



Article Multicomponent Low Initial Molar Ratio of SiO₂/Al₂O₃ Geopolymer Mortars: Pilot Research

Barbara Słomka-Słupik^{1,*}, Paulina Wiśniewska² and Wiktor Bargieł²

- ¹ Department of Building Structures, Faculty of Civil Engineering, Silesian University of Technology, 44-100 Gliwice, Poland
- ² Faculty of Civil Engineering, Silesian University of Technology, 44-100 Gliwice, Poland

Correspondence: barbara.slomka-slupik@polsl.pl

Abstract: Alkali-activated binders have the potential to consume various types of waste materials. Low initial molar ratios of SiO₂/Al₂O₃ geopolymer mortars were considered in this article. Here we studied alkali-activated binders produced with photovoltaic glass powder in 5%; kaolin clay in 15%; ground granulated blast furnace slag in 30%; alumina-lime cement in 30%; and, interchangeably, fly ash from coal combustion in 5%, fly ash from biomass combustion in 5%, or granulated autoclaved cellular concrete in 5%. The influence of clay dehydroxylation, curing conditions, glass presence, and a kind of waste material was investigated. According to the experimental results, strength (compressive and tensile) gradually increased with increasing time and with the use of calcined clay. Significant improvement in compressive strength was seen with the additional 3 days curing time in 105 °C when non-sintered clay was used. The presence of photovoltaic glass in alkali-activated mortars immobilised mercury and arsenic but released zinc, chromium, and sulphates. The microscopic observations confirmed the greater densification of the microstructure of the binder made of calcined clay due to its greater surface development and dehydroxylation. The binder of non-calcined clay was granular, and the interfacial transitional zone was more porous. The C-A-S-H gel seemed to be the main phase. XRD examination confirmed the presence of C-A-S-H, C-S-H, zeolites, and many other phases in minor amount. The presented research was a pilot study, and its main goal was to develop it further.

Keywords: geopolymer; alkali activation; anthropogenic raw materials; PV glass powder; kaolin clay; alumina-lime cement; autoclaved cellular concrete; slag; fly ash

1. Introduction

In this article, the use of different secondary materials in the mass of a binder or building mortar to perform a multicomponent low initial molar ratio of SiO_2/Al_2O_3 geopolymers was considered. Particular attention was paid to waste glass from photovoltaic (PV) panels, as few studies indicated its use as a geopolymer mass component. According to the IRENA report from 2016 [1], it was expected that, by 2050, the amount of photovoltaic modules that reach the end of their life will increase to 5.5–6 million tons. However, now, according to the brochure [2] shown in Figure 1, 1.7 to 8 million tonnes of cumulative PV waste will be generated by the end of 2030 and 60 to 80 million tonnes by the end of 2050. The last report [3] from November 2019 noted the increased awareness and research on end-of-life management of solar PV in the field of reducing, reusing, and recycling.

Recently, due to the trends in the world in the field of decarbonisation [4–10], many scientists are conducting research on cementless binders [11–16]. Most often, these are geopolymer binders [17–30]. Some of them use glass as a component: waste cathode ray tube (CRT) glass [20,21], liquid-crystal display (LCD) glass [22], and glass powder (GP) [23–27]; as well as huge amounts of municipal recycled glass, industrial recycled glass, glass derived from lighting equipment, borosilicate glass from pharmaceutical package,



Citation: Słomka-Słupik, B.; Wiśniewska, P.; Bargieł, W. Multicomponent Low Initial Molar Ratio of SiO₂/Al₂O₃ Geopolymer Mortars: Pilot Research. *Materials* 2022, *15*, 5943. https://doi.org/ 10.3390/ma15175943

Academic Editors: F. Pacheco Torgal and Ndue Kanari

Received: 22 July 2022 Accepted: 24 August 2022 Published: 28 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fluorescent lamps, glass produced by DC plasma treatment of waste, and even thin-film transistor liquid display panels [28]. However, there are not many scientific articles that exactly indicate the use of glass from photovoltaic panels as a component of binders. Skripkiūnas et al. [31] investigated the properties of concrete containing various quantities of copper indium selenide (CIS) solar module waste by replacing a certain part (up to 40%) of sand and observed that the compressive strength of the specimens was higher when the sand aggregate was replaced by CIS solar module waste particles from 5 to 20%. Máčalová et al. [32] replaced 100% of natural aggregates with recycled glass from PV panels in concrete made of Portland cement. The awareness of the harmful effect of glass on cement concrete, which is related to the alkali–silica reaction (ASR), is commonly present [17,33,34]. Hao et al. [35] examined the compressive strengths of metakaolinite-based geopolymer with solar panel waste glass after 28 days of curing. The geopolymer samples contained solar panel waste glass in the amount of 10 and 20% of the total mass. The strength was higher, 63 MPa, when 10% of glass was used and 49 MPa when 20% of glass was used. Several studies showed that waste glass in powder form can be successfully incorporated as supplementary cementitious material both in alkaline-activated and cement binders. Using different types of waste glass in geopolymer production is caused by the amorphous nature and pozzolanic properties of these materials [27,28].



Figure 1. Potential value creation through PV end-of-life management. Source: irena.org [2].

Geopolymerisation is mainly a developing field of research for utilising solid waste and by-products. From a chemical point of view, it is a geosynthesis of naturally occurring silico-aluminates or other pozzolanic compounds, silica, and alumina source that can dissolve in the alkaline solution—it can act as a source of geopolymer precursors and thus is able to undergo geopolymerisation [36]. The alkaline solution or component is an activator; it is a compound of the elements of the first group in the periodic table, mainly NaOH and KOH. Products of geopolymerisation are also used as immobilisers of metals [37–42]. Setting of the geopolymeric mixture quickly occurs without time for the formation of a proper crystal structure resulting in a microcrystalline, amorphous, or semiamorphous structure depending on the reaction conditions [43]. Undoubtedly Davidovits is considered the precursor of this field of science even before the 1980s [44]. Davitovits stated that the satisfactory properties of the synthesised products can be obtained if the following proportions are kept: M_2O/SiO_2 , 0.2–0.48; SiO_2/Al_2O_3 , 3.3–4.5; H_2O/M_2O_3 , 10-25; and M_2O/Al_2O_3 , 0.8–1.6 [36,45]. However, according to Van Jaarsveld [43], based on [46], Davidovits and co-workers indicated that certain compositional criteria have to be met for geopolymerisation to occur. These include the following: the molar ratio SiO₂:M₂O must be between 4.0:1 and 6.6:1 in the aqueous soluble silicate solution, where M is an alkali metal cation; the aluminosilicate oxide must contain Al, which is readily soluble; and the overall molar ratio Al_2O_3 :SiO₂ must be between 1:5.5 and 1:6.5. As can be seen, these criteria are not unambiguous; therefore, after [43], it must be assumed that while

using waste reactants for the reaction, one should develop his or her own criteria that are adequate to these substrates.

The geopolymeric aluminosilicate has been grouped in three families depending on the atomic ratio Si/Al, which may be 1, 2, 3, or >3 [36,45]. Amorphous to semi-crystalline three-dimensional aluminosilicate structures have been listed: the poly(sialate) type (Si–O– Al–O–), poly(sialate-siloxo) type (Si–O–Al–O–Si–O–), and poly(sialate-disiloxo) type (Si–O– Al–O–Si–O–Si–O–) [44]. However, it should be noted that Provis and Van Deventer [18] mentioned that the sialate nomenclature of Davidovits "implies certain aspects of the geopolymer gel structure which do not correspond to reality".

The general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina was proposed by Glukhovsky in the 1950s [47]. The mechanism of the Glukhovsky model is composed of simultaneous reactions of destruction–coagulation– condensation–crystallisation. The first step consists of a breakdown of the covalent bonds Si–O–Si and Al–O–Si, which happens when the pH of the alkaline solution rises, so those groups are transformed into a colloid phase. Then an accumulation of the destroyed products occurs, which interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed and crystallised structure.

One of the most important source materials for geopolymer is fly ash [15,19,20,26,28]. It is a secondary material, is waste from energy processes, is generally available, and comes from the combustion of coal and/or biomass [13,28,48,49]. The ash from the combustion of hard coal is mainly used in the production of cement [19,28]. It contains large amounts of reactive silica, but the amount of calcium is too small for the pozzolanic reactions to occur when the ash comes into contact with water [19]. The geopolymerisation process consists of exciting aluminium and silicon atoms with a strongly alkaline compound so that it is dissolved to form a geopolymer paste, of which the main phase is the C–S–H gel [18,30,50].

Another precursor of geopolymers is clay [24,25,51–54]. Similar to fly ash, clay minerals are diverse and the resources of aluminosilicates are available worldwide [51]. The use of clays in the production of mechanically strong geopolymers requires its preliminary treatment. This can be accomplished by thermal, mechanical, or chemical means [51]. Better pozzolana properties are obtained by burning; loss of combined water and OH-groups causes the crystalline network of the clay mineral to be destroyed, while silica and alumina remain in an unstable amorphous state that reacts with calcium hydroxide [52]. The most popular in the production of geopolymers is metakaolin, which is obtained during calcinations of kaolinitic clays at temperatures ranging from 500 to 800 °C, depending on the clay [52–54].

