28 days of curing, the specimens' density decreased

to 13.9–24.1%. It is seen that with the increase of PG in composition, the density decreases more visibly, possibly due to the presence of AAS, which stops PG hydration, and more unbounded water can evaporate during curing [52].

3.2. Ultrasonic Pulse Velocity

The patterns in the density are mirrored in how the BFA-PG pastes' structure develops, as illustrated in Figure 4. For the water-mixed samples with both BFA and PG, there was a notable rise in the UPV values from day 2 to day 7, followed by a more gradual increase up to day 28. This suggests that the structure formation predominantly occurred within this timeframe. For the sample B100-P0, the UPV value initially rose during the first seven days but then experienced a slight decline by day 28. As the proportion of PG in the paste increases, so does its UPV value. The sample B0-P100, containing only PG, consistently samples the highest UPV value.

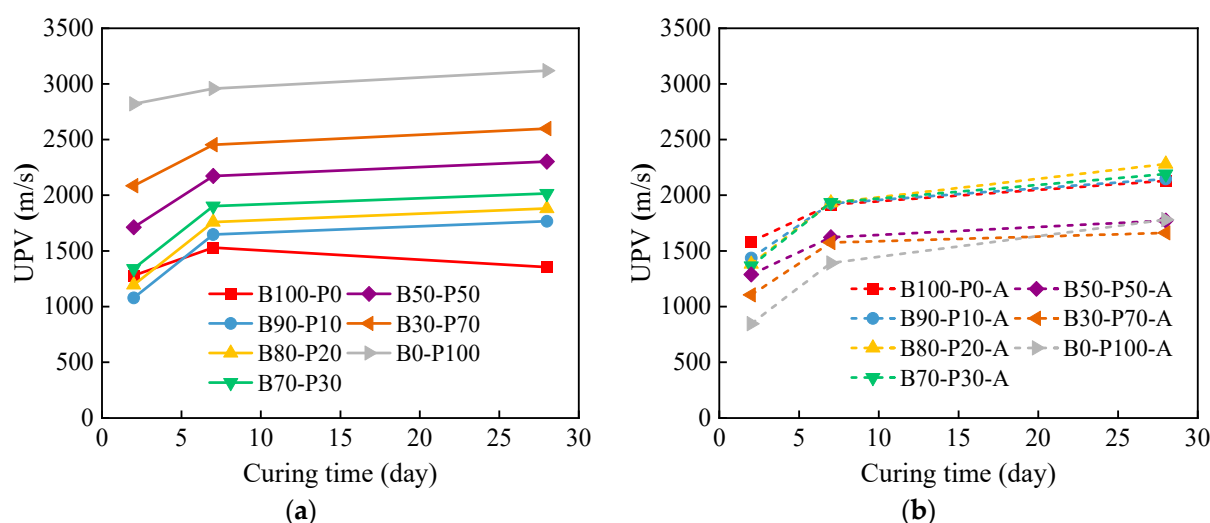


Figure 4. UPV value of BFA-PG specimens cured during 28 days: (a) with water; and (b) with AAS.

The AAS influence on the structure development is the same as presented in the UPV test (Figure 4b). The presented tendencies are contrary to the water-mixed samples. The UPV values of the PG-based samples are lowest, but for the BFA-based samples the highest. The UPV values of the samples with both BFA and PG containing AAS are lower than those of the sample mixed with water (up to 20–35%) while, for pure PG-based samples, more than three times. The main compaction of the structure took place during the first seven days when the UPV increase reached 4–6%. Then, during 28 days, the UPV values increase up to 8–10%. This difference confirms that in the samples with AAS, the structure densification due to the reaction of the components is slightly retarded, and the UPV values are lower. The UPV values of the samples mixed with water after 28 days of curing are slightly less than, or the same as, those samples containing AAS.

3.3. Compressive Strength

Following a seven-day curing period, the water-mixed specimens' compressive strength increased from 2.74 to 15.84 MPa as the PG amount rose from 0 to 100 wt%, as shown in Figure 5. The most visible strength increments were observed when the amount of PG exceeded 50 wt%. After 28 days of curing, the specimens' compressive strength further rose from 3.02 to 26.53 MPa with the rising PG content, suggesting that the specimens with more than 50 wt% PG have superior mechanical properties.

