



Sustainable Fly Ash Based Geopolymer Binders: A Review on Compressive Strength and Microstructure Properties

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Abstract: As a result of global warming, the pursuance of low-carbon, sustainable building materials has been prioritized. The development of geopolymer/cement-less binders can be considered an innovative and green way forward to minimize carbon footprint and tackle industrial waste material utilization. However, the chemical composition and properties of industrial waste-derived geopolymer binders varies considerably based on the chemical compositions of the source materials. This review paper presents a comprehensive understanding of the role of different chemical compositions (namely SiO₂, Al₂O₃, CaO, Fe₂O, and MgO) available in contemporary industrial wastes and the development of geopolymer binders. Subsequently, the compressive and microstructure properties of various FA-based geopolymer binders have been discussed to exhibit the feasibility of FA as a reliable source material. Significant findings and research gaps have been considered to aid future research works. Indeed, they provide guidelines for the commercial implementation of FA-based geopolymer binders as a low-carbon alternative to Portland cement.

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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/). **Keywords:** geopolymer; compressive strength; low-carbon composites; microstructure; waste management; green binders

1. Introduction

Cement production contributes nearly 5–8% of global CO₂ emissions [1]. For this reason, issues such as climate change, due to global warming, are considered severe areas of concern. In order to significantly scale down carbon emissions, efforts have been made to develop and implement greener alternatives to cement. The greener (low-carbon) alternatives could not only curb carbon emissions, but also provide an effective waste management strategy to achieve the sustainable development goals of the 21st century. Geopolymer (cement-less) binders are the most promising green building material. Figure 1 demonstrates the use of industrial wastes for the production of geopolymer composites which, from an environmental perspective, leads to several benefits.

Since the inception of the term '*geopolymers*' by J. Davidovits in 1978, research and development in the field of geopolymers has steadily increased and is now considered a highly dynamic area of scientific investigation from both the commercial and environmental viewpoint. The formation of geopolymers includes a reaction between aluminosilicate raw materials (industrial wastes) and an aqueous alkaline composition (usually a mixture of alkali hydroxides and silicates). The result is the inorganic polymer matrix, consisting of a three-dimensional framework of covalently bonded Si-O-Al-O (polysialate), with outstanding strength and microstructural and durable properties compared to cement-based materials [2–6]. However, as proposed in various studies [7–9], the reaction mechanism is a multiphase and complex process and still requires extensive investigation.

On the other hand, the rise in manufacturing industries calls for effective industrial waste management strategies. Therefore, developing industrial waste-derived geopolymer binders could potentially be the solution, promoting the concept of a circular economy

—waste to wealth [7,8]. The various industrial wastes contain a significant amount of aluminium (Al) and silicon (Si), which are essential for the formation of a strong and durable geopolymer matrix [9,10] and serve as source material in the preparation of geopolymer binders. In some studies [11,12], the presence of magnesium oxide (Mg) and iron (Fe), alongside Al and Si, in some source materials have also been reported to be beneficial for the strength development of resulting geopolymer binders. For this reason, the utilization of such wastes for the production of eco-friendly mortars and concrete could be a step forward in reducing our dependence on cement [13].

Over the last decade, numerous researchers have determined FA as an exceptional geopolymer binder due to its physical and chemical characteristics, aiding in geopolymerization reactions. A high amount of alumino silicate content in fly ash facilitates increased reactivity, with a higher degree of geopolymerization in an alkaline environment, while supporting the reduction of hydration heat and thermal cracking. The development of aluminosilicate gel and the early strength gain of FA-based geopolymers has been demonstrated upon premature high-temperature curing while increasing the rate of geopolymerization due to the requirement of higher activation energy of fly ash. Due to their amorphous nature, FA-based geopolymers possess excellent durability against acid and alkali attacks compared with other geopolymer binders.

This review article discusses some of the latest developments in FA-based geopolymer binders with-GGBFS, RM, IOT, FCA, MK, and SF as source material combinations. Particular focus has been given to the use of these contemporary wastes that require sincere attention to be reused in order to avoid the deterioration of the environment. Particular emphasis has been provided on the role of chemical compositions of these wastes during geopolymerization. There is a lack of studies that clearly describe the role of these particular wastes. However, this paper does not intend to offer an in-depth overview of all the factors/properties of FA-based geopolymer binders. Instead, it emphasizes the importance and selection of source materials for geopolymerization. Further, it concentrates only on the compressive strength and microstructure properties (XRD, SEM, FTIR).



Figure 1. Utilization of industrial wastes for the production of geopolymer composites-leading to several merits.

2. Scope of the Study

The current knowledge regarding geopolymers suggests that the selection of source material is crucial for enabling enhanced end properties. The source materials, whose reactivity is maximum and could be readily dissolved, facilitate a better degree of polymerization, thus requiring less curing time. To this end, FA is considered to be an effective source material, owing to its availability, reactivity and chemical compositions, which in turn provide superior properties to the final geopolymer products. Several researchers have therefore investigated many such industrial wastes as a primary or secondary source, along with fly ash as a material combination [14,15].

It is understood from the past literature that the chemical property is the deciding factor when selecting the source materials for the production of geopolymer binders. Hence, the scope of this review includes the initial discussion of the chemical compositions (SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO) of the desired source materials (FA, GGBFS, RM, IOT, FCA, MK, SF) and their influence upon the geopolymer binder structure formation. It is worth reiterating that this study primarily reviews the properties of FA-based geopolymer binders in two sections: Part-I looks at the compressive strength properties, and part-II at the microstructure properties (XRD, SEM, FTIR) of the geopolymer binder system, derived from FA in combination with IOT, RM, FCA, GGBFS, MK, SF (respectively).

3. Chemical Properties of Industrial Wastes/Source Materials

The rise in the manufacturing industries to attend to the needs of 21st-century civilization has led to a significant generation of industrial waste. With the ultimate aim of achieving a circular economy and sustainable development, these wastes could be utilized efficiently for making geopolymer binders. It is imperative to study the chemical properties of each of these wastes before their implementation as source materials. The chemical compositions play a significant role in the formation of the geopolymer network (Si-O-Al-O), geopolymer gels (C-A-S-H/N-A-S-H) [16–18], that in turn determine the strength and other characteristics of the final product. Hence, understanding geopolymer binders requires the utmost attention to the chemistry involved. The SiO₂ and Al_2O_3 content in the source materials are responsible for the formation of the principal geopolymer network (-Si-O-Al-), while the CaO, Fe_2O_3 , MgO contents provide additional mineral compounds, such as calcium aluminosilicate hydrate (C-A-S-H), magnesium aluminosilicate hydrate (M-A-S-H) and ferrosiliate (-Fe-O-Si-O-) type gels, respectively. These additional mineral phases improve the binder matrix, leading to a denser binder structure. Therefore, in this section, the authors' primary focus is on the chemical properties, and in particular, SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO of FA, GGBFS, RM, IOT, FCA, MK and SF, before moving toward the strength and microstructure properties.

According to Davidovits, geopolymerization involves the formation of the Si-O-Al-O network [19]. Therefore, the presence of a high amount of Si and/or Al makes industrial waste a potential candidate for geopolymerization. However, apart from oxides of Si and Al, the oxides of Ca, Fe, and Mg are also responsible for geopolymer compound formation. These minerals co-exist alongside the primary polymer chain of Si-O-Al-O-, which further influences the strength of the overall binder matrix.

The chemical compositions (esp. SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO %) of the FA, GGBFS, IOT, RM, FCA, MK, and SF are graphically presented in Figure 2. Table 1 shows that the chemical compositions of each of these wastes vary across the source of their origin (region) and method of processing.



Figure 2. The graphs show the distribution of SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO (Wt.%) in the industrial wastes [17,19–28].

			(Chemical C	ompositi	ons (Wt.%	.)
	Industrial Source & Region	Authors	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO
	NTPC Ramagundam Thermal Power Plant, India	[27]	60.11	26.53	4.00	4.25	1.25
ASH	Tarong Power Plant, Australia	[28]	75.66	19.00	0.30	1.38	0.00
ТХ	Gladstone Power Station, Australia	[29]	47.83	28.49	5.51	11.38	1.43
Ц	Cates Electrical Prod. Plant, Turkey	[30]	54.08	26.08	35.58	6.68	2.67
	Lethabo Power Plant, South Africa	[31]	56.45	30.27	4.59	3.58	1.06
	Nippon Steel & Sumitomo Metal Corporation, Japan	[32]	30.53	13.67	46.00	0.33	5.09
FS	Vizag steel plant, India	[33]	30.61	16.24	34.48	0.58	6.79
GGB	JSW Iron and Steel Plant, Bellary, India	[34]	32.52	17.14	34.22	1.22	9.65
	Rourkela Steel Plant, India	[35]	30.82	21.06	32.02	1.37	9.52
	Esfahan Steel Company, Iran	[36]	35.85	13.39	37.71	1.06	9.10
	Lake Superior Iron Ore District facility, USA	[37]	68.77	0.8675	0.275	28.17	0.74
	Copper-iron mine, Zibo city, China	[38]	70.32	5.1	4.71	10.93	4.51
IOT	Iron ore tailing dam, Brazil.	[39]	30.00	21.20	0.10	47.80	-
	Iron Ore mine site, Kuancheng Chengde, China	[40]	67.58	8.70	5.78	7.42	4.37
	Iron ore tailings dam, Ouro Preto, Brazil.	[41]	40.00	8.70	0.00	48.90	-
	Rio Tinto Aluminium company, Canada	[42]	10.52	22.12	1.36	38.92	0.10
	Hindalco Industries, Belgaum, India	[43]	9.93	18.1	2.3	42.9	-
βM	Tan Rai Bauxite Plant, Vietnam	[44]	4.52	18.98	0.87	49.90	-
1	Aluminium Smelter, Alcoa, Spain	[45]	5.67	14.63	1.88	52.25	3.35
	Zhaofeng Aluminium Company, China	[46]	21.43	22.72	16.49	9.98	0.00
	Balasore Alloys Limited, India	[47]	19.60	11.2	4.2	6.1	15.6
ČĂ	Balasore Alloys Limited, India	[48]	19.10	10.91	3.14	7.84	23.60
Щ.	Balasore Alloys Limited, India	[24]	19.10	10.91	3.14	7.84	23.60
×	C~ LUZ (Nové Strašecí, Czech Republic)	[49]	55.01	40.94	0.55	0.55	0.14
IW	Astrra Chemicals, Chennai, India	[50]	47.64	50.22	0.05	0.24	0.05
	Hongle, Inc. (Henan, China).	[25]	53.65	43.12	0.17	0.76	0.06
	Counto Microfine Products Pvt.Ltd., Goa, India	[15]	93.67	0.83	0.31	1.30	0.84
SF	Shenhua Junggar Energy Corporation, Junggar, China	[51]	95.72	0.09	0.23	0.63	0.37
	SMS ASIA Pvt. Ltd., Rourkela, India	[26]	93.67	0.83	0.31	1.30	0.84

Table 1. Chemical compositions of FA, GGBFS, IOT, RM, and FCA; detected from XRF analysis.