Alkaline activation must also include the ground granulated blast furnace slag (GG-BFS). The chemical component of GGBFS mainly consists of the CaO–SiO₂–MgO–Al₂O₃ system, gehlenite (2CaO·Al₂O₃·SiO₂), akermanite (2CaO·MgO·2SiO₂), and depolymerised calcium aluminosilicate glass. The glass content of the slag should be in excess of 90% to show satisfactory properties. The major binding phase in alkali-activated ground granulated blast furnace slag (AA GGBFS) is the C–S–H gel, unlike geopolymers, which are assumed to be the result of the formation of three-dimensional zeolite such as polymers [55].

In order to increase the amount of lime and aluminium in geopolymers, alumina-lime cement (ALC) can be used. Lime is needed for pozzolanic reactions, and aluminium in the available secondary materials is relatively little, taking into account silicon. It was found that calcium has a positive effect on the comprehensive strength of geopolymeric binds, and the formation of Ca compounds in geopolymers is greatly dependent on the pH and Si/Al ratio [56,57]. The addition of a sufficient quantity of Ca to geopolymers in the form of calcium hydroxide can lead to the formation of phase-separated Al-substitute calcium silicate hydrate (C–(A)–S–H) and geopolymer (N–A–S–H) gels [55]. Li et al. [55] emphasised also that Ca²⁺ is capable of acting as a charge-balancing cation within the geopolymeric binding structure. On the other hand, the role of aluminium is also significant because its availability controls the properties of geopolymers, such as setting characteristics, flexural strength, acid resistance, microstructure, and strength development profile [55].

The curing process for geopolymers is also of great importance. Complete geopolymerisation reactions were observed when curing at 40–85 °C [58]. Most studies confirmed the increase in the strength of geopolymers matured at higher temperature; however, Gołek and Deja [59] noticed that accelerating hydration by increasing the temperature or pressure results in the creation of favourable conditions for the growth of crystalline phases, which is the main reason for the observed drops in strength.

Various components have been and still are used in the production of geopolymers, which are examined in terms of composition, curing temperature, alkali concentration, water/solid ratio, strength, shrinkage property, performance in chemical exposure, resistance to freeze–thawing effect or aggressive attack, and heat resistance. To summarise, precursors can be materials rich in Si (such as fly ash or slag) and materials rich in Al (clays) naturally occurring, can come from industrial processes, and can be categorised as waste. The commonly used activators, in turn, are as follows: NaOH, Na₂SO₄, waterglass, Na₂CO₃, K₂CO₃, KOH, K₂SO₄, or a little amount of cement clinker and others [36,60–64].

The aim of the article was to compare the mechanical and material properties of mortars made on standard sand to determine the strength of the binders. These mortars were made of components containing aluminates and silicates, which bind after activation with an alkaline sodium solution. The properties were compared depending on the kaolin clay (KC)—fired and unfired—in the mixture. The influence of the secondary material was also highlighted. However, the amount of aluminium was increased in the mixtures. The value of SiO_2/Al_2O_3 in the designed blends was low, around 2 (Si/Al~1), so poly(sialate) type (–Si–O–Al–O–) geopolymer should be considered.

2. Methods and Materials

2.1. Methods

2.1.1. XRF: X-ray Fluorescence Method

X-ray fluorescence (XRF) is a common method used in the cement industry to test the chemical composition of cement and other additives and powders. Tests were carried out according to PN-EN ISO 12677:2011 [65] on samples grounded to a grain size less than 100 µm and dried at 105 °C to constant weight. Dried samples were ignited at 1025 °C, and the loss of ignition was determined. In order to prepare the fused cast bead used for analysis, the sample ignited to constant weight was fused with a mixture of lithium tetraborate (66.67%), lithium metaborate (32.83%), and lithium bromide (0.5%) produced by Spex CertiPrep (Metuchen, NJ, USA). The chemical composition analysis was performed using a MagiX PW2424 spectrometer produced by PANalytical (Malvern Panalytical Ltd., Enigma Business Park, Grovewood Road, Malvern, UK) calibrated using a series of certified reference materials JRRM 121-135, JRRM 201-210, and JRRM 301-310 (The Technical Association of Refractories, Japan (TARJ), Xiamen, China).

2.1.2. Grain Size Distribution

Two devices were used for the research: the LS 13 320 Particle Size Analyzer Beckman Coulter (Life Sciences Division Headquarters, 5350 Lakeview Parkway S Drive, Indianapolis, IN, USA) and mainly a Horiba LA-300 device (HORIBA, Ltd., Miyanohigashi, Kisshoin, Minami-Ku, Kyoto, Japan). The grain analysis was performed in an accredited laboratory on the basis of the ISO 13320: 2009 [66] laser diffraction method. This method is applicable to particle sizes ranging from approximately 0.1 μ m to 3 mm. The study was conducted in isopropanol. This instrument can accurately measure particle sizes in a range of 0.1–600 microns. The Mie mathematical model was used to calculate the particle size distribution. The measurement characteristics were as follows: dispersant-isopropanol; ultrasounds, 5 s; Laser T%, 86.0.

2.1.3. Thermal Analysis (DTA/DTG/TA)

The clay specimen was tested using an STA 409 PC thermal analyser by NETZSCH (Netzsch Gerätebau GmbH, Wittelsbacherstr. 42, Selb, Germany) coupled with a QMS

403 C Aëolos quadrupole mass spectrometer (Netzsch Gerätebau GmbH, Wittelsbacherstr. 42, Selb, Germany). Simultaneous differential thermal analysis (DTA), thermogravimetric (TG) analysis, differential thermogravimetric (DTG) analysis, and measurement of gases separated from the sample (EGA) were performed. The sample (33.0 mg) was placed in an Al_2O_3 crucible and heated from 40 °C to 1000 °C at a rate of 10 °C/min with an airflow of 30 mL/min.

2.1.4. Strength Test

The strength test was carried out according to PN-EN 196-1 [67], which concerns the strength of cement mortars. The test on bending and compressive strength was conducted in a Controls apparatus (CONTROLS S.p.A., model 65, Cernusco sul Naviglio, Italy), and the results were automatically given after the device was properly set.

2.1.5. Leaching Test

PV glass and mortars were leached to determine their harmfulness to the natural environment after binding in a geopolymer matrix. The water extract was made in accordance with PN-EN 12457-2: 2006 [68] (for ACC) and PN-EN 12457-4: 2006 [69] (for mortars) with the ratio of liquid to solid phase = 10 L/kg. Metals were marked with the ICP-OES method according to PN-EN ISO 11885: 2009 [70]. Chlorides and sulphates were determined according to PN-EN ISO 10304-1:2009 + AC 2012 by ion chromatography [71]. Mercury was tested according to PN-EN ISO 12846: 2012 using the CVAAS method (cold vapour ion absorption spectrometry) [72]. The leaching tests were performed in an accredited external laboratory using approved methods.

2.1.6. Total Carbon and Sulphur Examination

Prior to testing, the sample of fly ash was ground to a grain size below 63 μ m using a grinder with a tungsten carbide lining and then dried at 105 °C to a constant weight.

The carbon and sulphur content was determined using a Leco SC 144 DR sulphur and carbon analyser by Leco (3000 Lakeview Ave. St. Joseph, MI, USA) with a resistance furnace. The test sample was burnt at a temperature of 1350 °C in a stream of oxygen. The content of CO_2 and SO_2 in the resulting gas was determined by measuring the absorption of infrared radiation.

2.1.7. SEM (Scanning Electron Microscopy) Examination

The morphology of the tested sample was determined using a TESCAN Mira 3 LMU scanning electron microscope equipped with an EDS from Oxford Instruments (TESCAN, Abingdon, UK), supported by Aztec software. The specimens were carbon-coated using a Quorum Q150T ES sputter (Quorum Technologies Ltd., Guelph, ON, Canada). The tests were conducted on fractures or powdered material using the SEM-BSE (backscattered electron detector) operating mode or SEM-SE (secondary electron detector). The activation energy of fluorescent radiation used for SEM-EDS analysis was 15 keV.

2.1.8. XRD: X-ray Diffraction

For phase composition analysis, an X'Pert Pro MPD X-ray diffractometer, produced by PANalytical (Westborough, MA, USA), was used. The measurements were conducted at room temperature using monochromatic Cu K α radiation. Qualitative analysis with the support of the ICDD PDF4+ database was performed employing HighScore v4.9 software (Malvern Panalytical Ltd., Malvern, UK, 2020). The test was conducted on powdered samples. Quantitatively, the phases were determined by the Rietveld method using Siroquant computational program (40 Hoskins St., Mitchell, ACT, Australia).

2.2. Characterisation of Components

Materials for the design of binder mixtures with their chemical composition are presented in Table 1. To determine the chemical composition of used components, the XRF method was involved.