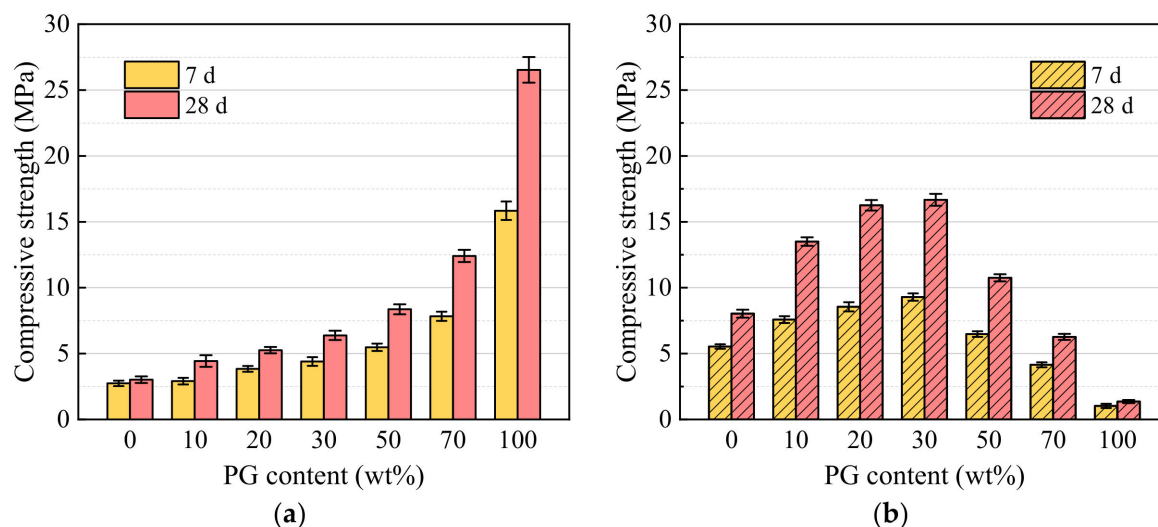


Figure 5. Compressive strength of BFA-PG specimens cured during 28 days: (a) with water and (b) with AAS.

As pointed out in research [21], the calcined PG specimen compressive strength grows to 3.5 MPa. When calcined PG was replaced (up to 30 wt%) with different additives (rice husk ash, porcelain or ceramic waste), the compressive strengths of specimens that included ceramic and porcelain wastes were 3.9 and 3.0 MPa. However, because of the high SiO_2 content in the rice husk ash, specimens containing it had a compressive strength that was 43% higher than the specimen containing only pristine PG. Bearing in mind the results reviewed and based on our results, it can be concluded that BFA, in combination with PG and mixed with water, worsens the mechanical properties of samples compared to pure PG specimens.

When AAS was used in compositions, the BFA impact on the BFA-PG specimens changed fundamentally. After seven days of curing, the compressive strength of the specimen reaches 5.54 MPa when only BFA is applied in the composition. This value is about two times higher than in the water-mixed samples. Increasing the PG amount in the composition until 30% increases the compressive strength of the samples to 9.29 MPa. The compressive strength value is about 2.1 times higher than in the same compositions of water-mixed specimens.

Further increase of the PG amount no longer contributes to compressive strength growth. Samples having 50% of PG reach just 6.48 MPa compressive strength. A higher amount of PG (70–100%) decreases the compressive strength to 4.15–1.03 MPa. This value is about 2–15 times lower than in water-mixed PG samples. Following a curing period of 28 days, the compressive strength of the specimens containing PG in all compositions showed an increase of approximately 30–90% (compare to 7-days strength).

For the pure BFA-based sample, the compressive strength growth is about 45%. Higher compressive strength values (16.25 and 16.67 MPa) are observed for compositions with BFA/PG ratios 4 and 2.33. For these compositions, the compressive strength is up to 3.1 times higher than in the same water-mixed compositions. This BFA/PG ratio ensures the highest strength values, and alkali activation significantly benefits the BFA and PG synthesis reactions (Figure 5b). In research [32], the same evaluated effect was observed with different amounts of BFA replacement to PG (hemihydrate type) in the presence of 10 M NaOH and sodium silicate. After solidification of the samples at 60 °C for 24 h and keeping them at ambient temperature for 26 days, the sample with 10–20% BFA replacement to PG shows the highest compressive strength—12–16 MPa. The use of less alkali activator, in our case, allowed us to reach higher compressive strength than is pointed out in [32].

3.4. XRD Study

After 28 days of curing, XRD tests were conducted to analyse the reaction products of specific specimens (B100-P0, B80-P20, B50-P50, and B0-P100), as depicted in Figure 6. In specimen B100-P0, the primary minerals identified were quartz and calcite, along with the presence of dicalcium silicate, portlandite, and lime. These minerals are also predominant in the raw state of the BFA, as shown in Figure 1. Comparing the BFA powder's XRD curve in Figure 1, it is observed that the intense lime peaks around $30\text{--}45^\circ 2\theta$ are reduced, suggesting the consumption of the lime when the BFA reacts with water.