Role of SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO in the Formation of Geopolymer Binder Structure

The reaction process leading to the formation of a geopolymer binder structure is complicated and is controlled by various parameters [52]. The most significant factor remains the reactivity of SiO₂, Al₂O₃, CaO, MgO, and Fe₂O₃ present in the source materials used, which are discussed herein.

The initial step, in the case of geopolymerization, is the dissolution of SiO_2 and Al_2O_3 from the source materials under an alkaline environment, which leads to the development

of Si-OH and Al-OH bonds [53]. Subsequently, due to subsequent condensation and polymerization reactions, a 3D network structure is produced that involves the tetrahedral networks of $[SiO_4]^-$ and $[AlO_4]$, linked via shared oxygen atoms [54]. However, these tetrahedral connection types of $[SiO_4]$ and $[AlO_4]$ are often very distinct and intricate; therefore, it can be implied that the properties of the final geopolymer product vary with different connection types [19]. For this reason, it is crucial to select source materials with an optimum composition of SiO₂ and Al₂O₃ in order to achieve enhanced geopolymer properties [20].

The CaO in the source materials does not participate in the core geopolymer network formation, i.e., Si-O-Al-. However, it aids in the formation of hydration products such as C-S-H (a space-filler) and a geopolymer gel, i.e., C-A-S-H, inside the geopolymer binder structure [55]; however, this geopolymer gel also comprises of Al and Si in a tetrahedral connection type, as mentioned earlier. It is also acknowledged that the final orientation and properties of geopolymer structures vary depending on the CaO content in the source materials [56]. Several researchers have favored the presence of CaO in the source materials to achieve improved properties [57–60]. Furthermore, the hardening time of geopolymers is also significantly affected by the presence of low/high CaO content in the source material [61]; hence, the role of CaO is considered crucial during the selection of source material for geopolymerization.

The presence of iron oxide (from the iron-rich source materials) is indicated by the replacement of Al³⁺ by Fe³⁺ (ferric ions) in the geopolymer binder structure (Si-O-Al), yielding a *Ferro-sialate* network (-Fe-O-Si-O-Al-O-) [62,63]. In contrast, some studies in the past have also found that iron, in its Fe²⁺ (ferrous) state, remains inert and does not participate in the geopolymerization process [64]. However, Lemougna et al. [65] noticed that some of the ferrous ions are present in the tetrahedral connections of the Si-O-Al network. This observation is corroborated by Kaze et al. [66], who reports that crystalline phases of ferrous ions exist, such as fayalite and siderite, in the final geopolymer binder system. Hence, it is confirmed that the presence of iron in its ferric or ferrous state affects the performance of the geopolymer binder structure and its formation.

The role of MgO in the source materials has been studied in [11,67,68]. It is demonstrated that the existence of MgO did not aid in developing or reorganizing the geopolymer chain (Si-O-Al). However, its presence led to the formation of *hydrotalcite*. This magnesium and aluminium hydroxycarbonate mineral form act as a filler agent while aiding in accelerating the generation of hydration products such as C-S-H. This reveals that, although MgO does not participate in the core development of geopolymer tetrahedral network formation, it necessitates forming other chemical compounds that directly affect the final geopolymer binder structure.

In this section, it is understood that it is a matter of significance to study the chemical compositions of the source materials (FA, GGBFS, IOT, RM, FCA) and their involvement in the formation of binder structure, which will ultimately influence the end properties. In this context, it is now essential to understand the effect of these source materials on the properties (esp. compressive strength and microstructure), and the subsequent sections (Part I and II) attempt to study this exclusively.

4. Part I: Review of Compressive Strength Properties

The industrial wastes considered for this study-FA, GGBFS, IOT, RM, FCA, MK, SFcarry unique chemical compositions of SiO₂, CaO, Fe₂O₃, Al₂O₃, MgO % (see Table 1). Different combinations of these source materials have been investigated worldwide to prepare geopolymer binders. However, in this section, the authors have first discussed the compressive strength properties of the geopolymer binders resulting from 100% FA, a combination of FA and GGBFS, followed by the RM, IOT, FCA, MK, SF-based geopolymer binders combined with FA. FA is widely available and is a worthy candidate for geopolymerization because of its chemical composition and easy availability. For the clarity of readers, it is also mentioned that the source material compositions containing only 100% FA are not considered for this review study. This is because the geopolymers prepared from 100% FA has certain limitations, such as a slow setting (100% FA) [69] and low early-age strength gain (100% FA) [70]. In addition, the geopolymerization of other industrial wastes is beneficial from waste management and environmental protection perspectives. Hence, efforts have been made worldwide to utilize these wastes while simultaneously supplementing them with FA for enhancing geopolymer reactions. The research involving a blended source material combination of FA where FA is present as one of the source materials (RM, IOT, FCA, MK, SF) have reported promising results, some of which are discussed in this study.

4.1. FA-Based Geopolymer Binder

Tho-In et al. [71] utilized high-calcium FA to manufacture geopolymer binder pastes (100% FA) under a heated curing regime of approximately 60 °C for 48 h, generating a 7-day compressive strength of 45.7 MPa. Their investigation included Na_2SiO_3 and NaOH as the alkaline activator with alkaline solution/binder (0.6) and Si/Al (3.02).

Another study, by Nagajothi and Elavenil [72], explored the application of 100% FA as a source material in geopolymer concrete under ambient curing conditions. The mix proportions for the casting incorporated M-Sand, Coarse aggregate, and alkaline solution, with NaOH/Na₂SiO₃ (2.5) and SiO₂/Al₂O₃ ratio of 2.36, achieving a 28-day compressive strength of approximately 30.7 Mpa. Furthermore, the control mixtures (100% FA) of geopolymer mortars, developed by Al-mashhadani et al. [30], activated by a mix of NaOH-12 M and Na₂SiO₃, obtained a 7-day and 28-day compressive strength of around 60.75 Mpa and 60.45 Mpa, respectively, through heat curing of 80 °C for 24 h, followed by room temperature conditions. Table 2 provides data from previous studies concerning the compressive strength of FA-based geopolymer binders.

Authors	Specimen Type	Source Materials	Molarity of NaOH	Curing Regime	28-Day Compressive Strength (Mpa)						
[71]	Paste	100% FA	12 M	Oven (60 °C + 48 h)	N/A						
				Ambient	41.3						
[73]	Mortar	100% FA	14 M	Oven (30 °C + 18 h)	50						
				Oven (60 °C + 18 h)	63						
[30]	Mortar	100% FA	12 M	Oven (80 °C + 24 h)	60.45						
[74]	Concrete	100% FA	12 M	Oven	N/A						
[, -]	Concrete	100% FA	12 111	$(60 {}^{\circ}\text{C} + 48 \text{h})$	N/A						
		100% FA			26.1						
[75]	Concrete	100% FA	12 M	12 M	12 M	12 M	12 M	12 M	12 M	(75 °C + 24 h)	14
		100% FA		(, - , - , - , - , - , - , -	13.7						
[76]	Mortar	100% FA	10 M	Oven (60 °C + 48 h)	34.3						
[72]	Concrete	100% FA	8 M	Ambient	30.7						
[77]	Mortar	100% FA	10 M	Oven (60 °C + 48 h)	N/A						
[78]	Mortar	100% FA	4 M	Oven (60 °C + 24 h)	8.18						

Table 2. Compressive strength of FA-based geopolymer binders.

4.2. FA-GGBFS-Based Geopolymer Binder

Recently, in a study by Nagajothi and Elavenil [72], FA was blended with GGBFS as a source material to produce geopolymer binders for manufacturing concrete. GGBFS replaced FA in 0%, 10%, 20%, and 30% by wt., while manufacturing sand (M-sand) substituted natural sand. The compressive results of the resulting geopolymer concrete increased by 17–41%. The authors of the study concluded that the increase of GGBFS content in the mix increased the Si/Al ratio, which subsequently improved the amount of Si-O-Si bonds in the system, thereby elevating the strength gain.

Saha and Rajasekaran [79] also attempted to improve the compressive strength properties of FA-based geopolymer paste by combining GGBFS at desired levels. From Figure 3, it was found that the compressive strength escalated with the increasing molarity of NaOH and GGBFS%; the highest 28-day compressive strength of 78 MPa was attained by the mix with 16 M NaOH and 50% GGBFS. The authors attributed this significant growth in the compressive strength to the formation of C-S-H gels in the mixture (because of the CaO content from the GGBFS) and the 3-D geopolymer network of Si-O-Al.

The coexistence of C-S-H gel and C-A-S-H/N-A-S-H gels have been established in a study by El-Hassan and Ismail [73], where geopolymer mortars were prepared with FA, GGBFS and desert dune sand as fine aggregates. The molarity of NaOH was fixed at 14 M, and the compressive strength results were assessed. The authors stressed that the simultaneous production of C-A-S-H/N-A-S-H gels and C-S-H gels led to the increased compressive strength of the mixes. As shown in Figure 4, the compressive strength of 100% FA mix samples was less than those containing 25% and 50% GGBFS. However, the water requirement of GGBFS particles was high, due to the presence of calcium. Therefore, the compressive strength was reduced for the mix containing 100% GGBFS and was drier than other mixes. Table 3 provides data from past works concerning the compressive strength of FA-GGBFS-based geopolymer binders.