Component (PL Abbreviation)	PV Glass(S1)	Kaolin Clay	Ground Granulated Blast Furnace Slag	Alumina- Lime Cement (CG-40)	Autoclaved Cellular Concrete (SOL.1)	Fly Ash from Coal Combustion (WR25.1)	Fly Ash from Biomass Combustion (PLB_T1)
Abbreviation used in this article	PVG	KC	GGBFS	ALC	ACC	FAC	FAB
				Content,	wt.%		
Silica as SiO ₂	72.39	47.46	40.43	3.05	67.45	43.53	60.25
Aluminium as Al ₂ O ₃	1.10	36.75	7.88	42.52	2.32	25.30	5.87
Sodium as Na ₂ O	13.41	0.02	0.46	0.08	0.26	2.22	0.72
Calcium as CaO	9.01	0.23	43.27	35.87	17.26	4.42	11.47
Iron as Fe_2O_3	0.05	0.92	0.81	15.31	1.00	6.80	2.86
Magnesium as MgO	3.09	0.24	6.97	0.50	0.29	2.61	3.51
Potassium as K ₂ O	0.02	0.88	0.29	0.09	0.60	4.67	6.91
Titanium as TiO ₂	0.02	0.24	0.28	2.01	0.06	1.39	0.39
Manganese as MnO	< 0.01	0.02	0.16	0.07	0.02	0.07	0.37
Phosphorus as P ₂ O ₅	< 0.01	0.08	0.02	0.06	0.04	3.41	1.63
Chromium as Cr ₂ O ₃	0.01	0.01	0.01	0.08	0.01	-	0.02
Zirconium as ZrO ₂	< 0.01	< 0.01	< 0.01	0.05	< 0.01	-	0.04
LOI (550 °C)	0.31						
LOI (1025 °C)		13.35	0.46	0.29	10.44	26.31	5.88

Table 1. Chemical composition of components for preparation of binder mixtures.

2.2.1. PVG: PV Glass

Glass from photovoltaic panels came from a recycler (Thornmann Recycling Sp z o.o., Toruń, Poland) in the form of crushed pieces up to 1 cm in size. The glass was not contaminated with a black layer of encapsulant and solar cells. Chemically, it can be classified as soda-lime glass powder. The cross-section and structure of the panel are shown in Figure 2. To prepare the geopolymeric mixtures, the glass was ground, sieved, and tested in a particle size analyser (Beckman Coulter). The results of PVG (PV glass) powder have the following parameters: mean, 97.19 μ m; median, 85.67 μ m; d₁₀, 4.669 μ m; d₅₀, 85.67 μ m; d₉₀, 200.5 μ m; and with phases amounts <3%: 1.284 μ m; <25%, 25.08 μ m; <50%, 85.67 μ m; <75%, 166.0 μ m; and <97%, 227.8 μ m (Figure 3).



Figure 2. Structure of a photovoltaic panel: (a) own photo; (b) elements of the construction of a photovoltaic panel. Source: BRIJ http://www.brijencapsulants.com/2020/12/28/six-main-components-solar-panel/ (accessed on 28 December 2020).



Figure 3. PV Glass powder grain distribution.

2.2.2. KC: Kaolinite Clay

In this examination, kaolin clay (SEDLECKY KAOLIN a.s. 362 26 BOZICANY, Czech Republic, mining date: 15 April 2021) in a powdered form was used. Based on the DTA/TG test result shown in Figure 4, kaolin clay (designated as KC-0) was burned at 600 °C for 1 h in a laboratory ceramic furnace to prepare metakaolin powder specimen, designated as KC-1 in this article.



Figure 4. DTA, DTG, and TG analysis of kaolin clay GK-0.

The mass spectrometer recorded m/e lines from 1 to 70. The thermogram showed a loss of sample mass by 11.13% related to the separation of water from the sample. The maximum water release was at a temperature of 537 °C. The process reached the highest speed at a temperature of 527 °C (minimum on the DTG curve). The weight loss was accompanied by an endothermal heat effect with a minimum on the DTA curve at 528 °C. The temperature range corresponded to the dehydroxylation reaction. The selected temperature of 600 °C for dehydroxylation of the used clay was chosen to ensure that complete dehydroxylation took place, taking into account the rising part of the graph. At

temperatures 339 °C and 464 °C in the mass spectrum of the released gases, there were small maxima of the released CO_2 from the sample.

During the microscopic observations (comparable with [54]), it was noticed that the KC-1 clay, after the calcination process, had a more developed specific surface due to a slightly larger number of smaller agglomerates and separated plates (Figure 5b) than non-sintered kaolin clay KC-0 (Figure 5a). The background is a carbon tape.





The XRD analysis of the KC-0 sample showed the highest amount of not only kaolinite but also quartz, muscovite, montmorillonite, and dawsonite (comparable with [54]). However, the KC-1 sample is mainly the amorphous phase; quartz and KAl₃Si₃ (muscovite) were identified. In the KC-0 sample, the main phase is kaolinite, which means that in the KC-1 sample, the metakaolin is amorphous. There is also muscovite after dehydroxylation in KC-1, which has retained its structure.

2.2.3. ALC: Alumina-Lime Cement

Alumina-lime cement was used because of its high calcium and aluminium content. Calcium is needed for pozzolanic reactions, and aluminium is needed to enrich the mixture with this element. It was produced from two raw materials, bauxite and limestone, by sintering at a temperature of 1250–1550 °C in a rotary kiln. According to the XRD examination, the main phase in this cement is CA and the accompanying phases are C₄AF, C₁₂A₇, and C₂AS (where C = CaO, A = Al₂O₃, F = Fe₂O₃, and S = SiO₂). Its production is controlled according to the PN-EN 14647 standard. Unfortunately, this component is not an anthropogenic mineral but is needed to increase the amount of aluminium and calcium in the mixtures.

2.2.4. GGBFS: Ground Granulated Blast Furnace Slag

Ground granulated blast furnace slag (GGBFS) by Górażdże Cement S.A. (Chorula, Poland), which came from the Ekocem production plant (Dąbrowa Górnicza, Poland), met the standard requirements according to PN-EN 15167-1 [73]. Its specific surface area according to Blaine was 3850 cm²/g, and it was delivered and stored in a sealed container. The use of slag as a binder involves the use of an alkaline activator. Together with sodium metasilicate, it acts as a binder in the mixture [13]. Using X-ray diffraction, it was confirmed that the slag contained approximately 98% amorphous phase.

Figure 6 shows the phase composition of the used GGBFS. The main component of the slag was the amorphous phase and a small amount of calcite. Other typical phases of blast furnace slag were also identified from the group of silicates—melilites, i.e., gehlenite and merwinite (island silicate) [74]. There was also a hydrated basic aluminium magnesium carbonate—hydrotalcite. Hydrotalcites (HTCs) are a class of high-temperature chemical sorbents that have been widely investigated for application in sorption-enhanced reactions [75].



Figure 6. Phase composition of GGBFS.

2.2.5. ACC: Autoclaved Cellular Concrete

Autoclaved aerated concrete is made of cement, lime, gypsum, aluminium powder or aluminium paste as a blowing agent, sand, and water. The production process of aerated concrete consists of exposing it to saturated water vapour in steam autoclaves. Most often, saturated steam with a temperature of 180 to 190 °C and a pressure of 1.0 to 1.3 MPa is used. ACC, in this examination, was used as a secondary material, and the results of its XRD analysis are shown in Table 2 and Figure 7. Phase identification and quantitative composition were performed using the X-ray diffraction method according to PN-EN 13925-1:2007 (described in the previous paragraph). Elements of concrete blocks were prepared from the non-contaminated remains from the construction site by grinding in a ball mill and screening through sieves. The fraction that passed through a sieve with a mesh of 65 μ m was used for the tests.

Table 2. Phase composition of autoclaved cellular concrete (ACC).

Phase	Amount, wt.%			
Amorphous phase	26.6			
Quartz	38.4			
Tobermorite	24.1			
Calcite	4.0			
Anorthite	1.5			
Microcline	2.1			
Anhydrite	2.0			
Gypsum	1.5			



Figure 7. Phase composition of autoclaved cellular concrete.

Particle and cumulative size distribution studies were also performed, obtaining the following parameters: d_{10} , 14.61 µm; d_{50} , 66.54 µm; and d_{90} , 142.40 µm. A Horiba LA-300 device was involved. The examination chart is shown in Figure 8.





2.2.6. FAB: Fly Ash from Biomass Combustion

Fly ash from biomass combustion (FAB) was used as a secondary material; the results of its XRD analysis are shown in Table 3 and point to many different phases. Some of these may come from the contaminants in the soil collected during harvesting. However, the amorphous phase contains more than half of the total mass. Phase identification and quantitative composition were performed using the X-ray diffraction method (described in an earlier paragraph).

Amount, wt.%	
51.3	
26.6	
0.5	
0.4	
2.9	
1.8	
6.6	
6.7	
0.7	
0.1	
1.3	
0.3	
0.6	
	Amount, wt.% 51.3 26.6 0.5 0.4 2.9 1.8 6.6 6.7 0.7 0.1 1.3 0.3 0.6

Table 3. Phase composition of Fly Ash from biomass combustion (FAB).

