

Review

Property-Guided Selection of Fly Ash Across Binder Chemistry Windows

Man Feng ¹, Zhiliang Zhou ^{2,*} , Lilin Yang ¹, Xue Bai ¹, Ning Xie ¹ , Tong Gao ³ and Menglei Yue ^{4,*}

¹ Shandong Provincial Key Laboratory of Preparation and Measurement of Building Material, School of Materials Science and Engineering, University of Jinan, Jinan 250022, China; fengman@stu.ujn.edu.cn (M.F.); yanglilin2019@163.com (L.Y.); 202321100342@stu.ujn.edu.cn (X.B.); mse_xien@ujn.edu.cn (N.X.)

² Key Laboratory of Advanced Marine Materials, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

³ School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China; gt1980614889@163.com

⁴ Guizhou Provincial Architectural Design & Research Institute Co., Ltd., No. 28 Lincheng West Road, Guanshanhu District, Guiyang 550081, China

* Correspondence: zlzhou@qdio.ac.cn (Z.Z.); 15285079296@139.com (M.Y.)

Highlights

What are the main findings?

- FA performance is governed by feedstock properties and binder chemistry windows.
- OPC favors fine, low-carbon, glass-rich FA with later pozzolanic contribution.
- CSA and MKPC mainly use FA as a filler or regulator rather than a strong reactant.
- In geopolymers, FA acts as a reactive precursor controlled by activator compatibility.

What are the implications of the main findings?

- FA route selection should prioritize ash-binder matching, not dosage alone.
- Source-specific qualification is essential before FA enters binder systems.
- Beneficiation can upgrade marginal ash and broaden viable deployment pathways.
- Property-guided FA deployment supports lower-carbon and more reliable binders.

Abstract

Fly ash (FA) recycling into cementitious binders offers a promising route to simultaneously reduce the environmental burden of high-impact construction materials, divert industrial waste from disposal pathways, and generate engineering value from an existing aluminosilicate residue. FA has therefore been widely incorporated into ordinary Portland cement (OPC), calcium sulfoaluminate (CSA) cement, magnesium potassium phosphate cement (MKPC), and alkali-activated/geopolymer systems, where it can improve workability, mechanical strength, durability and promote hydration reactions, depending on the binder chemistry. However, these benefits are not always successful: FA addition may also reduce early-age strength, delay setting, limit reactivity, impair fluidity, or produce under-reacted matrices when ash properties are mismatched with the chemistry window of the target binder. Rather than revisiting these systems as isolated application categories, this review develops a property-guided framework for interpreting and selecting FA across major cementitious routes. It first highlights why FA should not be treated as a single material. Key descriptors include glass content, fineness, calcium level, carbon residue, mineralogy, and beneficiation state. The review then compares four representative binder environments to clarify the role of FA shifts from pozzolanic contributor to filler-dominated hydration modifier to functional regulator, and finally



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to reactive precursor, including the calcium hydroxide (CH)-rich Portland systems, CH-poor CSA systems, phosphate-bonded MKPC systems, and alkali-activated/geopolymer systems. The central conclusion is that the key question is not simply where FA can be used, but which FA is best matched with which binder chemistry and for what performance objective.

Keywords: fly ash; supplementary cementitious materials; Portland cement; calcium sulfoaluminate cement; magnesium potassium phosphate cement; geopolymer; property-guided deployment; pathway selection

1. Introduction

Cementitious binders are under increasing pressure to reduce their environmental footprint because many widely used systems rely on energy-intensive raw materials and processing routes. Portland cement is the most prominent example, but the challenge extends beyond conventional cement and concrete to special cements and alkali-activated binders. Meanwhile, fly ash (FA), as a large-volume industrial by-product rich in reactive or potentially reactive aluminosilicate phases, continues to create disposal and land-use pressures when insufficiently utilized [1]. These two issues together create a clear opportunity: incorporating FA into cementitious systems can reduce the consumption of more carbon-intensive binder components, divert industrial residue from disposal pathways, and create engineering value from an existing by-product. Under suitable conditions, FA may also improve fresh-state behavior, later-age reaction, microstructural development, and durability-related performance [2,3]. Accordingly, FA reuse in construction binders should be understood not simply as waste management, but as an integrated environmental, economic, and materials-engineering strategy [4–6].

Among the available recycling routes for FA, its incorporation into cementitious binders remains the most mature and technically productive pathway because it combines large-volume utilization with measurable engineering benefit. In OPC systems, FA is well known to improve durability and, under suitable formulations, long-term mechanical performance [7]. In CSA systems, FA can modify hydration behavior, although its later reaction is often limited [8]. In magnesium phosphate systems, FA has been shown to improve strength, water resistance, and dimensional stability primarily through formulation effects [9]. In geopolymer systems, FA can play an even more fundamental role as the reactive aluminosilicate precursor itself [10,11]. These observations show that FA is not merely consumed as a waste additive; rather, it can deliver distinct but meaningful functions across different binder chemistries.

However, FA incorporation does not automatically lead to improved performance. In Portland systems, high replacement levels may reduce early-age strength, delay setting, and increase carbonation susceptibility because FA reacts more slowly than clinker at early ages [12]. In CSA systems, excessive FA may depress strength because the lower-portlandite, lower-pH environment limits classical pozzolanic participation and shifts the contribution toward filler effects [8]. In MKPC systems, FA can prolong setting and alter fluidity even when it later benefits dimensional stability or water resistance [9]. In geopolymer systems, unsuitable combinations of FA quality, activator composition, and curing regime may result in insufficient dissolution and under-reacted matrices [10]. These contrasting outcomes indicate that failure usually occurs when FA properties are mismatched with the chemistry environment of the target binder.

The key issue, therefore, is not simply whether FA can be used in cementitious materials, but how a given FA should be matched to a suitable binder chemistry according to its intrinsic characteristics and attainable reactivity [5,13–15]. This review adopts a property-guided perspective in which reactive glass content, fineness, calcium level, unburned carbon, mineralogy, and beneficiation state are treated as the primary descriptors for pathway selection. From this viewpoint, CH-rich OPC systems generally favor ashes with sufficient fineness and pozzolanic potential; CSA systems often use FA mainly through filler and hydration-regulating effects; MKPC systems benefit more from microstructural and rheological modification than from high chemical reactivity; and geopolymer systems require adequate reactive aluminosilicate content together with a suitable response to alkali activation. Because these descriptors can be identified through routine physicochemical characterization, and because source-specific upgrading methods such as classification, milling, screening, and compositional adjustment can broaden the usable range of marginal ashes, this strategy is also practically deployable.

Existing reviews have already made major contributions to understanding FA in Portland cement, CSA cement, MKPC, geopolymers, and broader ash-utilization pathways [1–3,6,8–11]. The gap is therefore not a lack of high-quality literature, but a fragmentation of perspective: most reviews are organized around single binder families or broad application inventories, and thus do not explicitly answer a cross-system question that is highly relevant in practice—how different fly ashes should be allocated to suitable binder systems to maximize benefit while minimizing mismatch-induced failure. By shifting the emphasis from application listing to property-guided pathway selection, the present review connects FA heterogeneity with binder chemistry, clarifies why the same ash can play fundamentally different roles across different systems, and provides a more rational basis for source-specific qualification, upgrading, and deployment. This review differs from previous studies by proposing a property-guided framework that links fly ash characteristics directly to binder chemistry windows and functional roles. Rather than treating fly ash as a generic supplementary material, this review emphasizes how source-specific properties determine whether fly ash should be used as a pozzolanic contributor, filler-dominated hydration regulator, microstructural modifier, or aluminosilicate precursor.

Because this review relies on a property-guided framework, several recurring terms are defined here to avoid ambiguity. “Reactive glass fraction” refers to the chemically accessible portion of the amorphous aluminosilicate-rich glass phase that can dissolve and participate in pozzolanic, alkali-activated, or other binder-specific reactions. “Particle accessibility” describes the extent to which reactive fly ash surfaces are exposed to and reachable by the reacting solution, which depends on fineness, particle-size distribution, morphology, agglomeration, and beneficiation processes such as classification or milling. “Chemistry window” refers to the characteristic reaction environment of a binder system, including pore-solution alkalinity, calcium hydroxide availability, dominant hydration or gel-forming pathway, ion balance, and curing regime. These definitions distinguish intrinsic ash descriptors from the system-specific conditions that determine their actual contribution. The overall property-guided logic of this review is summarized in Figure 1, which links fly ash descriptors, binder chemistry windows, optimization criteria, and dominant functional roles across OPC, CSA, MKPC, and alkali-activated/geopolymer systems.

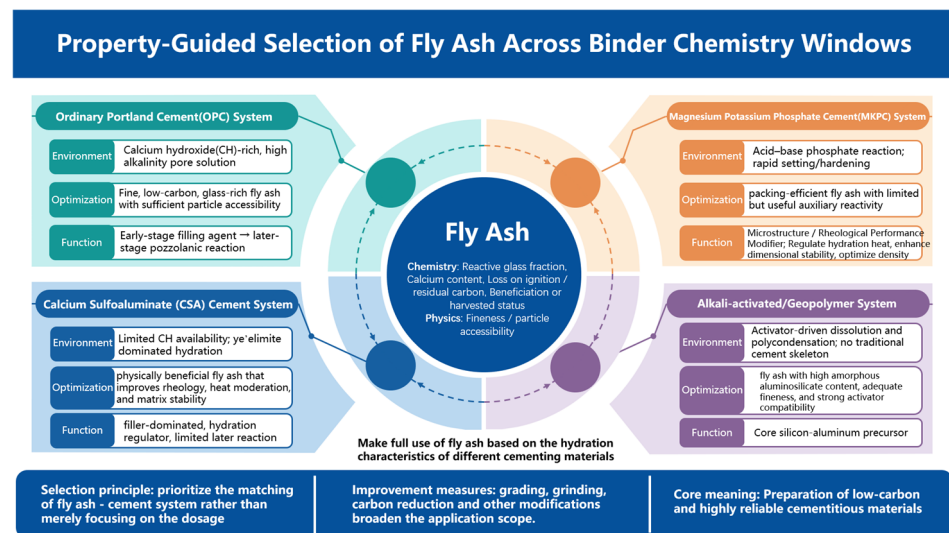


Figure 1. Graphical abstract summarizing FA role across binder systems.

2. Feedstock Heterogeneity of Fly Ash

As established in the Introduction, the successful utilization of fly ash depends on the compatibility between its intrinsic properties and the chemistry window of the target binder [3,16]. This relationship makes a feedstock-side analysis indispensable to any rigorous discussion of fly ash deployment. Before examining the behavior of fly ash in OPC, CSA, MKPC, or geopolymer systems, it is necessary to define the material basis of that behavior, namely, the source-dependent heterogeneity of fly ash and the key attributes that control its engineering value [14,17,18]. Fly ash should be viewed not as a uniform material, but as a group of combustion-derived aluminosilicate powders whose performance varies with source, collection method, mineralogy, physical properties, and post-processing treatments.

2.1. Historical Production and Utilization Patterns

Historical production and utilization data show that fly ash is a high-volume industrial by-product with uneven distribution across countries, regions, and industrial sectors. Cement and concrete applications remain the dominant utilization pathway for fly ash worldwide. Figure 2a presents the global production and utilization of coal fly ash [17,19]. Currently, only one-quarter of total fly ash output is effectively utilized. Major producers such as India and China have utilization rates below 50%. The utilization distribution across four countries is presented in Figure 2b [20]. The use of high-volume fly ash (with fly ash content above 30%) to replace cement clinker significantly enhances fly ash utilization while reducing carbon dioxide emissions and overall costs. Some of the fly ash is also used to manufacture industrial products, such as zeolites and composite hydrogels [3,16]. This pattern demonstrates that fly ash is not a niche additive, but a multi-sector resource whose allocation cannot be evaluated by replacement ratio alone. Large-scale utilization necessarily involves differentiation among ash qualities, end uses, and performance requirements [17,18].

Recent studies have further shown that supply quality and supply pathway are now as important as total tonnage [5]. Fresh high-quality fly ash is no longer uniformly available, whereas reclaimed or harvested ashes are becoming increasingly important supplementary sources. Reclaimed or ponded ashes, however, should not be treated as simply “older” versions of fresh fly ash. Long-term storage can induce carbonation, partial hydration, agglomeration, moisture-driven segregation, and enrichment of soluble salts or other contaminants. These changes may reduce reactive glass accessibility, alter Ca-bearing

phases, increase coarse fractions, change LOI or residual carbon distribution, and introduce batch-to-batch variability. Therefore, the use of recovered ashes requires storage-history-sensitive qualification before they are assigned to any binder route. Under these conditions, the central practical issue is no longer merely the total quantity of fly ash available, but the quality of the ash entering a given application and the qualification or beneficiation measures required before use [13]. Selective deployment has therefore become a necessary principle of rational fly ash utilization.