Authors	Specimen Type	Source Materials	Molarity of NaOH	Curing Regime	28-Day Compressive Strength (MPa)
[80]	Concrete	50% FA + 50% GGBFS	8	Ambient temperature	41
[81]	Concrete	70% FA + 30% GGBFS	8	Room temperature	45
[82]	Concrete	60% FA+ 40% GGBFS	16	Ambient temperature	49.53
[83]	Concrete	80% FA + 20% GGBFS	6	Ambient temperature	38
[84]	Concrete	70% FA + 30% GGBFS	8	Oven	41.26
[85]		62% FA + 38% GGBFS	10	Ambient temperature	39.9
[86]	Concrete	50% FA + 50% GGBFS	8	Oven 60 $^\circ\mathrm{C}$ 24 h	61.9
[87]	Concrete	80% FA + 20% GGBFS	10	20 °C in sealed containers (>90% relative humidity, RH)	39
[88]	Concrete	90% FA + 10% GGBFS	10	Oven 60 °C 24 h	45.62

Table 3. Compressive strength of FA-GGBFS-based geopolymer binders.

Authors	Specimen Type	Source Materials	Molarity of NaOH	Curing Regime	28-Day Compressive Strength (MPa)
[89]	Concrete	20% FA+ 80% GGBFS	12	Oven 80 °C 24 h	21.35
[78]	Mortar	50% FA + 50% GGBFS	4	Ambient temperature	42
[72]	Concrete	70% FA + 30% GGBFS	8	Ambient temperature	42.2
[75]	Concrete	70% FA + 30% GGBFS	12	75 °C + Ambient temperature	52.3
[74]	Concrete	70% FA + 30% GGBFS	12	Oven 60 °C + Ambient temperature	47.2

 Table 3. Cont.



Figure 3. 28-day compressive strength of the FA-GGBFS geopolymer paste [79]. Reprinted with permission from [79]. Copyright 2017 Elsevier.



Figure 4. Compressive strength of FA-GGBFS geopolymer mortars [73].

4.3. FA-RM-Based Geopolymer Binder

The use of RM as the sole source material for the preparation of geopolymer binders is considered less successful due to its low Al_2O_3 and high Fe_2O_3 (see Table 1). For this reason, supplementary sources with a higher aluminium content, such as FA, are encouraged. Moreover, in some cases, the RM is subjected to pre-treatment with Na_2O , and it was found that the compressive strength improved with this method of pre-treatment [90].

In a study by Hu et al. [12], geopolymers were manufactured using pre-treated RM and FA. It was found that the geopolymer binders with FA (50 wt.%) (i.e., by weight of the source material mix) increased in compressive strength; the highest 28-day compressive strength of 23.8 MPa was achieved. The results indicated that the Fe³⁺, from RM substituted Al³⁺ in the aluminosilicate geopolymer structure consisting of Si and Al, significantly improved the strength of the geopolymer binders.

Hu et al. [91] studied the utilization of high-volume RM to make geopolymer binders along with class C-type FA (high calcium content) and class F-type FA (low calcium content). A weight ratio of 50:50 (RM:FA) was selected for preparing mix samples under ambient conditions, using NaOH only as an activator. The results indicated that the mixes prepared with class C FA achieved better strength (15.2 MPa) than those prepared with class F FA (0.8 MPa). It was also found that the mixes with class F FA exhibited a slow reaction rate under ambient conditions compared to the class C FA-based geopolymer binders because of the presence of more active CaO content. This augmentation in strength, due to the presence of high CaO, acted as a filler by forming C-S-H gels as hydration products along with geopolymer gels (C-A-S-H/N-A-S-H). This fact is corroborated by van Deventer et al. [92], who stated that the active CaO content in the class C FA plays a significant role in the precipitation of Si and Al constituents from the source materials involved, thereby causing fast setting under ambient conditions and facilitating improved strength characteristics. Table 4 provides data from past works concerning the compressive strength of FA-RM-based geopolymer binders.

Authors	Specimen Type	Source Materials	Molarity of NaOH	Curing Regime	28-Day Compressive Strength (MPa)
[93]	Concrete	15% RM + 15% FA	8	Ambient temperature	38
[94]	Paste	20 RM + 80% FA	12.5	Oven 35 °C 48 h	64
[95]	Paste	50 RM + 50% FA	8	Autoclave	31.7
[96]	Paste	5% RM + 95% FA	6	Oven 60 °C 24 h	41.38
[97]	Mortar	40% RM + 60% FA	10	Ambient temperature	13.49

Table 4. FA-RM-based geopolymer binders.

4.4. FA-IOT-Based Geopolymer Binder

Kuranchie et al. [22] studied the feasibility of using IOT as the sole source material for the preparation of geopolymer binders, where sodium silicate was included in a powdered form as an activator solution (31% of the mix by wt.). It was found that the prepared samples required high-temperature curing (80 °C) to achieve satisfactory compressive strength results (50.58 MPa) after seven days of curing time. Further, when the curing time increased to 14 or 28 days, the compressive strength declined drastically as the polymerization process reached its maximum at seven days, after which no dissolution occurred. Moreover, it was mentioned in a study by Xiaolong et al. [98] that, due to the comparatively low reactivity of IOT, its use as single source material for the preparation of geopolymers is limited. Slow hardening time, insufficient compressive strength at 28-day curing and inadequate durability characteristics make it a less preferable single aluminosilicate material for geopolymerization. Thus, the addition of supplementary aluminosilicate materials, such as FA, GGBFS and IOT, is essential to achieve improved product end properties.

In a study by Duan et al. [99], the application of IOT and FA to prepare geopolymer pastes was investigated, and the compressive strength properties were evaluated. The FA was partially substituted by IOT, ranging from 0–30% at a 10% gap (by wt.). Figure 5 demonstrates the compressive strength results after 28 days. It can be understood that the geopolymer samples containing 20% IOT and 80% FA revealed the maximum compressive strength of 49 MPa under ambient conditions (without any need for high-temperature curing). The explanation of this strength behavior of a mix containing 20% IOT was partly attributed to the filling effect of IOT particles, which links the gaps inside the matrix, thus providing a dense microstructure and improving strength. Another reason for compressive strength increment is the presence of CaO in both IOT and FA. At 20% IOT, the reactivity of IOT was highest, and this active CaO generated sufficient C-S-H gels in the system that improved the strength of the pastes. However, when the IOT content was increased to 30%, the compressive strength declined due to the low reactivity of IOT, which reduced the rate of geopolymerization, generating fewer geopolymer gels (CA-S-H/N-A-S-H) and consequently led to decreased strength.



Figure 5. Compressive strength IOT-FA-based geopolymer [99]. Reprinted with permission from Ref. [99]. Copyright 2016 Elsevier.

Within comparison to other source materials, the dissolution rate of aluminium is low in the case of IOT (under an alkaline environment) [100]. Hence, as previously mentioned, using FA or GGBFS along with IOT becomes necessary. However, due to the ease and abundance of its availability and to promote waste management, many researchers have also investigated the use of high-volume IOT as fine and coarse aggregates [101–104] for concrete production, and the results are promising.

4.5. FCA -FA-Based Geopolymer Binder

FCA is one of the contemporary source materials used in the preparation of geopolymer binders, along with FA. Saha et al. [105] examined the feasibility of FCA- and FA-based geopolymer concrete, using 13 M NaOH and Na₂SiO₃ solution as alkali activators. The natural coarse aggregates were replaced by recycled coarse aggregates (RCA), up to 50%, and the compressive strength of the samples was evaluated. The results revealed that effective geopolymerization occurred due to a combination of FCA and FA to achieve adequate strength. The authors essentially recommended a 20% replacement of RCA to be used in manufacturing concrete for sustainable infrastructure solutions. In another study by Mishra et al. [24,48,106], several geopolymer mixes were prepared by varying FA mix proportions from 20% to 80% in the source mix. The alkaline solutions of sodium hydroxide and sodium silicate were used to activate these sources. It was observed that a mixture containing FCA and FA in a 60:40 ratio could be best suited for geopolymerization, resulting in a 28-day compressive strength of 29.3 MPa under ambient curing conditions.

4.6. FA-MK-Based Geopolymer Binder

Duan et al. studied the strength development of FA-based geopolymer paste by including MK with replacement percentages (0%, 5%, 10%, 15%, 20%) under ambient curing conditions for 28 days [107]. Subsequently, the specimens were exposed to 5% sodium sulfate solution (Na₂SO₄) for 28, 90 and 180 days. The compressive strength of the cubic specimens ($100 \times 100 \times 100$) mm³ was measured under loading rates of 0.6 MPa/s. The results illustrated in Figure 6 reveal strength loss after sodium sulfate solution exposure regardless of the replacement level of fly ash by metakaolin. However, the geopolymer gains strength by increasing the replacement level of metakaolin from 5% to 20%.



Figure 6. Compressive strength of geopolymer with different metakaolin content before and after exposure to sodium sulfate solution [107]. Reprinted with permission from Ref. [107]. Copyright 2016 Elsevier.

Another study, by Zhang et al., observed a 15% increase in the compressive strength of MK-based geopolymer with 10% FA replacement, while recording a 5%, 8% and 22% decrease with 20%, 30% and 40% replacement with FA, as depicted in Figure 7 [108]. The authors proclaimed the gel content and extent/rate of reaction between the binder mix and the alkaline activator to be a prime factor in compressive strength development. Contact between the activator solution and the mix binder particles decreased with a constant liquid/solid ratio of 0.6 and higher fly ash replacement levels, resulting in a longer initial reaction time.



Figure 7. Effects of fly ash content on compressive strength of geopolymers at 7 d and 28 d after curing at 25 °C [108]. Reprinted with permission from Ref. [108]. Copyright 2014 Elsevier.

4.7. FA-SF-Based Geopolymer Binder

Adequate replacement of SF in FA-based self-compacting geopolymer concrete was perceived by Memon et al., with substitution levels of 0, 5, 10, and 15 wt.% [109]. Parameters such as (w/b) ratio and binder content were kept constant, at 0.33 and 400 kg/m³. The molds were initially cured at 70 °C for two days, and later cured at ambient temperature to acquire a maximum 28-day compressive strength of 55.02 MPa (6.9%), with 10% replacement of SF, as displayed in Figure 8. The obtained strength was inferred due to the pozzolanic reactivity and pore-filling capability of SF, resulting in a denser microstructure. Moreover, the addition of SF also provides additional SiO₂, which is beneficial during geopolymerization reactions to form a geopolymer matrix with a denser gel structure [110].



Figure 8. Effect of SF on compressive strength [109]. Reprinted with permission from Ref. [109]. Copyright 2013 Springer Nature.

5. Part II: Review of Microstructural Properties

This section discusses the microstructural properties of geopolymer binder systems. The properties such as X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier-Transform Infrared spectroscopy (FTIR) are reviewed in light of the wastes analyzed in this study. In general, the microstructure properties vary according to the source materials used and, therefore, heavily influences the final compressive strength development of the geopolymer binders.

