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Engineering and Life Cycle Assessment (LCA) of Sustainable Zeolite-Based Geopolymer Incorporating Blast Furnace Slag

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Abstract: This study aims to investigate the preparation of zeolite-based geopolymer composites incorporating blast furnace slag at various temperatures and varying amounts of blast furnace slag as potential sustainable building and construction materials. The primary objectives were to use mining waste streams for geopolymer production and assess the mechanical behavior of these hybrid geopolymers, along with performing a life cycle assessment (LCA) to compare their environmental impact with conventional concrete. It was observed that the hybrid geopolymers attained a maximum mechanical strength of 40 MPa. Remarkably, substituting just 20% of the material with blast furnace slag resulted in a 92% improvement in compressive strength. To assess environmental impacts, a cradle-to-gate LCA was performed on different geopolymer mix designs, focusing particularly on the global warming potential (GWP). The results indicated that geopolymer concrete generated a maximum of 240 kg CO₂-e/m³, which was 40% lower than the emissions from ordinary cement, highlighting the environmental advantages of geopolymer materials. Further, X-ray diffraction was used to determine the mineral composition of both raw and developed composites. Solid-state nuclear magnetic resonance (NMR) was applied to study the molecular structure changes upon incorporating blast furnace slag. The initial setting time and shrinkage of the geopolymers were also investigated. Morphological characteristics were analyzed by scanning electron microscopy (SEM). Thermal analyses confirmed the stability of the geopolymers up to 800 °C. Geopolymer composites with high thermal stability can be used in construction materials that require fire resistance. This study not only enhances the understanding of geopolymer composite properties but also confirms the substantial environmental advantages of utilizing geopolymerization in sustainable construction.



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1. Introduction

The production and use of ordinary Portland cement (OPC) in construction have increased at an annual growth rate of approximately 4% over the past decade and are driven by rapid urbanization and growing industrial projects [1]. However, this growth negatively impacts environmental sustainability, as OPC production significantly contributes to anthropogenic CO₂ emissions. Notably, the production of one ton of OPC leads to the release of about 0.8 tons of CO₂, primarily during the calcination process at temperatures between 1400 and 1500 °C [2–4]. This scenario highlights the urgent need for environmentally sustainable alternatives to OPC [3].

Geopolymer technology significantly contributes to sustainable construction through its environmentally friendly attributes. Primarily, it reduces the construction industry's carbon footprint by utilizing industrial by-products like fly ash, blast furnace slag (BFS), and

metakaolin as base materials, thereby minimizing reliance on carbon-intensive OPC. The production of geopolymers involves lower CO₂ emissions compared to OPC, addressing one of the major sources of greenhouse gases in the construction sector. Additionally, the use of industrial by-products in geopolymer synthesis not only diverts them from storage facilities, reducing waste, but also conserves raw materials by decreasing the demand for raw natural resources [3,5–12]. Moreover, geopolymers exhibit superior mechanical properties, thermal stability, and chemical resistance, which translate into longer-lasting, more durable structures [13,14]. This durability means fewer frequent repairs and replacements, further diminishing the overall environmental impact through reduced material consumption and waste over the building's life cycle. In essence, geopolymer technology expresses the principles of sustainability in construction by lowering emissions, repurposing waste, and enhancing building longevity.

Blended geopolymer systems, combining low- and high-calcium source materials, offer a balanced approach to construction materials by leveraging the strengths of each category while mitigating their weaknesses [15–17]. Low-calcium geopolymers, sourced from materials like metakaolin or mined zeolite, are valued for their thermal stability and chemical resistance. They are highly suitable for fire-resistant coatings and structures in construction [15,18]. Their ability to withstand high temperatures also makes them ideal for insulating furnaces and industrial equipment [15]. In the field of metallurgy, these geopolymers can serve as protective coatings for metals, effectively preventing oxidation and corrosion under extreme heat [19]. However, they often require longer setting times and higher curing temperatures [3,20–27]. High-calcium geopolymers, derived from BFS, for example, are known for their quick setting times and enhanced mechanical properties, making them suitable for infrastructure applications, but they can suffer from low workability and high drying shrinkage when used alone [3,28,29]. Blending these types of materials results in geopolymers that exhibit the quick setting and robust mechanical properties of high-calcium materials, along with the stability and chemical resistance of low-calcium materials, improving overall performance and versatility for sustainable construction [30–35].

A comprehensive review of existing literature reveals that a diverse array of low-calcium precursors, when combined with BFS, have been employed to create hybrid geopolymer systems. However, mined zeolite waste, despite its abundance and cost-effectiveness, has rarely been used in geopolymer production, either as a primary or a supplementary component. To our knowledge, the specific blend of zeolite and BFS for geopolymer synthesis has yet to be explored. Furthermore, there is a noticeable gap in understanding the environmental impacts and the engineering properties of such unique geopolymer composites manufactured using two waste streams. Therefore, the aim of this study is to assess the feasibility of using mined zeolite and BFS in geopolymer production. Additionally, we aim to conduct an economic analysis and a sustainability assessment through LCA analyses, providing critical insights into the environmental impacts, global warming potential in particular, of these novel composites in construction applications [8,24,36].

2. Materials and Methods

2.1. Zeolite and BFS

The experiments used waste zeolite sourced from an Australian mine, featuring particle sizes less than 54 µm. Ground BFS with an average particle size under 35 µm was supplied by Independent Cement and Lime Pty. Ltd., (Melbourne, Australia) Particle size significantly influences geopolymerization efficiency and the properties of the resultant geopolymers by affecting different stages of the geopolymerization reaction. Generally, finer zeolite particles (<125 µm) provide a larger surface area, accelerating the dissolution of aluminosilicate materials, which leads to higher mechanical strength compared to larger particles. The effect of varying particle sizes on the properties of geopolymer materials was explored in a separate study [8,37]. Further details are available in supplementary section. The chemical compositions of both the mined zeolite and BFS were analyzed using X-ray

fluorescence (XRF), as documented in Table 1. According to the table, the mass ratios of silicon to aluminum (Si/Al) in the mined zeolite and BFS were 4.9 and 2.1, respectively. It was noted that impurities such as quartz in the mined zeolite were not part of its structural framework, which could potentially alter the actual Si/Al ratio, as referenced in [38].

Table 1. Chemical composition of mined zeolite and BFS using XRF analyses.

	Component Oxide (wt.%)											
	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	MgO	Na ₂ O	TiO ₂	P ₂ O ₅	SO ₃	MnO	LOI ¹
Mined zeolite	67.49	12.18	3.04	1.83	1.43	0.95	0.94	0.21	0.03	0.01	0.06	11.83
BFS	32.35	13.32	41.81	0.32	0.29	5.31	0.21	0.55	0.02	2.73	0.21	1.51

¹ LOI: loss on ignition at 1050 °C.

2.2. Chemicals

A 40% *w/w* sodium hydroxide solution, acquired from Chem-Supply Pty Ltd. (Gillman, Australia), was diluted to achieve a concentration of 5 M. Additionally, a sodium silicate solution (grade D) with a SiO₂/Na₂O mass ratio ranging between 1.95 and 2.05, obtained from PQ Australia Pty Ltd. (Malvern, PA, USA), was used as-is in the experiments.

2.3. Sample Preparation

Zeolite ore, 5 M sodium hydroxide, and sodium silicate liquid were combined using a mechanical stirrer for 20 min to create a consistent slurry. BFS was then incorporated into the blend at a BFS/solid mass ratio of 10%, 20%, or 30% [39], with sufficient water added to achieve a water/solid mass ratio of 7.7%. The ratios of solid to liquid and sodium hydroxide to sodium silicate were maintained at 1.3 and 3.5, respectively, throughout the process. Adding BFS at the end was crucial due to its rapid setting properties, as premature addition could cause early hardening of the mixture, hindering the dissolution of the mined zeolite. The prepared slurry was cast into cylindrical molds (100 mm in height and 50 mm in diameter) and cured at ambient temperature, 40 °C, and 60 °C for up to 28 days. We considered 5 repetitions for each sample to ensure the reliability and reproducibility of the results. All samples were sulfur-capped prior to the compressive strength testing. The experiment's procedure is detailed in Figure 1. To avoid excessive drying during thermal curing, samples were hermetically sealed. For accuracy, all tests and characterizations were conducted in triplicate, with average results reported. Details of sample coding and synthesis methods are outlined in Table 2.

Table 2. Sample names and variables studied.