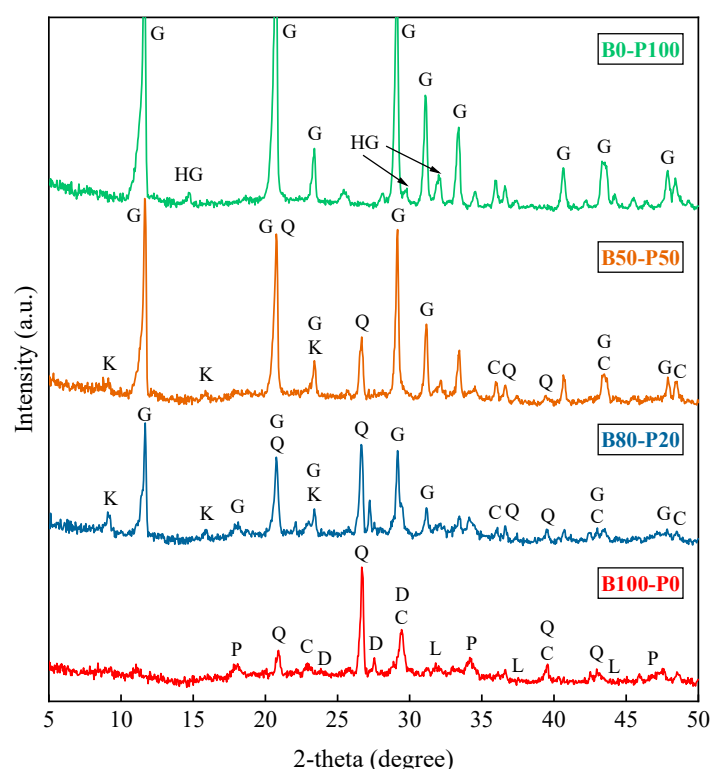


Figure 6. XRD curve of BFA-PG specimens with water after 28 days of curing. (HG—hemihydrate gypsum, P—portlandite, Q—quartz, L—lime, D—dicalcium silicate, C—calcite, G—gypsum, K—kottenheimite).

The primary minerals in the B80-P20 specimen are gypsum, quartz, kottenheimite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)_2$), and calcite. The presence of gypsum is indicative of the PG hydration process. The quartz and calcite in the sample originate from the BFA. Kottenheimite, a new mineral formed in this context, results from the reaction between the PG and BFA. The mineral kottenheimite ($\text{Ca}_3\text{Si}(\text{OH})_6(\text{SO}_4)_2$) is formed by the presence of the PG mineral and BFA minerals. The BFA is the supplier of SiO_2 . The PG dissolves and participates in the solid product formation. The PG is a supplier of SO_4^{2-} and Ca^{2+} ions, enhancing the formation of secondary reaction products, such as kottenheimite. It can be noticed that the mineral kottenheimite has a higher density (1930 kg/m^3) than the BFA, which has a density of 1852 kg/m^3 .

In the B50-P50 specimen, the mineral composition is similar to the B80-P20 specimen, but there is a noticeable increase in the intensity of the gypsum peaks and a decrease in the intensity of the kottenheimite peaks. The XRD pattern of the hydrated PG (specimen B0-P100) predominantly displays the mineral gypsum, with small amounts of hemihydrate gypsum also detected. The reaction products in the samples containing AAS, such as B100-P0-A, B80-P20-A, B50-P50-A, and B0-P100-A, remained consistent, as verified by XRD tests conducted after 28 days of curing, shown in Figure 7. Notably, the main mineral composition of the specimen B100-P0-A did not show significant changes.