5.1. XRD

5.1.1. FA-Based Geopolymer Binder

Sasui et al. [78] employed NaOH (Cem. C) and NaOH+Na₂SiO₃ (CemN.C) alkaline solutions in 100% FA-based geopolymer mortars. XRD patterns of the mixture specimens indicate the different crystalline phases and the difference in the crystallinity percentage of FA upon activation by Cem. C (24.23%) and CemN.C (19.72%). The intensity of hydroso-dalite (formation due to high SiO₄ and AlO₄ in contrast with CaO) was higher in Cem. C, resulting in lower strength than CemN.C due to the amorphous silicate supplied from Na₂SiO₃. Calcite peaks around 20 (28°), in both compositions, indicated the availability of unreacted Ca, as it was not associated with C-S-H development. Moreover, the formation of a low-intensity hump between 2 (18°–35°), in Figure 9a, and high-intensity hump between 20 (23°–38°), in Figure 9b, could be associated with the formation of an amorphous compound in gel due to the presence of amorphous silica.



Figure 9. (a,b) XRD patterns of 100% FA-based samples [78].

In another study, Tho-In et al. [71] investigated the XRD patterns of the 7-day ovencured geopolymer paste (100% FA), as illustrated in Figure 10. The hardened paste exhibited a glassy matrix, which can be established through the broad hump in Section $25^{\circ} < 2\theta < 35^{\circ}$ and the low-intensity peaks of calcite (CaCO₃) and quartz (SiO₂) signifies their poor crystallinity behavior; as a result, there was a significant degree of geopolymerization.



Figure 10. XRD pattern of 100% FA-based samples [71]. Reprinted with permission from Ref. [71]. Copyright 2018 Elsevier.

Activation of 100% FA-based geopolymer mortar through NaOH and varying modulus of Na₂SiO₃ (1.5, 3.3) was undertaken by Lv et al. [111] to comprehend the consequential effects on the strength and microstructure of the resulting geopolymer mortar. Figure 11 illustrates the XRD data of the ambient cured mortar with a notifiable hump between 2θ ($20^{\circ}-35^{\circ}$), indicating primary hydration gel products (N-A-S-H) in the amorphous phase, generated by the geopolymerization reaction in the system. As the dosage of Na₂SiO₃ increased in Figure 11a, minor changes in the diffraction peaks of the spectrum can be spotted around 2θ (21°), as the diffraction peaks of quartz and mullite decrease as the dosage increases, proving that increased dosage and low modulus of Na₂SiO₃ can contribute to adequate activation of fly ash, leading towards suitable strength development. Figure 11b does not indicate any results in the reaction products, in contrast with Figure 11a, as the rise of SiO₂ content and decrease of Na₂O in Figure 11b lead to insufficient alkali content in the system. No significant development in the diffraction peaks of the spectrum can be witnessed as the sodium silicate dosage increases.



Figure 11. (**a**,**b**) XRD patterns of 100% FA-based samples [111]. Reprinted with permission from Ref. [111]. Copyright 2021 Springer Nature.

5.1.2. FA-GGBFS-Based Geopolymer Binder

In a study by Saludung et al. [112], the XRD test was carried out to understand the microstructure evolution of the FA-GGBFS geopolymer binder system. The GGBFS was replaced from 0–60% by wt. of the FA at a 15% interval. Figure 12 presents the XRD test results of the raw FA and the geopolymer pastes, with varying quantities of GGBFS. It can be observed that a broad, amorphous hump is seen at 15–38° (2- θ) for FA, which suggests its high reactivity. For the pastes containing 0% GGBFS, a slight shift is noticed in the amorphous hump (15–40°) that confirms the development of geopolymer gels. The peaks of mullite (M) and quartz (Q) found in the case of raw FA alone are also seen even after exposure to an alkali solution and the inclusion of GGBFS. However, when GGBFS was introduced into the system (15–60%), the overall XRD pattern of the geopolymer pastes remained unchanged. At the same time, a new diffraction peak was formed around 30° (2 θ) as a result of the generation of C-S-H gel. Moreover, the intensity of this peak increased with the increase in GGBFS inclusion in the paste. It is also important to note that the samples with 0% GGBFS exhibited no peak conforming to C-S-H gels as FA does not contain a sufficient quantity of active calcium in it, which can participate in geopolymerization.



Figure 12. XRD patterns of FA-GGBFS geopolymer specimens [112].

Similarly, Kamath et al. [113] studied the XRD patterns of the geopolymer binder system made up of FA and GGBFS, with the addition of metakaolin (5%, 10%, 20% by weight). At seven days of ambient curing, the FA-GGBFS mixes containing 20% metakaolin attained the highest compressive strengths. The corresponding XRD pattern of the mixtures is presented in Figure 13. From the figure, it is identified that the peaks of SiO₂, i.e., quartz (Q), dominate the spectrum in the case of all the geopolymer mix samples. However, the intensity of these peaks reduced when the quantity of GGBFS increased in the binder system. This reduction in the intensity is partly attributed to the fineness of metakaolin and the increased CaO contents, for which the constituents of SiO₂ underwent full alkaline activation to form various aluminosilicate gels that govern the strength development. The hump around 20–40° (2 θ) exhibits the formation of gels such as C-S-H, C-A-S-H and N, C-A-S-H in all the mixes. This co-existence of the gels is also described in [114,115], to the higher strength gain of the geopolymer binders.



Figure 13. XRD patterns of FA-GGBFS-based geopolymer sample with 20% MK [113]. Reprinted with permission from Ref. [113]. Copyright 2021 Elsevier.

5.1.3. FA-RM-Based Geopolymer Binder

Yang et al. [116] examined the changes in the XRD patterns of RM-FA-based geopolymer binders, which were exposed to room and elevated temperatures (400–1000 °C), as shown in Figure 14. It is observed that each XRD pattern exhibits a broad hump between $20^{\circ}-40^{\circ}$ (20), which indicates its amorphous characteristics. The FA selected for this experimentation is reported to consist of mullite and quartz, also found in all of the RM-FA geopolymer samples. The figure illustrates that until 800 °C, there is no significant change in the XRD patterns. A new mineral compound–Nepheline, is found in the XRD patterns of the samples cured at 800 °C and 1000 °C, and this has been established in [117]. However, as reported, the formation of Nepheline caused serious volume expansion that resulted in stress and cracks formation. Eventually, the geopolymer matrix collapsed, leading to rapid strength loss when cured at 800 °C or above.

Zhang et al. [118] analyzed the microstructural changes, with the help of XRD patterns of the geopolymer binder made with RM, and class F fly ash (FFA) cured at 80 °C for varying time periods (1 h, 2 days, and 120 days). Primarily, the binder consisted of 80% FFA. Figure 15 presents the XRD patterns of geopolymer samples and raw materials–RM, FFA. It is observed that the amorphous behavior of FFA is characterized by the hump between $16-30^{\circ}$ (2 θ) in its XRD pattern. However, after two days of curing, it is found that there is a

shift in this hump to 16° – 38° (2 θ). The individual centers are distinguished on the XRD patterns, as shown in Figure 15. The generation of reactive geopolymer gels is responsible for this shift in the hump, confirmed in previous findings [119].



Figure 14. XRD pattern of the RM-FA geopolymer after exposure to elevated temperatures [116]. Reprinted with permission from Ref. [116]. Copyright 2019 Elsevier.



Figure 15. XRD spectra of RFFG samples cured at 80 °C; (Q: Quartz, M: Mullite, K: Kaolinite, Na: Nacrite, He: Hematite, and Ca: Calcite) [118]. Reprinted with permission from Ref. [118]. Copyright 2018 Elsevier.

5.1.4. FA-IOT-Based Geopolymer Binder

In a study by Duan et al. [120], the geopolymer binders were prepared with IOT and fly ash, activated by a combination of 10 M NaOH and Na₂SiO₃ solution, where IOT replaced 30% (by wt.) in the mix. The microstructure phase compositions of the resulting geopolymer were characterized using XRD analysis. The XRD pattern is shown in Figure 16. It is reported that, following the subsequent geopolymerization, the mineral phases such as anatase, calcite, mullite and quartz, which existed in the raw materials (IOT and FA) are also present in the XRD pattern of the resulted geopolymer samples. However, the sharp intensity of their peaks is transformed into broad peaks (in geopolymer), which signifies the dissolution of particles of IOT and FA under an alkaline environment, which leads to the formation of an amorphous aluminosilicate structure during the reaction process.



Figure 16. XRD patterns of IOT-FA (30:70) based geopolymer sample [120]. Reprinted with permission from Ref. [120]. Copyright 2016 Elsevier.

XRD patterns of IOT as a single source material for geopolymerization have previously been studied in Kuranchie et al. [22], where it is confirmed that partial dissolution of the constituent minerals present in IOT occurs to form geopolymer gels that enhance the strength of the samples.

However, the studies related to the XRD characterization of geopolymer binders made with IOT-FA are very limited. Therefore, further studies relating to XRD analysis of geopolymer binders made with IOT-FA are required in order to examine and understand the microstructure changes of the resulting binder systems.

5.1.5. FCA-FA-Based Geopolymer Binder

Mishra et al. studied the XRD patterns of geopolymer samples formed by incorporating 60% FCA and 40% FA in the source material mix [24,48,106]. The XRD pattern revealed the presence of peaks of mineral compounds, with the chemical formula KAlSi₃O₈, that belong to the K-feldspar group, quartz, forsterite (magnesium silicate), and donathite. The change in the chemical composition of the source material mix with the inclusion of FCA led to the formation of some new mineral compounds. It is also evident that quartz from FA, forsterite (magnesium silicate), donathite from FCA remained unreacted during the geopolymerization process. The MgO from FCA could have led to the formation of Mg-bearing gel phases, namely N-M-A-S-H or M-A-S-H, but no such peaks were detected due to their amorphous character.

5.1.6. FA-MK-Based Geopolymer Binder

Yang et al. studied the XRD patterns of ambient cured MK-based geopolymer with varying FA replacements (0, 10, 20, 30 wt.%) [121]. The authors analyzed the XRD patterns

of the source materials. They deduced the presence of broad aluminosilicate humps at divergent positions owing to the physical characteristics of the amorphous elements available in FA (20–35°) 2 θ and MK (22–30°) 2 θ . Figure 17 displays the availability of Mullite, Quartz and Kaolinite phases, from 22–40°, 2 θ in the geopolymer specimens at an elevated angle, corresponding to the evolution of tangled aluminosilicates binder gel.