Sample Code	BFS/Total Solid (%)	Temperature (°C)
ZS10–25 °C	10	25
ZS10–40 °C	10	40
ZS10–60 °C	10	60
ZS20–25 °C	20	25
ZS20–40 °C	20	40
ZS20–60 °C	20	60
ZS30–25 °C	30	25
ZS30–40 °C	30	40
ZS30–60 °C	30	60

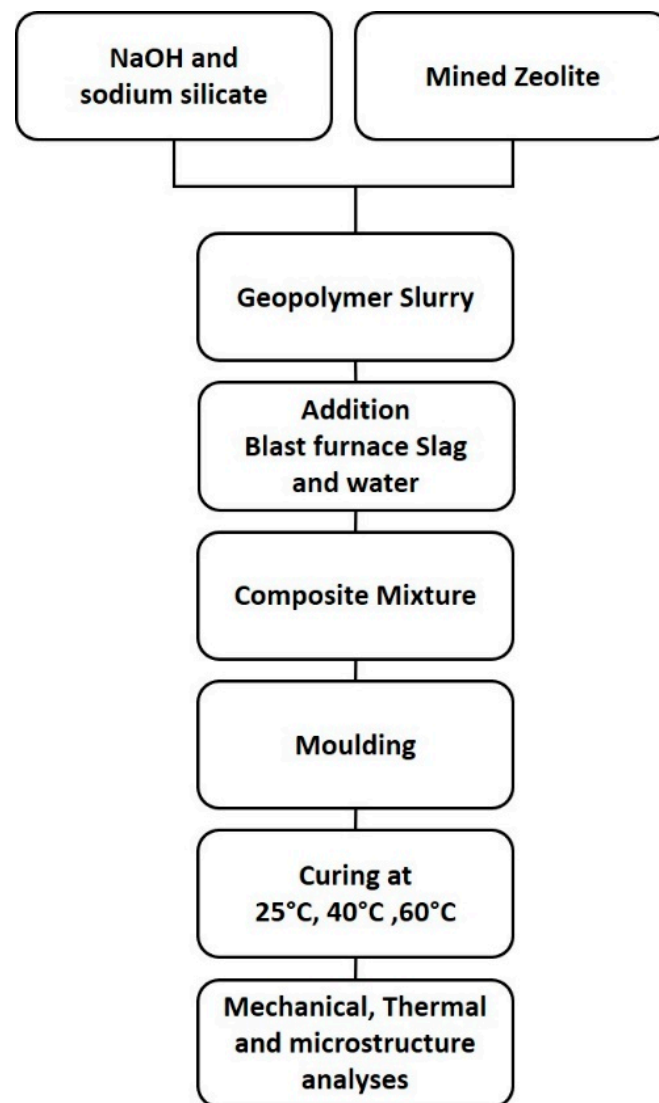


Figure 1. Geopolymer composite production process.

2.4. Environmental Sustainability Assessment

The life cycle inventory (LCI) for geopolymer production was developed on a laboratory scale to assess the environmental impacts of its production process, as depicted in Figure 2. This LCI encompasses both the inputs and outputs related to the geopolymerization process, including the extraction of raw materials, transportation, and manufacturing [40,41]. In this study, components like BFS, chemical solutions, and mine waste, along with energy and water inputs, were taken into account. The study primarily focuses on evaluating the global warming potential (GWP) at an industrial scale, as environmental impacts can vary significantly with changes in energy and resource needs. Therefore, the functional unit for analysis is set at 1 cubic meter (1 m³) of concrete. To calculate emissions from production, data regarding energy requirements, mixing, and curing processes were collected from primary sources and analyzed using GaBi software version 10.5.1.124. The study adheres to relevant standards and guidelines such as ISO 14040 and ISO 14044 and specifically follows EN 15804 for LCAs of construction materials [42–45]. Information was sourced both from literature and software or local databases, with more detailed information available in the supplementary section.

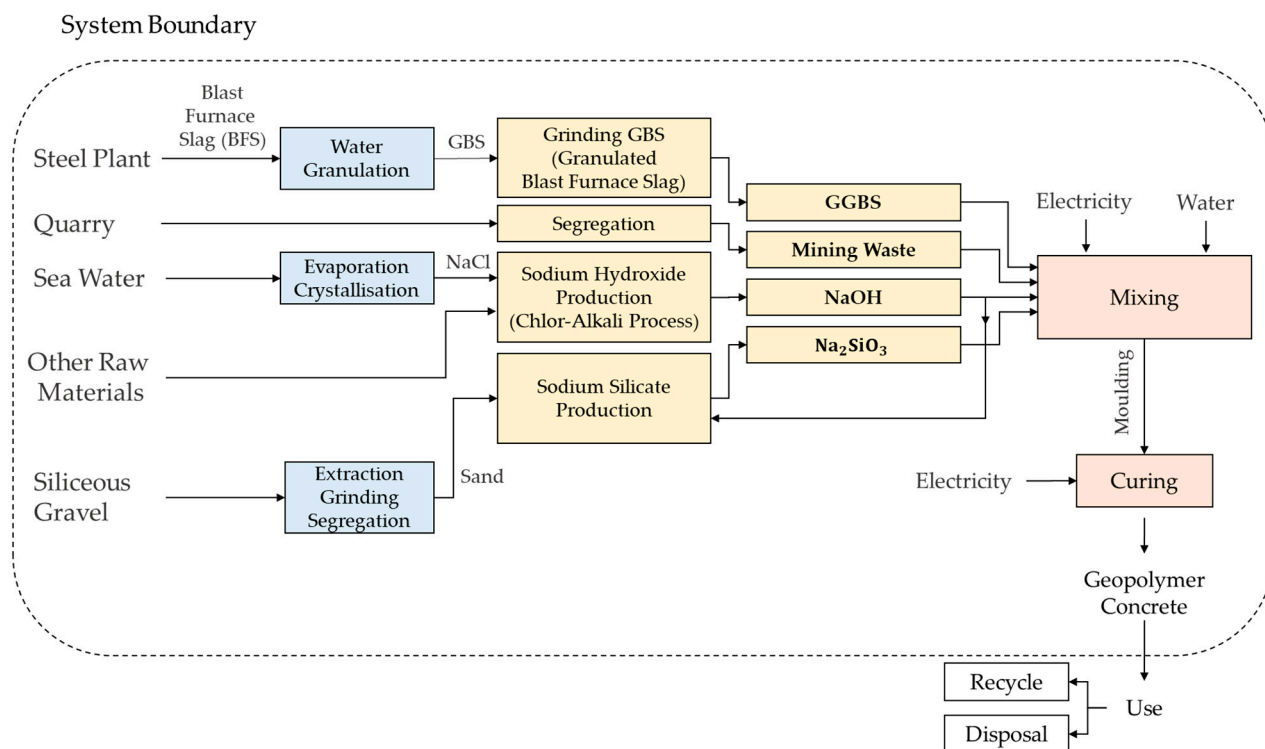


Figure 2. Life cycle assessment of the geopolymerization process of mine waste.

2.5. Economic Analyses

The economic feasibility of the technology was assessed using an economic analysis method, focusing on the costs and benefits within the defined system boundary. This economic analysis (EA) involved estimating both the capital and operating costs and performing a cost–benefit analysis. This was to evaluate how key assumptions and uncertainties affect the economic viability of the geopolymer production process using mine waste streams [42]. The unit of measure for the analysis was set at 1 cubic meter (1 m³). In this study, the costs associated with equipment and infrastructure for batching, mixing, and placing concrete were assumed to be the same for both geopolymer and conventional concrete production. This assumption establishes a baseline for comparison and simplifies the economic analysis. Further details of these analyses can be found in the supplementary section.

2.6. Characterization Methods

2.6.1. Mechanical Strength

To determine the mechanical strength of geopolymers, a compressive strength test was conducted. Before performing the compression test, all samples were unwrapped, demolded, and sulfur-capped, according to ASTM C617 [46]. Then, the compressive strength of capped samples was examined as stated by ASTM C 39/C 39M—03 [46] using the Instron 6027 instrument (MA, USA). The load rate and pre-load values were 1 mm/min and 100 N, respectively.

2.6.2. Initial Setting Time

The measurement of the initial setting time was conducted using a Vicat apparatus operated manually, in compliance with ASTM C 191 standards. This device includes a steel needle, 1 mm in diameter and 50 mm long, which is initially positioned and secured to rest on the paste's surface. The needle is then released, allowing it to drop into the paste. During each test, both the time and the depth of needle penetration were recorded. It is recommended to conduct these tests at 15 min intervals, continuing until the needle penetrates to a depth of 25 mm. The initial setting time is defined as the duration from the

first mixing of solid precursors with activator solutions and/or water to the point when the needle achieves a penetration depth of 25 mm.

2.6.3. Particle Size Distribution

Mastersizer 3000 apparatus (Malvern PAN analytical, Almelo, The Netherlands), with an agitator velocity of approximately 3000 rpm, was used for the particle size distribution of solid precursors. Before the measurement, all samples were scattered continuously in deionized water so that the obscuration acquired a satisfactory level of 10%.

2.6.4. Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS)

To analyze the microstructure and morphology of samples and to detect spatial elemental distributions, scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS) (JEOL 7001f, Tokyo, Japan) for chemical analysis were employed with a voltage of 5 kV to take secondary electron images. The gold coating was conducted using a Leica EM SCD005—cool sputter coater in an argon environment. The pressure in the vacuum compartment was adjusted to 0.05 mbar, and the sputter current was fixed at 30 mA.

2.6.5. X-ray Diffraction (XRD)

For qualitative and quantitative analysis of the crystals, XRD analysis with an X'Pert Pro diffractometer (40 kV and 40 mA) was employed. Tests were set up for X-ray powder diffraction utilizing the corundum (Al_2O_3 , Baikowski International) inner standard with a particular wt.% to a precisely measured bit of the geopolymers [47]. Then, the micronized samples (slurry of corundum, sample powders, and 10 mL of ethanol) were dried overnight. The fine powders were backloaded and squeezed into test disks. The disks were pivoted during analysis. Phase detection was attained by PANalytical Highscore Plus (V4) and MDI Jade (V4.1) with copious databases such as PDF4+. Quantitative analysis was performed using the Rietveld method as implemented in TOPAS (V5, Bruker).

2.6.6. X-ray Fluorescence (XRF)

The XRF was used to detect the main elements of the mined zeolite and geopolymers. For this, samples were combined with a mix of lithium metaborate and lithium tetraborate flux, including 0.5 wt.% lithium iodide (LiI) as a wetting agent. Disk preparation was conducted by melting down the abovementioned mixture for 30 min at 1050 °C using a Claisse TheOx fusion apparatus. Chemicals' compositions were revealed utilizing PANalytical's WROXI solution, and key elements were reported as oxide%. Loss-on-ignition (LOI) was attained using different analysis techniques.