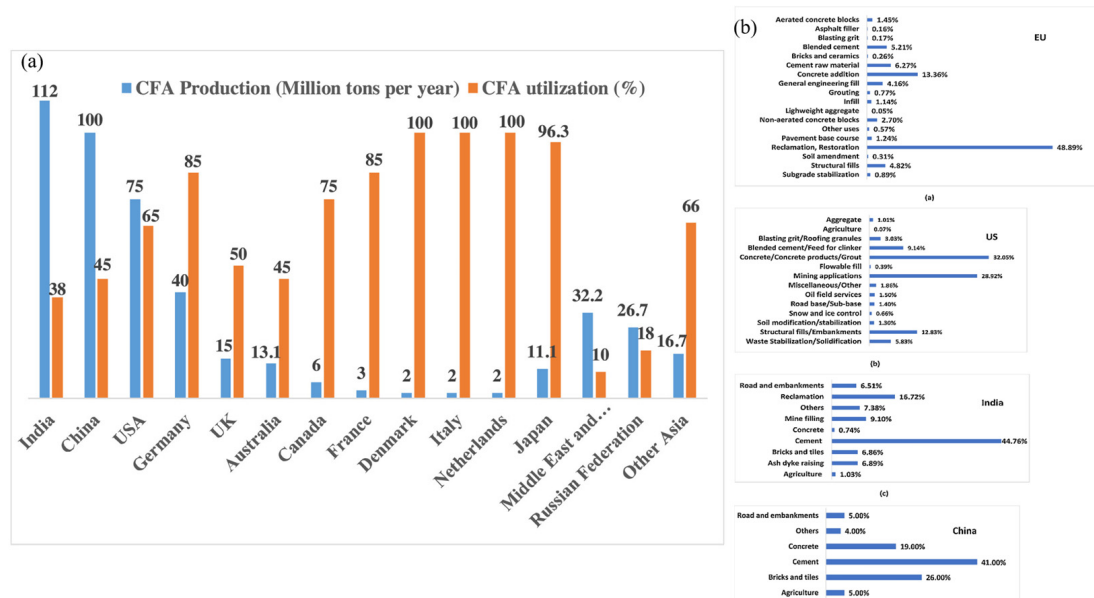


Figure 2. Historical production/utilization and sectoral utilization patterns of coal fly ash. Panel (a) compares production and utilization across major regions, and panel (b) summarizes the principal utilization sectors in the EU, United States, India, and China. Together, these trends show why FA must be treated as a selectively allocated resource rather than a generic filler. Adapted from [3,16–18].

A further distinction should be made between dry-collected fly ash and wet, ponded, or reclaimed fly ash. Dry-collected fly ash is usually closer to the condition required for direct use in concrete, provided that fineness, LOI, chemical composition, and activity requirements are satisfied. By contrast, wet or ponded fly ash may contain higher moisture, agglomerated particles, partially hydrated or carbonated phases, soluble salts, and stronger within-deposit heterogeneity [5,13]. Therefore, wet fly ash usually requires beneficiation before it can be used as a concrete addition. A practical upgrading sequence may include representative sampling and homogenization, dewatering and drying, screening or deagglomeration, classification or milling to adjust fineness, carbon reduction when LOI is excessive, washing or soluble-salt control when needed, and final conformity testing. For concrete use in Europe, this treatment should aim to satisfy the chemical, physical, and quality-control requirements of EN 450-1 for siliceous fly ash used as a type II addition in concrete [21].

This shift from tonnage-centered utilization to quality-centered allocation establishes the first layer of the review logic [5]. Once selective deployment is recognized as necessary, the discussion must move from utilization statistics to the material characteristics that distinguish one fly ash from another in engineering terms [13].

2.2. Physicochemical Characteristics of Fly Ash

The engineering behavior of fly ash is fundamentally governed by its physicochemical heterogeneity. Typical fly ash contains spherical particles, solid or hollow cenospheres, vari-

able surface textures, low bulk density, and substantial differences in color and composition arising from source-dependent mineralogy, iron content, and unburned carbon. Its typical morphology is shown in Figure 3 [20]. These characteristics are directly linked to engineering performance rather than serving as merely descriptive features. Spherical morphology contributes to the ball-bearing effect and improved workability, whereas glassy phase content, particle accessibility, and chemical composition determine dissolution potential, reaction kinetics, and the extent to which fly ash can contribute beyond a simple filler function [14]. Fly ash is commonly classified as Class F or Class C according to ASTM C618. Class F fly ash is primarily pozzolanic, whereas Class C fly ash exhibits both pozzolanic and cementitious properties because of its generally higher calcium content. This classification provides a useful starting point, but it is not sufficient for predicting performance across different binder systems. Class F fly ash is often more suitable when long-term pozzolanic reaction, chloride-resistance improvement, and stable later-age performance are prioritized. In contrast, Class C fly ash may be advantageous when early reactivity or early strength is required, but its performance is usually more sensitive to mixture chemistry, sulfate balance, curing conditions, and exposure environment. Therefore, the Class F/Class C distinction should be used together with more specific descriptors, including fineness, reactive glass fraction, CaO content, LOI, mineralogy, and beneficiation state.

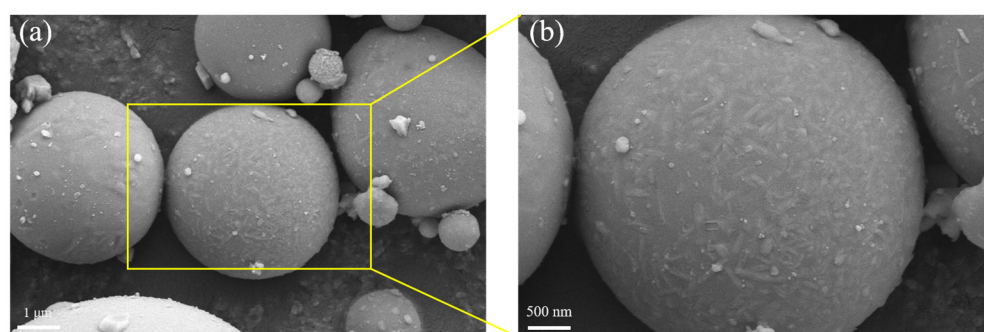


Figure 3. Typical fly ash morphology and SEM micrographs. (a) SEM image of fly ash, and (b) is a magnified image of the surface of fly ash. The spherical particle geometry, cenospheres, and accessible surface features illustrated here are directly relevant to discussions of workability, packing, and reactivity.

Particle-size distribution should also be interpreted relative to the target binder system. In OPC systems, finer fly ash fractions are generally preferred when later pozzolanic contribution, portlandite consumption, and pore refinement are desired. In CSA systems, the particle-size requirement is less directly linked to strong pozzolanic reaction and more closely related to packing, nucleation, rheology regulation, and dilution of ye'elimite- and sulfate-bearing phases [8,14,22–28]. In MKPC systems, particle-size distribution and spherical morphology mainly regulate flowability, heat release, packing density, and the continuity of the phosphate-bonded matrix [29–32]. In geopolymer systems, smaller particle size and higher surface accessibility can promote alkaline dissolution, but the benefit still depends on activator composition and curing temperature [10,11,33–36]. Thus, the same particle-size distribution may be favorable in one binder route but less decisive or insufficient in another.

Recent reactivity-focused studies have reinforced this interpretation by showing that the intrinsic pozzolanic reactivity of siliceous fly ash can be significantly improved through classification and milling [14]. However, the magnitude of this improvement should be regarded as ash- and process-dependent rather than universal. Classification and milling are most effective when the as-received ash contains a substantial reactive glassy fraction that is locked in coarse or poorly accessible particles. By contrast, ashes with

low reactive glass content, high crystalline residue, high residual carbon, or already fine particle-size distribution may show smaller gains, and excessive grinding may increase water demand or reduce the beneficial spherical morphology of fly ash particles. These findings demonstrate that the suitability of a given ash for a specific utilization route is not fixed at the moment of collection. An as-received ash with only marginal suitability for one application may become substantially more competitive after beneficiation [7]. Feedstock assessment and feedstock upgrading therefore form an integrated decision framework rather than two independent steps [26].

The significance of physicochemical heterogeneity lies not only in the fact that different fly ashes are different, but in the fact that their differences are measurable, interpretable, and technologically actionable [3,17]. This understanding provides the basis for converting feedstock heterogeneity into pathway-relevant descriptors for deployment across different binder systems [14].

2.3. Feedstock Attributes and Pathway Compatibility

Once fly ash is recognized as a property-sensitive feedstock, the logic of pathway selection becomes explicit. The key issue is not whether fly ash, in the abstract, can be used in OPC, CSA, MKPC, or geopolymer systems. The more informative question concerns which combinations of feedstock properties make a given ash more compatible with one chemistry environment than another. Feedstock-side analysis therefore constitutes the necessary basis for interpreting binder-side performance [1,3,14,17].

Low-carbon, fine ashes with abundant and chemically accessible glass are generally more attractive for Portland and geopolymer routes, where dissolution potential, reaction accessibility, and later-age reactivity are especially important [14,37]. In this review, the term “glass-rich” should not be interpreted simply as a high total amorphous content. A distinction must be made between the total glassy fraction and the truly reactive glassy fraction of fly ash. The total glassy fraction refers to the overall amorphous aluminosilicate-rich phase present in the ash, which is commonly estimated by quantitative phase analysis such as XRD/Rietveld analysis with an internal standard. This value represents the potential reservoir of glassy material. However, not all of this reservoir is necessarily reactive in a given binder environment. The truly reactive glassy fraction refers to the portion of the amorphous phase that is chemically accessible, dissolvable, and able to participate in the dominant reaction pathway under the pore-solution chemistry, pH, temperature, and curing conditions of a specific binder system. Therefore, total glass content and reactive glass content should not be treated as equivalent. For property-guided selection, reactive glass is more appropriately inferred from dissolution behavior, portlandite consumption, reaction degree, heat evolution, strength activity, or gel formation, rather than from total amorphous content alone [7,14,37]. By contrast, ashes with lower intrinsic reactivity can still perform valuable functions in systems where filler effects, rheology regulation, heat moderation, or microstructural densification are dominant [8,10,11]. The engineering value of fly ash is therefore determined not by an intrinsic classification as suitable or unsuitable, but by the degree to which its measurable attributes align with the dominant functional requirements of a given binder system.

This descriptor-based view is especially important because the Class F/Class C distinction, although useful, is not a complete classification scheme for all fly ashes [5,17,18]. Many practical sources fall between these two categories or deviate from conventional coal-combustion ashes, including intermediate-composition ashes, co-combustion ashes, and reclaimed or ponded ashes [5,13]. These materials should not be excluded a priori, but they require source-specific qualification because their performance may be affected by non-standard calcium levels, altered glass chemistry, residual carbon, soluble salts,

sulfates, phosphates, chlorides, unburned residues, partial hydration, carbonation, agglomeration, or weathering-induced changes. For recovered ponded or landfilled ashes in particular, qualification should include representative sampling across the deposit, moisture and particle-size assessment, LOI/residual carbon measurement, XRD/TGA evidence of carbonation or hydration products, soluble ion analysis, and leaching or contamination screening where relevant. Therefore, in the property-guided framework, such ashes are evaluated through measurable descriptors, including fineness, LOI, reactive glass accessibility, CaO content, mineralogy, soluble ion content, and beneficiation response, rather than by Class F/Class C labels alone [14,15,26].

These descriptors establish the feedstock-side basis for the selective deployment of fly ash [14]. However, feedstock properties alone do not determine performance outcomes. The same ash can perform very different functions in different cementitious systems because binder chemistry environments interpret feedstock properties in fundamentally different ways [8–10]. The next section therefore shifts the discussion from feedstock heterogeneity to binder-side chemistry, in order to clarify how the same material attributes are translated into distinct functional roles across OPC, CSA, MKPC, and geopolymer systems. To make this feedstock-side logic explicit, Table 1 summarizes the key fly ash attributes considered in this review and their pathway implications. The table shows how compositional descriptors, physical descriptors, source condition, and beneficiation response jointly determine whether a given ash is more suitable for pozzolanic contribution, filler/nucleation effects, rheological regulation, or precursor use.

Table 1. Typical pathway implications and mechanisms caused by different feedstock attributes of fly ash. Adapted from [8,10,11,14,37].