Figure 17. XRD patterns of the geopolymer paste with 7 days of autogenous curing [121]. Reprinted with permission from Ref. [121]. Copyright 2017 Elsevier.

5.1.7. FA-SF-Based Geopolymer Binder

The microstructure of SF- and FA-based geopolymer has been evaluated by Li et al. [122] through XRD analysis. The geopolymer was cured in ambient conditions with a fixed binder/liquid ratio (2.5) and varying SF inclusions (0, 2, 4 wt.%). Figure 18 illustrates the primary crystalline peaks in the geopolymer with quartz, mullite and lower hematite phases originating from the included FA. The appearance of zeolite was deduced as the secondary reaction product originating during geopolymerization. At 20 (26.5°), the intensity of mullite and quartz was high, mostly with 4% SF inclusion. The authors concluded that the high intensity resulted from the lower dissolution of aluminosilicate and the progression of chemical reactions to form the geopolymer network. Table 5 shows the XRD peaks obtained from different geopolymer binder compositions involving FA.

Table 5. XRD peaks of geopolymers with different binder compositions.

Binder Composition	XRD Peaks	Reference
FA (100%)	Quartz, Magnetite, Mullite, Arghonite, Calcite, Albite, Hydrosodalite	[78]
FA (100%)	Calcite, Quartz	[71]
FA (100%)	Quartz, Mullite	[111]
FA (70%)-GGBFS (30%)	Quartz, Mullite	[112]

FA (50%)-GGBFS (50%)	Albite, Mullite, Hydrotalcite	[123]
FA (80%)-RM (20%)	Quartz, Mullite	[116]
FA (80%)-RM (20%) (800–1000 °C)	Quartz, Mullite, Nepheline	[116]
FA (80%)-RM (20%)	Quartz, Mullite, Kaolinite	[118]
FA (70%)-IOT (30%)	Quartz, Mullite, Anatase	[120]
IOT (100%)	Quartz, Sodian, Goethite, Birnessite	[22]
FCA (60%)-FA (40%)	Quartz, forsterite, K- feldspar mineral donathite, silvine	[24,48,106]
FA (30%)-MK (70%)	Mullite, Quartz, Kaolinite	[121]
FA (98%)-SF (2%)	Quartz, Mullite, Hematite, Zeolite	[122]
and and a fail and a fail of the fail of t	Q - Quartz M - Mullite H - Hematite Z - Zeolite	
and a second and a second and a second and a second a sec	4%	
the second secon	2%	
and and the second seco	M Q 0%	

Table 5. Cont.

Binder Composition

Figure 18. XRD patterns of fly ash geopolymers with varying silica fume contents [122].

Bragg's Angle (2θ)

50

60

70

8(

40

5.2. SEM

20

10

5.2.1. FA-Based Geopolymer Binder

30

SEM micrographs of 100% FA-based geopolymer mortars, developed by Al-mashhadani et al. [30], are illustrated in Figure 19a. From the figure, it is revealed that there existed some unreacted FA over the geopolymer matrix, which correlates positively with the strength behavior of the composite under compression. The unreacted FA does not behave as a reinforcement material, but instead strengthens the matrix with age due to the bonding strength offered by the complex reaction between the surface of the particles. A micrograph with a magnification of 10,000, in Figure 19b, demonstrates a fly ash particulate reacting with prism-shaped pillars, primarily composed of Si and Al constituents, implying that Si-O and Al-O bonds are the primary chemical reactions that produce this binder. Alternatively, these prism-shaped pillars could be identified as an Al-tobermorite phase whose formation was mostly facilitated by abundant Al constituents from sand [124].



Figure 19. (**a**,**b**) SEM images of 100% FA-based samples [118]. Reprinted with permission from Ref. [30]. Copyright 2018 Elsevier.

The scanning electron microscopic characterization of 100% FA-based geopolymer concrete was conducted by Hu et al. [75], as depicted in Figure 20, to observe the morphology, effect of natural and recycled aggregate on the resulting microstructure and interfacial transition zone (ITZ) of the geopolymer matrix. Distinctive differences can be witnessed in the microstructure of the geopolymer specimens: S00 (containing natural aggregates) and S00R00 (containing recycled aggregates). S00 and S00R00 revealed the formation of multiple porosities and a non-uniform structure, accompanied by evident cracks, as the geopolymer matrix had numerous defects and was not dense, owing to the absence of a secondary binder which could lead the weak point to change from the geopolymer matrix to the ITZ between the geopolymer matrix and aggregates.



(a) S00

(a) S00R100

Figure 20. (**a**,**b**) SEM images of 100% FA-based samples [75]. Reprinted with permission from Ref. [75]. Copyright 2019 Elsevier.

Wongsa et al. [77] analyzed the microstructure and morphology of 100% FA (high calcium) based seven-day geopolymer mortar. Figure 21 shows the SEM micrograph of the fractured specimen surface, with a porosity of around 27.1%, exhibiting a smoother surface validating dense and homogenous geopolymerization matrix with notifiable unreacted FA particles at the fracture surface. The authors outlined the controlled geopolymer mortar as a well-interconnected aluminosilicate network of high calcium fly ash geopolymer composite.



Figure 21. SEM images of 100% FA-based samples [77]. Reprinted with permission from Ref. [77]. Copyright 2020 Elsevier.

5.2.2. FA-GGBFS-Based Geopolymer Binder

Al-Majidi et al. [125] analyzed the SEM micrographs of the FA-GGBFS mix, cured under ambient conditions for 28 days, to study the microstructural changes in the geopolymer pastes. Figure 22 presents the SEM images of the binder system containing 10% GGBFS subjected to $10,000 \times$ magnification. It is reported in the study that the inclusion of GGBFS contributes to the strength enhancement of the geopolymer paste samples. The figure shows that amorphous clusters of GGBFS particles are present together with moderately reacted FA particles inside the geopolymer matrix. In the study, it is emphasized that during geopolymerization, the reactions occur at the external edge of the particles, followed by the subsequent deposition of the reaction products, rather than complete dissolution. The micrograph demonstrates this behavior, which has also been confirmed by Izquierdo et al. [126]. In addition, as GGBFS is a source of high calcium, this leads to the significant formation of C-A-S-H gel in the matrix [127], which enabled the development of a denser microstructure compared to binders made out of FA only. Hence, consequent improvements in the compressive strength were identified with the inclusion of GGBFS into the geopolymer binder system.



Figure 22. SEM analysis of a 10% slag sample after 28 days of curing, 10,000 magnification [125]. Reprinted with permission from Ref. [125]. Copyright 2016 Elsevier.

In a study by Panda et al. [128], the authors evaluated the possibility of using FA and GGBFS to prepare geopolymer mortars for the additive manufacturing of the structural elements. They mixed 28.85% FA with 1.68% GGBFS and 3.36% silica fume (by wt.), and

the resultant geopolymer mortar mix was subjected to 3D printing methods. The SEM micrographs of the printed geopolymer sample are presented in Figure 23. From the figure, it is evident that the incorporation of GGBFS has aided the formation of sufficient geopolymer gels, eventually producing a hardened and compact microstructure. It is also comprehended from the micrograph that a minor amount of unreacted FA particles is present inside the matrix. In contrast, most FA particles followed complete dissolution when they came in contact with the alkaline solution. Furthermore, as seen in the figure, the existence of micro-pores within the matrix is the probable cause for the strength reduction of the printed geopolymer samples at later ages.



Figure 23. SEM micrograph of Fly ash-GGBFS geopolymer [128]. Reprinted with permission from Ref. [128]. Copyright 2017 Elsevier.

5.2.3. FA-RM-Based Geopolymer Binder

To study the microstructural changes in the geopolymer matrix composed of RM and FA, Singh et al. [129] analyzed the SEM characteristics of the samples cured under ambient conditions. Figure 24a–c represents the ambient cured samples: (a) GRM30 (with 30% RM), and (b) GRM50 (with 50% RM) under 6 M NaOH, along with (c) GRM30 under 10 M NaOH. It is reported in the study that the compressive strength improved with the addition of RM to the binder system. Figure 24a,b reveals that the geopolymer samples, when activated under 6 M NaOH, exhibited better strength due to significant alkalinity and the improved microstructural packing of RM-FA particles inside the matrix. In the case of 50% RM addition, i.e., GRM50 under 6 M, the amount of unreacted RM particles increased in the matrix, for which the strength enhancement is lower than the sample, containing 30% RM (GRM30). However, when activated under 10 M NaOH, although a compact microstructure is observed, the samples could not reach optimal strength, which might be due to the whitish deposition of excess unreacted alkali leading to less effective geopolymerization, as seen in Figure 24c.

Toniolo et al. [130] investigated the SEM images of the geopolymer binders made with wastes comprising RM and FA, where 30% RM replaced FA (by wt.). The alkaline solution adopted for this study was a mix of Na₂SiO₃ and NaOH, at a mass ratio of 2.5. The compressive strength of 60 MPa was attained by this mix proportion, which is better than the strength obtained from 10% and 20% RM inclusion. The corresponding SEM micrograph (30% RM–70% FA) is shown in Figure 25. From the figure, it is revealed that the 30% RM-FA-based geopolymer sample has a dense microstructure, which explains its improved strength gain. In addition, the RM particles can agglomerate by themselves, filling the pores/gaps left behind by the FA particles after their dissolution. Therefore, the final microstructure became more compact, enhancing the compressive strength.



Figure 24. SEM image of ambient cured paste (**a**) GRM30–6 M, (**b**) GRM50–6 M, (**c**) GRM30–10 M [129]. Reprinted with permission from Ref. [129]. Copyright 2018 Elsevier.



Figure 25. SEM image of RM-FA (30:70) based geopolymer sample [130].