2.6.7. Solid-State Nuclear Magnetic Resonance (Solid-State NMR)

Solid-state NMR experiments were conducted to analyze the molecular structure, purity, and composition of geopolymer materials. These experiments were carried out using a Bruker Avance III spectrometer, equipped with a 300 MHz (1H) magnet and a 4 mm magic-angle spinning probe with a double air bearing. Powdered samples were placed in a zirconia rotor with a Kel-F cap, spinning at 5 kHz for ^{29}Si and 8 kHz for ^{27}Al . The ^{29}Si spectra were obtained using a Cross-Polarization Magic Angle Spinning (CPMAS) pulse sequence along with 100 kHz tppm15 proton decoupling and a single-pulse sequence with identical decoupling. A repetition time of 120 s, deemed sufficient for complete relaxation, was used for single-pulse spectra. For the ^{27}Al spectra, a 1 μs single pulse with a 2 s repetition time was employed.

2.6.8. Thermogravimetric (TG)/Differential Scanning Calorimetry (DSC)

DSC and TG analyses were applied to characterize the trapped water type and thermal tolerance of zeolite and geopolymers. For this, a TG-DSC apparatus (STA 449F3, Netzsch,

Germany) was employed in an air environment with a heating rate of 10 °C/min up to 1200 °C.

3. Results

3.1. Mineralogical Characterization of Mined Zeolite, BFS, and Geopolymers

Figure 3 displays the XRD patterns of the mined zeolite, BFS, and their geopolymer variants cured under various conditions for 28 days. Detailed quantitative analysis and crystal PDF numbers are available in the supplementary documents. In summary, the mined zeolite consists of approximately 28.1% clinoptilolite/heulandite, around 20% quartz, and roughly 19.1% stilbite, with minor quantities of feldspar, mordenite, plagioclase, and chabazite. Additionally, 21.5% of the zeolite is made up of amorphous elements like amorphous SiO₂ [8] and a small fraction of smectite. The unaltered BFS is composed of about 5% gypsum, 1% kilchoanite, trace amounts of quartz and calcite, and approximately 94% amorphous components. Newly formed phases in the geopolymers include zeolite-X, zeolite-A, zeolite-P, chabazite, and sodium aluminum silicate hydrate in a partially crystalline form (“N-A-S-(H)”; PDF: 00-047-0162), calcium aluminum silicate hydrate (“C-A-S-H”; PDF: 01-076-8380), and sodium carbonate hydrate.

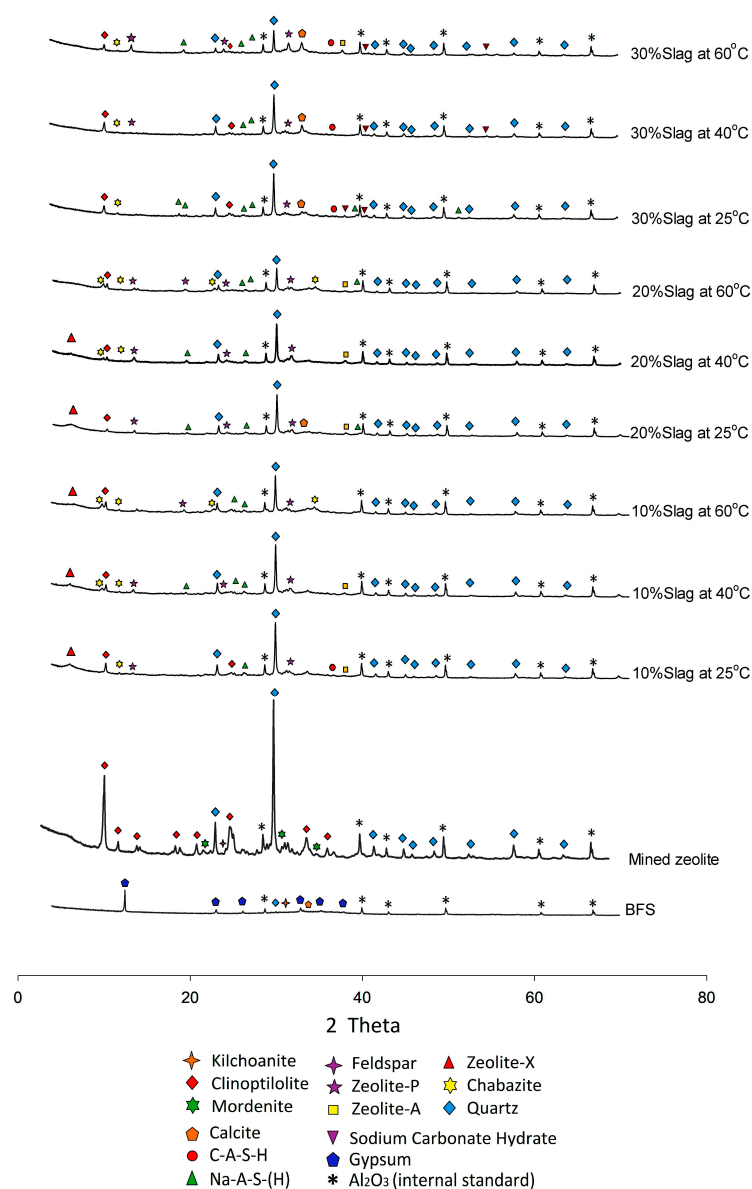


Figure 3. XRD diffractograms of BFS, mined zeolite, and geopolymer compositions.

The degree of crystallinity and the specific development of these phases are influenced by both the BFS content and the curing conditions. For instance, the formation of calcite is notably observed in samples with 30% BFS. The schematic (Figure 4) effectively demonstrates the influence of temperature and BFS levels on the formation and evolution of various zeolite structures in composite materials. In all samples, sodium carbonate hydrate was present, but it was particularly abundant in those cured at 60 °C, with the sample ZS10–60 °C containing the highest concentration, approximately 12%. The C-A-S-H gel was predominantly observed in samples containing 30% BFS, while the N-A-S-(H) gel was prevalent across all samples, attributed to the high amount of mined zeolite used. The representation of each zeolite type in the diagram correlates to its relative percentage in the sample. For example, in the sample ZS10–25 °C, about 80% of the synthetic crystals are zeolite A, and around 20% are zeolite X. These results highlight the intricate process of geopolymer synthesis and the critical impact of both starting materials and curing conditions on the geopolymers' final characteristics. The formation of specific mineral phases in relation to changes in BFS content and curing temperatures is crucial for enhancing the mechanical properties and broadening the potential uses of these geopolymers in construction and other sectors. The molecular configuration of the synthesized geopolymers and the factors affecting their molecular structure were examined in NMR. For more in-depth information on this analysis, please refer to the supplementary documents [13,48–52].

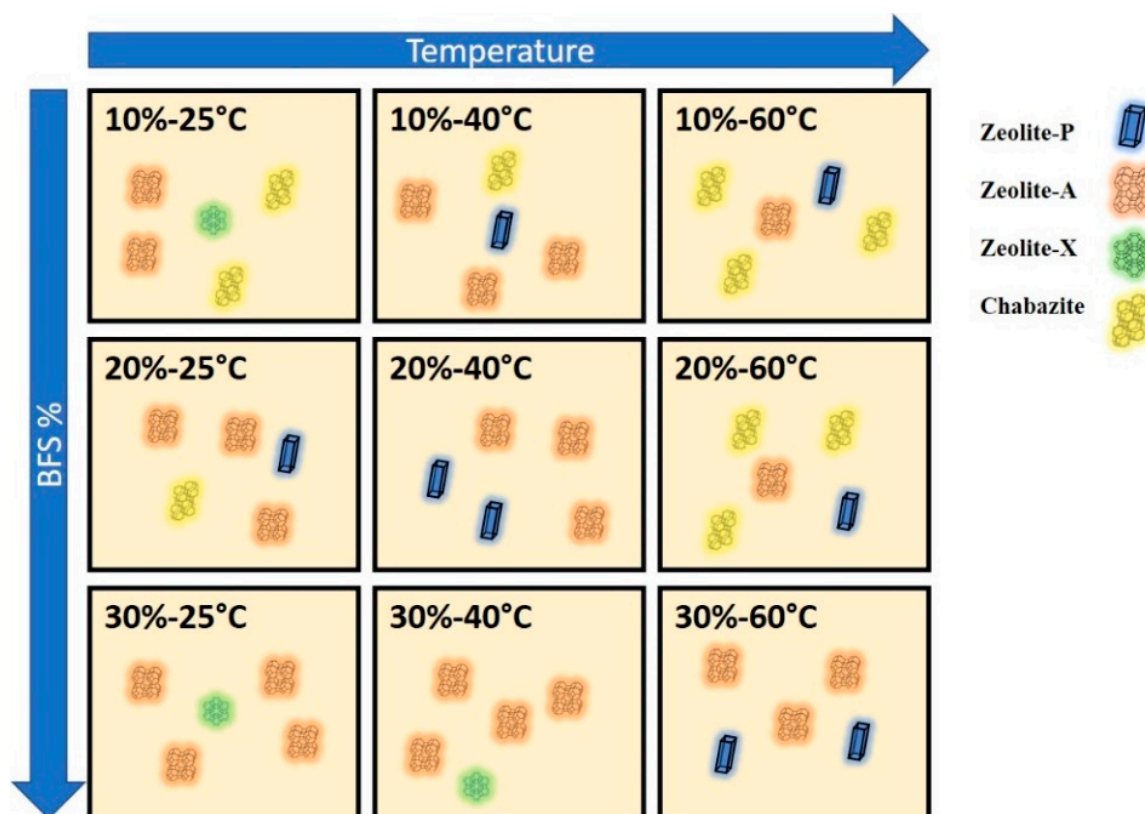


Figure 4. A schematic representation showing how variations in temperature and BFS content influence the formation of different zeolite structures, based on quantitative XRD analyses.