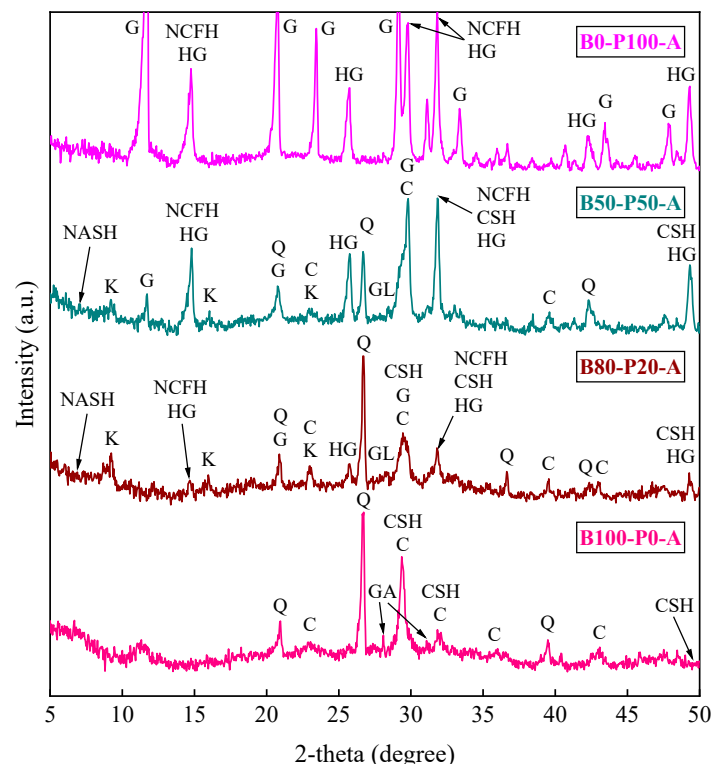


Figure 7. XRD curve of BFA-PG specimens with AAS after 28 days of curing. (HG—hemihydrate gypsum, Q—quartz, C—calcite, G—gypsum, K—kottenheimite, GL—glauberite, GA—gaylussite, CSH—calcium silicate hydrate, NASH—sodium aluminium silicate hydrate, NCFH—sodium calcium sulphate hydrate).

The crystalline phases, such as the quartz in the raw BFA, remained unchanged after the BFA pastes were activated. The study [45] reported the same observations. There is an increased rate of calcite, C-S-H and gaylussite minerals crystallisation [53], whose presence regulates the increase in the compressive strength of the AAM pastes based on BFA. The study [54] also discovered weakly crystallised C-(A)-S-H gels in such compositions due to the availability of the Ca^{2+} precipitated rapidly with CO_3^{2-} to produce calcite and gaylussite. The conversion of the initially precipitated CaCO_3 into subsequent phases significantly affects how quickly the reaction proceeds.

The presence of the AAS entirely alters the mineral crystallisation in the paste containing PG. It should be emphasised that the formation of gypsum is severely inhibited when alkali is present in the compositions. For sample B80-P20-A, the intensity of peaks of the mineral kottenheimite increased, but the quartz and calcite peaks' intensity did not change. The gypsum crystallisation in the B80-P20-A specimen is much smaller than in the pure PG specimen. Somewhat more intense peaks of unhydrated hemihydrate gypsum are observed. Some portlandite, C-S-H, and glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) are identified [54,55]. The same observations are presented in studies [56–58], proving that alkalies retard gypsum creation and possible new products created in the presence of PG can be hydration products, such as cesanite ($\text{Ca}_{1.31}\text{Na}_{4.32}(\text{OH})_{0.94}(\text{SO}_4)_3$), which are responsible for the increasing strength properties [59]. In our case, the reaction between sodium ions from the AAS and BFA minerals resulted in the mineral sodium aluminium silicate hydrate (N-A-S-H, $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot 216\text{H}_2\text{O}$) development [38,60]. The mineral sodium aluminium silicate hydrate is also responsible for the increasing strength properties [32,56]. Its density according [61] is 2300 kg/m^3 . Generally, such types of minerals possess density varies from 2200 kg/m^3 to 3005 kg/m^3 [62]. Additionally, sodium calcium sulphate hydrate (N-C-F-H, $\text{Na}_{0.84}\text{Ca}_{2.58}(\text{SO}_4)_3\cdot \text{H}_2\text{O}$), density 2500 kg/m^3 , was identified [50]. We suppose that the excess of Na ions promotes the formation of N-C-F-H on the surface of unreacted hemihy-

hydrate particles, which can cover the surface of these products and block the hydration of hemihydrate gypsum.

With an increased amount of PG in the composition (specimen B50-P50-A), the gypsum peak intensity falls to a very low level. The peak intensity of hemihydrate gypsum, compared to the B80-P20-A composition, significantly increases, which proves our assumption that thin films of hydration products block the hydration of hemihydrate gypsum. We can underline that the gypsum creation in the presence of the alkalies is strongly suppressed. It can be pointed out that the kottenheimite, portlandite, C-S-H, and sodium aluminium silicate hydrate peaks' intensity decreased, whereas the sodium calcium sulphate hydrate peaks' intensity increased. The amorphous phase is less apparent in this composition.

The XRD pattern of the pure B0-P100-A shows that the presence of AAS shows the domination of mineral gypsum. Small amounts of hemihydrate gypsum and sodium calcium sulphate hydrate are observed. Mineral kottenheimite is not identified.