5.2.4. IOT-FA-Based Geopolymer Binder

In a study by Duan et al. [99], IOT was blended with FA to prepare geopolymer binders. The mix containing 20% IOT (by wt. of the FA) achieved the maximum compressive strength of 49 MPa and 25 MPa, under standard room temperature and seven thermal cycles (200 °C), respectively. The SEM analysis was conducted to investigate the microstructure of the samples and is shown in Figure 26a–d. From Figure 26a, it is observed that, in the case of the reference sample (containing 0% IOT), micro-cracks in the matrix are formed after 28 days. These micro-cracks are developed due to stress development in the matrix, thereby leading to high porosity and less strength gain. However, from Figure 26b, it is observed that the mix containing 20% IOT carries a denser microstructure in comparison to the reference sample. No pores or micro-cracks are formed, making the microstructure more compact with reduced porosity and, therefore, showed improvement in the compressive strength when cured under standard room temperature. In Figure 26c, following the seven thermal cycles at 200 °C, a very loose structure is observed for the microstructure of the mix containing 20% IOT, with a certain degree of porosity and cracks. However, compared to the mixture containing 0% IOT (Figure 26d), it is found that the microstructure of the 20% IOT sample is denser and offers better thermal resistance in terms of compressive strength. Therefore, it is understood that increasing temperatures increases stress inside the matrix, which ultimately forms pores/cracks, making the microstructure lose. This negatively affects the strength development of the samples. However, the inclusion of 20%



IOT into the FA-based geopolymer binder systems is beneficial and effective in case of high temperatures.

(c) IOT20-7 thermal cycles-200 °C (d) Refer



Figure 26. SEM image of IOT-FA (**a**) Reference and (**b**) IOT20 (**c**) IOT20–7 thermal cycles 200 °C (**d**) reference–7 thermal cycles 200 °C [99]. Reprinted with permission from Ref. [99]. Copyright 2016 Elsevier.

In another study by Duan et al. [120], geopolymer binders were prepared using IOT and FA as source materials, where IOT replaced 30% by wt. of FA. The authors investigated the effectiveness of geopolymers for the removal of Cu^{2+} . Two samples were prepared, with and without H₂O₂ (a foaming agent). After 28 days of curing, the SEM study was conducted to differentiate and identify the microstructures of the resulting geopolymer samples. Figure 27a,b shows the microstructures of reference geopolymer and porous geopolymer (with H₂O₂), respectively. As seen from the figures, following the geopolymerization, the matrix embodied the aluminosilicate gels. It is observed that the SEM micrograph of the reference geopolymer exhibits a low degree of porosity accompanied by dense microstructure. On the other hand, the porous geopolymer (with H₂O₂) indicated a high degree of porosity and, consequently, a less dense microstructure.



Figure 27. SEM image of IOT-FA (**a**) Geopolymer (**b**) Porous geopolymer [120]. Reprinted with permission from Ref. [120]. Copyright 2016 Elsevier.

5.2.5. FA-FCA-Based Geopolymer Binder

Mishra et al. revealed that the concrete samples made with FCA (60%) and FA (40%) demonstrated a dense heterogeneous geopolymer gel matrix, as shown in Figure 28a [106].

The porous gel phase indicated the partially reacted FCA or FA. In addition, the small dot-spots represent carbonates of Na and Ca, resulting from the reaction of excess unreacted alkalis with atmospheric CO₂. Further, from Figure 28b, it is also revealed that between the binder and aggregate phase (ITZ), a large number of microcracks exists; this validates the weak structure of the ITZ.



(a) Detailed gel structure

(b) Micrograph showing aggregate and binder phase

Figure 28. SEM images (**a**) Mix involving FCA and FA, (**b**) Mix involving FCA and FA (aggregate and binder phase) [106]. Reprinted with permission from Ref. [106]. Copyright 2022 Springer Nature.

5.2.6. FA-MK-Based Geopolymer Binder

The microstructure of MK- and FA-based geopolymer was evaluated by Zhang et al. through SEM analysis [108]. Figure 28 shows the development in the microstructure of MK-based geopolymer with 40% FA inclusion from 1, 7 and 28 curing days. Corrosion craters can be seen on the surface of fly ash from the first day of reaction, in Figure 29a, where the aluminosilicate glass in the fly ash particles has receded from the mullite needles that were previously trapped within the fly ash particle. After seven days, as shown in Figure 29b, the glass has further retreated, stipulating a higher degree of geopolymerization, while the visible pores and reaction products seem more continuous and compact. Finally, in Figure 29c, the 28-day geopolymer gel had become more compact with reduced pore sizes due to the continued reaction.



Figure 29. SEM images of (a) GFA40-1 Day, (b) GFA40-7 Day, (c) GFA40-28 Day [108]. Reprinted with permission from Ref. [108]. Copyright 2014 Elsevier.

5.2.7. FA-SF-Based Geopolymer Binder

SEM analysis of FA-based geopolymers with SF replacement of 0, 2 and 4 wt.% was undertaken by Li et al. to observe the effect of SF on the mechanical strength of the composite [122]. Figure 30a illustrates the FA control mix geopolymer microstructure, indicating a smooth surface with open pores, cracks and a relatively loose matrix. Introduction of 2 wt.% SF in Figure 30b revealed a denser and homogenous microstructure with a low amount of unreacted fly ash. In contrast, 4 wt.% SF in Figure 30c resulted in broader cracks, a high amount of unreacted fly ash and loose microstructure. The authors concluded that introduction of 2 wt.% SF to be optimum in enhancing the strength of FA-based geopolymer as the compressive strength results supported the microstructural study.



Figure 30. SEM micrographs of fly ash geopolymers with (**a**) 0 wt.%, (**b**) 2 wt.% and (**c**) 4 wt.% of silica fume [122].

5.3. FTIR

5.3.1. FA-Based Geopolymer Binder

In a study by Tho-In et al. [71], an FTIR investigation of control geopolymer pastes (100% FA), as in Figure 31, was undertaken to comprehend the molecular chemical bonds in a heat-cured geopolymer paste at the age of seven days. The penetrating bands at 3450 cm⁻¹ and 1650 cm⁻¹ pertained to the vibrations of O-H (stretching) and H-O-H (bending) bonds, indicating the presence of absorbed water during geopolymerization. The band at 1450 cm⁻¹ exhibited a stretching vibration of O-C-O in carbonate groups, whereas the bands 450 cm⁻¹ were developed due to the bending and stretching of O-Si-O and Si-O-Si bonds. The band at 1050 cm⁻¹ presented the highest intensity owing to the increased rate of geopolymerization and the asymmetric stretching vibrations of Si-O-X (X = tetrahedral silicon) bonds.



Figure 31. FTIR Spectra of 100% FA-based samples [71]. Reprinted with permission from Ref. [71]. Copyright 2018 Elsevier.

El-Hassan et al. [131] conducted FTIR spectroscopy studies to determine the polymerization degree and reaction products of 100% FA-based geopolymer concrete, cured for 7 and 28 days, under varying temperature conditions (A-Ambient conditions, 30 °C, 60 °C). From Figure 32a, we observe the stretching vibration mode of Si–O–X (X = Si or Al) on the 820 cm⁻¹. A decreased polymerization degree of silica was identified for the 30 °C cured specimen because of the shift in wavenumber towards a lower wavelength. A band at 1420 cm⁻¹ was spotted for ambient cured samples, indicating the formation of Na₂CO₃ through the carbonation of unreacted NaOH. The bands from 1600–3600 cm⁻¹ were linked to –OH bending and H–O–H stretching vibrations and were similar for all the geopolymer mixes. The presence of water and the occurrence of geopolymer reactions in the concrete specimens can be authenticated through these bands. Growth in H–O–H stretching vibrations at the 3500 cm⁻¹ bands were spotted in Figure 32b, in contrast with Figure 32a, validating that extended curing could assist in the growth of geopolymerization reactions and yield more polymerization products.



Figure 32. (a,b) FTIR spectra of 100% FA-based samples [131].

Morsy et al. [132] analyzed the reaction of utilizing different sodium silicate/sodium hydroxide-10 M (S/N) ratios (M1-0.5, M2-1.0, M5-2.5) on the microstructure of 100% FA geopolymer mortar. Figure 33 depicts a broad constituent around 1004 cm⁻¹ because of the Si–O–Si and Al–O–Si asymmetric stretching vibration, and the graph became sharper while moving towards lower bands (995, 979 and 975 cm⁻¹) when the S/N ratio rises from 0.5 to 2.5. The bands between 995 cm⁻¹ and 790 cm⁻¹ were allocated towards Al–OH and Al–O, respectively. The primary transmittance bands for the mortars lie between 900–1300 cm⁻¹ as M2 obtains the maximum compressive strength. This could be attributed to the combined effect of the increased curing temperature, S/N ratio (1.0) and Si/Al ratio resulting in an extensively accelerated geopolymerization process.



Figure 33. FTIR spectra of 100% FA-based samples [132,133].

5.3.2. FA-GGBFS-Based Geopolymer Binder

Samantasinghar and Singh [133] examined the FTIR bands of geopolymer binders composed of FA and GGBFS, 0-100% at intervals of 20%, including 100% FA and 100% GGBFS mixes, cured under ambient conditions. For comparison, the FTIR spectra of individual source materials (FA and GGBFS), and the resulting FA-GGBFS geopolymers are shown in Figure 34a,b, respectively. In Figure 34, FA-GP and GGBS-GP represent the mixes containing a minimum of 50% of either FA or GGBFS, respectively. It is observed from the figures that, due to the occurrence of some new peaks and the difference in peak locations, the FTIR spectra of geopolymers made up of FA and GGBFS differ from the individual source materials. In Figure 34b, the peaks at low frequencies $(449-560 \text{ cm}^{-1})$ indicate the presence of silicates. The symmetric stretching vibration of the Si-O-Al bond is designated by the peaks in the range of 686-896 cm⁻¹, while the peaks identify the asymmetric stretching vibration of the Si-O-Al bond at 968 and 1088 cm⁻¹. Compared with the FTIR spectra of source materials, the shifting of the peaks in the case of geopolymers reveals the formation of aluminosilicate gels occurs because of the presence of silicon and aluminium in the source materials. This shifting of the peaks influences the strength development in the resulting geopolymer samples. In Figure 34b, in the case of GGBFSbased geopolymers, the bands formed at 1414 and 1486 cm⁻¹ result from O-C-O bond stretching, which signifies that the GGBFS absorbed the CO₂ during geopolymerization. Some minor peaks, at 1652, 1657 and 2925 cm⁻¹, reveal the existence of bound water, generated due to H-O-H bond bending. The broad bands observed at 3464 and 3474 cm^{-1} are because of the stretching of O-H bond units. These O-H bond units are also witnessed in the FTIR spectra of source materials; however, the peaks are not sharp in source materials. The observations carried out in this study are also confirmed in past studies [134,135].