3.2. Morphology Analyses of Synthetic Zeolites

Morphological analyses of the samples were performed using SEM. An SEM image, illustrated in Figure 5a, reveals the cubical crystalline structure of zeolite A, a formation that was corroborated by XRD analysis. It was observed that zeolite A frequently forms in the geopolymers, with the inclusion of BFS, which is rich in calcium, playing a crucial role in its development, particularly under hydrothermal conditions [53]. Additionally, SEM/EDS identified spherical crystals of zeolite P, as shown in Figure 5b, and crystals of

chabazite, as depicted in Figure 5c. The process by which amorphous aluminosilicate gels convert into crystalline zeolites remains incompletely comprehended. For further details on the morphology, including EDS images and analysis of the identified crystals, refer to the supplementary documents.

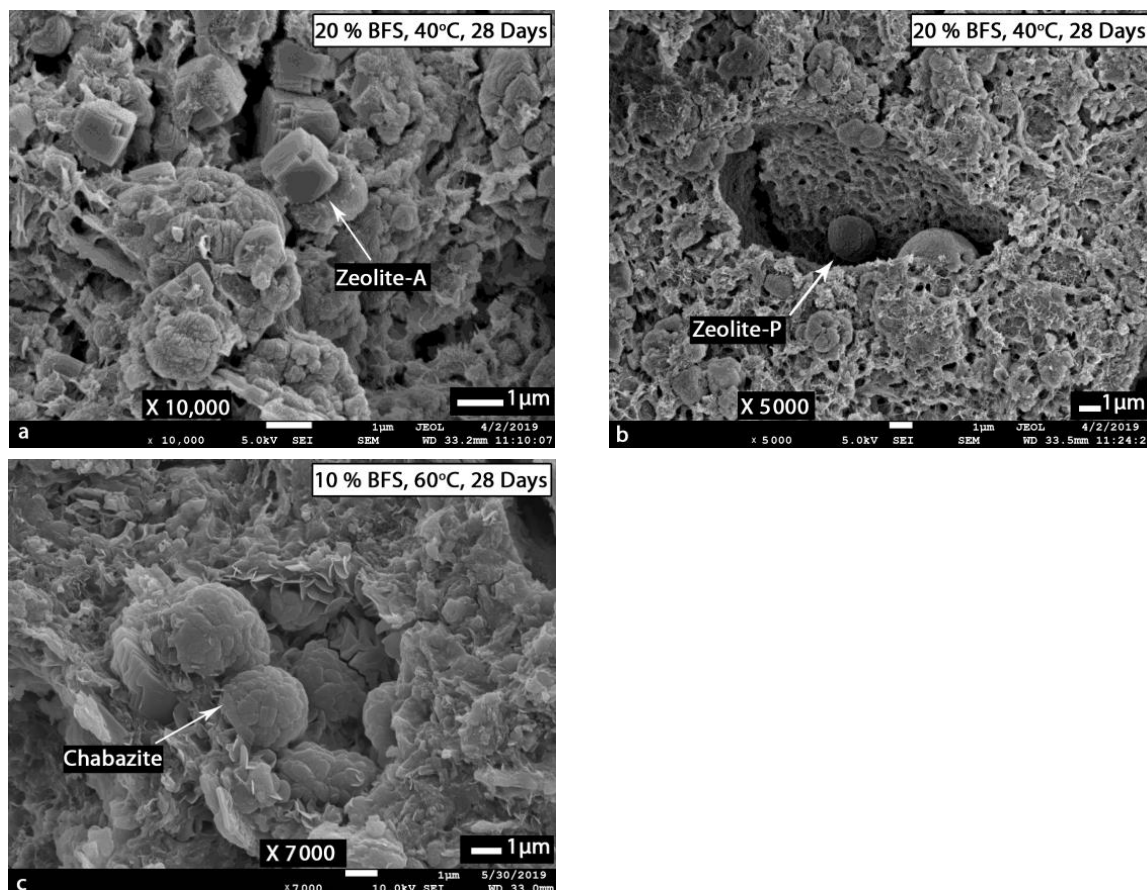


Figure 5. Synthesized zeolites produced during geopolymerization: (a) zeolite-A, (b) zeolite-P, and (c) chabazite.

3.3. Initial Setting Time

Based on the Vicat test results at ambient conditions (Figure 6), samples demonstrated a quicker initial setting with increased BFS content. This aligns with earlier observations that BFS reacts more rapidly at room temperature with reaction solutions, unlike mined zeolite, whose geopolymerization reaction takes longer [54]. This suggests that the primary product in these samples was likely a C-A-S-H gel type. The initial setting times for the samples ZS10–25 °C, ZS20–25 °C, and ZS30–25 °C were 191, 237, and 550 min, respectively. Setting time analysis was not conducted for the sample without BFS, as this test occurred at room temperature, and samples lacking BFS needed heat (at least 40 °C) to set [55]. A notable trend was observed: the setting time increased significantly when reducing BFS content from 20% to 10%, but the change was less pronounced when decreasing from 30% to 20%. The initial formation of C-A-S-H gel likely enhances BFS dissolution, creating momentum for the reaction to continue. Consequently, a higher BFS content tends to promote faster and more extensive formation of C-A-S-H, thereby reducing the initial setting time. This observation is consistent with previous research examining the setting times of mixtures containing fly ash and BFS binder [56].

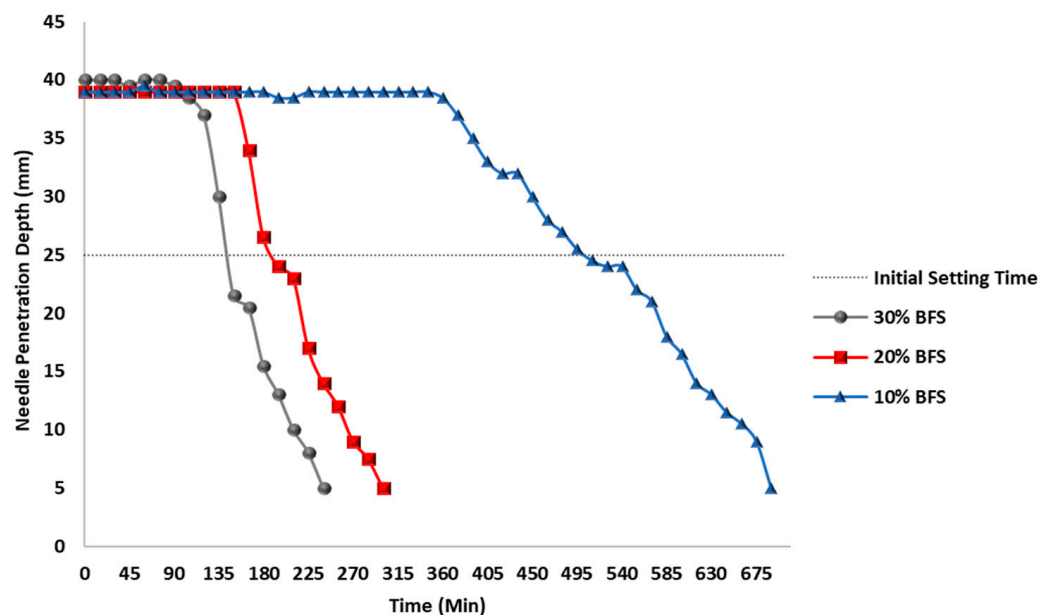


Figure 6. Initial setting time of the geopolymer composites.

3.4. Mechanical Properties of Geopolymers

Figure 7 illustrates the variation in compressive strength over time for samples created using different zeolite/BFS mass ratios that were subjected to various curing temperatures. At room temperature, samples containing 10% BFS consistently exhibited an increase in strength over time. Increasing the BFS content to 20% not only maintained this consistent strength gain but also resulted in a higher overall mechanical strength. The most significant finding in this condition was observed in the sample with 30% BFS (ZS30–25 °C), which achieved an average compressive strength of 17.3 MPa after two weeks of curing. However, this strength level plateaued thereafter, indicating that the initial reactions, while rapid, likely reached completion or a state of stability by the 28 day mark.

The increase in strength observed in the sample is linked to the formation of C-A-S-H, as confirmed by the results obtained from XRD analysis (Figure 3). The C-A-S-H gels contain water within their structure, leading to a decrease in the sample's permeability, which in turn improves its mechanical strength. Similar to Portland cement systems, these gels are composed of layers of tetrahedral silicate chains. Within the interlayer regions of these chains reside calcium cations, water of hydration, and alkalis. Furthermore, specific alkali cations serve to offset the net negative charge that occurs when Al^{3+} ions replace Si^{4+} in the sites of the tetrahedral chains [3].

These findings align with previous research [57], indicating that BFS, when used as a secondary precursor, promotes strength development, particularly at lower temperatures where activation reactions in low-calcium systems are limited [54]. Figure 8 presents SEM images of geopolymers cured under varying conditions and with different BFS content after 28 days. The images reveal that samples cured at room temperature exhibit a noticeably irregular and non-uniform morphology, correlating with their lower mechanical strength.

Notably, increasing the curing temperature to 40 °C generally enhanced the strength of most samples, except for ZS30–40 °C, which initially displayed almost a similar strength to the room temperature sample and gradually reached 17.8 MPa after 28 days. The impact of increasing the temperature to 40 °C was even more pronounced in the early strength development of samples with 20% and 10% BFS, with the strength doubling or tripling, respectively, compared to the ambient temperature samples after 7 and 14 days of curing. However, the samples containing 10% and 20% BFS display a drop or a plateau in strength development after 14 days, indicating a more rapid initial reaction at this temperature, which may suggest that the reaction stabilizes and stops progressing beyond the 14 days.

This temperature increase led to a more uniform and denser microstructure in ZS30–40 °C after 28 days of curing, where particles were uniformly linked, as observed in SEM images (Figure 8).