Feedstock Attribute	Why It Matters	Typical Pathway Implication
Total glassy fraction/amorphous content	Indicates the potential reservoir of amorphous aluminosilicate-rich material, but does not by itself prove actual reactivity	Useful as an initial screening descriptor, especially for OPC and geopolymer routes, but must be interpreted together with glass chemistry, fineness, and binder environment
Reactive glassy fraction/binder-accessible glass	Represents the portion of the glassy phase that can dissolve and participate in the target reaction pathway under specific pore-solution chemistry, pH, temperature, and curing conditions	More decisive than total glass content for Portland pozzolanic contribution and geopolymer precursor performance; should be inferred from dissolution, portlandite consumption, reaction degree, heat evolution, strength activity, or gel formation
Fineness/particle accessibility	Controls packing, nucleation, and reaction kinetics	Finer ashes are generally more attractive for Portland and geopolymer routes; coarse ashes may need beneficiation
Calcium content	Changes the preferred reaction logic and gel assemblage	High-Ca ashes do not follow the same pathway logic as low-Ca siliceous ashes
Loss on ignition/residual carbon	Influences admixture demand, air entrainment, and consistency of fresh behavior	High (loss of ignition) LOI may complicate Portland deployment unless controlled or upgraded

Table 1. *Cont.*

Feedstock Attribute	Why It Matters	Typical Pathway Implication
Beneficiation response/harvested status	Determines whether classification, milling, carbon reduction, or screening can convert a marginal ash into a route-compatible feedstock	Improvement depends on ash type, reactive glass accessibility, particle-size distribution, residual carbon, processing intensity, and the reactivity test used; therefore, upgrading should be validated by performance-based indicators rather than fineness alone
Non-standard source status: intermediate, co-combustion, reclaimed/ponded/landfilled ash	These ashes may deviate from fresh Class F/Class C behavior because storage can induce carbonation, partial hydration, agglomeration, moisture-driven segregation, soluble salt enrichment, contamination, and strong within-deposit heterogeneity	Requires representative sampling, storage-history-sensitive characterization, beneficiation when needed, and mixture-level validation before route selection
Dry/wet source condition	Dry-collected ash is generally closer to direct use, whereas wet/ponded ash may contain moisture, agglomerates, soluble salts, carbonated/hydrated phases, and stronger heterogeneity [5,13]	Wet ash usually requires homogenization, drying, deagglomeration, classification/milling, carbon reduction, washing if needed, and conformity testing before binder route selection [21]

3. Binder Chemistry Windows and Functional Roles of Fly Ash

Section 2 established that FA is a property-sensitive feedstock whose engineering value cannot be inferred from its name alone. The next analytical step is to determine how these feedstock properties are translated into function once fly ash enters a cementitious system. This translation is governed primarily by the binder environment rather than by fly ash properties in isolation [4,8–11]. In practical terms, the availability of calcium hydroxide, the alkalinity and ionic composition of the pore solution, the dominant reaction pathway, and the curing regime collectively determine whether fly ash acts mainly as a physical assistant, a pozzolanic reactant, a filler-dominated regulator, or a true precursor. Accordingly, the same fly ash cannot be expected to play the same role across OPC, CSA, MKPC, and geopolymer systems, even when its feedstock descriptors remain unchanged. The same distinction also applies to the glassy phase of fly ash: a high total amorphous fraction does not guarantee the same reactive contribution across different chemistry environments, because dissolution and reaction are controlled by the binder pore solution, alkalinity, calcium availability, temperature, and curing regime.

This binder-side perspective provides the conceptual bridge between feedstock heterogeneity and system-specific performance. In CH-rich Portland systems, fly ash is introduced into an environment where portlandite is available and long-term pozzolanic reaction can gradually develop; hence, its contribution commonly evolves from early packing and flow modification toward later chemical participation [7,12]. This pattern is consistent with blended-cement studies showing that finer or more reactive fly ash accelerates portlandite consumption and improves the later contribution of the ash in cement systems, while durability-oriented studies continue to show that Class F fly ash can significantly reduce porosity, sorptivity, and chloride permeability at later ages even when early strength is lower [14,37].

The logic changes markedly in CH-poor CSA systems. Martin et al. showed that increasing fly ash content accelerated CSA hydration primarily through a filler effect, whereas dissolution rims after 90 days indicated that the reaction degree of the fly ash remained only about 20%–30% [8]. More recent work further showed that both Class C and Class F fly ash can slightly improve workability and modify early-age heat evolution in CSA pastes, but strength development remains highly dependent on replacement level and ash type [22]. These observations indicate that, in CSA systems, fly ash is generally better interpreted as a hydration-regulating and filler-dominated component than as a strongly reacting pozzolanic phase [23].

A further shift occurs in phosphate-bonded MKPC systems. Here, the governing chemistry is no longer hydration in a CH-rich environment, but the rapid acid–base reaction between MgO and phosphate species to form a phosphate-bonded skeleton [9,38]. Under this phosphate-bonded environment, the role of fly ash is usually not to serve as the principal reactive framework. Instead, experimental studies have shown that properly dosed fly ash can improve particle-size distribution, refine microstructure, moderate heat release, and optimize compressive strength, whereas excessive replacement dilutes the active MKPC matrix and becomes counterproductive [29]. Recent comparative studies and reviews on MKPC also support this interpretation, emphasizing that the value of fly ash in this system lies in functional regulation and formulation optimization rather than maximal substitution [30].

The reaction environment changes most fundamentally in alkali-activated and geopolymer systems [10]. In these binders, fly ash is no longer primarily an additive to another cementitious matrix; instead, it may become the principal aluminosilicate precursor from which the gel network is formed. Under this route, the decisive variables are the dissolution potential of the ash, activator composition, and curing schedule. Studies on low-calcium fly ash geopolymer concrete have shown that curing conditions strongly affect pore structure and microstructural development, while recent reviews of one-part geopolymers have emphasized that hydration/activation stages, flowability, setting, shrinkage, and efflorescence are all highly sensitive to precursor–activator compatibility [11,33,34]. Thus, in geopolymer systems, fly ash should be analyzed primarily as a precursor whose suitability depends on reactivity and activation response rather than as a supplementary filler or delayed pozzolan [35].

As a result, these chemistry environments reveal a clear cross-system progression in the role of fly ash. In Portland systems, fly ash commonly evolves from physical assistance to later pozzolanic contribution [7]. In CSA systems, its contribution is dominated by filler-driven hydration effects with limited later reaction [8]. In MKPC systems, it functions mainly as a microstructural and rheological regulator within a phosphate-bonded matrix [9]. In geopolymer systems, it becomes the precursor itself [10]. This progression is not merely a convenient way of organizing the literature; it is the central interpretive line of the present review because it explains why the same feedstock descriptors can lead to very different engineering outcomes across binder families.

On this basis, the remainder of the review is organized not as a sequence of independent binder-specific case summaries, but as a progressive examination of how different binder systems assign different functional identities to fly ash. The following sections therefore move from CH-rich Portland systems to CH-poor CSA systems, then to phosphate-bonded MKPC systems, and finally to alkali-activated/geopolymer systems, in order to show how fly ash shifts from supplementary participant to functional regulator and, ultimately, to principal precursor. This binder-side comparison is summarized in Table 2, which links each chemistry window with the dominant functional role of fly ash and the representative performance implications emphasized in this review. Together with

Table 1, this table establishes the two-part logic of the review: feedstock attributes define the potential of fly ash, while binder chemistry determines how that potential is expressed.

Table 2. Binder-side chemical features and dominant role of fly ash originating from different binder-side perspective. Adapted from [7–10].

Chemistry Window	Binder-Side Chemical Features	Dominant Role of Fly Ash	Representative Implications Emphasized in This Review
CH-rich OPC	Portlandite available; sustained alkaline pore solution; hydration + later pozzolanic coupling	Packing aid + later pozzolanic reactant	Fresh-state modification, later strength gain, pore refinement, chloride/sulfate resistance
CH-poor CSA	Limited CH availability; ye’elimite-dominated hydration; rapid early reactions	Filler-dominated hydration regulator with limited later reaction	Workability adjustment, hydration acceleration by filler effect, modest reaction degree at later age
Phosphate-bonded MKPC	Acid–base phosphate reaction; rapid setting/hardening; non-Portland chemistry	Functional regulator/microstructural modifier	Heat moderation, particle packing, dimensional stability, optimized rather than maximal addition
Alkali-activated/geopolymer	Activator-driven dissolution and polycondensation; precursor-controlled gel formation	Principal aluminosilicate precursor	Activator sensitivity, curing sensitivity, gel-network formation, precursor–activator compatibility

4. Fly Ash in Portland Cement Systems

Portland cement systems preferentially accommodate fly ashes that are fine, low in residual carbon, rich in chemically accessible glass, and predominantly spherical in morphology. This preference arises because the Portland binder environment requires fly ash to perform a dual function: an early physical role in improving particle packing and rheological behavior, followed by a later chemical role through pozzolanic reaction with portlandite [4,14,15,37]. However, these feedstock descriptors should not be interpreted independently of the surrounding mix design. In OPC-based systems, the effective contribution of fly ash is also governed by cement chemistry, portlandite availability, alkali and sulfate balance, water-to-binder ratio, complementary mineral additions, replacement level, and curing regime [4,12,37,39–41]. Thus, the most suitable fly ash for an OPC system is not defined by ash properties alone, but by the compatibility between ash properties and the full binder–mixture–curing environment. Fly ashes that lack sufficient fineness, chemically accessible glass, or particle accessibility are generally less capable of making this transition from physical assistance to chemical contribution, whereas carbon-rich ashes may further compromise admixture compatibility and fresh-state control [26,42,43].

A further distinction is also necessary within the Portland route itself. Low-calcium Class F fly ash is usually the more robust option when the design objective emphasizes later-age performance and durability, because it follows a clearer pozzolanic route and has been repeatedly associated with improved pore refinement and chloride resistance under adequate curing [2]. Higher-calcium Class C fly ash, by contrast, may be attractive when greater early reactivity is desired because of its cementitious character, but its behavior is more system-specific and should not be assumed to provide the same long-term balance automatically [42]. Recent comparative work at equal replacement levels also reported that Class F fly ash outperformed Class C fly ash in later-age strength and durability, even though the two classes play different roles in fresh-state behavior and early hydration [43]. Thus, the practical question is not whether Class F or Class C fly ash is universally

better, but which ash chemistry is better matched with the intended OPC mixture and exposure condition.

4.1. System-Level Modulators in Portland–Fly Ash Binders

The performance of fly ash in OPC systems should be understood as a coupled outcome of ash properties and system-level variables. Cement chemistry determines the early hydration rate, the supply of portlandite for pozzolanic reaction, and the alkali–sulfate environment in which fly ash dissolution occurs. Therefore, a fine and reactive ash may show different apparent reactivity when blended with different Portland cements. Cements or mix designs that provide sufficient portlandite and a stable alkaline pore solution can better support the later pozzolanic contribution of Class F fly ash, whereas systems with limited alkalinity or insufficient curing may require finer or more reactive ashes to achieve comparable later-age benefits [4,37].

The water-to-binder ratio further modifies this response. A lower w/b ratio can enhance packing density and reduce capillary porosity, thereby increasing the durability benefit of fine fly ash. However, it may also restrict moisture availability and ion transport during later curing, which can limit the extent of pozzolanic reaction if curing is inadequate. A higher w/b ratio provides more reaction space and easier ionic transport, but it also increases the initial porosity that must be refined by subsequent hydration and pozzolanic products. Therefore, fly ash fineness and glass reactivity should be selected together with w/b ratio and curing condition, rather than as isolated feedstock criteria [12,39].

Complementary mineral additions can also shift the role required of fly ash. In binary OPC–FA systems, fly ash is expected to provide both packing and later pozzolanic contribution. In ternary or blended systems containing slag, silica fume, limestone, or other SCMs, the required function of fly ash may change because the co-addition can modify early hydration, nucleation, pore refinement, calcium/alumina availability, and hydrate assemblage. Under such conditions, the most suitable fly ash is not necessarily the most reactive ash, but the ash that best complements the other mineral additions and the target performance of the binder.

Curing regime is another decisive modulator. Adequate moist curing is essential for sustaining the delayed pozzolanic reaction of fly ash and for converting its early dilution effect into later microstructural benefit. Elevated-temperature or otherwise accelerated curing can increase the apparent reactivity of moderately reactive ashes, whereas low-temperature or insufficient moist curing places greater demand on ash fineness, particle accessibility, and reactive glass content. This explains why the same fly ash may exhibit different strength and durability contributions under different curing regimes [39–41].

Accordingly, the OPC selection rule proposed in this review should be read as a conditional guideline: fine, low-carbon, chemically accessible glass-rich fly ash is generally favorable, but its actual benefit depends on ash–cement– w/b –co-SCM–curing compatibility.

4.2. Fresh-State Performance

The fresh-state behavior of Portland–fly ash systems is controlled by both feedstock attributes and mix-design variables. Among the feedstock descriptors, particle shape, fineness, and residual carbon are especially important [44,45]. When fly ash particles are predominantly spherical and have smooth accessible surfaces, they commonly reduce interparticle friction, improve packing, and lower water demand at a given workability level [46,47]. Chindaprasirt and co-workers showed that finer fly ash fractions reduced the water requirement of mortar mixes, which they attributed to the more spherical shape and smoother surface of the finer particles [27,28]. In concrete, the same group further found that replacing cement with fly ash lowered the water-to-binder ratio required to maintain

comparable slump, and that the benefit became stronger as fly ash fineness increased. These results explain why properly selected fly ash often improves workability in OPC systems even before meaningful pozzolanic reaction occurs.