Particle and cumulative size distribution studies were also performed, obtaining the following parameters: d_{10} , 3.55 µm; d_{50} , 19.99 µm; and d_{90} , 69.96 µm. A Horiba LA-300 device was involved. The examination chart is shown in Figure 9.



Figure 9. Particle size distribution and cumulative size distribution of FAB—fly ash from biomass combustion.

2.2.7. FAC: Fly Ash from Coal Combustion

The examined ash came from the ammonia removal experimental process and contained very large amounts of ammonia, 11.5% of total carbon, and 0.19% of total sulphur. The parameters of the particle and cumulative size distributions were as follows: d_{10} , 16.02 µm; d_{50} , 106.74 µm; and d_{90} , 307.87 µm (Figure 10). A Horiba LA-300 device was involved.

2.2.8. Standard Sand

CEN standard sand was added to the mixture in the amount of 67.2% of the total mass of the mixture in order to make mortars of beams with dimensions of 4 cm \times 4 cm \times 16 cm for binder strength tests according to PN-EN 196-1 [67].



Figure 10. Particle size distribution and cumulative size distribution of FAC—fly ash from coal combustion.

2.2.9. Alkaline-Activating Solution

An activating solution was prepared using sodium metasilicate pentahydrate Na₂SiO₃·5H₂O, sodium hydroxide NaOH, and distilled water with a conductivity of 0.06 μ S in mass proportion 1:2:10.2. The activator was prepared in such a way that the temperature did not excessively rise, i.e., metasilicate was first dissolved using a magnetic stirrer (dissolution is an endothermic reaction), and then sodium hydroxide was added (dissolution is an exothermic reaction). Two types of an activating agent were selected because NaOH is usually used for fly ash and metasilicate for slag [13].

2.3. Selection of Ingredients Proportions, Preparing Mixtures

As it is commonly known, the preparation of the geopolymer blend requires the calculation of the ratios of the oxides or elements present in the precursor (Al, Si) and then the quantity and quality of the activator as well as the amount of water. Based on Table 1, a diagram of the mass ratios of selected oxides that are most often analysed in the synthesis of geopolymers is shown in the case of each ingredient (Figure 11).

As can be seen, the composition of the substrates was mainly aluminosilicates with an emphasis on a higher silicon content than aluminium. Even kaolin clay is richer in silica than alumina. This meant that it was decided to additionally use the substrate alumina-lime cement. Calcium is present in greater quantity only in the slag, and this was another reason why ALC was used to create either the C–A–S–H or C–S–H phase. Most of the components contained trace amounts of sodium. Sodium was found only in glass (PVG).

It was decided to prepare 3 types of mixtures, named M5, M6, and M7, in the same proportions but replacing only 1 waste component—autoclaved cellular concrete (ACC) or fly ash from coal combustion (FAC) with higher amount of ammonia ions or fly ash from biomass combustion (FAB). In addition, each of the mixtures was differentiated, in the type of kaolin clay, to calcined and non-calcined to determine the effect of thermal activation of the kaolin clay.

The mixtures M5, M6, and M7 were prepared on the basis of the computational analyses of the chemical composition of the dry components (without the standard sand). The following proportions were proposed—presented in the form of percentage by mass in Figure 12 and in the molar oxide and atomic elemental forms in Table 4. In Table 5, the mass ratios of the components of the mixtures are given.



Ternary Phase Diagram for Components

Figure 11. Ternary phase diagram of mass ratios for $Na_2O/Al_2O_3/SiO_2$ oxides in components used for mixture preparation.

Ternary Phase Diagram for powders in Mixtures



Figure 12. Ternary diagram of mass percentage ratios of Al, Si, and Na oxides in M5, M6, and M7 mixtures including all dry components of binder (without standard sand).

Table 4. Molar ratio of Si, Na, and Al oxides and atomic ratio of Si, Na, and Al in the designed mixtures M5, M6, and M7 for binder components.

Mixture	0	xide Molar Rat	io	Atomic Ratio			
	SiO ₂ /Al ₂ O ₃	Na ₂ O/SiO ₂	Na ₂ O/Al ₂ O ₃	Si/Al	Na/Si	Na/Al	
Mixture 5	2.28	0.33	0.75	1.14	0.66	0.75	
Mixture 6	2.33	0.33	0.76	1.17	0.65	0.76	
Mixture 7	2.12	0.34	0.73	1.06	0.69	0.73	

Table 5. Quantitative and qualitative compositions of mixtures, in %.

Component		Type of	f Mixture	with Cor	% Mass of Binder Component			
		M.5.0	M.5.1	M.6.0	M.6.1	M.7.0	M.7.1	%
PVG	PV glass	1.1	1.1	1.1	1.1	1.1	1.1	5
FAB	Fly ash from biomass combustion	1.1	1.1					
ACC	Autoclaved cellular concrete			1.1	1.1			5
FAC	Fly ash from coal combustion					1.1	1.1	
KC-0	Kaolin clay	3.2		3.2		3.2		15
KC-1	Sintered kaolin clay		3.2		3.2		3.2	15
GGBFS	Slag	6.5	6.5	6.5	6.5	6.5	6.5	30
ALC	Alumina-lime cement	6.5	6.5	6.5	6.5	6.5	6.5	30
A.1	Na ₂ SiO ₃ ·5H ₂ O	1.1	1.1	1.1	1.1	1.1	1.1	5
A.2	NaOH	2.2	2.2	2.2	2.2	2.2	2.2	10
SS	Standard sand	67.2	67.2	67.2	67.2	67.2	67.2	-
DW	Distilled water	11.2	11.2	11.2	11.2	11.2	11.2	-

Based on a polymeric model of Davidovits [45,64], a poly(sialate) type (-Si-O-Al-O–) structure can be expected in the prepared mixtures $2[Al(OH)_4]^- + [SiO_2(OH)_2]^{2-}$, Si/Al = 1, beside the C–S–H phase.

3. Results with Analysis

3.1. Composition Analysis

It is commonly known that the influences of the molar ratios of SiO_2/Al_2O_3 and Na₂O/Al₂O₃ affect the microstructure and compressive strength of geopolymer binders. In this article, low initial molar ratios of SiO_2/Al_2O_3 (around 2) structures were considered, which favours the condensation of poly-(sialates), with an atomic ratio of Si/Al = 1. High strength and durability systems, in turn, can be achieved when initial molar ratios of SiO_2/Al_2O_3 are around 3.5–4.5 [64].

Juengsuwattananon et al. [64] examined the reaction products of metakaolin-rice husk ash geopolymer with initial molar ratios of SiO_2/Al_2O_3 (2.0–7.0), Na_2O/Al_2O_3 (0.6–1.6), and Na₂O/SiO₂ (0.20-0.72). Moreover, the specimens were cured at 30 °C for 1-90 days before the examination of the phase and microstructure and mechanical properties as well. The highest strength was achieved when the initial molar ratios of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 were 4.0 and 1.0, respectively.

Based on the diagram prepared by Juengsuwattananon et al. [64], the composition data for samples M.5.1, M.6.1, and M.7.1 are placed in the red circle in Figure 13. On this basis, it can be assumed that the designed AA-binders were mainly zeolite + geopolymeric phase + unreacted raw materials. However, there were many other compounds in the composition of mortar components, such as calcium, which also have a great influence on the formation of the microstructure and material properties.



MK = Metakaolin, ZS, ZA, ZY, ZX, ZF = Sodalite, Zeolite type A, Y, X, Faujasite

Figure 13. Ternary mixed design composition of geopolymer pastes with different ratios of $SiO_2/Al_2O_3,\ Na_2O/Al_2O_3,\ and\ Na_2O/SiO_2$ from the article prepared by Juengsuwattananon et al. [64] with own mixture data.

3.2. Strength Tests

The strength tests were carried out as follows. After 7 days, the bars were demoulded and cured in a laboratory room (22 \pm 2 °C) in air. After 7, 14, and 28 days, the bar from each series was tested for its flexural strength. One of the halves was immediately tested for compressive strength, and the other was placed for 3 days in a specialised ventilated dryer for building materials at 105 $^{\circ}$ C. After these 3 days, the compressive strength of the second half was tested on the 10th, 17th, and 31st days of hardening.

Bending and compressive strength test results for mixtures with KC-0 kaolin clay and KC-1 calcined kaolin clay mortars are shown in Figures 14–17.

It can be clearly seen that the calcination of the clay contributed to the increase in the mechanical properties of the mortars. By analysing the graph shown in Figure 14, autoclaved concrete ACC (mortar M.6.0) caused a rapid increase in strength, but in the first 7 days, the bonding reactions were very slow. In the first 7 days, the specimens were not dried out possibly due to water-absorbing clay and curing covered in moulds. As a result of replacing clay with calcined clay, the M.5.1 samples with biomass combustion ash were able to match the strength of the M.6.1 samples with ACC. The least stable was the development of bending strength in the case of samples M.7 with ash with a high content of ammonia.