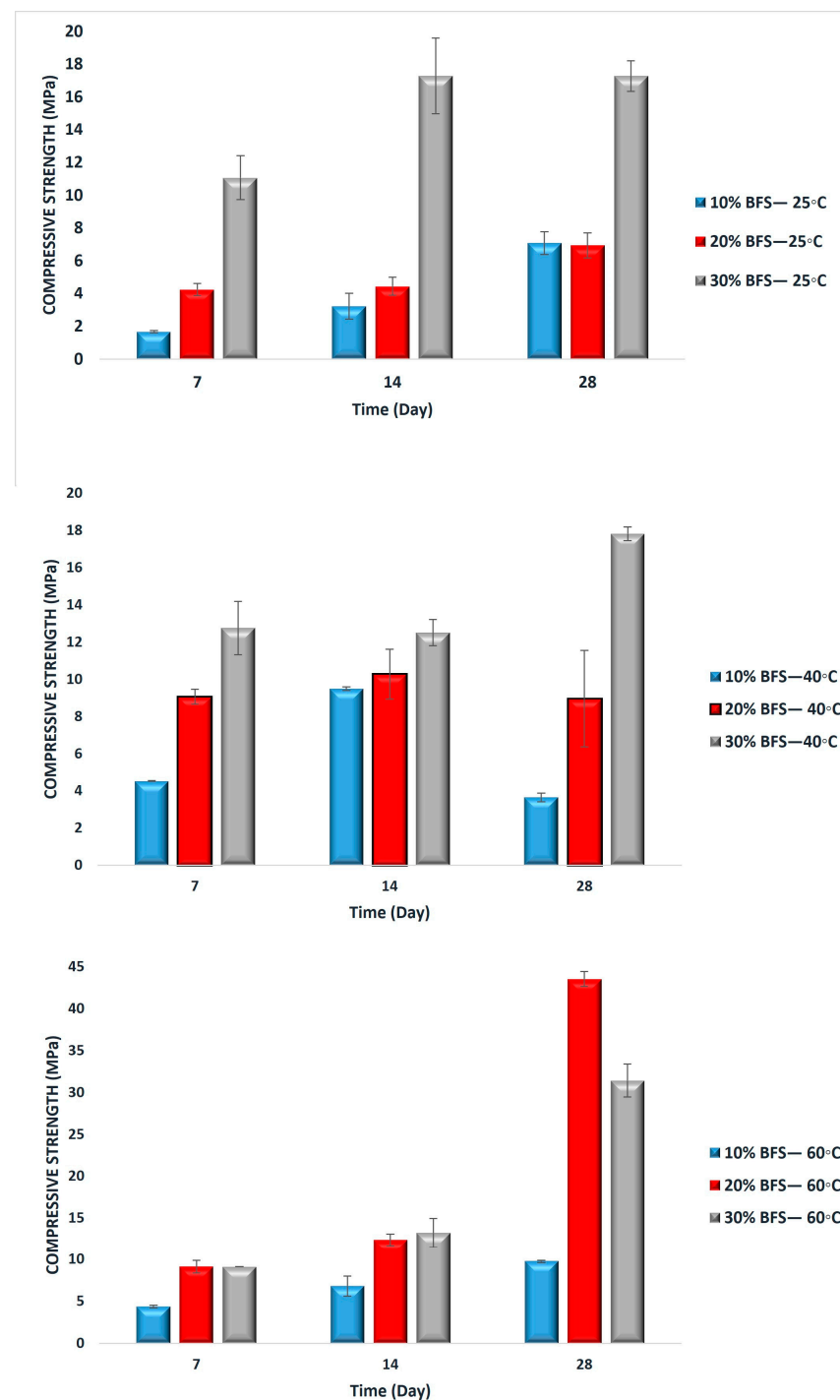


Figure 7. Compressive strength of geopolymer composites cured at 25, 40, and 60 °C.

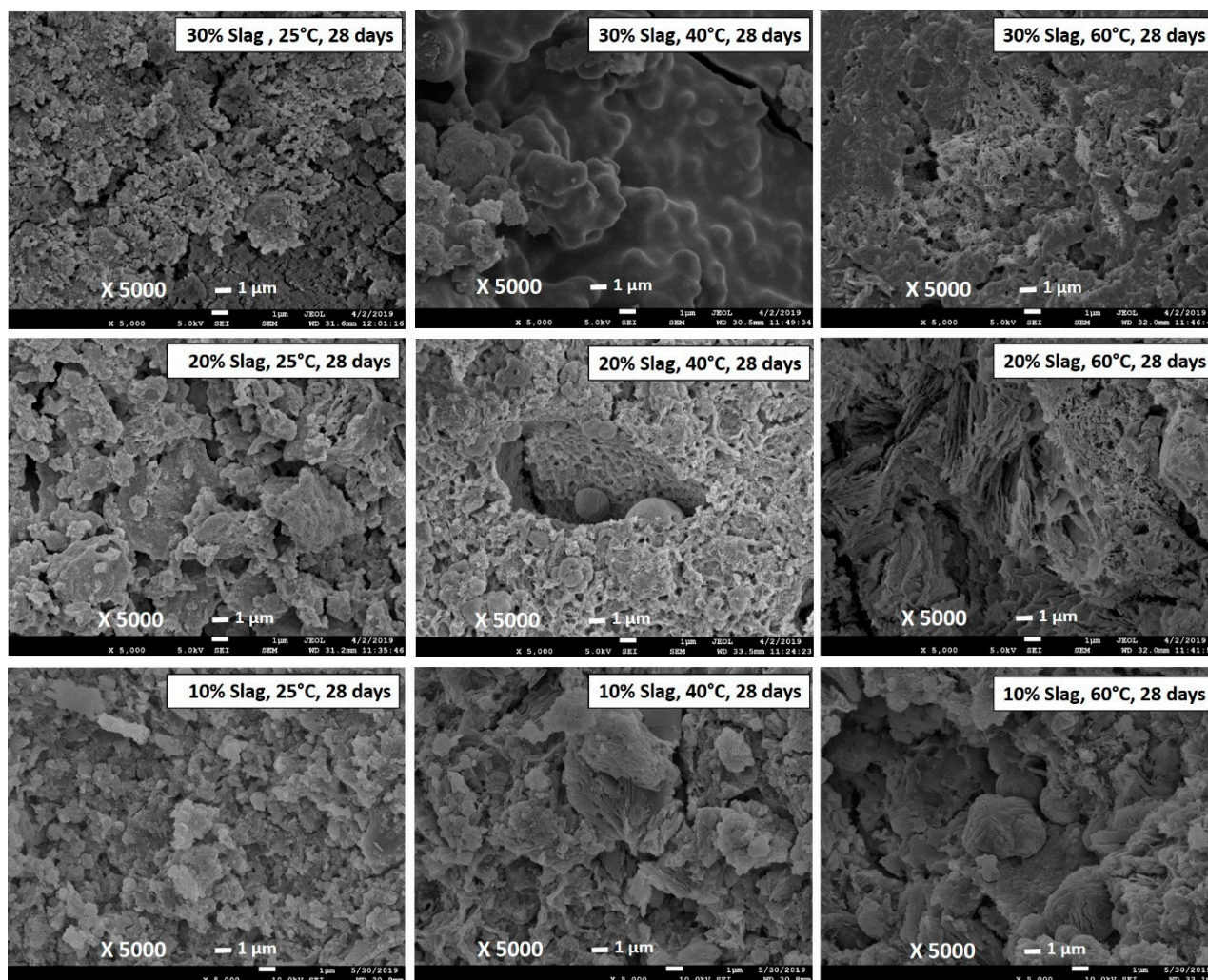


Figure 8. Microstructure of geopolymer composites.

Further increasing the temperature to 60 °C does not substantially affect the early strength of most samples after 7 and 14 days. However, significant improvement in strength was observed after 28 days. ZS20–60 °C exhibited a dramatic increase in strength, reaching an average value of 43 MPa after the same period, a substantial enhancement compared to lower temperature curing conditions, while the strength of samples containing 30% BFS reached an average value of 31 MPa after 28 days.

This phenomenon suggests that a higher BFS content does not necessarily ensure greater compressive strength in the blended systems. The study demonstrated that the simultaneous presence of C-A-S-H and N-A-S-(H) gels, a highly cross-linked aluminosilicate gel, enhanced the mechanical strength of the mixed systems [3]. For similar blended systems, the mechanical strength of binders appears to be enhanced when C-A-S-H and N-A-S-(H) gels coexist [58,59].

The production of N-A-S-(H)-type gels is heavily dependent on the curing temperature, occurring more prominently at higher temperatures [54]. Similar gel coexistence trends have been identified in BFS-metakaolin blended binders [60]. N-A-S-(H)-type gels offer excellent chemical and thermal resistance, while C-A-S-H -type gels provide chemical binding to water, reducing permeability. The N-A-S-(H) gel may also aid in anion-binding mechanisms that retard chloride ingress, thereby increasing the service life of reinforced concrete by delaying corrosion initiation in embedded steel [3].

Thermal curing is essential for blended systems with a high proportion of low-calcium precursors to achieve optimal gel coexistence and maximal compressive strength. At

room temperature, BFS-based geopolymers were more prevalent. However, at elevated temperatures, such as 60 °C, there is a more controlled and effective interaction between the low- and high-calcium precursors, leading to improved material properties [61]. The idea of combining less reactive aluminosilicates with a smaller quantity of a more reactive calcium source, such as BFS, and adding alkalis to accelerate the reaction has been suggested for valorizing wastes or by-products [58,59]. Based on XRD results, the formation of sodium carbonate hydrate, observed in all samples, was more pronounced in those cured at 60 °C, especially in the sample with the lowest strength (10% BFS), supporting the idea that higher carbonation correlates with reduced strength [62]. SEM images (Figure 8) also established that the ZS20–60 °C samples exhibited a greater integration of particles compared to the other samples.