At the same time, fresh-state benefits are not governed by fineness alone [44,45]. Residual carbon exerts a separate and often adverse influence because it interferes with admixture performance, especially air entrainment. The effect of unburned carbon is not limited to air entrainment. Carbon-rich or porous fly ash particles can adsorb mixing water and chemical admixtures, increase admixture demand, reduce dispersion efficiency, and increase variability in yield stress, plastic viscosity, slump retention, and setting behavior [15,44,45]. Therefore, LOI should be interpreted not only as a specification parameter, but also as a practical rheological-risk indicator. When the amount or surface activity of unburned carbon is high, carbon reduction, blending with low-carbon ash, or adjustment of admixture dosage may be required before stable fresh-state performance can be achieved [15,44,45]. Soong et al. [15] noted that ASTM C618 limits LOI to 6% largely because high-LOI fly ash is associated with poor air entrainment, segregation, and the adsorption of air-entraining admixtures, which in turn increases admixture demand. This means that a fly ash may appear acceptable in terms of size and broad chemistry yet still perform poorly in Portland mixtures if unburned carbon is not controlled. Accordingly, the fly ashes best suited to OPC are not simply fine, but fine and low in residual carbon.

Rheological compatibility with modern polycarboxylate ether (PCE) superplasticizers is particularly important in low-water and high-performance mixtures. Although PCE performance is not governed by LOI alone, residual carbon, porous particles, irregular morphology, and soluble ions can affect admixture adsorption, dispersion efficiency, slump retention, yield stress, and plastic viscosity [15,27,28,44,45]. As a result, two fly ashes with similar fineness and oxide composition may still require different PCE dosages. For this reason, PCE compatibility should be verified by paste or mortar flow tests, slump retention, setting time, and rheological measurements, rather than inferred from fineness or LOI alone [15,44,45].

These observations clarify the physical-entry condition for Portland deployment [44,45]. A suitable OPC fly ash is one that can improve rheology without introducing excessive admixture incompatibility [15,28]. In practical terms, this usually points to low-carbon, predominantly spherical, and adequately fine ashes; by contrast, porous, carbon-rich, or highly irregular ashes are less favorable unless beneficiation is used to improve their physical quality.

4.3. Long-Term Strength Development

The hardened-state role of fly ash in OPC systems is defined by the transition from early dilution to later pozzolanic contribution [39]. This transition occurs most effectively when the ash possesses sufficient reactive glass and adequate particle accessibility [7,14]. Sakai et al. [37] showed that increasing fly ash glass content increased the reaction ratio of fly ash during long-term curing, and further concluded that reactivity in fly ash cement is controlled by the basicity of the glass phase between 28 and 270 days. These findings are especially important because they identify the chemical form and reactivity of the amorphous phase, rather than bulk oxide composition or total glass content alone, as decisive parameters for Portland suitability. In this sense, the total glassy fraction should be regarded as a potential compositional reservoir, whereas the reactive glassy fraction represents the binder-accessible part of that reservoir that can dissolve, consume portlandite, and contribute to secondary C–S–H/C–A–S–H formation. Thus, in OPC systems, a chemically appropriate ash is not simply one with high $\text{SiO}_2 + \text{Al}_2\text{O}_3$ content or high total amorphous

content, but one with a sufficiently reactive glass phase that can actually participate in pozzolanic conversion.

Mechanistically, the pozzolanic activity of fly ash in OPC systems involves the alkaline dissolution of chemically accessible Si- and Al-bearing glassy phases, followed by reaction with portlandite and calcium-rich pore solution to form secondary C–S–H and C–A–S–H-type products [14,37,39]. This process is slower than clinker hydration, which explains the common early-age dilution effect, but it becomes increasingly important at later ages when sufficient moisture, alkalinity, particle accessibility, and reactive glass are available [26,27,37,39]. The long-term strength and durability benefits of fly ash therefore arise from both chemical and physical effects, including continued pozzolanic product formation, portlandite consumption, pore refinement, ITZ densification, and reduced connectivity of capillary pores [12,27,28,37]. However, the same portlandite consumption also contributes to the carbonation trade-off discussed in Section 4.4 [37,40,41,48,49].

Particle accessibility is equally decisive. Chindaprasirt et al. [27] showed that classified fly ash with a median particle size of 6.4 μm produced higher compressive strength and lower porosity than the corresponding original ash with a median particle size of 19.1 μm . In a related study, finer fly ash fractions improved strength, reduced water demand, and produced a denser cement matrix than coarser fractions. Kiattikomol et al. [26] further demonstrated that grinding coarse fly ash substantially increased its strength activity; when ground ash with particle size below 9 μm was used, the strength activity index exceeded 100% of the control within 28 days. Snellings et al. later confirmed the same logic from a reactivity perspective by showing that classification and milling increased the intrinsic pozzolanic reactivity of siliceous fly ash by about 57% and 40%, respectively. Together, these studies show that Portland suitability depends strongly on how much of the reactive fraction is actually accessible to the cement pore solution.

Calcium content further modulates this strength-development path. Mehta's comparative study [42] on 11 fly ashes identified calcium content and particle-size distribution as the most important parameters governing strength development rate, while Oner et al. [43] summarized the conventional distinction that Class F ashes are mainly pozzolanic whereas Class C ashes contain up to about 20% CaO and exhibit cementitious character. Accordingly, when early strength is a major design priority, higher-calcium ashes may be beneficial; when later-age stability and a more predictable pozzolanic route are prioritized, fine low-calcium Class F ashes are often the more reliable choice. The crucial point is that OPC does not simply reward "more ash" or "more fineness" in isolation; it rewards a coordinated combination of reactive glass chemistry, accessible particle size, and appropriate calcium level.

4.4. Durability Benefits and Trade-Offs

The Portland route remains highly attractive because properly selected fly ash can generate substantial durability benefits. Saha [12] reported that Class F fly ash concrete showed lower porosity, lower water sorptivity, and lower chloride permeability than plain concrete, with especially large reductions in sorptivity and chloride permeability between 28 and 180 days. Chindaprasirt et al. [28] likewise found that chloride resistance increased significantly with the incorporation of fly ash and that the improvement became stronger as fly ash fineness increased, owing to reduced water-to-binder ratio, reduced average pore size, and a denser interfacial zone. Acid and sulfate resistance also improve in many Portland–fly ash systems: Chindaprasirt's fineness study found improved resistance to sulfuric acid attack and sulfate expansion for all but the coarsest fractions, and Aydın et al. [50] showed that sulfuric acid resistance of steam-cured concrete improved significantly with high-volume fly ash incorporation. These findings explain why fine,

low-carbon, chemically accessible glass-rich fly ash is especially attractive in OPC when the design objective is long-term transport resistance.

This durability benefit, however, should be separated from carbonation resistance because chloride ingress and carbonation are not governed by identical controlling factors. The improvement in chloride resistance is mainly transport-controlled: fly ash can reduce water demand, refine capillary pores, densify the interfacial transition zone, and generate additional C–S–H/C–A–S–H through pozzolanic reaction, thereby lowering sorptivity and chloride permeability [12,28]. Carbonation resistance, by contrast, depends not only on transport resistance but also on the alkaline reserve of the binder [37,49]. Fly ash replacement reduces the clinker fraction and the initial amount of hydration products derived from clinker, while the pozzolanic reaction consumes portlandite [37,49]. As a result, even when the pore structure is refined, the capacity of the matrix to buffer CO₂-induced pH reduction may decrease. The trade-off is therefore not a contradiction: fly ash can simultaneously reduce chloride transport and increase carbonation sensitivity if the loss of alkaline reserve outweighs the benefit of pore refinement [12,28,37,49,50].

This mechanism explains why these advantages do not make the Portland route universally optimal. Sakai et al. [37] noted that fly ash-blended cement tends to be vulnerable to carbonation, and later experimental studies likewise reported increased carbonation depth as fly ash content increased, even when chloride resistance was improved. Similar studies on wet-stored or moistened fly ash also showed that Portland systems containing such ash can remain sensitive to carbonation and chloride-induced corrosion depending on ash condition and storage history [50]. Turk et al. [40] demonstrated that the carbonation resistance of self-compacting concrete decreased with increasing fly ash content, a trend also observed by Khunthongkeaw et al. [41] and Bai et al. [48]. This mechanism-dependent behavior is also evident under sulfate exposure, where pozzolanic consumption of calcium hydroxide and formation of additional C–S–H can reduce vulnerable portlandite and densify the pore structure [51]. Liu et al. [52] reported that fly ash substantially enhanced sulfate resistance, with 40% FA replacement performing better than 20% replacement. These findings indicate that fly ash durability performance should not be described simply as beneficial or detrimental; rather, its effect depends on the deterioration mechanism considered. In other words, the same feedstock attributes that make fly ash attractive for pore refinement and ion transport control do not automatically guarantee superior resistance to all forms of deterioration, and carbonation remains a principal trade-off that must be managed in OPC fly ash systems.

This trade-off becomes more pronounced at high replacement levels because early-age strength is often penalized by the low initial reactivity of many fly ashes. For this reason, recent studies have explored targeted activation strategies rather than abandoning the Portland route altogether. Joseph et al. [53] showed that Na₂SO₄ activation of Portland cement blended with 50 wt% Class F fly ash produced significant increases in both early and later-age strength, while also improving workability and refining pore structure. More recently, Liu et al. [54] reported that combining seawater with calcined layered double hydroxides provided a mild chemical activation route for high-volume fly ash Portland systems and improved early-age strength. These studies are important not because activation is always necessary, but because they show that the Portland chemistry window itself can be tuned when otherwise suitable fly ash lacks sufficient early reactivity. The rational Portland route is therefore not “the more fly ash, the better,” but a controlled balance among ash quality, replacement level, curing, and—when necessary—targeted activation.

5. Fly Ash in CSA and MKPC Systems

Section 4 showed that the Portland chemistry window preferentially accommodates fine, low-carbon, glass-rich fly ash capable of evolving from early physical assistance to later pozzolanic contribution. In non-Portland systems, however, the suitability criteria shift substantially because the governing reaction environments are fundamentally different. In CSA systems, the lower-pH, portlandite-poor hydration environment reduces the scope for conventional Portland-style pozzolanic contribution, so fly ash is favored primarily for its packing efficiency, rheological moderation, nucleation effects, and limited auxiliary reactivity [8]. In MKPC systems, where hardening is governed by an acid–base phosphate reaction rather than silicate hydration, the chemical reactivity of fly ash becomes secondary to its physical ability to regulate rheology, packing, heat evolution, and dimensional stability [9,38]. These chemistry windows therefore favor fly ash mainly as a non-precursor functional component rather than as a classical SCM or a true aluminosilicate precursor.

5.1. Fly Ash in CSA Cement

The hydration chemistry of calcium sulfoaluminate (CSA) cement differs fundamentally from that of OPC. The main mineral phases in CSA cement are ye'elimite ($C_4A_3\bar{S}$) and belite (C_2S) [55]. During early hydration, ye'elimite reacts rapidly with calcium sulfate and water to form ettringite (AFt) and aluminum hydroxide (AH_3), producing an early framework that contributes to rapid setting and early strength development [56]. Meanwhile, belite hydration can form C-S-H at later ages, and C-S-H together with AH_3 can fill the voids within or around the ettringite framework, further improving matrix compactness and mechanical performance [57]. A schematic of this hydration process is shown in Figure 4.

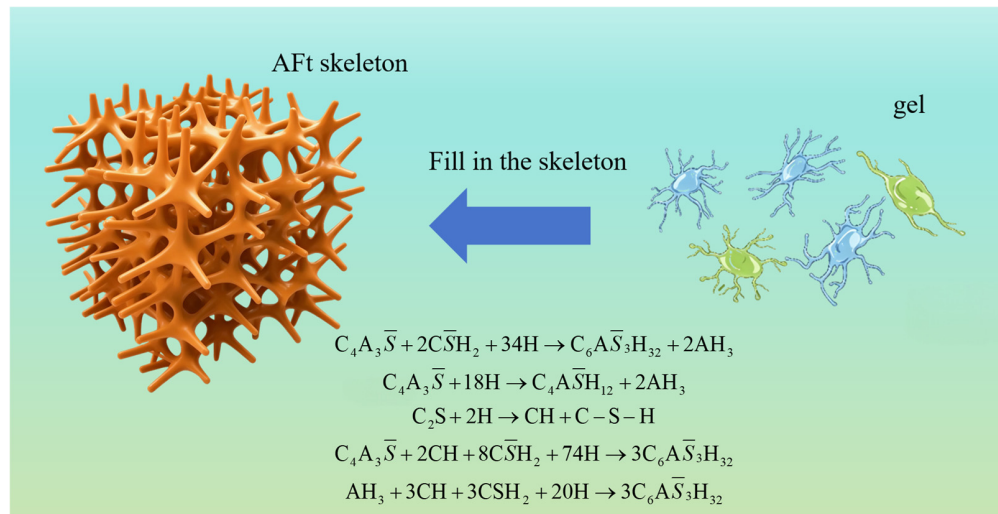


Figure 4. Schematic hydration process of calcium sulfoaluminate cement. The sequence highlights the rapid formation of ettringite from ye'elimite hydration and the later contribution of belite hydration. This CH-poor hydration environment explains why fly ash in CSA systems should be discussed mainly as a filler-dominated hydration regulator with limited Portland-style pozzolanic contribution.