It can be concluded that the presence of AAS in the BFA-PG-based samples due to sodium ions' participation in the reactions, significantly reduces gypsum crystallisation, but increases the crystallisation of the new denser phases such as kottenheimite, sodium aluminium silicate hydrate, and sodium calcium sulphate hydrate. These new minerals are responsible for the increasing strength properties of the specimens. In the B80-P20-A composition, where BFA/PG ratio is 4:1, the alkali activation significantly benefits the BFA and PG synthesis reactions. The alkaline activator breaks the Si-O-Si bonds and further forms Si-O-Na⁺ bonds, joining SO₄²⁻ and Ca²⁺ ions in the new phasis.

3.5. DTA/TG Study

The TG-DTA tests were adopted to analyse the differences between water-mixed samples and samples activated with AAS. Figure 8 displays the test outcomes. Pure BFA water-mixed samples show two endothermic peaks, one belonging to water released at a temperature of 100 °C and another at the temperature interval of 700–760 °C, corresponding to the breakdown of CaCO₃. The burnt-out organic portion of BFA is represented by the exothermic peak in the 300–500 °C temperature range [54,63].

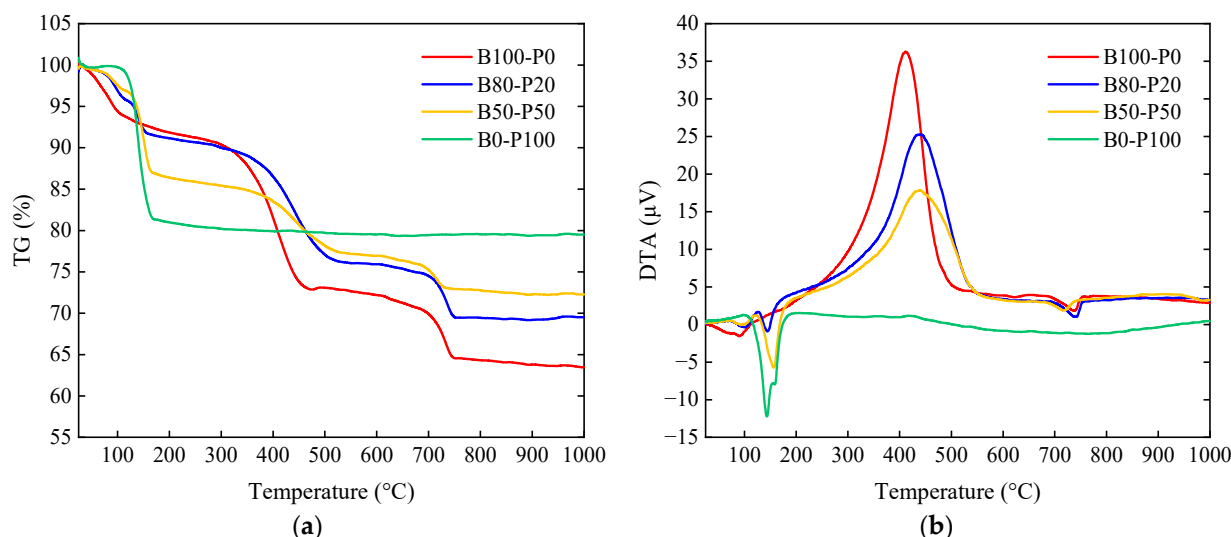


Figure 8. TG (a) and DTA (b) curves of BFA-PG-based pastes with water.

In the pure PG sample, two endothermic peaks at 145 and 170 °C belong to gypsum dehydration to hemihydrate [55]. In the composition where both BFA and PG are mixed with water, three above-mentioned endothermic peaks and one exothermic peak are observed. With increased PG amount in the compositions, the endothermic peaks at 145 and 170 °C are more visible, but the exothermic peaks belonging to the BFA organic part burning decrease. The decomposition of calcite at 700–760 °C is less visible with

an increase in the amount of PG. According to the weight loss results, with a rise of PG quantity in the composition (from 0 to 100%), the mass loss of physically bound water decreases from 6 to 0%. At high temperatures (around 100–110 °C), the decomposition of C-S-H and kottenheimite in the specimens with BFA may occur [64,65]. In the 100–200 °C temperature range, the weight loss increases up to 2.6 times, with an increase in the PG amount in composition. The mass losses reach 8% in the pure BFA sample, 10 and 14% in the B80-P20-A and B50-P50-A samples, and 21% in the pure PG sample. The mass loss increased due to gypsum dehydration to hemihydrate, kottenheimite, and sodium calcium sulphate hydrate dehydration.