Figure 34. (**a**) FTIR spectra for FA and GGBFS (**b**) FTIR spectra for 28 day-cured FA-GGBFS based geopolymer samples [133]. Reprinted with permission from Ref. [133]. Copyright 2018 Elsevier.

In an effort to understand the bond characteristics, Qiu et al. [123] examined the FTIR spectra of the geopolymer pastes made up of FA and GGBFS, after eight days of curing under room temperature conditions. Figure 35a,b exhibits the FTIR spectra of FA-GGBFS samples activated with 8 M NaOH and 16 M NaOH solutions, respectively. In the figures, FxByNz denotes Fx-FA%, By-GGBFS%, and Nz-molarity of NaOH. Following the activation by 8 M and 16 M NaOH, the FTIR spectra exhibit the shifting of Si-O-Al bonds to a low-frequency region (997 cm⁻¹); this indicates the pattern of new aluminosilicate compounds such as N-A-S-H gels [136]. Simultaneously, the formation of N-A-S-H gels is also revealed by bands at 780 and 580 cm⁻¹ due to symmetric stretching vibrations of Al/Si-O-Si bonds [137]. These modifications are similar in the case of samples activated by 8 M and 16 M NaOH. However, in the case of the FTIR spectra of 16 M NaOH, the peaks are sharper, suggesting the formation of more N-A-S-H gels in the matrix; this observation is in line with [138,139]. In addition, the increase in the intensity of the O-H bands at 1650 and



 3420 cm^{-1} is supported by the inclusion of OH⁻ from NaOH solution in both the samples (8 M NaOH and 16 M NaOH).

Figure 35. FTIR of FA and BFS and geopolymer pastes with (**a**) 8 M NaOH solution and (**b**) 16 M NaOH solution [123].

5.3.3. FA-RM-Based Geopolymer Binder

Mucsi et al. [140] investigated the inclusion of RM (0–30% by wt.) into the FA-based geopolymer binder system to enhance the compressive strength of the samples. The compressive strength test results demonstrated that up to 15% RM addition, there is an improvement in the strength of the samples. The FTIR spectra of the RM-FA-based geopolymer samples are displayed in Figure 36. From the figure, it is observed that the peaks which appear in the bands 3390–3370 cm⁻¹ are identified with -OH groups, while the peaks at 1640 cm⁻¹ are associated with H-O-H bending vibrations [136]. The asymmetric stretching vibrations due to the existence of Al/Si-O-Si bonds are exhibited by the peaks at 1100–445 cm⁻¹. After adding RM (5%, 10%, 20%, 30%), the newly developed mineral bonds are indicated by the peaks at 670 cm⁻¹ and 612 cm⁻¹. The presence of the carbonate group resulting from the interaction of the activator and CO₂ is revealed in the matrix from the bands at 1410–1425 cm⁻¹. In addition, the peak intensity decreased to 1414 from 1421 cm⁻¹ after the addition of RM, which indicates the alteration in the formation of carbonate compounds inside the matrix.



Figure 36. FTIR spectra of RM-FA-based geopolymer pastes [140].

Similarly, in a study by Chandra et al. [141], FTIR analysis was conducted for the geopolymer binder consisting of 80% RM and 20% FA by wt., which was activated by an alkaline solution composed of 90% 8 M NaOH and 10% Na_2SiO_3 solution. Figure 37 displays the FTIR spectra after 28 days of curing. From the figure, the appearance of the new bands is confirmed by the peaks at 1643 and 3438.33 cm⁻¹. It is noticed that, due to

the presence of symmetric and asymmetric stretching of Si-O and Al-O bonds in the matrix, there happens to be a shift of the peaks to lower frequency regions (991.03 cm⁻¹). Hence, chemical modifications of the matrix and the formation of Si-O and Al-O bonds resulted in effective geopolymerization of the binder samples.



Figure 37. FTIR spectra of RM-FA (80:20) based geopolymer pastes [141]. Reprinted with permission from Ref. [141]. Copyright 2011 American Society of Civil Engineers.

5.3.4. FA-IOT-Based Geopolymer Binder

To date, no Study has been conducted to investigate the bond characteristics of an IOT-based geopolymer binder system prepared with FA.

5.3.5. FA-FCABased Geopolymer Binder

Mishra et al. found that the FTIR spectra of the specimen mix involving FCA (60%) and FA (40%) indicated the presence of asymmetric stretching of -Si-O-T (T = Si or A) band at 1007 cm⁻¹, as shown in Figure 38 [24,48,106]. The figure shows that the free and bound water molecules corresponding to the-OH groups are detected at 3440 cm⁻¹ and 1650 cm⁻¹. The bands at 600 cm⁻¹ correspond to the stretching vibration of -Mg-O-Mg-O- and signify the presence of N-M-A-S-H or M-A-S-H type (Mg bearing) gel phases. Similarly, the bands at 1430–1450 cm⁻¹ indicate the presence of C-O bonds due to efflorescence. As the source material mix containing FCA and FA have high iron content, the bands at 458 cm⁻¹ and 484 cm⁻¹ indicate the presence of a Fe-O bond that can be linked to the chain of Fe-O-Si-O-Al-O-.



Figure 38. FTIR spectra of FCA-FA geopolymer binder sample [106]. Reprinted with permission from Ref. [106]. Copyright 2022 Springer Nature.

5.3.6. FA-MK-Based Geopolymer Binder

No FTIR study has been reported to date regarding the combination of MK-FA-based geopolymer specimens

5.3.7. FA-SF-Based Geopolymer Binder

In a study by Li et al., ambient cured geopolymers, with different doses of SF (0, 2, 4 wt.%), were characterized by FTIR analysis to examine the functional groups and bond vibration frequencies in the composite [122]. Absorption bands in Figure 39 were found to be in close resemblance to the control specimen with O-H stretching vibrations corresponding to 3300 cm⁻¹. The band at 983 cm⁻¹ was supported by the development of an amorphous Al-Si gel phase through the alkali activation of amorphous fly ash. The introduction of SF increased the wavenumber from 983 cm⁻¹ to 990 cm⁻¹ without generating any additional bands associated with the generation of the Si bond-rich geopolymer network. Table 6 demonstrates the FTIR spectra of geopolymers with different binder compositions.



Figure 39. FT-IR spectra of un-exposed fly ash geopolymers with varying silica fume content addition [122].

Binder Composition	FTIR Bands (cm ⁻¹)	Reference
FA	450, 1050, 1450, 1650, 3450	[71]
FA (100%)	559.3, 873.6, 962.3, 1421, 1640, 3375	[140]
FA (100%)	983, 1522, 1659, 2346, 3377, 3633	[122]
FA (50%)-GGBFS (50%)	580–780, 997, 1650, 3420	[123]
FA (30%)-GGBFS (50%)-MK (20%)	495, 1170, 1510, 1660, 3600	[113]
FA (70%)-RM (30%)	612.3, 670.1, 957.5, 1100, 1415, 1641, 3384	[140]
FA (20%)-RM (80%)	452.69, 720.98, 991.66, 1453.8, 1644.56, 3441.59	[141]
FCA (60%)-FA (40%)	447, 458, 484, 600, 1007, 1430–50, 1650, 3440	[106]
FA (98%)-SF (2%)	986, 1521, 1660, 2343, 3376, 3643	[122]
FA (96%)-SF (4%)	990, 1520, 1660, 2346, 3383, 3632	[122]

Table 6. FTIR bands of geopolymers with different binder compositions.

Many techniques have been used by researchers worldwide to analyze the microstructure properties of geopolymer samples (paste, mortar, concrete). The tests are conducted with the help of instruments that have a respective degree of precision, influencing the results and our understanding. The types and specifications of the instruments used in the microstructure characterization of FA-based geopolymer binders are presented in Table 7 below:

Binder System	Specimen Type	Analysis Type	Instrument	Specifications	References	
		SEM	Thermoscientific ApreoS	Size (10 μm–20 μm)	-	
		EDX	Oxford Instruments INCA		-	
		XRD	Rigaku, D/max-2400	Test range (5° – 85°), Scanning speed (10°/min)	-	
		FTIR	Nicolet, NEXUS 670		[111]	
		BET	Micromertics, Inc., Trister 3020/ASAP2020M		. [111]	
	Paste	²⁹ Si NMR	Bruker AVANCE III 600M		-	
		Unconfined Compressive Strength	TDW-10-300	Loading rate (2400 N/s \pm 200 N/s)		
		XRD	Malvern Panalytical, EMPYREAN	Cu-Ka radiation, 20 values of 10–90		
		FTIR	Bruker, TENSOR 27	Wavenumbers (600–4000 cm ⁻¹), Transmission mode	[1 (0]	
		Vibrating Specimen Magnetometer (VSM)	Quantum Design, Inc., VersaLab TM	Magnetic field range of -10 kOe to 10 kOe at room temperature (25 °C)	. [172]	
FA (100%)	Mortar	SEM	JWEL JSM 6360A	Magnification (5000×-15,000×), Size (1 μm-5 μm)	[132]	
		FTIR	Jasco-6100	Absorption mode up to 4000 cm^{-1}		
		XRD	Philips PW 1390 Diffractometer	Scanning speed (2°/min)	-	
		Micro-Computed Tomography (CT)	Newton 5G System	110 kV microfocus X-ray source	[30]	
		Thermal Conductivity	ISOMET2114		[77]	
		XRD	D/Max-2200 Ultima/PC	2θ (5° to 100°)	[78]	
		SEM-EDX	LYRA3 XMU	Specimens coated with Platinum		
		SEM-EDX	EVO 18	LaB ₆ filaments electron source	[72]	
		Thermal conductivity	ISOMET2114	ASTM D5930-17	[143]	
		FTIR	Varian 3100 FT-IR Spectrometer	Transmittance mode (400 to 4000 cm ^{-1}), Resolution (1 cm ^{-1})		
	Concrete	SEM	JEOL-JSM 6390A	High-Vacuum SEM mode and Energy-Dispersive X-ray analysis	[131]	
		DSC	DSC Q200	Heating rate of 10 °C/min, Constant flow of nitrogen gas (50 mL/min)	-	
		SEM-EDX	LYRA3 XMU	Specimens coated with Platinum		
					-	

 Table 7. Types and specifications of instruments used in microstructure characterization.