Among the non-Portland hydration systems, CSA cements clearly demonstrate that the fly ash best suited to a binder is not always the ash with the highest Portland-style pozzolanic potential. In CSA systems, suitable fly ashes are generally those with good packing efficiency, relatively low residual carbon, and sufficient fineness to provide nucleation and rheological benefits without relying on strong portlandite-driven reactivity [8]. When the target is improved later-age strength rather than mere dilution, more reactive or

higher-calcium ashes can be advantageous; by contrast, when ettringite stabilization and flow retention are prioritized, lower-calcium Class F ashes may still be attractive despite their weaker later reaction [22,23]. In other words, the CSA route does not primarily reward pozzolanic aggressiveness; it rewards compatibility with a ye'elimite-dominated, CH-poor hydration environment.

Reported studies further show that fly ash can modify the rheology and hydration behavior of CSA cement [24]. In CSA pastes containing fly ash and silica fume, the plastic viscosity of low-water-to-binder-ratio mixtures can be reduced, whereas that of high-water-to-binder-ratio mixtures may increase; meanwhile, the pastes generally exhibit shear-thinning behavior. These results indicate that the effect of fly ash on CSA rheology is mixture-dependent rather than universally fluidizing. Other studies have shown that fly ash in CSA cement acts primarily through filler and nucleation effects rather than through strong pozzolanic reactivity [25]. When the fly ash replacement level exceeds approximately 30%, compressive strength may decrease because the lower alkalinity and limited portlandite availability of CSA systems restrict the classical pozzolanic activation of fly ash. Higher water content may accelerate belite hydration and promote stratlingite formation only under high water-to-cement ratios and long curing conditions. Therefore, partial replacement of CSA cement with fly ash is technically feasible, but its benefit depends on dosage, water-to-binder ratio, sulfate balance, and curing condition.

This preference is consistent with the chemistry of CSA hydration. Martin et al. [8] showed that increasing fly ash content accelerated CSA hydration through a filler effect, while dissolution rims around fly ash particles after 90 days indicated a reaction degree of only about 20%–30%. The same study also showed that 7.5 mass-% fly ash produced higher compressive strength than the fly-ash-free reference at constant water-to-cement ratio, and that up to 15 mass-% fly ash could be incorporated without strength loss. Martin et al. further noted that CSA pore solutions are generally lower in pH than Portland systems at early ages and usually do not form portlandite, which explains why fly ash in CSA cannot be expected to behave like a conventional Portland pozzolan.

More recent evidence confirms that fly ash selection in CSA systems should be framed around functional fit rather than generic substitution. Mondal et al. [22] reported that both Class C and Class F fly ash slightly improved CSA paste workability at fixed water-to-binder ratio, accelerated hydration mainly through filler effects rather than pozzolanic effects, reduced 1-day compressive strength, and increased 28-day strength. The same study found that Class C fly ash produced a higher heat of hydration and higher later-age strength than Class F fly ash, whereas Class F fly ash stabilized ettringite more strongly [23]. This distinction is highly relevant for route selection: Class C or other more reactive/calcium-bearing ashes are better suited when later-age strength gain is emphasized, whereas fine Class F ashes are more suitable when the design objective is hydration regulation, placement control, and ettringite preservation within the CSA matrix.

Mechanistically, fly ash in CSA systems should be described as filler-dominated but not phase-neutral. Its contribution to ettringite stability is mainly indirect. Fine fly ash particles can provide nucleation surfaces for ettringite precipitation, while fly ash replacement dilutes ye'elimite and sulfate-bearing phases and thereby modifies the sulfate-to-aluminate balance. Low-calcium Class F fly ash tends to disturb the Ca–Al–S balance less and may help preserve ettringite, whereas higher-calcium Class C fly ash may increase heat release and later-age strength but can also alter the hydrate assemblage more strongly [22,23]. Possible AFm or monosulfate formation should therefore be interpreted mainly as a consequence of sulfate availability, aluminate balance, calcium availability, and pore-solution chemistry, rather than as a direct fly-ash-driven reaction. In terms of porosity evolution, moderate fly ash replacement can refine the matrix through particle packing,

nucleation, and improved particle-size distribution, whereas excessive replacement may dilute CSA hydration, reduce the amount of binding hydrates, disturb the AFt/AFm balance, and increase porosity [8,22,23].

The CaO content of fly ash further modulates this phase balance. Low-Ca fly ash mainly acts as a physical filler and nucleation substrate, with limited chemical contribution to CSA hydration; therefore, it tends to preserve the ettringite-dominated hydrate assemblage by causing less disturbance to the Ca–Al–S balance. By contrast, high-Ca fly ash can increase calcium availability and may enhance early heat release and later-age strength when the sulfate balance is appropriate. Under sulfate-sufficient conditions, the additional calcium-bearing and nucleation effects may favor ettringite formation. However, when sulfate availability is insufficient relative to reactive aluminate and calcium, high-Ca fly ash may promote the formation of AFm-type hydrates such as monosulfate or otherwise modify the aluminate hydrate assemblage. Therefore, the effect of fly ash CaO content in CSA systems should be interpreted through the coupled balance among calcium supply, sulfate availability, aluminate release, and clinker dilution, rather than by treating high CaO content as universally beneficial [8,22,23].

In addition to CaO content, alumina availability is important for CSA and other sulfate-bearing binder systems. High-alumina fly ash may supply additional reactive Al species when its glassy phase is sufficiently accessible. In the presence of adequate calcium and sulfate, this additional Al source may contribute to ettringite formation or stabilization. However, if sulfate availability is insufficient relative to reactive aluminate, the system may shift toward AFm-type hydrates such as monosulfate or other aluminate-bearing phases. Therefore, the influence of high-alumina fly ash should be evaluated through the coupled Ca–Al–S balance rather than by Al_2O_3 content alone [8,22,23,55–57]. XRD/TGA evidence of AFt, AFm, portlandite consumption, and pore-structure evolution should be used to verify whether the ash promotes ettringite formation, phase conversion, or dilution-dominated behavior [8,22,23].

Beyond coal fly ash–CSA blends, CSA chemistry has also been investigated for the immobilization of cesium, heavy metals, and municipal solid waste incineration fly ash, which provides extended evidence for the compatibility of CSA binders with calcium- and alumina-bearing residues [58,59]. For example, CSA cement has been reported to effectively immobilize cesium and heavy metals, and the encapsulation of cesium was largely unaffected by phase transition in sulfoaluminate cement [58]. Chu et al. [59] used CSA cement to solidify untreated municipal solid waste incineration fly ash and prepare ecological mortars. Increasing the replacement level reduced workability, mechanical strength, and hydration heat, while increasing drying shrinkage, chloride migration, and porosity. Nevertheless, heavy-metal leaching concentrations met relevant standards, and at a 15% substitution level, the ecological mortar reduced energy consumption, carbon emissions, and production cost by 14.90%, 14.63%, and 4.03%, respectively. Although these examples are not equivalent to conventional coal fly ash use, they reinforce the broader point that CSA performance is highly sensitive to residue chemistry, replacement level, and pore-structure evolution.

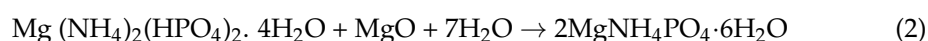
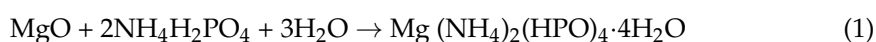
The rational use of fly ash in CSA systems is therefore centered on fine, low-carbon, packing-efficient ashes, with ash calcium content serving as a tuning parameter for heat release, ettringite preservation, AFm/monosulfate tendency, and pore-structure evolution rather than as a simple indicator of higher quality [8,22,23]. High CaO content may increase reactivity and strength development, but it can also shift the AFt/AFm balance if sulfate availability is not matched. Fly ash in this chemistry window should be interpreted mainly as a filler-dominated hydration regulator with limited later reaction, but not as a phase-neutral diluent. Its practical contribution lies in controlling nucleation, ettringite

preservation, AFt/AFm balance, and porosity evolution within a dosage- and chemistry-dependent window. Compared with OPC, systematic studies on coal fly ash in CSA systems remain relatively limited and require further investigation.

5.2. Fly Ash in MKPC Systems

The selection logic changes again in magnesium potassium phosphate cement (MKPC) systems. MKPC belongs to the broader family of magnesium phosphate cements (MPCs), which are widely used in rapid repair and cold-weather repair applications because of their rapid hardening, high early strength, low water requirement, near-neutral pH, and low drying shrinkage [38,60]. A typical phosphate-bonded system contains dead-burned magnesia (DBM, mainly MgO), phosphate salt, water, and retarders such as sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) or borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) [61]. Dead-burned magnesia is generally produced by high-temperature calcination of magnesite, and its reactivity is strongly affected by calcination temperature, particle size, and MgO crystallinity. In ammonium-based magnesium phosphate cement, MgO reacts with ammonium phosphate to form struvite-type products, whereas in MKPC, potassium dihydrogen phosphate is used and K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) becomes the principal binding phase [60,62,63].

The representative reaction sequence in ammonium-based magnesium phosphate cement can be expressed as follows [62,63]:



To improve the chemical stability of the struvite-type binding phase, potassium dihydrogen phosphate can be used instead of ammonium dihydrogen phosphate, forming K-struvite as the main binding phase in MKPC [60]:



The stability of struvite-type phases is sensitive to pH and mixture proportion. At low pH, struvite may transform to newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), which can reduce strength [64]. Therefore, Mg/P ratio, water-to-binder ratio, retarder dosage, and mineral additions must be controlled to stabilize the phosphate-bonded skeleton. This point is especially relevant when high-Ca fly ash is used, because additional calcium may compete with Mg-bearing species for phosphate, modify the Ca–Mg–K–P balance, and favor the formation of calcium-containing phosphate phases if the formulation is not properly balanced.

Within this phosphate-bonded environment, fly ash is not necessarily selected for the highest glass reactivity or the strongest classical pozzolanic potential. Instead, it is commonly incorporated to reduce material cost, moderate hydration heat, improve workability, reduce water demand, and optimize the packing structure. In some MPC/MKPC formulations, fly ash has been incorporated at relatively high replacement levels, even up to about 50 wt%, to mitigate heat-induced cracking and improve formulation economy [65–68]. The spherical morphology of fly ash particles can enhance paste flowability through a ball-bearing effect, while suitable particle-size distribution can improve packing density and matrix compactness.

The role of fly ash in phosphate-bonded systems remains formulation-sensitive. Many studies describe fly ash mainly as an inert filler or diluent that improves particle packing, workability, and compatibility between phosphate cement and mineral additions [64,66,69]. Other studies suggest that fly ash may also make a limited chemical or interfacial contribution to strength development, possibly through surface reactions or amorphous Si/Al/Ca-bearing phosphate-related products formed during hydration [70]. However, the evidence

for direct incorporation of fly ash-derived species into the main phosphate network remains suggestive rather than conclusive, because these secondary products are not always clearly resolved by XRD or thermal analysis. Therefore, in this review, fly ash is not treated as a primary phosphate-network former, but as a formulation-sensitive regulator with possible limited chemical participation.

Similar packing-based mechanisms have also been reported for combined fly ash and silica fume systems. Fly ash and silica fume can exhibit ball-bearing and micro-aggregate effects: the former improves flowability and particle dispersion, whereas the latter fills pores and microcracks, increasing matrix density [71,72]. In fiber-reinforced or repair-oriented phosphate cement systems, such densification may also improve interfacial friction between the matrix and fibers. Although silica fume is not the focus of this review, these observations support the broader interpretation that fine mineral additions improve MPC/MKPC performance mainly through particle packing, rheological control, and microstructural densification.

Experimental studies further confirm that FA/MKPC systems are governed by formulation balance rather than maximum fly ash replacement. Xu et al. [29] showed that considering fly ash as more than a purely inert diluent helped explain the improved fresh performance, optimized microstructure, and higher mechanical strength of FA/MKPC mortars. SEM observations indicated possible local reaction at fly ash particle surfaces, although secondary phases derived from fly ash were not clearly resolved by XRD or TGA. The same work highlighted the importance of the magnesia-to-fly-ash ratio and the KDP-to-(magnesia + fly ash) ratio in optimum FA/MKPC design. This evidence supports limited interfacial participation rather than definitive proof that fly ash becomes a major component of the K-struvite phosphate network. In a follow-up study, Xu et al. [30] used a relatively high-CaO fly ash and showed that 50 wt% replacement of magnesia gave the highest compressive strength, whereas 70 wt% should be treated as an upper limit because higher replacement caused substantial strength loss. This result indicates that high-Ca fly ash can be beneficial within an optimized formulation window, probably because it improves packing, modifies reaction kinetics, and contributes to a denser matrix. However, at very high fly ash contents, the system no longer remains governed only by the $\text{MgO-KH}_2\text{PO}_4$ reaction. Additional calcium potassium hydrogen phosphate formed, and K-struvite destabilized under water exposure, contributing to poor strength retention. Therefore, high-Ca fly ash influences K-struvite durability in a dual way: moderate replacement may improve matrix compactness and mechanical performance, whereas excessive replacement may consume phosphate, promote competing Ca-containing phosphate phases, dilute the MgO-based skeleton, and reduce the water stability of the K-struvite-bearing matrix.