Flexural strength - specimens with CK-0

Figure 14. Bending strength of mortars with kaolin clay CK-0.



Flexural strength - specimens with CK-1

Figure 15. Bending strength of mortars with calcined kaolin clay CK-1.

The obtained compressive strengths of the test specimens generally were also very low, in the range up to 14 MPa (unburned clay) and 19 MPa (calcined clay). The strongly noticeable difference was between the samples heated for an additional 3 days in 105 °C and non-heated ones made of non-calcined clay (Figure 16). It appears that curing at 105 °C

has stronger developing strength effects than calcination of clay. In the case of samples with KC-1 clay (Figure 17), the strength achieved on the 28th day under normal conditions was equal to that obtained on the 17th day after 3 days of drying. However, specimens on the 10th day of curing were stronger than on the 14th day of curing. It is not known, however, how this increased hardening temperature will affect the further development of strength, which is another interesting research direction.



Compressive strength - specimens with CK-0

Figure 16. Compressive strength of mortars with kaolin clay.



Compressive strength - specimens with CK-1

Figure 17. Compressive strength of mortars with calcined kaolin clay.

3.3. Leaching Test

Leaching was prepared in the case of ground PV glass to check that it did not contain harmful metals after the granulation process and in the case of two mortars: mixture designed M.5.1 and M.5.1.1. The M.5.1.1 mixture is the same as M.5.1 (Table 5), but the PV glass content was eliminated to check the influence of PV glass. The mixtures M.5.1 and M.5.1.1 were cured for 28 days in natural conditions and then dried for 3 days at 105 °C. In the total mass of M.5.1, PV glass was just 1.1%. The effects of removing PV glass from the mortar mixture were as follows: better binding of sulphates, better binding of zinc and chromium, but the release of larger amounts of mercury and arsenic (Table 6).

Component	PV Glass (PVG)	Specimen M.5.1	Specimen M.5.1.1
Chlorides as Cl ⁻	<1.00	<1.00	<1.00
Sulphates as SO_4^{2-}	<1.00	16.6	11.2
Zinc as Zn	< 0.001	0.005	0.003
Cadmium as Cd	< 0.001	< 0.001	< 0.001
Copper as Cu	0.005	< 0.001	< 0.001
Lead as Pb	0.006	< 0.001	< 0.001
Nickel as Ni	< 0.001	< 0.001	< 0.001
Barium as Ba	0.020	< 0.001	< 0.001
Chromium as Cr	< 0.001	0.029	0.025
Mercury as Hg	0.00020	0.06	0.11
Arsenic as As	< 0.01	0.029	0.035
Molybdenum as Mo	< 0.02	< 0.02	< 0.02
Cobalt as Co	< 0.01	< 0.01	< 0.01
Tin as Sn	< 0.02	< 0.02	< 0.02

Table 6. Water extract of selected components of mixtures, in mg/dm^3 .

3.4. SEM Examination

The microscopic examination consisted of comparing the microstructure of the M.6 series samples in relation to the strength results. Sample M.6.0 was made with non-calcined clay and sample M.6.1 with calcined clay. Both samples were cared for in natural conditions without being dried at 105 ° C. Their endurance was tested on the 28th day of hydration. As can be seen from the photos in Figure 18, these two microstructures differed. The maps of the content of the elements in the studied area show larger oval forms with a high silicon content; these are grains of sand. The 100-fold magnification does not show that the matrix of the binder M.6.0 (Figure 18a) is mechanically significantly weaker than that of M.6.1 (Figure 18b); it is even more uniform. However, at higher magnifications (Figure 18e,f), there is clearly less coherence of its elements. In addition, the ITZ (interfacial transitional zone) was more porous in the case of sample M.6.0 (Figure 18e), which can be seen, in particular, by the slag grain on the right side of the image. The fact that it is a slag grain is evidenced by the distribution of the content of magnesium and calcium (Figure 18g). Perhaps a brighter matrix of M.6.1 (Figure 18b), compared with M.6.0 (Figure 18a), indicates a lower water content in the structure. Too much water can hinder the bonding processes and cause disintegration.



(a)

Figure 18. Cont.



(b)







Figure 18. SEM images: (a) BSE, M.6.0, mag.: $100 \times$; (b) BSE, M.6.1, mag.: $100 \times$; (c) map of Si distribution, M.6.0, mag.: $100 \times$; (d) map of Si distribution, M.6.1, mag.: $100 \times$; (e) BSE, M.6.0, mag.: $1k \times$; (f) BSE, M.6.1, mag.: $1k \times$; (g) maps of elements distribution, M.6.0, mag.: $1k \times$; (h) maps of elements distribution, M.6.1, mag.

During observations carried out at a magnification of $10 \text{ k} \times$, crystalline or other regular forms were not generally visible in the mass. A small piece of the phase morphologically



similar to the honeycomb can be seen only in the very centre of the image of sample M.6.0 (Figure 19); probably it is the C–A–S–H phase.

Figure 19. (a) SEM-SE image of M.6.0, mag.: $10k \times .$ (b) SEM-SE image of M.6.0, mag.: $10k \times .$ Points in which EDS analysis was performed.

Without wishing to lower the resolution of the photo shown in Figure 19a, the locations of point analyses are shown above in Figure 19b. Table 7 shows the content of the elements with the comparison in the graphs. Probably, in point 22, the C–A–S–H gel in a form similar to a honeycomb can be seen and, in point 23, a chemically active grain surface of SiO₂.

Spectrum Label	Spectrum 19	Spectrum 20	Spectrum 21	Spectrum 22	Spectrum 23	Spectrum 24
С	2.94	3.84	4.03	1.58	2.89	
О	52.09	55.74	55.36	37.83	56.36	32.86
Na	3.29	4.60	3.60	4.98	0.82	1.62
Mg	0.22	1.01	0.49	2.99		
Al	12.50	13.66	15.00	15.97	1.16	12.27
Si	10.58	12.65	14.99	13.09	37.62	4.84
S	0.12	0.22	0.20	0.44	0.03	0.58
К	0.17	0.12	0.13	0.31		0.13
Ca	14.22	6.88	5.56	18.81	0.78	36.68
Ti	0.53	0.15		0.72		0.38
Fe	3.33	1.13	0.64	3.28	0.33	10.64

Table 7. Content of elements in analys	sed points, in wt.%.
--	----------------------

Elemental analysis of EDS confirmed that hydration products were mainly calcium aluminosilicate hydrate (C–A–S–H) or calcium–sodium aluminosilicate hydrate C–(N)–A–S–H type gels [76] or even with built-in magnesium near slag grains (point 27 in Figure 20a).

The granules seen in Figure 19a are more dissolved in Figure 20a. Fewer voids, larger clusters, and less oblong granules and forming conglomerates with each other, the flake and fibrous phase make the matrix denser in the case of M.6.1 (Figure 20) than in the case of M.6.0 specimen (Figure 19). Similar reports were also noted by Siddika et al. [17]. Therefore, with the fineness in particle size and thermal preparation of KC-0 to KC-1, the microstructure of the AA-binder becomes denser.



Figure 20. (a) SEM-SE image of M.6.1, mag.: $10k \times .$ (b) SEM-SE image of M.6.1, mag.: $10k \times .$ Points in which EDS analysis was performed.

Table 8 shows the content of the elements pointed in Figure 20b with the comparison in the graphs. It seems that in point 25, the C–A–S–H gel can be identified; in 26, a glass; in 27, C–A–(Na,Mg)–S–H; in 28 and 29, C–A–S–H; in 30, C–A–S–H enriched with metals (Fe, Ti); and in 31, C–A–S–H from clay flakes.

Spectrum Label	Spectrum 25	Spectrum 26	Spectrum 27	Spectrum 28	Spectrum 29	Spectrum 30	Spectrum 31
С	3.21	4.87	4.12	3.49	2.72	1.24	5.59
0	51.93	53.71	50.47	54.80	54.12	33.45	51.94
Na	4.65	5.71	7.90	4.01	2.04	4.80	8.66
Mg	0.10	0.07	4.12	0.61	0.42	0.28	2.84
Al	6.48	5.39	11.16	9.18	8.01	6.78	11.96
Si	6.49	27.49	9.81	6.67	5.17	7.53	11.18
S	0.08	0.12	0.23	0.22	0.21	0.18	0.20
K	0.07	0.14	0.14			0.18	0.26
Ca	14.80	2.28	10.06	16.87	20.28	11.53	6.36
Ti	6.12		0.19	0.32	1.62	17.40	
Fe	6.07	0.23	1.83	3.84	5.40	16.63	1.02

Table 8. Content of elements in analysed points, in wt.%.

3.5. XRD Examination—Crystalline Phases

M.6.0 and M.6.1 pastes (prepared without the standard sand) marked M.6.0.z and M.6.1.z, respectively, were tested for crystalline phase composition (Figures 21 and 22). Large amounts of sand in mortars can significantly raise the background, and phases present in minor amount will not be noticed. These samples differently matured, however, for 2 weeks in moulds followed by 2 weeks at 105 °C because they were very moist.