3.5. Mass Loss and Shrinkage Behavior

Drying shrinkage, the reduction in volume due to the loss of internal pore water, is a critical factor in cementitious materials as it can lead to cracking and adversely affect the durability of binders. Hence, understanding and managing shrinkage behavior is vital to the development of geopolymers [30]. As shown in Figure 9, the shrinkage values (measured as length change) at room temperature were found to increase with the increasing BFS content. Notably, the highest degree of shrinkage was observed in the sample with the highest amount of BFS (30%) and cured at ambient temperature. This data indicate that a balanced mix of low-calcium precursor and BFS can significantly mitigate shrinkage, performing better in this respect than other geopolymers with a higher BFS content [30].

In the ZS10–25 °C samples, the high content of mined zeolite plays a crucial role in retaining moisture within the composites, acting as a water reservoir due to its high adsorption capacity. This feature effectively prevents excessive water evaporation and combats self-desiccation in composites [22]. However, it was observed that drying shrinkage in almost all samples increased over time under the given conditions, with the exception of ZS20–25 °C. This trend aligns with findings by Ye et al. [63], highlighting that the gradual drying of geopolymers can lead to a significant increase in drying shrinkage. A similar pattern was observed for the compressive strength of such samples, which suggests a correlation between compressive strength and shrinkage value. Corresponding to the trend in shrinkage value at room temperature, the mass loss in the samples was found to increase with both time and BFS content, as illustrated in Figure 10. The relationship between mass loss and shrinkage becomes particularly noticeable when low-calcium precursors are used in geopolymers. To mitigate these effects, the addition of aggregates has been proposed to reduce mass loss and, consequently, shrinkage. It was also noted that the extent of mass loss at ambient conditions was higher compared to that at elevated temperatures, possibly due to air movement around the samples, further influencing the drying process [30].

With an increase in curing temperature to 40 °C, all samples exhibited a decrease in shrinkage. Thermal treatment at this temperature helped to decrease the porosity and limit pore conductivity in the geopolymers, leading to reduced pore water content and, consequently, lower shrinkage [30]. In line with the ambient condition findings, the maximum shrinkage strain at 40 °C was seen in ZS30–40 °C, approximately three times lower than at ambient conditions. Fluctuations in shrinkage and mass loss over time (as shown in Figures 9 and 10) may be attributed to the dynamic nature of the geopolymerization process, involving the formation, disintegration, or transformation of various Al- and Si-rich gels. According to Li et al. [64], the development of Al-rich gels or nano-zeolites in the geopolymer matrix can lead to the expansion of the product. This is mainly due to the fact that the nanoscopic pores or voids formed during the geopolymerization process are insufficiently large to hold all the generated water or guest molecules. As a result, there is a net increase in the volume of the geopolymer product. Conversely, the cavities within amorphous Si-rich gels are larger (mesoporous), and the formation of inaccessible pores is less frequent. This explanation might be the reason for lower shrinkage (or expansion) at higher ages. For example, for ZS30–40 °C, shrinkage

initially decreased after two weeks and increased after 28 days. This could be due to the initial formation of Al-rich gels or zeolite structures and the later partial decomposition of these zeolites, coupled with the formation of amorphous Si-rich gels. FTIR results support this, showing the development of Al-rich gels after two weeks, followed by Si-rich gels after 28 days (supporting documents; section G) [64]. Understanding the shrinkage behavior of geopolymers, especially those made from multiple precursors, including crystalline materials like mined zeolite, is complex.

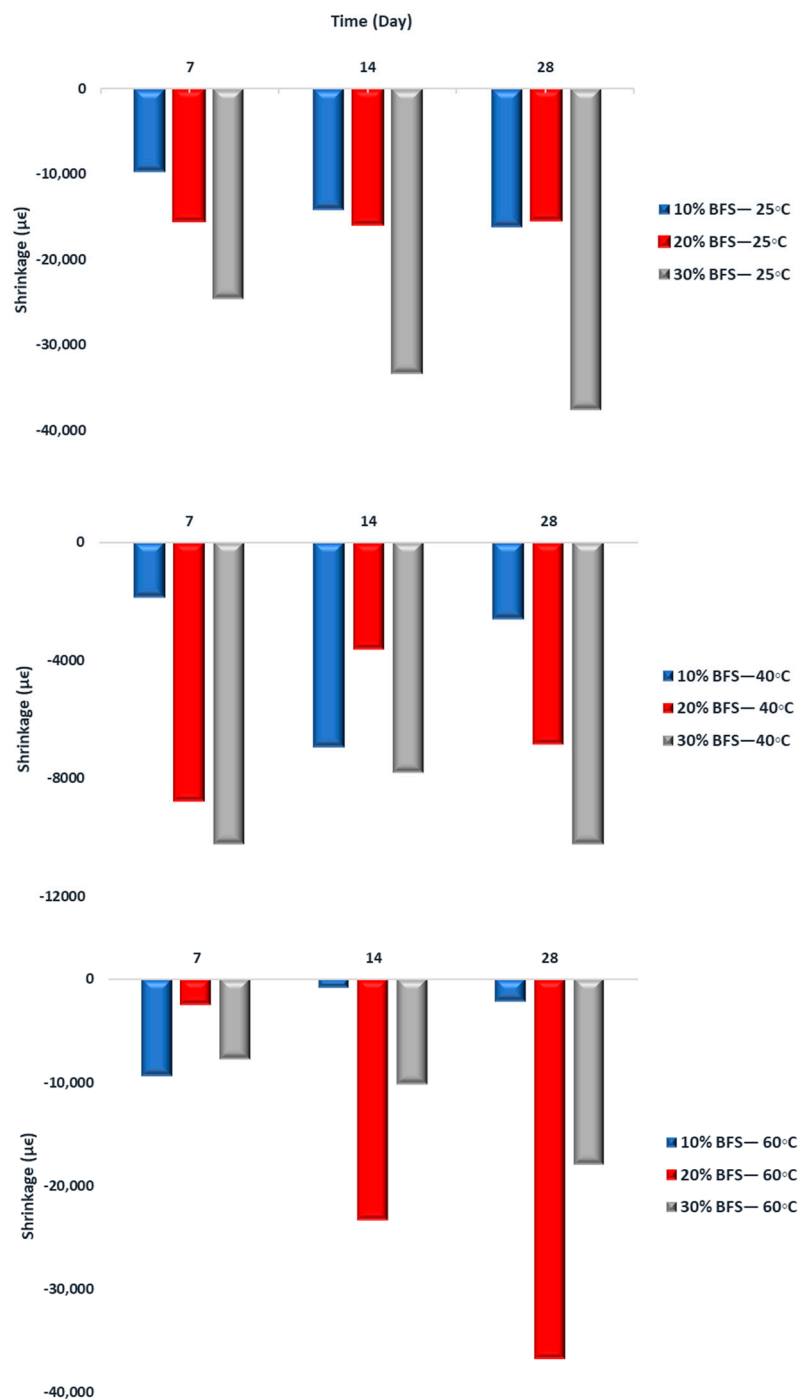


Figure 9. Shrinkage value of geopolymer composites cured at 25, 40, and 60 °C.

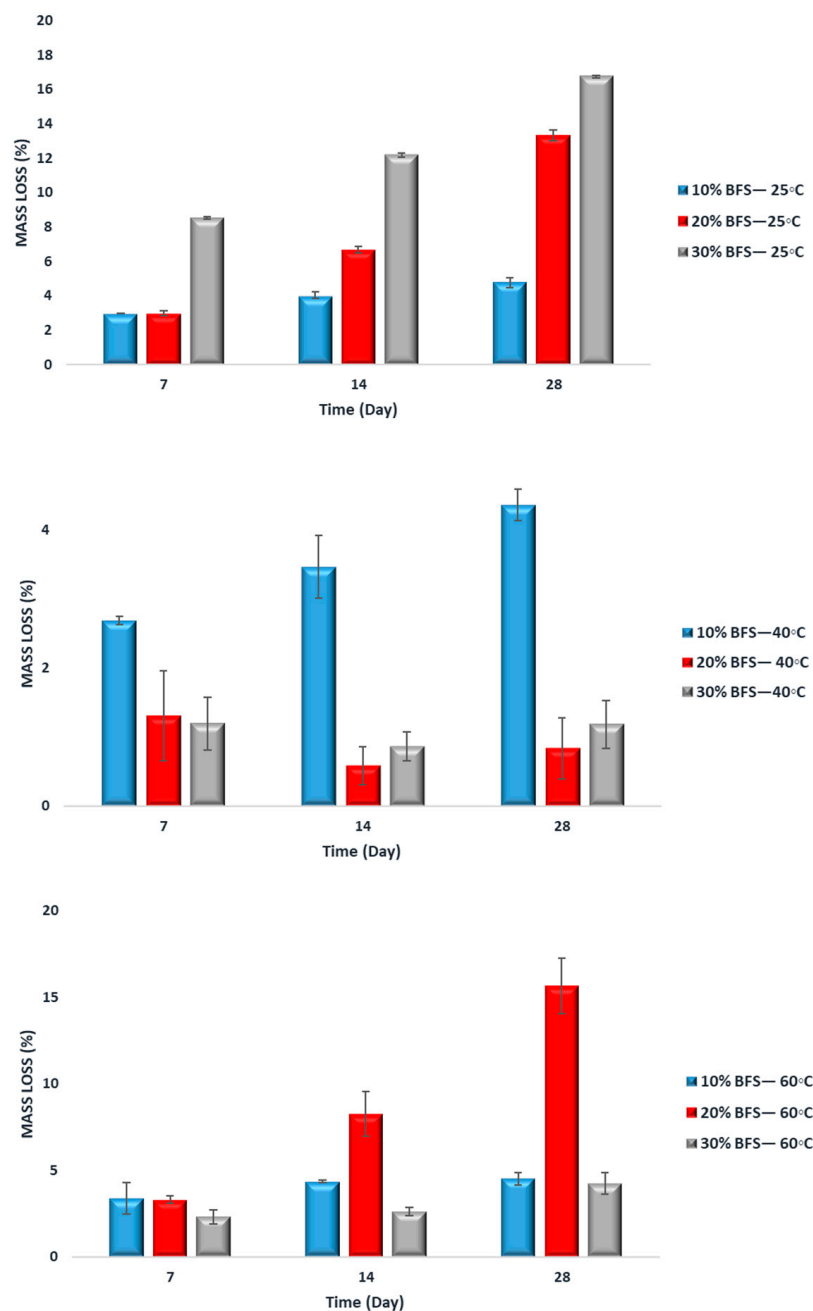


Figure 10. Mass loss of geopolymer composites cured at 25, 40, and 60 °C.