Workability studies further clarify which physical traits are desirable. Li et al. [31] found that replacing MgO with 10%–20% fly ash enabled MKPC paste to satisfy self-compacting requirements for narrow-crack repair applications. Although fly ash increased early plastic viscosity, it also reduced early static yield stress and improved thixotropy because of the dispersing and tumbling effects of the spherical particles; these mixes also developed a denser 1-day microstructure and higher 1-day strength. Closely related results were reported for magnesium ammonium phosphate cement, where spherical fly ash reduced plastic viscosity, improved fluidity, prolonged setting time, improved late-age strength and water resistance, and reduced drying shrinkage [32].

Collectively, the chemical descriptors that dominate Portland suitability, such as strong pozzolanicity or maximum reactive glass fraction, are not the leading selection criteria in MKPC systems [9,29,30]. More decisive factors include particle morphology, rheological behavior, water demand, heat moderation, packing density, FA/MgO ratio, phosphate/binder balance, and compatibility with K-struvite stability. For high-Ca fly ash, this compatibil-

ity should be judged by whether Ca-bearing secondary phosphates are suppressed and whether K-struvite remains stable under water exposure. For this reason, MKPC represents a further step away from the Portland interpretation of fly ash: the ash is no longer evaluated mainly as a cement replacement, but as a formulation-sensitive functional regulator whose value lies in optimized design rather than maximum substitution.

6. Fly Ash in Geopolymer Systems

The geopolymer route differs fundamentally from both Portland and non-Portland blending routes because fly ash is no longer introduced primarily as a supplementary component within another binder skeleton. Instead, it becomes the aluminosilicate feedstock from which the binding gel network is produced. For this reason, the fly ashes best suited to geopolymer systems are generally those with high amorphous aluminosilicate content, sufficient fineness, strong dissolution potential under alkaline activation, and good compatibility with the selected activator and curing regime [10,11]. When predictable geopolymerization, later-age stability, and durability are the priority, low-calcium fly ash remains the most established and robust option. High-calcium fly ash can also be used, especially when rapid setting or early strength is desirable, but it usually introduces greater sensitivity in workability and mix control.

This selection logic follows directly from geopolymer chemistry. In alkali-activated systems, performance is controlled not by portlandite availability or filler-induced hydration acceleration, but by the dissolution of reactive aluminosilicate phases, their reorganization in alkaline solution, and the subsequent formation of a gel-rich network [10,11,33,34]. Consequently, fly ash suitability is governed by precursor–activator compatibility rather than by replacement ratio alone. Gunasekara et al. [35] showed that curing conditions strongly affect the geopolymeric reaction, strength evolution, and pore structure of brown-coal-fly-ash-based geopolymer materials, while Yılmaz et al. [36] specifically investigated low-calcium-fly-ash geopolymer mortars and showed that curing temperature and duration decisively affect their mechanical and durability performance. These results explain why fine, reactive, activator-compatible ashes are preferred in geopolymer systems: even a chemically promising ash may perform poorly if its dissolution behavior does not match the activator chemistry or curing schedule. The basic geopolymerization process is summarized in Figure 5, including fly ash dissolution, silica/alumina species release, oligomer nucleation, polymerization, and representative polysialate structural units.

In practical terms, the compatibility among fly ash, alkaline activator, and curing regime should be assessed through a stepwise screening procedure rather than inferred from ash class alone. The first step is feedstock characterization, including particle-size distribution, fineness, LOI, CaO content, total amorphous content, reactive glass accessibility, and crystalline mineralogy [10,11]. The second step is activator screening, in which NaOH/KOH concentration, alkali dosage, silicate modulus, sodium silicate-to-hydroxide ratio, and liquid-to-binder ratio are varied to determine whether the ash dissolves sufficiently without causing flash setting, excessive viscosity, or severe efflorescence [10,33,34]. The third step is curing-regime screening, including ambient curing, sealed curing, and elevated-temperature curing with controlled temperature and duration [33–36]. The purpose is to determine whether the selected activator can produce sufficient dissolution, gel formation, and pore refinement under a curing condition that is realistic for the target application.

Compatibility should then be judged using both reaction indicators and engineering indicators. Reaction indicators include heat evolution, setting time, dissolution response, FTIR band shift, XRD amorphous hump change, N–A–S–H/C–A–S–H gel formation, bound water, and microstructural densification observed by SEM or porosity measure-

ments [10,11,33–35]. Engineering indicators include flowability, early and later-age compressive strength, shrinkage, efflorescence, water absorption, and durability under the intended exposure [10,11,36,73]. A compatible fly ash–activator–curing combination should show sufficient gel formation and strength development without unacceptable rapid setting, under-reaction, excessive shrinkage, or efflorescence. Conversely, low strength with large unreacted fly ash fractions indicates insufficient activator strength or inadequate curing, whereas rapid setting, high viscosity, or efflorescence indicates that the activator dosage or silicate modulus may be excessive.

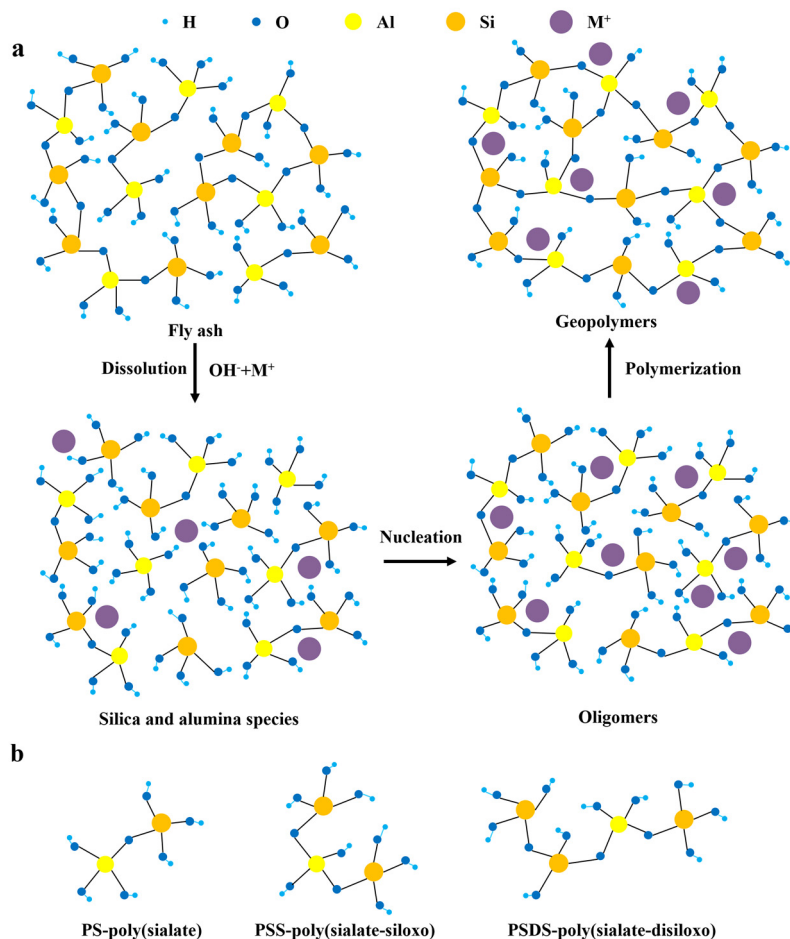


Figure 5. Geopolymerization schemes. Panel (a) summarizes the dissolution–reorganization–polymerization sequence, and panel (b) illustrates the classical polysialate families. Together they show why FA in this route must be discussed as precursor rather than replacement filler.

The assessment should also distinguish low-calcium and high-calcium fly ashes. Low-calcium fly ash commonly requires stronger alkaline activation or elevated-temperature curing to achieve sufficient dissolution and N–A–S–H gel formation [11,33,34,36]. High-calcium fly ash may develop strength more rapidly and may partially form C–A–S–H-type products, but it is more sensitive to rapid setting, workability loss, and activator imbalance [10,74]. Therefore, compatibility is not defined by high amorphous content alone, but by whether the activator and curing regime convert the accessible glass into a stable gel network while maintaining workable fresh behavior and acceptable dimensional stability.

This distinction also requires separating low-calcium fly ash geopolymers from calcium-rich hybrid alkali-activated systems. In low-calcium fly ash systems, the binding phase is generally dominated by N–A–S–H gel formed through alkaline dissolution and polycondensation of aluminosilicate glass. In calcium-rich systems, such as Class C fly ash, high-Ca fly ash, or fly ash blended with slag or other Ca-rich precursors, the reaction

products may shift toward mixed gel assemblages in which N–A–S–H, C–A–S–H, and C–(N)–A–S–H coexist. This mixed gel formation can improve early strength and ambient-temperature reactivity, but it also increases sensitivity to activator dosage, silicate modulus, setting control, shrinkage, efflorescence, and durability. Therefore, calcium-rich hybrid binders should be interpreted as hybrid alkali-activated systems rather than as simple extensions of classical low-calcium fly ash geopolymers [10,11,73,74].

Calcium content is therefore a key descriptor not only for reactivity and workability, but also for gel assemblage and practical route assignment. Alkali-activated Class C fly ash systems can deliver high strength, but their workability is often poor and must be controlled through mix-design adjustments such as silica modulus, retarders, or mixing strategy [10]. By contrast, low-calcium fly ash systems are more commonly associated with predictable geopolymerization pathways and durable binder formation, although they often rely more strongly on thermal or otherwise optimized curing [11,36]. This contrast means that low-calcium, amorphous, sufficiently fine fly ash is generally the safer choice when the goal is robust geopolymer formation, whereas high-calcium fly ash is better understood as a higher-reactivity but more sensitive precursor that can accelerate setting and complicate fresh-state control.

At the same time, the geopolymer route is flexible enough to exploit hybrid precursor design. Nuaklong et al. [74] showed that partially replacing high-calcium fly ash with low-calcium fly ash improved the durability profile of high-calcium-fly-ash geopolymer mortar, and that a 50:50 blend of high- and low-calcium fly ash provided high early strength together with excellent potential in an acidic environment. This result is particularly instructive for the logic of this review, because it shows that geopolymer route selection should be based on matching ash chemistry with the performance target, activator strategy, and curing condition, rather than on a binary low-Ca/high-Ca classification. Thus, selective deployment becomes even more important in geopolymer systems.

This comparison highlights a distinct practical implication for geopolymer systems. In Portland systems, the key question was whether the ash could evolve from physical assistance to pozzolanic contribution. In CSA and MKPC systems, the key question was whether the ash could function effectively as a hydration or microstructural regulator. In geopolymer systems, the key question becomes whether the ash itself is a suitable precursor. Accordingly, some ashes that are only moderately attractive in Portland blends can become highly valuable in geopolymer binders if their amorphous aluminosilicate content, fineness, and activator compatibility are favorable [10,11,36]. Conversely, geopolymerization is not a universal answer for all ashes, because activator demand, curing sensitivity, rapid setting in high-calcium systems, and durability under specific exposures remain decisive constraints [73,74].

7. Boundary Evidence for Chemistry-Dependent Fly Ash Functionality

Although this review focuses on cementitious binders, selected non-binder valorization routes are briefly included as boundary evidence for the central property–chemistry interaction concept. These examples are not intended to provide a separate review of zeolite, hydrogel, or other non-binder applications, nor are they proposed as equivalent alternatives to cementitious reuse. Instead, they serve a specific interpretive function: they show that fly ash reactivity and functionality are not fixed material constants, but depend on how ash chemistry, processing environment, and target function are matched. This boundary perspective strengthens the binder-focused framework because it clarifies why the same ash may behave as a pozzolanic contributor in OPC, a filler or regulator in CSA/MKPC, a precursor in geopolymers, or a feedstock for non-binder products under different chemical environments. Related environmental assessments of mineral eco-binders derived from

secondary raw materials further support the need to evaluate valorization routes by both material function and environmental performance [6].

Among these non-binder routes, zeolite synthesis offers the clearest example. Under alkaline activation or hydrothermal treatment, fly ash can serve as a silicon–aluminum source for the formation of zeolitic phases, and the resulting products depend strongly on ash composition, alkalinity, temperature, and crystallization conditions [75,76]. This route is conceptually important because it shows that fly ash is not limited to Portland-type pozzolanicity or cement replacement. When the chemical environment is sufficiently altered, the same aluminosilicate feedstock can function as a precursor for an entirely different class of crystalline aluminosilicate products. This example is relevant to the binder-focused discussion because it parallels the geopolymer route: in both cases, the useful role of fly ash depends on whether the aluminosilicate phase can dissolve and reorganize under the imposed alkaline environment, although the final products differ.