The main phase of the samples M.6.1.z and M.6.0.z is the amorphous phase. Other crystalline phases, detected in smaller amounts, may be derived from the components such as gehlenite (from slag), tobermorite (from ACC), or muscovite (from kaolin clay). The following zeolites were identified in the M.6.1.z sample: sodalite (Na₈[Cl₂(AlSiO₄)₆], PDF#014-6619), cancrinite ((Na₇Ca, \square)₈(Al₆Si₆)O₂₄(CO₃,SO₄)₂·2H₂O, PDF#011-2478), and Linde type A (Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·27 H₂O, PDF#011-3551); and in the M.6.0.z sample, sodalite and MCM-70 (siliceous framework formula Si₁₂O₂₄, PDF#074-8993) were identified. Zeolitic phases demonstrate the effective formation of an aluminosilicate 3D structure. Cancrinite and sodalite were also identified by Toniolo et al. in soda-lime waste glass in fly ash-based geopolymers [26]. There is no evidence of the formation of the sodium

aluminosilicate hydrate (N–A–S–H) type gel, and only calcium aluminosilicate hydrate (C–A–S–H) type gels, in the hardened binder (Si-bearing katoite, PDF#038-0368). Katoite is, in turn, presumably a hydrated CA (CaO·Al₂O₃, PDF#008-8343) phase from Ca–Al–cement. There are some differences between the samples; for example, in M.6.0.*z*, there was no Si-bearing katoite but brownmillerite—a typical phase in the cement composition, which in this composition does not occur in a reacted form. Tobermorite in M.6.0.*z* was richer in water and keno-structured, as it is known that the C–S–H gel is the major binding phase in alkali-activated slag. In M.6.1.*z*, there were no potassium-containing phases of aluminosilicates or silicates, unlike in the case of M.6.0.*z*. Because of dehydroxylation, muscovite became reactive. However, in M.6.1.*z* (contrary to M.6.0.*z*), carbonate phases were detected—hydrotalcite and cancrinite. No crystalline sulphate phase was detected in sample M.6.1.*z*, but the sample had alunite (aluminium potassium sulphate). The sulphates were leachable from ACC and therefore likely reacted with the clay phases. As can be seen, the thermal pretreatment of the kaolin clay greatly contributes to the nature of the crystalline phases also due to the reactions taking place during the alkaline activation.

Phase composition requires an in-depth study also with other methods such as FTIR (Fourier-transform infrared spectroscopy), NMR (nuclear magnetic resonance) spectroscopy, and IR (infrared), which are common methods in the study of geopolymers [52–54,61,62,64].

4. Conclusions

As Provis [77] stated in 2013, still "geopolymers"—a commercial name for the alkali activation of kaolinite, limestone, and dolomite [78]—attract scientists and entrepreneurs. There has been more and more research in recent years, as we are increasingly focusing on reducing equivalent CO₂ emissions [79]. Historically, however, it is very important and should also not be forgotten that the alkali activation technology started with a patent obtained by Kühl in 1908 (US Patent 900,939) [77].

This study investigated the effect of incorporating PV glass powder, kaolin clay, ground granulated blast furnace slag, alumina-lime cement, and, interchangeably, an amount of fly ash from coal combustion or fly ash from biomass combustion or granulated autoclaved cellular concrete together in an alkali-activated matrix. As a replacement for kaolin clay, kaolin clay burned in 600 °C was introduced.

Strength tests carried out between the 7th and 31st days of hardening showed very low values, so it is not recommended to use these mixtures in industrial construction. Further research into the composition and care is needed. However, the use of clay after calcination increased the strength of the mortars. The bending strength values most rapidly increased when using ground AAC as compared with using fly ashes in mixtures with non-calcined clay. The samples needed to be treated at a higher temperature because they retained large amounts of moisture. The molar ratios of Na₂O/SiO₂ and Na₂O/Al₂O₃ of M5, M6, and M7 mixtures are in line with the values proposed by Davidovits, while the value of SiO₂/Al₂O₃ in the designed mixtures is much lower due to the greater amount of added aluminates, in the case when greater strength is desired. Therefore, a further research stage will be preparing mixtures with the same composition but without the alumina-lime cement.

Preliminary tests showed also that the presence of PV glass in mortars, prepared as described in this work, contributes to the better binding properties of mercury and arsenic. Unfortunately, zinc, chromium, and sulphates more readily released in the company of PV glass powder.

The microscopic observations confirmed the greater densification of the microstructure of the binder made of calcined clay due to its greater surface development and dehydroxylation. The main phase seemed to be C–A–S–H. The AA-binder of non-calcined clay was granular, and the ITZ was more porous. No crystals were found in fractures.

Diffractometry studies of crystalline phases confirmed the formation of zeolites. The research also confirmed that the binder is mainly the amorphous phase, containing C–A–S–H and, in small amounts, C–S–H gels.

Further research requires a longer curing time with temperature control and checking whether in the proposed systems increasing the Si/Al ratio increases the strength. In addition, other research directions have also been suggested because expanding knowledge about geopolymers is nowadays undoubtedly strongly recommended.

Author Contributions: Conceptualisation, B.S.-S. and P.W.; methodology, B.S.-S., P.W. and W.B.; software, B.S.-S.; formal analysis, B.S.-S.; investigation, B.S.-S. and W.B.; resources, B.S.-S. and P.W.; data curation, B.S.-S.; writing—original draft preparation, B.S.-S.; writing—review and editing, B.S.-S. and P.W.; visualisation, B.S.-S.; supervision, B.S.-S.; project administration, B.S.-S.; funding acquisition, B.S.-S., P.W. and W.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Polish Minister of Education and Science, grant number: SKN/SP/496162/2021.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank everyone who supported us.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Weckend, S.; Wade, A.; Heath, G. End-of-Life Management Solar Photovoltaic Panels. IRENA and IEA-PVPS. Available online: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2016/IRENA_IEAPVPS_End-of-Life_Solar_PV_ Panels_2016.pdf (accessed on 5 July 2016).
- IRENA. Future of Solar Photovoltaic: Deployment, Investment, Technology, Grid Integration and Socio-Economic Aspects (A Global Energy Transformation: Paper); International Renewable Energy Agency: Abu Dhabi, United Arab Emirates, 2019. Available online: https://irena.org/-/media/Files/IRENA/Agency/Publication/2019/Nov/IRENA_Future_of_Solar_PV_2019.pdf (accessed on 6 January 2020).
- 3. The International Renewable Energy Agency (IRENA). Future of Solar Photovoltaic. Deployment, Investment, Technology, Grid Integration and Socio-Economic Aspects. Available online: https://irena.org/Search?keywords=pv%20end%20of%20life (accessed on 6 January 2020).
- European Commission. Set of Documents. Available online: https://ec.europa.eu/info/strategy/priorities-2019-2024/europeangreen-deal_en (accessed on 11 December 2019).
- 5. Industrial Decarbonisation Strategy. Available online: https://www.gov.uk/government/publications/industrial-decarbonisationstrategy (accessed on 17 March 2021).
- 6. *The Long-Term Strategy of the United States: Pathways to Net-Zero Greenhouse Gas Emissions by 2050;* United States Department of State and the United States Executive Office of the President: Washington, DC, USA, 2021. Available online: https://www.whitehouse.gov/wp-content/uploads/2021/10/US-Long-Term-Strategy.pdf (accessed on 27 September 2021).
- Onyango, S. African Countries Are Joining the World in Decarbonising, but Is this Fair? Available online: https://www.theafricareport.com/131724/african-countries-are-joining-the-world-in-decarbonising-but-is-this-fair/ (accessed on 30 September 2021).
- 8. Japan 2021 Energy Policy Review, International Energy Agency. Available online: https://www.iea.org/reports/japan-2021 (accessed on 4 August 2021).
- 9. EU-Japan Centre for Industrial Cooperation. Green Technology. Set of Documents. Available online: https://www.eu-japan.eu/ tags/green-technology (accessed on 21 July 2021).
- 10. Lee, H.; Schrag, D. The Reforms Needed for 'Deep Decarbonisation' in China. Available online: https://chinadialogue.net/en/ climate/the-reforms-needed-for-deep-decarbonisation-in-china/ (accessed on 7 April 2022).
- 11. Yum, W.S.; Yu, J.; Jeon, D.; Song, H.; Sim, S.; Kim, D.H.; Oh, J.E. Mechanical and Durability Properties of Cementless Concretes Made Using Three Types of CaO-Activated GGBFS Binders. *Materials* **2022**, *15*, 271. [CrossRef] [PubMed]
- Parcesepe, E.; De Masi, R.F.; Lima, C.; Mauro, G.M.; Maddaloni, G.; Pecce, M.R. Experimental Evaluation of the Mechanical Strengths and the Thermal Conductivity of GGBFS and Silica Fume Based Alkali-Activated Concrete. *Materials* 2021, 14, 7717. [CrossRef] [PubMed]
- 13. Słomka-Słupik, B. Self-Immobilizing Metals Binder for Construction Made of Activated Metallurgical Slag, Slag from Lignite Coal Combustion and Ash from Biomass Combustion. *Materials* **2021**, *14*, 3101. [CrossRef] [PubMed]
- 14. Lee, J.; Lee, T.; Lee, S.; Choi, H. Performance Evaluation of Cementless Composites with Alkali-Sulfate Activator for Field Application. *Materials* **2020**, *13*, 5410. [CrossRef]