In the 200–550 °C temperature range, the weight loss of specimens is the same depending on the BFA and PG ratio in the specimens. With an increasing PG/BFA ratio, the mass loss (mass loss value at 550 °C) due to the organic part burning process decreases from 27% to 23%. The weight loss at this temperature range is not identified in the PG-based composition with no BFA. The weight loss in the temperature interval of 550–750 °C relates to the calcite decomposition, and the tendencies show that BFA, in which the composition CaCO_3 [45] is presented in significant amount, represents the essential mass loss (35.5%), whereas in compositions where the BFA and PG ratio is 1 (B50-P50-A) shows 1.33 times lower mass loss—27%. The mass loss is not identified in the composition where PG is the main component. The mass loss is minimal at the 750–1000 °C temperature range.

The TG-DTA tests were used to identify the obtained compounds formed during the hydration and alkali activation reactions. The samples prepared with AAS have the same endothermic and exothermic peaks as those prepared with water. However, due to the appearance of AAS reactions and new synthetic products, the temperature and mass loss during thermal effects differ significantly.

Until the temperature is 100 °C, the loss of mass, related to water evaporation and possibly the dehydration of sodium carbonate groups or CASH gel, is observed [54]. The presence of Na_2CO_3 (mineral natron, or thermonatrite) in the AAS can contribute to the growth of weight loss because this mineral can decompose in the temperature interval of 50–90 °C [54,64,65]. The weight loss at this temperature interval in the compositions with AAS is 2 times higher than in water-mixed compositions. The dehydration of C-S-H and kottenheimite in the temperature (around 100–110 °C) increases the weight loss. This assumption is confirmed by the XRD results (Figure 9). The weight loss at 100–200 °C in the specimens with BFA is 1.9–1.2 times higher than in the specimens with similar composition mixed with water. A higher amount of BFA is responsible for the higher weight loss in this temperature range.

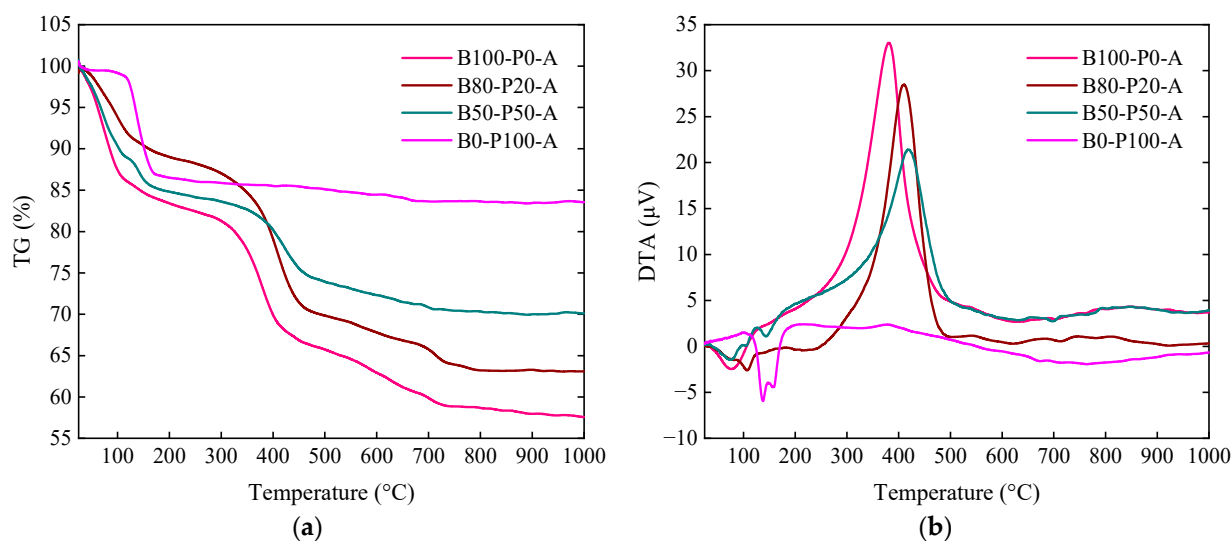


Figure 9. TG (a) and DTA (b) curves of BFA-PG-based pastes with AAS.