A similar boundary argument is supported by water-absorbing and hybrid polymer-related applications [34]. For example, a poor water-sorbing fly ash has been transformed into a high water-absorbing material with a reported water absorption capacity of about 310 g/g. This example indicates that fly ash can also be redirected into functional absorbent systems when its chemistry and processing conditions are appropriately modified. Such studies are not used here to expand the scope of the review beyond cementitious binders, but to reinforce the broader principle that the engineering value of fly ash depends on the interaction between feedstock properties, chemical environment, and target function.

Therefore, the non-binder examples are retained only as boundary cases that support the property-guided framework. They demonstrate that fly ash should be evaluated according to the function it can perform in a specific chemical environment. This conclusion directly reinforces, rather than replaces, the binder-focused route-selection logic developed for OPC, CSA, MKPC, and geopolymer systems.

8. Property-Guided Deployment Framework

To make the cross-system logic of the review more intuitive, the property-guided framework is visually summarized in Figure 1. The figure links key fly ash descriptors, including reactive glass fraction, calcium content, loss on ignition, residual carbon, beneficiation state, fineness, and particle accessibility, with the chemistry windows of OPC, CSA, MKPC, and alkali-activated/geopolymer systems. It further summarizes the binder environment, fly ash optimization criteria, and dominant functional role in each route. In this way, the central concept of the review is conveyed not only through text and tables, but also through a schematic visual framework.

8.1. Practical Workflow for Property-Guided Fly Ash Selection

The preceding sections show that the same fly ash may play different roles in different binder environments. However, for practical use, this conclusion must be translated into a decision-making process. Therefore, the property-guided framework is reformulated here as a practical workflow for fly ash selection and route assignment.

First, the fly ash should be characterized in terms of particle-size distribution, fineness, LOI or residual carbon content, bulk oxide composition, CaO content, total amorphous content, reactive glass fraction, mineralogy, morphology, and storage or beneficiation history. These descriptors define the initial suitability and risk profile of the ash.

Second, the target binder system and performance objective should be identified. The selection logic differs depending on whether the ash is intended for CH-rich OPC systems, CH-poor CSA systems, phosphate-bonded MKPC systems, or alkali-activated/geopolymer systems. The target performance should also be specified, such as early strength, later-

age strength, chloride resistance, carbonation resistance, rapid repair, low heat release, dimensional stability, or precursor reactivity.

Third, fly ash properties should be matched with the functional role required by the target binder. In OPC systems, fine, low-carbon fly ash with chemically accessible glass is favored when later pozzolanic contribution and transport resistance are desired. In CSA systems, fly ash is better selected for packing efficiency, nucleation, rheology regulation, and compatibility with ettringite-dominated hydration. In MKPC systems, spherical morphology, suitable fineness, water-demand control, and compatibility with the MgO–phosphate formulation are more important than high pozzolanic reactivity. In geopolymers systems, the decisive criteria are reactive aluminosilicate content, dissolution potential, activator compatibility, curing response, and target gel assemblage. Low-Ca systems are generally N–A–S–H-dominated, whereas Ca-rich hybrid systems may contain coexisting N–A–S–H, C–A–S–H, and C–(N)–A–S–H gels. These criteria should be validated through setting time, heat evolution, flowability, compressive strength, gel formation, porosity, shrinkage, and efflorescence tests.

Fourth, route-specific mismatch risks should be screened. For OPC systems, key risks include early strength loss, carbonation susceptibility, high LOI, and admixture incompatibility. For CSA systems, risks include excessive dilution, altered AFt/AFm balance, and porosity increase. For MKPC systems, risks include excessive heat release, poor rheology, dilution of the phosphate-bonded skeleton, and K-struvite destabilization when high-Ca fly ash is overdosed. For geopolymer systems, risks include under-reaction, rapid setting, efflorescence, shrinkage, and curing sensitivity.

Fifth, beneficiation or compositional adjustment should be applied when the as-received ash does not meet the requirements of the selected route. Classification and grinding can increase particle accessibility and pozzolanic reactivity, but the gain depends on ash type, processing intensity, and the reactivity metric used; carbon reduction can improve admixture compatibility; washing or screening can reduce salts or coarse impurities; and blending with low-Ca or high-Ca ashes, slag, limestone, silica fume, or activator modifiers can tune the chemistry of the system.

Finally, the selected route should be validated by mixture-level testing. Depending on the target binder and application, validation may include workability, setting time, heat evolution, early and later-age strength, porosity, water absorption, chloride migration, carbonation depth, sulfate resistance, water resistance, shrinkage, and phase assemblage. The complete procedure is summarized in Figure 6. Together, these steps transform the property-guided framework from a descriptive concept into a practical route-selection tool.

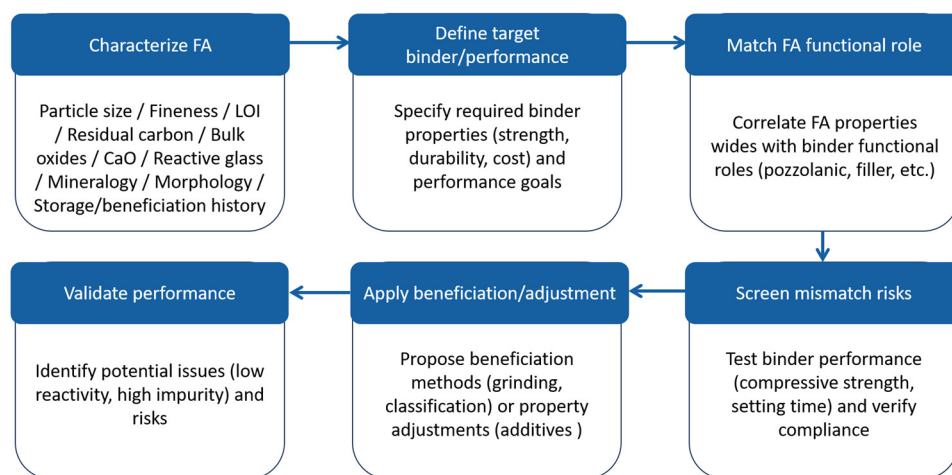


Figure 6. Practical workflow for property-guided fly ash selection.

8.2. Fly Ash-Binder Matching

When the evidence across binder families is placed on a single interpretive line, a property-guided deployment framework becomes more explicit. In Portland systems, the most suitable fly ashes are typically those with adequate fineness, low residual carbon, predominantly spherical morphology, and sufficient reactive glass to move from early physical assistance toward later pozzolanic contribution [7]. In CSA systems, by contrast, the most relevant criteria are packing efficiency, low admixture interference, and compatibility with a CH-poor hydration environment in which filler-dominated and hydration-regulating effects are more important than strong later pozzolanic reaction [8]. In MKPC systems, the leading criteria shift further toward rheological compatibility, heat moderation, and microstructural optimization within a phosphate-bonded reaction network [9]. In geopolymer systems, the central requirement is no longer supplementary contribution, but precursor suitability, which generally favors fly ashes with high amorphous aluminosilicate content, sufficient fineness, and strong compatibility with the selected activator and curing regime [10].

This descriptor-based framework is particularly important for intermediate-composition, co-combustion, and reclaimed or ponded ashes, which cannot be reliably assigned to a suitable route by Class F/Class C labels alone [5,13,17]. For these non-standard sources, route selection should begin with source-specific characterization rather than direct assignment to Class F or Class C [5,13]. If the ash contains excessive coarse particles, residual carbon, soluble salts, weathering-induced agglomerates, or storage-derived carbonate/hydrate phases, beneficiation steps such as drying, screening, classification, milling, washing, blending, or carbon reduction may be required before its compatibility with OPC, CSA, MKPC, or geopolymer systems can be judged [14,15,26].

This cross-system comparison clarifies that the phrase “suitable fly ash” has no universal meaning independent of binder chemistry. A fly ash that is highly attractive in one binder environment may be only marginally suitable in another. For this reason, rational route selection should be based on the functional role that a specific ash can realistically perform within a given binder environment, rather than on generic assumptions that all fly ashes can be evaluated by the same criteria. This matching logic is summarized in Table 3, which links fly ash chemistry, physical features, binder environment, functional role, and design priority. The table is intended to convert the binder-specific discussions in Sections 4–6 into a cross-system route-selection guide. It shows that the same fly ash property may carry different practical meanings in different binder systems: for example, fineness supports pozzolanic contribution in OPC, packing and nucleation in CSA, rheological regulation in MKPC, and alkaline dissolution in geopolymer systems.

This table synthesizes the evidence discussed in Sections 4–6. The OPC criteria are grounded in the established importance of fineness, reactive glass, and beneficiation-driven reactivity enhancement; the CSA criteria reflect the filler effect and limited later reaction reported for fly ash in CH-poor sulfoaluminate systems; the MKPC criteria follow studies showing that fly ash functions primarily as a formulation and microstructural regulator; and the geopolymer criteria are based on the precursor-centered role of fly ash and its strong sensitivity to activator chemistry and curing conditions [8–10,14].

To complement the qualitative fly ash–binder matching framework, Table 4 summarizes representative quantitative evidence from the studies discussed in this review. The purpose of this table is not to establish universal performance thresholds, because OPC, CSA, MKPC, and geopolymer systems differ substantially in reaction mechanism, curing regime, mixture proportion, and testing method. Instead, the table provides numerical anchors showing how specific fly ash properties and processing conditions, including fineness, particle accessibility, CaO content, beneficiation response, dosage, and activator

or phosphate balance, influence reaction behavior, strength development, and durability or stability performance.

Table 3. Property-guided matching matrix of fly ash properties, binder environments, functional roles, and design priorities, obtained from the cross-system evidence discussed in Sections 4–6 [8–10,14].

Binder System	Fly Ash Chemistry Generally Favored	Fly Ash Physical Features Generally Favored	Dominant Role of Fly Ash	Typical Design Priority
Blended Portland cement	Moderate-to-high chemically accessible glass fraction; low residual carbon; low-Ca/Class F generally preferred for later-age durability, whereas higher-Ca ashes may be useful for early reactivity; selection should be adjusted according to cement chemistry, w/b ratio, co-SCMs, replacement level, and curing regime.	Adequate fineness, high particle accessibility, predominantly spherical morphology	Packing aid followed by later pozzolanic reactant	Balance workability, later-age strength, pore refinement, durability, and ash–cement–mix–curing compatibility.
CSA-based systems	Compatibility with CH-poor hydration; limited but useful auxiliary reactivity; Class C or higher-Ca ashes may enhance heat release and later strength when sulfate balance is maintained, while Class F/low-Ca ashes may better preserve ettringite and reduce disturbance of the AFt/AFm balance	Fine, low-carbon, packing-efficient particles	Filler-dominated hydration regulator with limited later reaction	Rheology/setting control and acceptable later-age performance
MKPC-based systems	Chemical reactivity is secondary to compatibility with MgO–phosphate formulation; ashes should not destabilize the phosphate reaction skeleton	Good particle shape, suitable fineness, low water demand, strong packing benefit	Functional regulator/microstructural modifier	Workability control, heat moderation, dimensional stability, and matrix densification
Geopolymer/alkali-activated systems	High amorphous aluminosilicate content, good dissolution potential, low LOI; compatibility should be verified by activator-response and curing-response tests; low-Ca/Class F ashes are often robust but may require heat curing, whereas high-Ca ashes can react faster but are more sensitive to rapid setting and activator imbalance	Sufficient fineness and dissolution accessibility; compatibility with activator dosage, silicate modulus, liquid-to-binder ratio, and curing temperature/duration	Efficient gel-network formation, control of N–A–S–H versus hybrid C–A–S–H/C–(N)–A–S–H assemblages, acceptable setting/workability, low shrinkage/efflorescence, and precursor-activator-curing compatibility	Efficient gel-network formation, acceptable setting/workability, strength development, low efflorescence/shrinkage, and precursor-activator-curing compatibility

Table 4. Representative quantitative evidence supporting property-guided fly ash selection across binder systems.

Binder Route	Quantitative Evidence and Comparison	Main Performance Aspect	Property-Guided Implication
OPC–FA systems	Classified fly ash with a median particle size of 6.4 μm produced higher compressive strength and lower porosity than the corresponding original ash with a median particle size of 19.1 μm [27].	Strength development and pore refinement	Fineness and particle accessibility are critical for converting fly ash from a physical filler into a later pozzolanic contributor.
OPC–FA systems	Ground coarse fly ash with particle size below 9 μm achieved a strength activity index exceeding 100% of the control at 28 d [26].	Strength activity	Coarse ash can be upgraded by grinding when the reactive fraction is present but poorly accessible.
OPC–FA systems	Classification and milling increased the intrinsic pozzolanic reactivity of siliceous fly ash by approximately 57% and 40%, respectively, based on reactivity testing [14].	Pozzolanic reactivity	Beneficiation can increase measured reactivity, but the gain depends on ash type, processing method, and the reactivity test used.
OPC–FA systems	Class F fly ash concrete showed lower porosity, water sorptivity, and chloride permeability than plain concrete, with the improvement becoming more pronounced between 28 and 180 d [12].	Transport-related durability	Fly ash benefits in OPC are often delayed and linked to later pore refinement; chloride resistance and carbonation resistance should still be evaluated separately.
OPC–FA systems	Finer fly ash reduced water demand and improved chloride resistance; the improvement was greater as fly ash fineness increased [27,28].	Workability and chloride resistance	Fine, low-carbon fly ash with chemically accessible glass is generally favorable for OPC systems targeting long-term transport resistance.
CSA–FA systems	Martin et al. reported that fly ash accelerated CSA hydration mainly through a filler effect, while dissolution rims after 90 d indicated a fly ash reaction degree of approximately 20%–30% [8].	Reaction degree and hydration mechanism	Fly ash in CSA is not completely inert, but its chemical contribution is limited compared with its filler/nucleation effect.
CSA–FA systems	In the same CSA study, 7.5 mass% fly ash produced higher compressive strength than the fly-ash-free reference at constant water-to-cement ratio, and up to 15 mass% fly ash could be incorporated without strength loss [8].	Strength development and replacement limit	Moderate fly ash replacement can be beneficial in CSA, but the useful range is narrower and more formulation-sensitive than in OPC.