Raising the temperature further to 60 °C led to a decrease in the early-age shrinkage observed at 7 days for ZS30–60 °C and ZS20–60 °C samples. However, over a longer period, there was a notable increase in shrinkage with extended curing time. After 28 days of curing, ZS20–60 °C showed a maximum mass loss and shrinkage that was about 5 times higher than the shrinkage value of ZS20–40 °C. This high shrinkage value suggests that the material could no longer be considered porous but rather a granulated substance with micro-defects, with the drying behavior linked to the time-dependent reorganization of C-A-S-H gel nanoparticles [65]. The study also indicated a correlation between chemical shrinkage and natural carbonation, implying that the significant shrinkage noted could be attributed to the substantial amount of sodium carbonate hydrate (approximately 10%) present in these samples [62].

In Figure 10, we observe distinct trends in mass loss correlated with varying percentages of BFS under different treatment temperatures. At 25 °C, an increase in the percentage

of BFS is directly linked to an increase in mass loss, while the mass loss data at higher temperatures (40 °C and 60 °C) do not exhibit a clear, consistent trend in relation to BFS percentages. This deviation could be attributed to several factors. Unlike the behavior at room temperature, where the reaction is predominantly driven by BFS and zeolite behaves more passively, at temperatures of 40 °C and 60 °C, zeolite waste becomes more reactive in an alkaline solution [8]. This change in reactivity alters the dynamics of the reaction. The activation of zeolite at these higher temperatures contributes to the development of new reaction products. Both BFS and zeolite contribute to the formation of different types of gels—C-A-S-H and N-A-S-(H), each possessing unique chemical structures and varying water demands [54]. The concurrent formation of these gels at elevated temperatures results in a more complicated system. This complexity is primarily due to the different water consumption patterns of these gels compared to those at lower temperatures [3]. There might be a competitive interaction between the gels for the water necessary for their formation and stability. This competition introduces an intricate balance between water consumption and retention within the geopolymer matrix, which could influence mass loss trends. Additionally, at higher temperatures, there is a greater likelihood of the formation of crystalline and nanostructures within the zeolite [64]. These structures are fundamental in affecting the water dynamics within the geopolymer, particularly their ability to influence water retention and loss through their pore size and structure [64].

3.6. Thermal analyses

DSC and TG analyses were used to identify the types of water contained within and to assess the thermal stability of both zeolite and geopolymers. Figure 11 illustrates the trends in mass loss and phase changes for both mined zeolite and ZS30 samples, where the temperature was progressively increased from 25 °C to 1200 °C at a rate of 10 °C per minute. The total mass loss observed in zeolite (Figure 11a) was about 7.76 wt.%, primarily due to the evaporation of water. The initial weight loss, occurring around 100 °C, was linked to the release of external and weakly bound water, followed by a subsequent mass loss near 300 °C. The evaporation of more firmly bound water took place below 700 °C [66]. Beyond 700 °C, no further decrease in mass was recorded. An exothermic peak, observed near 900 °C, indicated the collapse of the zeolitic crystal structure.

The TG analyses of the ZS30 geopolymer series revealed varying water evaporation levels: approximately 25.5 wt.% for ZS30–25 °C, 11.5 wt.% for ZS30–40 °C, and 13.8 wt.% for ZS30–60 °C. This total evaporable water content in all geopolymer samples was higher than in raw zeolite, aligning with previous findings about the increased water absorption capacity of geopolymers [8]. Among these, the ZS30–25 °C sample exhibited the highest water content. This is attributed to the fact that curing at elevated temperatures, like 40 °C and 60 °C, facilitates the evaporation of surface and loosely bound water to some extent. Approximately 47% of the total water loss in ZS30–25 °C occurred before reaching 150 °C, whereas the loss was around 17% for samples cured at 40 °C and 60 °C, respectively. This suggests a higher presence of external and loosely bound water in samples prepared under ambient conditions.

In the DSC profiles of all samples, two significant endothermic peaks were identified in the range of 25–200 °C. The initial peak, appearing between 100 and 120 °C, signaled the loss of water that was physically bonded, while the subsequent peak, occurring in the 155–190 °C range, was linked to the evaporation of water from pores. Particularly, the sample labeled ZS30–60 °C displayed the greatest content of pore water among all samples. Beyond 200 °C, a consistent reduction in mass was observed in all geopolymers, likely attributable to the dihydroxylation of the C-A-S-H geopolymer gels. Around 800 °C, an exothermic peak was detected, indicative of the breakdown of the aluminosilicate gel and calcium carbonate species. Notably, the samples ZS30–40 °C and ZS30–60 °C demonstrated a more pronounced integrated area at this peak compared to the ZS30–25 °C sample, implying a more substantial development of C-A-S-H gels.

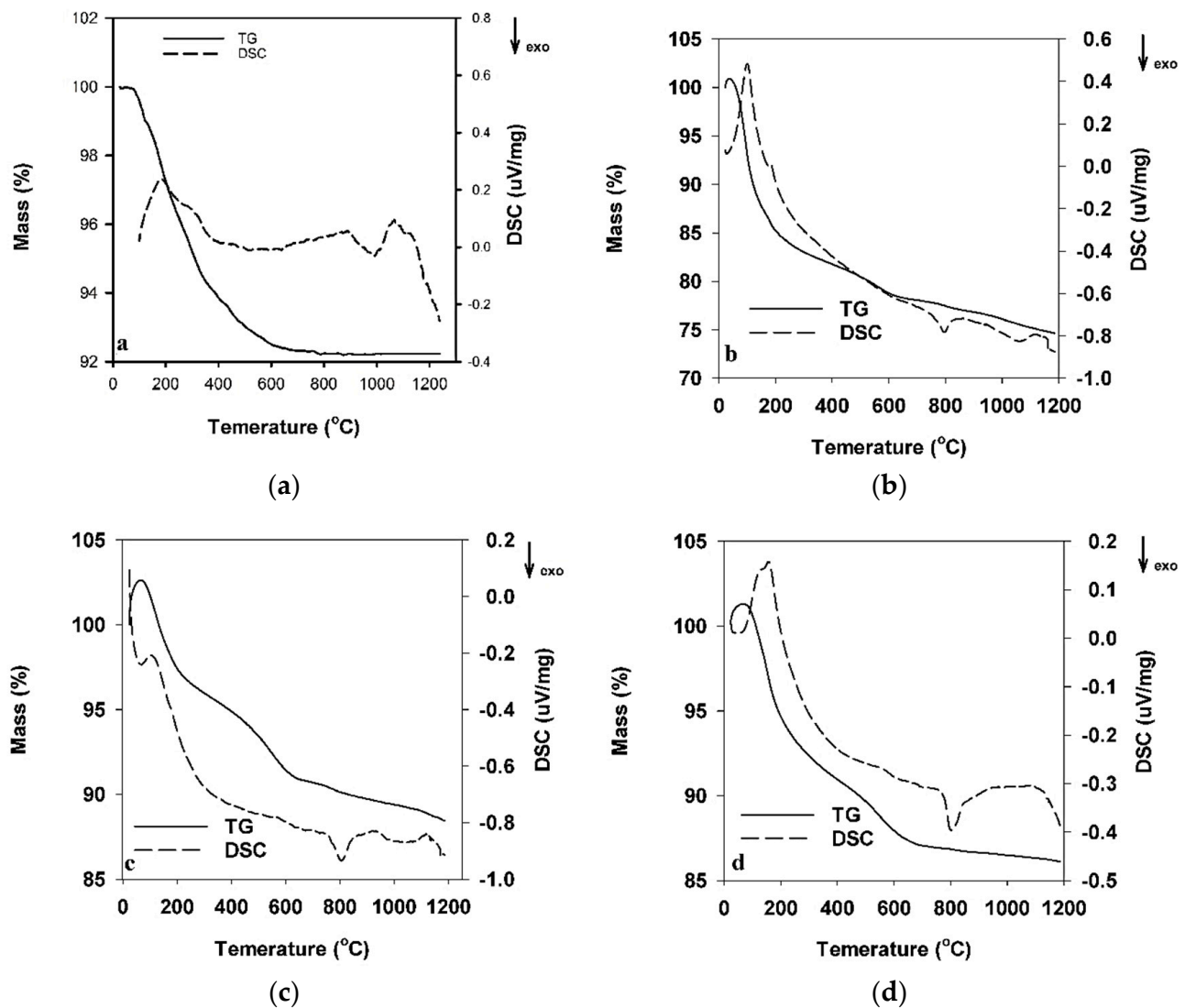


Figure 11. TG and DSC diagrams for (a) mined zeolite waste and geopolymer composites with 30% BFS cured at (b) 25 °C, (c) 40 °C, and (d) 60 °C.