Binder System

FA-GGBFS

Instrument	Specifications	References	
Bruker AXS D2	2 θ (10–65°), Cu K α X-ray source		
DTA-TG (DTG-60H)	Heating rate of 10 °C/min from room temperature to 1000 °C	[112]	
Bruker 400 MHz Avance III NMR spectrometer		-	
Stemi 508	Monitor cracking in samples	[144]	
D8 Diffractometer	Voltage of 40 KV using CuKa radiation, 20 scanning range of 5° – 50°	- [145]	
COXEMEM-30PLUS	Magnification (2 kx–20 kx)	[143]	
Oxford, Carl Zeiss	Magnification (1000 kx)		
Rigaku Mini-flex 600	Broad-angle measurement (5–130°) 2θ		
JASCO FT///IR-6300	Wavelength range $(400 \text{ to } 4000 \text{ cm}^{-1})$	[113]	
JASCO FT///IR-6300	wavelength range $(400 \text{ to } 4000 \text{ cm}^{-1})$	-	
Panalytical Empyrean	Elemental composition		
I-Cal 8000	Heat of geopolymer reaction		
GeminiSEM			
Cameca SX- 100	Raw Materials composition	[91]	
Rigaku Geigerflex	Cr Kα radiation, Voltage (37.5 kV), Current (25 mA)	-	
	Instrument Bruker AXS D2 DTA-TG (DTG-60H) Bruker 400 MHz Avance III NMR spectrometer Stemi 508 D8 Diffractometer COXEMEM-30PLUS OXford, Carl Zeiss Rigaku Mini-flex 600 JASCO FT///IR-6300 JASCO FT///IR-6300 Panalytical Empyrean I-Cal 8000 GeminiSEM Cameca SX- 100 Rigaku Geigerflex	InstrumentSpecificationsBruker AXS D22θ (10–65°), Cu Kα X-ray sourceDTA-TG (DTG-60H)Heating rate of 10 °C/min from room temperature to 1000 °CBruker 400 MHz Avance III NMR spectrometerHeating rate of 40 °C/min from room temperature to 1000 °CBruker 400 MHz Avance III NMR spectrometerMonitor cracking in samplesStemi 508Monitor cracking in samplesD8 DiffractometerVoltage of 40 KV using CuKa radiation, 2θ scanning range of 5°-50°COXEMEM-30PLUSMagnification (2 kx-20 kx)Oxford, Carl ZeissMagnification (1000 kx)Rigaku Mini-flex 600Broad-angle measurement (5–130°) 2θJASCO FT///IR-6300Wavelength range (400 to 4000 cm ⁻¹)JASCO FT///IR-6300Elemental compositionI-Cal 8000Heat of geopolymer reaction GeminiSEMCameca SX- 100Raw Materials compositionRigaku GeigerflexCr Kα radiation, Voltage (37.5 kV), Current (25 mA)	

Table 7. Cont.

Specimen Type

Paste

		SEM	JEOL JSM-7000F	Secondary electron mode		
FA-RM	Paste	FTIR	Bruker Optics Vetex70	Transmittance mode (500–1600 cm ^{-1}), Resolution (2 cm ^{-1})	[116]	
		XRD	PANalytical B. V	Cu Kα radiation, 40 mA, 40 kV		
		XPS	Axis-Ultra Dld-600 W	Al K α radiation, 10 mA, 15 kV		
		Mössbauer Spectroscopy	Topologic 500A	Proportional Counter attachment		
		FTIR	Bruker Vetex70	Wavenumber range of $(450-4000 \text{ cm}^{-1})$		
		SEM FEI, Sirion 200 High va Acceleration		High vacuum mode, Acceleration voltage (10 kV)	[12]	
		Thermogravimetric Analysis (TGA)	NETZSCH STA 409 PC	Heated in nitrogen atmosphere from 25 °C to 1000 °C at 5 °C/min		
		SEM/Energy Dispersive X-ray Spectroscopy (EDX)	JSM-5610LV	Accelerating voltage of 15 kV		
FA-IOI	Paste	SEM	Zeiss SUPRA 55-VP FEG-SEM	operated at 15 kV and having resolution capacity of 1–4 nm.	[99]	
		XRD	Diffractometer	2θ value was kept in a range of 10–90° and the scanning rate at 2.4° per minute		
FA-FCA		FTIR	PerkinElmer Spectrum GX FTIR spectrometer	-	[106]	
		Petrography	Optical microscope (Laica made)	set to view under $20 \times$ to $50 \times$ magnification		
		SEM	A ZEISS EVO MA18	_		

Binder System	Specimen Type	Analysis Type	Instrument	Specifications	References
FA-MK		XRD	Thermo ARL9900 machine	Co Ka radiation, with a scanning rate of 2.4/min from 8 to 80 2 h	[107]
	_	SEM	JEOL JSM-6460 LA	Magnification of 500 & 1000 \times	-
FA-SF		XRD	Shimadzu X-ray Diffractometer (XRD-6000)	-	[120]
FA-SF		FTIR	PerkinElmer FTIR spectrometer	scanned from 650 cm ^{-1} to 4000 cm ^{-1} with a resolution of 4 cm ^{-1}	_ [120]

Table 7. Cont.

6. Discussion

This study discussed the effect of chemical compositions of the source materials, especially the role of SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO, in the formation of a geopolymer binder structure. Table 1 highlights the chemical compositions (SiO₂, Al₂O₃, CaO, Fe₂O₃, MgO) of the source materials considered for the study: FA, GGBFS, RM, IOT, FCA, MK, and SF. It is found that the chemical compositions of every source material vary under the influence of the method of their generation. Therefore, it is critical to study each source material combination before reaching any solid base of knowledge regarding the end properties of the geopolymer binders. The significance of chemical oxides, namely SiO₂, Al_2O_3 , CaO, Fe₂O₃, and MgO, has been described in the formation of a geopolymer binder structure. With the exception of SiO_2 and Al_2O_3 , the geopolymerization also depends on the presence of CaO, Fe_2O_3 , and MgO in the source materials. These industrial wastes may therefore serve as a filler or participate in the geopolymer reactions by the formation of alumino-silicate (C-A-S-H/N-A-S-H/M-A-S-H) gels, thus making the geopolymer matrix denser. The geopolymerization highly depends upon the dissolution character of the source materials, which are composed of varying percentages of SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO, and it is likely that not every oxide of silicon/aluminium/calcium/iron/magnesium will participate in the reaction process.

Following the role of chemical compositions, in part I, the study reviews the compressive strength properties of 100% FA, along with some blended geopolymer binder systems: FA-GGBFS, RM-FA, IOT-FA, FCA-FA, MK-FA and SF-FA. The compressive strength review demonstrates that there are primary geopolymer gel formations–C-A-S-H/N-A-S-H/C-S-H- that aid in the strength development of the geopolymer products. The RM and IOT contain a high amount of Fe₂O₃, while FCA and GGBFS are rich in MgO; hence, the role of MgO and Fe₂O₃ is crucial, and, in turn, influences the strength development of geopolymer products. However, as seen in Tables 2–4, the percentage combination of source materials, curing temperature conditions and the molarity of NaOH also significantly impacts the development of strength.

Geopolymerization is a complex phenomenon, and the trend of compressive strength properties is not simple enough to come to any general conclusion. Therefore, part II of the study highlighted the microstructural characteristics (XRD, SEM, FTIR) of the geopolymer binder systems to understand the nature of the internal binder structure. Accordingly, the microstructure studies revealed that each binder composition based on FA provides better density and formation of geopolymer gels that complement the compressive strength properties. Each FA-based binder composition demonstrates the formation of several mineral compounds and associated geopolymer bonds that aid in strength development.

7. Outlook on the Utilization of FA-Based Geopolymer Binders

The easy availability, reliable chemical compositions, and desirable physical properties of FA create the prospects of its utilization in making commercial geopolymer binders. This also means that FA-based geopolymer binders, due to their promising properties, provide the opportunity to minimize the use of cement as a traditional binder material, leading to a low-carbon future. Moreover, the utilization of FA in the preparation of geopolymer binder aids in the conservation of natural resources [146].

Over the last decade, a variety of research has been devoted to improving FA-based geopolymer binders by incorporating other supplementary aluminosilicate wastes. The wastes considered in this review (GGBFS, RM, IOT, FCA, MK, and SF) are recognized to modify the properties of FA-based geopolymer binders. In addition to the use of fibers, nano-materials are observed to improve the mechanical strength and microstructure characteristics [147–150]. The pore structure of these binders suggests that durability increases in FA-based geopolymer binders as a result of the incorporation of additional wastes in the matrix. Therefore, the implementation of FA-based geopolymer binders becomes a new pathway along with several other industrial wastes, as discussed in this review. Other prospects include emerging applications in geopolymer 3D printing, ceramic coatings, bricks, etc.

8. Conclusions

In this paper, the findings of previous studies regarding the compressive strength and microstructure properties of the FA-based geopolymer binder combinations incorporating GGBFS, RM, IOT, FCA, MK, and SF are studied. Based on the extensive review, the following conclusions are presented:

- 1. Primarily, the chemical compositions of the FA, esp. SiO₂, Al₂O₃, CaO, Fe₂O₃, and MgO, play a significant role in the development of geopolymer microstructure.
- The formation of geopolymer network (Si-O-Al), along with C-A-S-H/N-A-S-H/M-A-S-H/K-A-S-H gels and several other additional/new mineral compounds, significantly influence the compressive strength and microstructure properties of the FA based geopolymer binders.
- 3. Advanced analyzing techniques, such as XRD and FTIR, are necessary to understand the complex chemical mechanism that facilitates geopolymerization.
- 4. It could be stated that owing to the excellent geopolymerization behavior, the RM, GGBFS, IOT, FCA, MK, and SF combined with FA could be used as an alternative binder to conventional cement-based binders.
- 5. As geopolymer binders involve different chemistry, compared to cement-water interaction, analyzing microstructure analysis and compressive strength properties provides us with a complete understanding to further address the research gaps and, thereby, improve the already developed FA-based geopolymer binders.

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Abbreviations

FA	Fly Ash
GGBFS	Ground Granulated Blast Furnace Slag
RM	Red Mud
IOT	Iron Ore Tailings
FCA	Ferrochrome Ash
MK	Metakaolin
SF	Silica Fume
XRD	X-ray Diffraction
SEM	Scanning electron Microscope
FTIR	Fourier-Transform Infrared Spectroscopy
RCA	Recycled Coarse Aggregates
М	Mullite
Q	Quartz
K	Kaolinite
Na	Nacrite
He	Hematite
Са	Calcite
ITZ	Interfacial Transition Zone
FFA	Class F Fly Ash

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