- Kwon, Y.-H.; Kang, S.-H.; Hong, S.-G.; Moon, J. Acceleration of Intended Pozzolanic Reaction under Initial Thermal Treatment for Developing Cementless Fly Ash Based Mortar. *Materials* 2017, 10, 225. [CrossRef]
- 16. Park, H.; Jeong, Y.; Jeong, J.-H.; Oh, J.E. Strength Development and Hydration Behavior of Self-Activation of Commercial Ground Granulated Blast-Furnace Slag Mixed with Purified Water. *Materials* **2016**, *9*, 185. [CrossRef]
- 17. Siddika, A.; Hajimohammadi, A.; Mamun, M.A.A.; Alyousef, R.; Ferdous, W. Waste Glass in Cement and Geopolymer Concretes: A Review on Durability and Challenges. *Polymers* **2021**, *13*, 2071. [CrossRef]
- 18. Provis, J.L.; Deventer, J.S.J. *Geopolymers. Structures, Processing, Properties and Industrial Applications*; A Volume in Woodhead Publishing Series in Civil and Structural Engineering; Woodhead Publishing: Sawston, UK, 2009. [CrossRef]
- Singh, N.B. 19-Fly Ash in the Construction Industry. In *Handbook of Fly Ash*; Kamal, K.K., Ed.; Butterworth-Heinemann: Oxford, UK, 2022; pp. 565–610. [CrossRef]
- 20. Gao, X.; Yao, X.; Xie, R.; Li, X.; Cheng, J.; Yang, T. Performance of fly ash-based geopolymer mortars with waste cathode ray tubes glass fine aggregate: A comparative study with cement mortars. *Constr. Build. Mater.* **2022**, 344, 128243. [CrossRef]
- Long, W.-J.; Zhang, X.; Xie, J.; Kou, S.; Luo, Q.; Wei, J.; Lin, C.; Feng, G.-L. Recycling of waste cathode ray tube glass through fly ash-slag geopolymer mortar. *Constr. Build. Mater.* 2022, 322, 126454. [CrossRef]
- Yoo, D.-Y.; Lee, S.K.; You, I.; Oh, T.; Lee, Y.; Zi, G. Development of strain-hardening geopolymer mortar based on liquid-crystal display (LCD) glass and blast furnace slag. *Constr. Build. Mater.* 2022, 331, 127334. [CrossRef]
- Derinpinar, A.N.; Karakoç, M.B.; Özcan, A. Performance of glass powder substituted slag based geopolymer concretes under high temperature. *Constr. Build. Mater.* 2022, 331, 127318. [CrossRef]
- Si, R.; Guo, S.; Dai, Q.; Wang, J. Atomic-structure, microstructure and mechanical properties of glass powder modified metakaolinbased geopolymer. *Constr. Build. Mater.* 2020, 254, 119303. [CrossRef]
- 25. Dadsetan, S.; Siad, H.; Lachemi, M.; Sahmaran, M. Extensive evaluation on the effect of glass powder on the rheology, strength, and microstructure of metakaolin-based geopolymer binders. *Constr. Build. Mater.* **2021**, *268*, 121168. [CrossRef]
- Toniolo, N.; Rincón, A.; Roether, J.A.; Ercole, P.; Bernardo, E.; Boccaccini, A.R. Extensive reuse of soda-lime waste glass in fly ash-based geopolymers. *Constr. Build. Mater.* 2018, 188, 1077–1084. [CrossRef]
- 27. Redden, R.; Neithalath, N. Microstructure, strength, and moisture stability of alkali activated glass powder-based binders. *Cem. Concr. Compos.* **2014**, 45, 46–56. [CrossRef]
- 28. Toniolo, N.; Boccaccini, A.R. Fly ash-based geopolymers containing added silicate waste. A review. *Ceram. Int.* 2017, 43, 14545–14551. [CrossRef]
- 29. Zhao, J.; Tong, L.; Li, B.; Chen, T.; Wang, C.; Yang, G.; Zheng, Y. Eco-friendly geopolymer materials: A review of performance improvement, potential application and sustainability assessment. *J. Clean. Prod.* **2021**, *307*, 127085. [CrossRef]
- Nikolov, A.; Rostovsky, I.; Nugteren, H. Geopolymer materials based on natural zeolite. Case Stud. Constr. Mater. 2017, 6, 198–205. [CrossRef]
- Skripkiūnas, G.; Vasarevičius, S.; Danila, V. Immobilization of copper indium selenide solar module waste in concrete constructions. *Cem. Concr. Compos.* 2018, 85, 174–182. [CrossRef]
- 32. Máčalová, K.; Václavík, V.; Dvorský, T.; Figmig, R.; Charvát, J.; Lupták, M. The Use of Glass from Photovoltaic Panels at the End of Their Life Cycle in Cement Composites. *Materials* **2021**, *14*, 6655. [CrossRef]
- Mariaková, D.; Jirkalová, Z.; Řepka, J.; Vlach, T.; Hájek, P. Utilization of photovoltaic panels waste glass in high-performance concrete. AIP Conf. Proc. 2021, 2322, 020020. [CrossRef]
- Stehlík, M.; Knapová, J.; Kostka, V. Possibilities of Use of Glass Recyclate from Photovoltaic Panels for Concrete Masonry Units. In IOP Conference Series: Materials Science and Engineering, Proceedings of the XXV International Conference and Meeting of Departments, CONSTRUMAT 2019, Zuberec, Slovakia, 29–31 May 2019; Volume 549, p. 012006. Available online: https: //iopscience.iop.org/article/10.1088/1757-899X/549/1/012006 (accessed on 10 May 2019).
- Hao, H.; Lin, K.-L.; Wang, D.Y.; Chao, S.-J.; Shiu, H.-S.; Cheng, Y.-W.; Hwang, C.-L. Elucidating characteristics of geopolymer with solar panel waste glass. *Environ. Eng. Manag. J.* 2015, 14, 79–87. Available online: http://www.eemj.icpm.tuiasi.ro/pdfs/ vol14/no1/10_49_Hao_12.pdf (accessed on 15 February 2015).
- Khale, D.; Chaudhary, R. Mechanism of geopolymerization and factors influencing its development: A review. J. Mater. Sci. 2007, 42, 729–746. [CrossRef]
- Komnitsas, K.; Zaharaki, D.; Bartzas, G. Effect of sulphate and nitrate anions on heavy metal immobilisation in ferronickel slag geopolymers. *Appl. Clay Sci.* 2013, 73, 103–109. [CrossRef]
- Xu, J.Z.; Zhou, Y.L.; Chang, Q.; Qu, H.Q. Study on the factors of affecting the immobilization of heavy metals in fly ash-based geopolymers. *Mater. Lett.* 2006, 60, 820–822. [CrossRef]
- 39. Palomo, A.; Palacios, M. Alkali-activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes: Part II. Stabilisation of chromium and lead. *Cem. Con. Res.* **2003**, *33*, 289–295. [CrossRef]
- 40. Medina, T.J.; Arredondo, S.P.; Corral, R.; Jacobo, A.; Zárraga, R.A.; Rosas, C.A.; Cabrera, F.G.; Bernal, J.M. Microstructure and Pb2+ Adsorption Properties of Blast Furnace Slag and Fly Ash based Geopolymers. *Minerals* **2020**, *10*, 808. [CrossRef]
- 41. Ariffin, N.; Abdullah, M.M.; Zainol, R.R.; Murshed, M.F. Geopolymer as an Adsorbent of Heavy Metal: A Review. In Proceedings of the AIP Conference Proceedings, Krabi, Thailand, 29–30 April 2017; Volume 1885, p. 020030. [CrossRef]
- Deja, J. Immobilization of Cr⁶⁺, Cd²⁺, Zn²⁺ and Pb²⁺ in alkali-activated slag binders. *Cem. Concr. Res.* 2002, 32, 1971–1977. [CrossRef]