The peak, relating to the endothermic effect at 125–180 °C in the DTA curve of B80-P20-A, B50-P50-A, and B0-P100-A compositions, corresponds to the process of the PG crystal losing crystal water [66,67]. As in the case of water-mixed samples, XRD results confirm this assumption. The research [68] states that gypsum can dehydrate to hemihydrate at temperatures between 95 and 180 °C. In the temperature range of 200 °C, decomposition occurs in N-A-S-H, which is identified in the XRD tests [32]. The weight loss in specimens is additionally affected by the breakdown of the mineral gaylussite. The decomposition of gaylussite happens in the 200–250 °C temperature range [69,70]. In the 200–240 °C temperature interval [71], chemically bounded water leaves the samples, and the last amounts of hemihydrate gypsum turn into CaSO_4 [66]. Beyond 240 °C, in the temperature interval until 550 °C, the typical exothermic peak at 420–430 °C corresponds to the burning out of the organic part of BFA [54,63]. In the pure PG specimen, the weight loss is less. It is important to note that in the temperature interval 200–550 °C, the weight loss of the AAS mixed specimens with BFA, due to the decomposition of newly created products is 25% higher than in the identical composition specimens mixed with water. The endothermic decomposition of CaCO_3 to CaO ranges from 550–750 °C. Compared to specimens of the same composition mixed with water, the weight loss of alkali-activated specimens containing BFA is 20% larger. These results show that, in the presence of AAS in the composition with BFA, some additional CaCO_3 is created. The weight loss of alkali-activated specimens containing BFA is 25% larger than that of water-mixed specimens in the temperature range between 750–1000 °C. That can happen because of mineral glauuberite decomposition. As pointed out in the literature, glauuberite decomposition happens at 910–930 °C [72].

3.6. Microstructure

The variations in the microstructure of the pure water hydrated by water PG and PG, activated with AAS, or pure BFA, mixed with water and activated with AAS, are observed in the SEM images Figures 10–12.

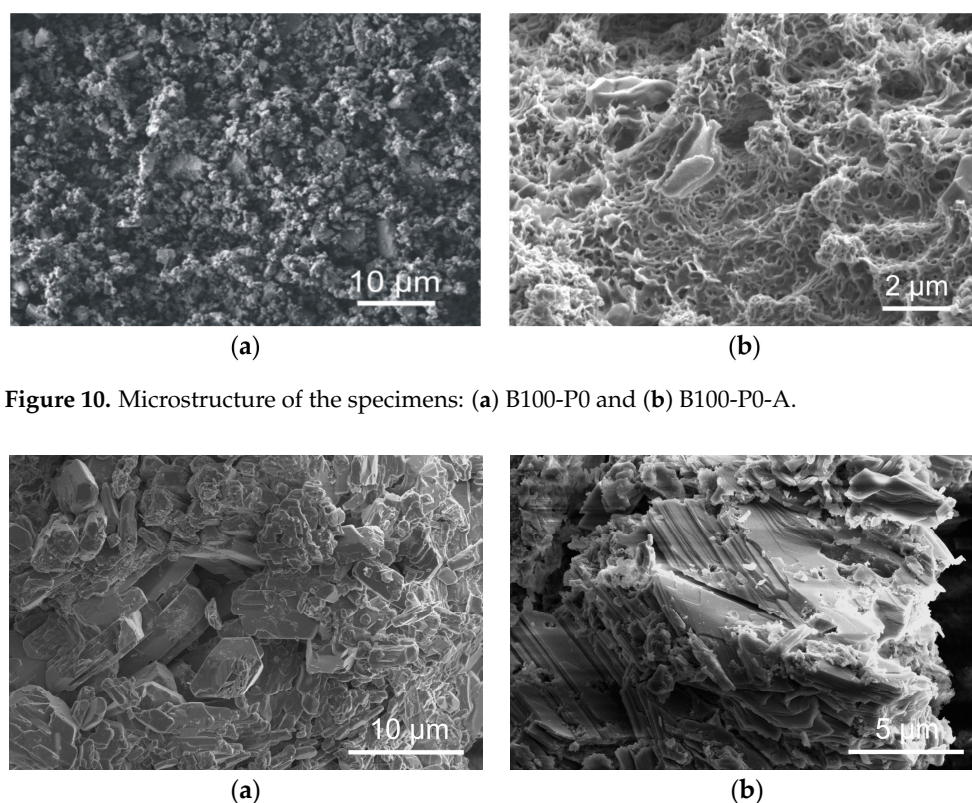


Figure 10. Microstructure of the specimens: (a) B100-P0 and (b) B100-P0-A.

Figure 11. Microstructure of the specimens: (a) B0-P100 and (b) B0-P100-A.