3.7. Environmental Impact Assessment and Economic Analyses

A comparative study of the GWP was conducted between geopolymer concrete and conventional cement concrete. The findings indicate that geopolymer concrete generates between 205 and 240 kg CO₂-e/m³ (Figure 12a), noticeably less than the 354 kg CO₂-e/m³ produced by conventional concrete [67]. This significant reduction, in the range of 30% to 40%, highlights the environmental advantages of geopolymerization. However, it is essential to consider the mechanical strength of the materials produced. The geopolymer concrete reached a maximum strength of 12 MPa after seven days, noticeably below the 30 MPa typically achieved by standard cement concrete within 24 h. This lower initial strength could restrict the use of geopolymer concrete or necessitate extra materials or processes to improve its strength. However, it is important to note that not all construction applications require high early mechanical strength. Many construction projects can accommodate materials like geopolymer concrete, which develops its full strength over a longer period of time.

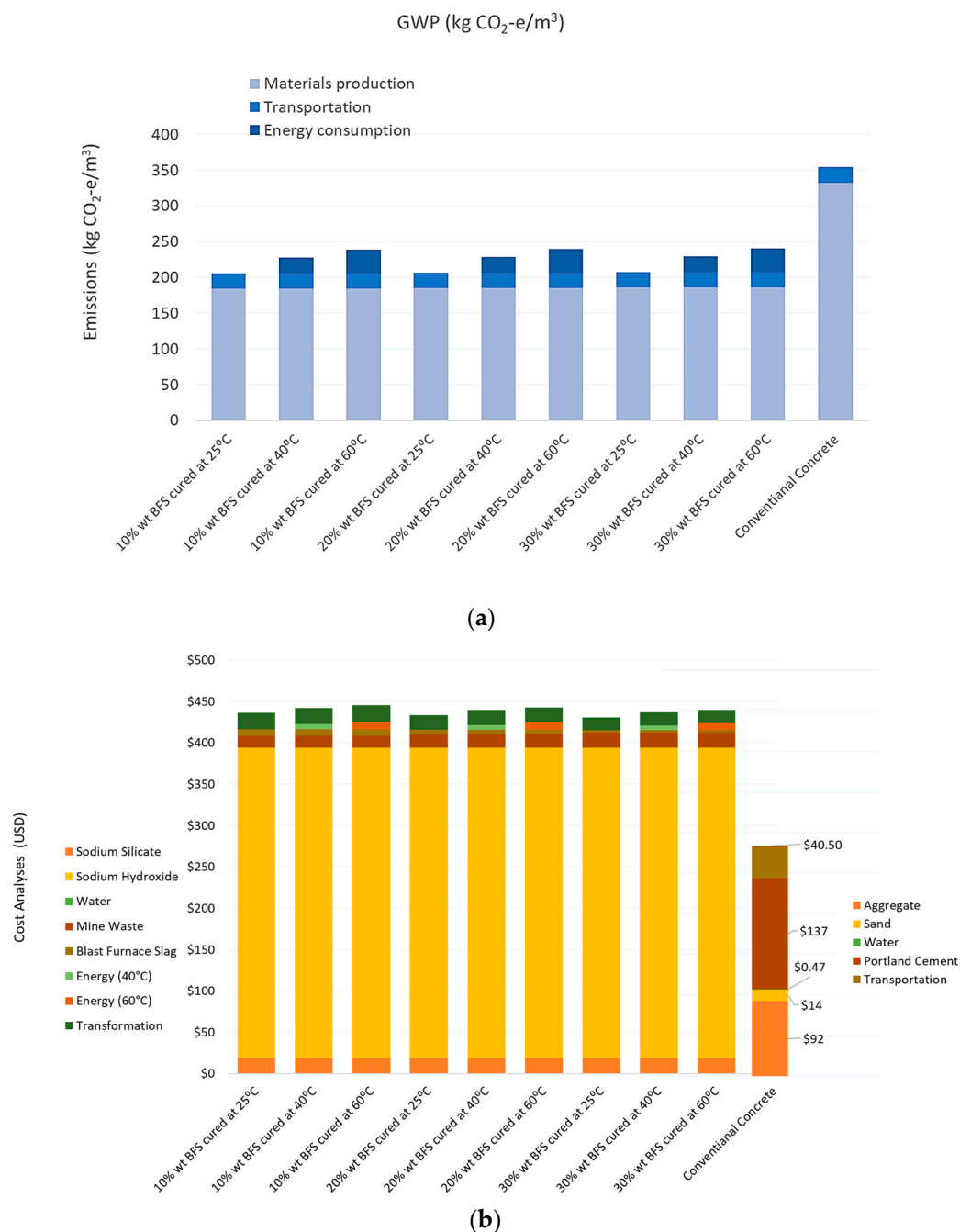


Figure 12. (a) Emissions from the geopolymerization process and (b) cost analyses of geopolymer production using mine wastes.

In terms of cost, geopolymer concrete, which is estimated between \$430 and \$445/m³, comes at a higher cost compared to conventional concrete, which has a total cost of \$283/m³ (Figure 12b). This price difference is primarily because of the chemicals involved in making geopolymer concrete. Nevertheless, the higher expenses may be justified by the environmental benefits offered by geopolymer concrete. It is also important to recognize that these prices are subject to change based on geographical location and market trends.

The utilization of geopolymer technology in the construction industry represents a significant improvement in sustainable and environmentally responsible practices. Geopolymers offer a compelling alternative to conventional Portland cement, primarily through their ability to incorporate quarry waste and by-products such as mined zeolite and BFS. This approach not only mitigates the environmental degradation associated with traditional

cement production but also addresses industrial waste management more effectively. Crucially, geopolymers are characterized by a substantially lower carbon footprint, primarily due to reduced greenhouse gas emissions during their production process. This attribute is particularly vital in the context of global climate change mitigation efforts. Moreover, the inherent properties of geopolymers, including enhanced durability and thermal stability, contribute to the extended lifespan of construction materials. This leads to a decrease in the frequency of repairs and replacements, further reducing the consumption of raw materials and the generation of waste over the lifecycle of a structure. The adoption and advancement of geopolymer technology in the construction sector not only aligns with but actively promotes sustainable development goals. This technology presents an innovative solution that balances the demands of modern construction with the urgent need for environmental conservation and sustainability.

3.8. Limitations and Future Research Opportunities

There is a lack of published information available on the long-term performance and various hardening properties of blended geopolymers, particularly those utilizing natural zeolite. This gap is highlighted by the major weakness in existing literature, which often focuses on the immediate mechanical strengths of geopolymers, neglecting their behavior under different environmental conditions and over prolonged periods. The current study contributes to this field by investigating the hardening characteristics and mechanical strengths of geopolymers with zeolite waste and BFS, highlighting their potential for sustainable material applications. However, it is recognized that this study is limited by its focus on constant solid-to-liquid ratios and quantities of alkaline activators, which constrains the exploration of varied compositions and their impacts. There is a significant opportunity for future research to explore the development of studies that explore varying ratios of alkaline activator solutions to solid components, the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio, and the quantities of the chemicals involved. Such research is essential to gain a more comprehensive understanding of the diverse factors influencing the performance of geopolymers, involving both their practical applications in various industries and their environmental sustainability. Moreover, an in-depth analysis of their performance as air-hardening, thermal-hardening, and hydraulic binders is essential. This thorough approach is crucial for advancing the field and unlocking the full potential of blended geopolymers as a sustainable material solution.

4. Conclusions

In this research, new composites made of zeolite and BFS geopolymers were created, and various characterization methods were used to understand the nature of the resulting composites. The effects of various factors, including BFS content, curing time, and temperature, on the properties of the composites were investigated. This study demonstrates that geopolymer concrete significantly reduces greenhouse gas emissions compared to conventional cement concrete, with a decrease of about 40%. Additionally, the findings showed that adding BFS influenced both the fresh and hardened properties of the paste. Interestingly, a higher BFS content did not always lead to increased compressive strength, although it contributed to a quicker initial setting. Thermal analysis indicated that these geopolymers are stable up to 800 °C, suggesting their suitability for fireproofing applications. Cost-wise, geopolymer concrete is more expensive due to the chemicals used in its production, but this could be offset by its environmental benefits. These findings highlight the need to balance environmental advantages with performance and cost considerations in the development and use of geopolymer concrete.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su16010440/s1>.

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Abbreviations

Al ₂ O ₃	aluminum oxide
ASTM	American Society for Testing and Materials
BFS	blast furnace slag
°C	degrees Celsius
C-A-S-H	calcium aluminum silicate hydrate
CaO	calcium oxide
CO ₂	carbon dioxide
CO ₂ -e	carbon dioxide equivalent
CPMAS	cross-polarization magic angle spinning
DSC	differential scanning calorimetry
EN	European Norm
Fe ₂ O ₃	iron (III) oxide
GHG	greenhouse gas
GWP	global warming potential
ISO	International Organization for Standardization
K ₂ O	potassium oxide
LCA	life cycle assessment
LCI	life cycle inventory
LOI	loss on ignition
M	molarity
MgO	magnesium oxide
MnO	manganese (II) oxide
N-A-S-H	sodium aluminum silicate hydrate
Na ₂ O	sodium oxide
NMR	nuclear magnetic resonance
NSW	New South Wales
OPC	ordinary Portland cement
PDF	portable document format
P ₂ O ₅	phosphorus pentoxide
QUT	Queensland University of Technology
SEM	scanning electron microscopy
SiO ₂	silicon dioxide
SMI	Sustainable Minerals Institute
SO ₃	sulfur trioxide
TG	thermogravimetric
TiO ₂	titanium dioxide
UQ	The University of Queensland
w/w	weight by weight
XRD	X-ray diffraction
XRF	X-ray fluorescence
μm	micrometer
με	microstrain

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