- 43. Van Jaarsveld, J.G.S.; Van Deventer, J.S.J.; Lorenzen, L. The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications. *Miner. Eng.* **1997**, *10*, 659–669. [CrossRef]
- 44. Davidovits, J. Geopolymers. J. Therm. Anal. 1991, 37, 1633–1656. [CrossRef]
- Davitovits, J.; Davitovits, M.; Davitovits, N. Process for Obtaining a Geopolymericalumno-Slicate and Products thus Obtained. US Patent No. 5,342,595, 30 August 1994. Available online: https://patentimages.storage.googleapis.com/1d/3e/be/2fa9a5 ebece332/US5342595.pdf (accessed on 25 June 2017).
- 46. Davidovits, J. Geopolymers of the first generation: SILIFACE-Process, Geopolymer 88. In Proceedings of the First European Conference on Soft Mineralurgy, Compiegne, France, 1–3 June 1988; Volume 1, pp. 49–67.
- Glukhovsky, V.D.; Rostovskaja, G.S.; Rumyna, G.V. High strength slag-alkaline cements. In Proceedings of the Seventh International Congress on the Chemistry of Cement, Paris, France, 30 June–5 July 1980; Volume 3, pp. 164–168.
- 48. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40–76. [CrossRef]
- 49. Demirbaş, A. Sustainable cofiring of biomass with coal. Energy Convers. Manag. 2003, 44, 1465–1479. [CrossRef]
- 50. Palomo, A.; Grutzeck, M.W.; Blanco, M.T. Alkali-activated fly ashes: A cement for the future. *Cem. Concr. Res.* **1999**, *29*, 1323–1329. [CrossRef]
- Khalifa, A.Z.; Cizer, Ö.; Pontikes, Y.; Heath, A.; Patureau, P.; Bernal, S.A.; Marsh, A.T.M. Advances in alkali-activation of clay minerals. *Cem. Concr. Res.* 2020, 132, 106050. [CrossRef]
- 52. Pytel, Z.; Małolepszy, J. Influence of Kaolin Clay Roasting Conditions on Its Pozzolanic Properties (In Polish, Wpływ Warunków Prażenia Gliny Kaolinowej Na Jej Własności Pucolanowe). In Proceedings of the II Scientific and Technical Conference on Materials Issues in Civil Engineering MATBUD '98, Kraków, Poland, 17–19 June 1998. Available online: https://www.researchgate.net/publication/298784978_WPLYW_WARUNKOW_PRAZENIA_GLINY_KAOLINOWEJ_NA_JEJ_WLASNOSCI_PUCOLANOWE (accessed on 21 July 2022).
- Lemougna, P.N.; Wang, K.; Tang, Q.; Melo, U.C.; Cui, X. Recent developments on inorganic polymers synthesis and applications. *Ceram. Int.* 2016, 42, 15142–15159. [CrossRef]
- Medri, V.; Fabbri, S.; Dedecek, J.; Sobalik, Z.; Tvaruzkova, Z.; Vaccari, A. Role of the morphology and the dehydroxylation of metakaolins on geopolymerization. *Appl. Clay Sci.* 2010, *50*, 538–545. [CrossRef]
- 55. Li, C.; Sun, H.; Li, L. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements. *Cem. Concr. Res.* **2010**, *40*, 1341–1349. [CrossRef]
- Yip, C.K.; Lukey, G.C.; van Deventer, J.S.J. The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. *Cem. Concr. Res.* 2005, 35, 1688–1697. [CrossRef]
- 57. Mozgawa, W.; Deja, J. Spectroscopic studies of alkaline activated slag geopolymers. J. Mol. Struct. 2009, 924–926, 434–441. [CrossRef]
- 58. Shilar, F.A.; Ganachari, S.V.; Patil, V.B.; Khan, M.Y.; Khadar, S.D.A. Molarity activity effect on mechanical and microstructure properties of geopolymer concrete: A review. *Case Stud. Constr. Mater.* **2022**, *16*, e01014. [CrossRef]
- 59. Gołek, Ł.; Deja, J. The hydration conditions of aluminosilicate glasses and the usable properties and phase composition of hardened pates. In Proceedings of the conference Dni Betonu, Wisła, Poland, 13–15 September 2008. Available online: https: //www.dnibetonu.com/wp-content/pdfs/2008/golek_deja.pdf (accessed on 24 September 2008).
- Chi, M.; Huang, R. Binding mechanism and properties of alkali-activated fly ash/slag mortars. *Constr. Build. Mater.* 2013, 40, 291–298. [CrossRef]
- Buchwald, A.; Hilbig, H.; Kaps, C. Alkali-activated metakaolin-slag blends—performance and structure in dependence of their composition. J. Mater. Sci. 2007, 42, 3024–3032. [CrossRef]
- 62. Swanepoel, J.C.; Strydom, C.A. Utilisation of fly ash in a geopolymeric material. Appl. Geochem. 2002, 17, 1143–1148. [CrossRef]
- 63. Lombardi, F.; Mangialardi, T.; Piga, L.; Sirini, P. Mechanical and leaching properties of cement solidified hospital solid waste incinerator fly ash. *Waste Manag.* **1998**, *18*, 99–106. [CrossRef]
- Juengsuwattananon, K.; Winnefeld, F.; Chindaprasirt, P.; Pimraksa, K. Correlation between initial SiO₂/Al₂O₃, Na₂O/Al₂O₃, Na₂O/SiO₂ and H₂O/Na₂O ratios on phase and microstructure of reaction products of metakaolin-rice husk ash geopolymer. *Constr. Build. Mater.* 2019, 226, 406–417. [CrossRef]
- 65. *PN-EN ISO 12677:2011;* Chemical Analysis of Refractory Products By X-ray Fluorescence (XRF)-Fused Cast-Bead Method. PKN: Warsaw, Poland, 2011.
- 66. ISO 13320:2009; Particle Size Analysis-Laser Diffraction Methods. Publication Date: 2009-10. Technical Committee: ISO/TC 24/SC 4 Particle Characterization. ICS: 19.120 Particle Size Analysis. Sieving. ISO: Geneva, Switzerland, 2009. Available online: https://www.iso.org/standard/44929.html (accessed on 6 January 2020).
- 67. PN-EN 196-1:2016-07; Metody Badania Cementu-Część 1: Oznaczanie Wytrzymałości (Cement Test Methods-Part 1: Determination of Strength). PKN: Warsaw, Poland, 2018.
- 68. PN-EN 12457-2:2006; Polish Version, Characterization of Waste-Leaching-Compliance Test for Leaching of Granular Waste Materials and Sludge-Part 2: One-Stage Batch Test with a Liquid/Solid Ratio of 10 L/kg for Materials with a Particle Size of less than 4 mm (no Reduction or with Size Reduction. PKN: Warsaw, Poland, 2006.

- 69. *PN-EN 12457-2:2006;* Polish Version, Characterization of Waste-Leaching-Compliance Test for Leaching of Granular Waste Materials and Sludge-Part 4: One-Stage Batch Test with a Liquid/Solid Ratio of 10 L/kg for Materials with a Particle Size of less than 10 mm (no Reduction or with Size Reduction. PKN: Warsaw, Poland, 2006.
- PN-EN ISO 11885:2009; English Version, Water Quality-Determination of Selected Elements by Inductively Induced Plasma Optical Emission Spectrometry (ICP-OES). PKN: Warsaw, Poland, 2009.
- 71. *PN-EN ISO 10304-1:2009*; English Version, Water Quality-Determination of Dissolved Anions by Ion Chromatography-Part 1: Determination of Bromides, Chlorides, Fluorides, Nitrates, Nitrites, Phosphates and Sulphates. PKN: Warsaw, Poland, 2009.
- 72. *PN-EN ISO 12846:2012;* English Version, Water Quality-Determination of Mercury-Atomic Absorption Spectrometry (AAS) Method with or without Enrichment. PKN: Warsaw, Poland, 2012.
- 73. *PN-EN 15167-1:2007*; Polish Version, Ground Granular Blast Furnace Slag for Use in Concrete, Mortar and Paste-Part 1: Definitions, Specifications and Compliance Criteria. PKN: Warsaw, Poland, 2007.
- 74. Bolewski, A.; Manecki, A. Mineralogia Szczegółowa (Detailed Mineralogy); Publishing house PAE: Warsaw, Poland, 1993.
- 75. Rackley, S.A. 7-Adsorption capture systems. In *Rackley, Carbon Capture and Storage*, 2nd ed.; Stephen, A., Ed.; Butterworth-Heinemann: Oxford, UK, 2017; pp. 151–185. [CrossRef]
- Samarakoon, M.H.; Ranjith, P.G.; De Silva, V.R.S. Effect of soda-lime glass powder on alkali-activated binders: Rheology, strength and microstructure characterization. *Constr. Build. Mater.* 2020, 241, 118013. [CrossRef]
- 77. Provis, J.L. Geopolymers and other alkali activated materials: Why, how, and what? Mater. Struct. 2014, 47, 11–25. [CrossRef]
- Palomo, A.; Krivenko, P.; Garcia-Lodeiro, I.; Kavalerova, E.; Maltseva, O.; Fernández-Jiménez, A. A review on alkaline activation: New analytical perspectives. *Mater. Construcción* 2014, 64, 315. [CrossRef]
- 79. Palomo, A.; Maltseva, O.; Garcia-Lodeiro, I.; Fernández-Jiménez, A. Portland Versus Alkaline Cement: Continuity or Clean Break: "A Key Decision for Global Sustainability". *Front. Chem.* **2021**, *9*, 705475. [CrossRef]