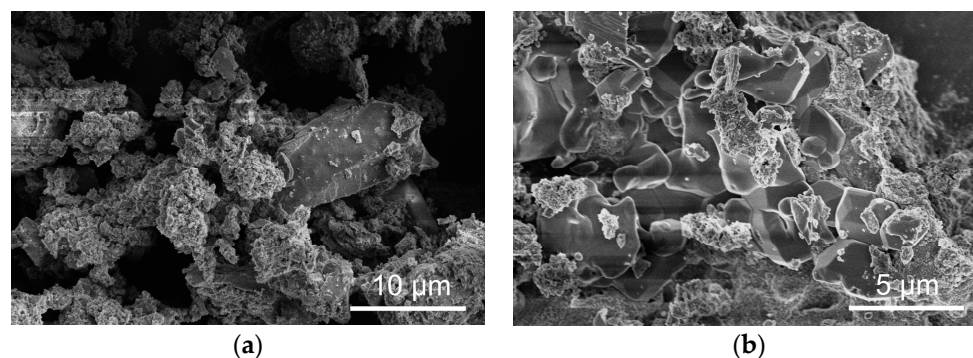


Figure 12. Microstructure of the specimens: (a) B80-P20 and (b) B80-P20-A.

In the BFA samples mixed with water, as depicted in Figure 10a, an inhomogeneous porous structure is evident, characterised by remnants of wood combustion and sand particles. Conversely, in the BFA samples activated by AAS, the structure appears more uniform, exhibiting a high concentration of fine pores (Figure 10b). The release of calcium from the BFA, which contributes to the activation reactions, yields the formation of a microstructure comprising a small, porous gel.

The PG sample displays well-crystallised gypsum crystals when hydrated with water, as seen in Figure 11a. In contrast, the structure of the PG sample activated by AAS, shown in Figure 11b, is noticeably different. The regular gypsum crystals have been disrupted, resulting in a visible structure of fractured gypsum crystal plates.

Figure 12a presents the samples with both BFA and PG prepared with water. These samples exhibit an inhomogeneous structure, characterised by visible voids and pores. Large gypsum crystals are apparent within this structure. The coarser gypsum crystals have crystallised, which is why there are evident empty spaces and cracks. This particular structural composition significantly reduces the samples' density and compressive strength.

When the BFA-PG mix is activated with AAS, a visible change in the structure is observed, as shown in Figure 12b. The structure becomes denser, with gypsum crystals losing their regular shape and the gel structure exhibiting no visible pores. The specimens' higher compressive strength at 28 days could have resulted from this more compacted microstructure. Overall, it is noteworthy that specimens demonstrating beneficial uniformity and a dense gel structure correlate with compositions that possess higher mechanical strength.

4. Conclusions

This study explores the potential of employing BFA and PG, which are hardly utilised, to mitigate environmental effect, reduce greenhouse gas emissions, address climate change, and conserve natural resources. The created composite can be used as a non-structural material in multistored construction and as a structural material for low-rise construction. This research established how the ratio of PG/BFA affected the mechanical strength, density, structure, and mineral composition of the water-mixed and alkali-activated BFA-PG pastes. The following conclusions were made:

The higher the PG/BFA ratio in water-mixed BFA-PG composition, the higher the density and UPV of the samples. The specimens' higher AAM density can be attributed to the denser structure formed in the alkali-activated BFA-PG composition. As expected, incorporating PG enhances the mechanical properties of water-mixed BFA-PG specimens. The water-mixed BFA-PG composition specimens have higher compressive strengths when the PG/BFA ratio is higher. Alkali-activated pure BFA specimens have compressive strengths up to twice as high as water-mixed specimens.

Increasing the BFA replacement up to 20–30% of PG in alkali-activated composition increases up to 2.1 times the compressive strength compared to pure BFA specimens and up to 3.1 times compared to the same composition water-mixed specimens.

A higher amount of PG (50–100%) significantly decreases compressive strength because the alkali activation reactions stop gypsum crystallisation. Such an amount of PG of 20–30% is sufficient for the highest mechanical properties.

The XRD test reveals that gypsum crystallisation occurs when the amount of PG in the water-mixed BFA-PG compositions increases. Furthermore, the mineral kottenheimite formation is seen as the result of the reaction between PG and BFA.

The presence of an alkali activator in the BFA-PG-based specimens significantly reduces the gypsum crystallisation, but due to presence of Na ions, Si-O-Na⁺ bonds formation and joining SO₄²⁻ and Ca²⁺ ions in the new phasis increases the new dense minerals, such as kottenheimite and sodium aluminium silicate hydrate crystallisation, which are responsible for the growth of strength, when the PG/BFA ratio is 1:4 and 3:7.

These new features will allow the utilisation of large amounts of BFA, obtaining a sufficiently lightweight binders that ensures high mechanical properties.

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