Table 4. Cont.

Binder Route	Quantitative Evidence and Comparison	Main Performance Aspect	Property-Guided Implication
CSA–FA systems	Other CSA studies reported that fly ash replacement levels above approximately 30% may reduce compressive strength because the low-CH, lower-pH environment limits classical pozzolanic activation [25].	Strength loss at excessive replacement	Excessive fly ash can dilute CSA hydration; dosage, sulfate balance, water content, and curing conditions must be controlled.
CSA–Class C/Class F FA systems	Mondal et al. reported that both Class C and Class F fly ash reduced 1 d compressive strength but increased 28 d strength; Class C fly ash produced higher heat release and later-age strength, whereas Class F fly ash stabilized ettringite more strongly [22,23].	Early/late strength and ettringite stability	CaO content should be treated as a tuning parameter for heat release, later strength, ettringite preservation, and AFt/AFm balance.
MKPC–FA systems	Xu et al. showed that optimized FA/MKPC design depends strongly on the magnesia-to-fly-ash ratio and the KDP-to-(magnesia + fly ash) ratio [29].	Formulation balance and strength	MKPC suitability is governed by FA/MgO and phosphate/binder balance rather than maximum fly ash replacement.
MKPC–high-Ca FA systems	A relatively high-CaO fly ash gave the best compressive strength at about 50 wt% MgO replacement, whereas 70 wt% replacement approached an upper practical limit because higher replacement caused substantial strength loss [30].	Strength optimization and replacement limit	High-Ca fly ash can improve MKPC performance within an optimized formulation window, but excessive replacement dilutes the phosphate skeleton.
MKPC–high-Ca FA systems	At very high fly ash contents, calcium potassium hydrogen phosphate formed and K-struvite destabilized under water exposure, contributing to poor strength retention [30].	Water durability and K-struvite stability	High-Ca fly ash must be screened for competing Ca-phosphate formation and K-struvite stability, not only for strength.
MKPC repair-oriented systems	Replacing MgO with 10%–20% fly ash enabled MKPC paste to satisfy self-compacting requirements for narrow-crack repair applications [31].	Flowability and repair workability	Spherical morphology and suitable dosage can improve rheology and repair applicability.
Magnesium phosphate cement systems	Spherical fly ash reduced plastic viscosity, improved fluidity, prolonged setting time, improved late-age strength and water resistance, and reduced drying shrinkage [32].	Rheology, strength, water resistance, dimensional stability	In phosphate-bonded systems, particle morphology and packing effects are more important than high pozzolanic reactivity.

Table 4. Cont.

Binder Route	Quantitative Evidence and Comparison	Main Performance Aspect	Property-Guided Implication
Low-Ca FA geopolymer systems	Curing temperature and duration strongly affected the mechanical and durability performance of low-calcium-fly-ash geopolymer mortars [36].	Strength development and durability	Low-Ca fly ash geopolymers require precursor–activator–curing compatibility rather than ash quality alone.
Brown-coal FA geopolymer systems	Curing conditions strongly affected geopolymeric reaction, strength evolution, and pore structure [35].	Reaction extent, strength, pore structure	Even chemically promising fly ash may underperform when its dissolution behavior does not match the activator chemistry or curing schedule.
High-Ca/low-Ca FA geopolymer systems	A 50:50 blend of high-calcium and low-calcium fly ash provided high early strength and strong potential in acidic environments [74].	Early strength and durability in acidic exposure	Hybrid precursor design can balance early strength and durability; route selection should not rely only on a binary low-Ca/high-Ca label.
Geopolymer/alkali-activated systems	Reviews of one-part geopolymers show that activator dosage, curing response, setting, shrinkage, and efflorescence are highly sensitive to precursor–activator compatibility [33,34,73].	Practical performance and durability risks	Geopolymer selection should be validated through setting, flowability, gel formation, shrinkage, efflorescence, and durability tests.

These examples confirm that quantitative criteria for fly ash selection must remain binder-specific. In OPC systems, fineness, particle accessibility, and later pozzolanic contribution are strongly linked to strength activity and transport-related durability. In CSA systems, the measurable contribution of fly ash is more limited and is expressed mainly through filler-driven hydration, moderate later reaction, ettringite stability, and replacement-level sensitivity. In MKPC systems, the decisive quantitative variables are not fly ash reaction degree, but FA/MgO ratio, phosphate/binder balance, and K-struvite stability. In geopolymer systems, quantitative performance depends strongly on activator composition, curing regime, calcium level, and target gel assemblage. Therefore, the numerical evidence supports the property-guided framework while also showing why a single universal threshold is not appropriate.

To further translate this framework into a practical selection tool, Table 5 summarizes an operational decision-making matrix that links measurable fly ash properties, recommended characterization methods, indicative screening criteria, suitable binder routes, and major mismatch risks. Indicative values are provided only where approximate numerical guidance is supported by the literature; for properties that cannot be reduced to fixed thresholds, the matrix instead specifies system-dependent screening criteria and validation methods. The criteria are not intended as universal acceptance limits or as a ranking system for assigning intrinsic quality labels to fly ash sources; instead, they serve as practical screening windows for identifying the most reasonable deployment pathway for a given ash and the additional validation or beneficiation required. For example, a fine, low-carbon, chemically accessible glass-rich ash is generally more suitable for OPC or geopolymer routes, whereas a lower-reactivity but spherical and packing-efficient ash may still be

useful in CSA or MKPC systems. Reclaimed or ponded ashes should first be screened for storage-induced carbonation, hydration, soluble salts, contamination, and heterogeneity before binder assignment. In this way, the matrix converts the property-guided concept into an operational route-selection procedure while preserving the central message of this review: suitability is determined by ash–binder compatibility rather than by fly ash class or replacement level alone.

Table 5. Operational decision-making matrix for property-guided fly ash route selection.

Fly Ash Property/Issue	Characterization Method	Indicative Screening Criterion/Interpretation	More Suitable Binder Route	Main risks and Required Validation	Main Supporting References
Fineness/particle accessibility	Laser particle-size analysis; Blaine fineness; 45 µm sieve residue; SEM	D50 < 10 µm is generally favorable; D50 around 6–7 µm is preferred when high reactivity is required; coarse ash may require classification or milling	OPC and geopolymer when pozzolanic or precursor reactivity is desired; CSA/MKPC when packing and nucleation are desired	Excessive grinding may increase water demand or reduce spherical morphology; validate by workability, setting, strength activity, heat evolution, and porosity	[7,14,26–28]
Total glassy fraction/amorphous content	XRD/Rietveld analysis with internal standard; quantitative phase analysis	High amorphous content indicates a potential reactive reservoir but does not directly prove actual reactivity	OPC and geopolymer as first-priority routes when the glass phase is chemically accessible	Risk of overestimating reactivity; confirm using dissolution, portlandite consumption, calorimetry, strength activity, or gel formation	[14,37]
Reactive glass accessibility	Dissolution test; CH consumption; calorimetry; strength activity index; FTIR/XRD evidence of reaction products	No universal percentage threshold is recommended; high reactive glass accessibility should be confirmed by dissolution, CH consumption, calorimetry, strength activity, or gel formation	OPC for later pozzolanic contribution; geopolymer for precursor use	Low accessibility may cause under-reaction; beneficiation or stronger activation/curing may be required	[14,33,34,37]
LOI/residual carbon	LOI test; TGA; carbon analysis	LOI ≤ 6% is a practical upper limit for many concrete applications; lower values are preferred for admixture-sensitive or air-entrained mixtures	OPC and CSA when workability and admixture compatibility are important	High carbon may increase admixture demand and impair air entrainment; carbon reduction or blending may be needed	[15,44,45]
CaO content/calcium level	XRF; XRD; TGA/DTG	Low-Ca/Class F ash favors stable later pozzolanic behavior and N–A–S–H-dominated geopolymer gels; high-Ca/Class C ash may improve early strength but increases formulation sensitivity	Low-Ca: OPC durability and low-Ca geopolymer; high-Ca: CSA strength tuning, Ca-rich hybrid alkali-activated systems, and selected MKPC systems	High Ca may alter sulfate balance in CSA, promote rapid setting in geopolymers, or destabilize K-struvite in MKPC; validate phase assemblage and durability	[22,23,30,42,43,74]
Particle morphology/sphericity	SEM; image analysis; flowability/rheology tests	Spherical particles favor ball-bearing effect, lower water demand, and packing efficiency	OPC fresh-state improvement; CSA and MKPC rheology regulation	Irregular or porous particles may increase water demand; validate by flowability, viscosity, and setting behavior	[3,15,27,28,31,32,49]

Table 5. Cont.

Fly Ash Property/Issue	Characterization Method	Indicative Screening Criterion/Interpretation	More Suitable Binder Route	Main risks and Required Validation	Main Supporting References
Mineralogy and crystalline phases	XRD; TGA/DTG; SEM-EDS where needed	High quartz/mul-lite/crystalline residue may reduce available reactive glass; carbonate or hydrate phases indicate storage-induced alteration	Route depends on reactive fraction; lower-reactivity ashes may still suit CSA/MKPC as fillers/regulators	Risk of low reactivity or altered phase balance; validate by strength, reaction degree, and phase assemblage	[3,8,14,17,37]
Soluble salts/contaminants/storage history	Ion chromatography; conductivity; leaching tests; moisture content; representative sampling	Important for co-combustion, ponded, landfilled, or reclaimed ashes; soluble salts, chlorides, sulfates, or contaminants require additional screening	Route selection only after source-specific qualification; possible use in OPC, CSA, MKPC, or geopolymer after treatment	Risks include efflorescence, corrosion, poor setting control, contamination, and batch heterogeneity; drying, washing, screening, or blending may be needed	[5,13,17]
Beneficiation response	Compare as-received and treated ash by particle size, LOI, strength activity, calorimetry, and dissolution	Classification, milling, carbon reduction, washing, or blending is useful only if it improves route-relevant performance	Marginal ashes can be upgraded for OPC/geopolymer reactivity or CSA/MKPC packing roles	Gains depend on ash type, grinding energy, classification method, and test used; avoid judging by fineness alone	[14,15,26]
OPC compatibility	Mortar/concrete workability; setting; strength activity; CH consumption; carbonation/chloride tests	Fine, low-carbon, chemically accessible glass-rich ash is preferred when later strength and transport resistance are desired	OPC blended cement/concrete	Risks include early strength loss, carbonation sensitivity, high LOI, and admixture incompatibility	[12,27,28,37,39–43]
CSA compatibility	Heat evolution; XRD/TGA for AFt/AFm; strength; porosity; rheology	Packing-efficient, low-carbon ash with controlled CaO content; Class F may favor ettringite preservation, while higher-Ca ash may improve later strength if sulfate balance is maintained	CSA-based binders	Risks include excessive dilution, AFt/AFm imbalance, porosity increase, and strength loss	[8,22–25]
MKPC compatibility	Setting; flowability; heat release; XRD for K-struvite and Ca-phosphates; water resistance	Spherical, suitably fine ash with controlled FA/MgO and phosphate/binder balance; high-Ca ash must not destabilize K-struvite	MKPC repair binders	Risks include poor rheology, excessive heat, dilution of phosphate skeleton, Ca-phosphate formation, and K-struvite destabilization	[9,29–32,49]
Geopolymer compatibility	Activator screening; setting; calorimetry; FTIR/XRD; strength; shrinkage; efflorescence	Low-Ca ash favors N–A–S–H-dominated gels but may require heat curing; high-Ca ash can form hybrid N–A–S–H/C–A–S–H/C–(N)–A–S–H gels but is more sensitive	Low-Ca geopolymer or Ca-rich hybrid alkali-activated binder	Risks include under-reaction, rapid setting, workability loss, shrinkage, efflorescence, and curing sensitivity	[10,11,33–36,73,74]

8.3. Beneficiation and Route Selection

The workflow and decision-making matrix lead to two broader implications. First, dosage-centered comparison is insufficient on its own. Testing one fly ash at several replacement ratios within a single binder family can reveal local trends, but it cannot determine whether that ash has been assigned to its most suitable binder route in the first place [4,5,13]. A more informative approach is to ask which role a given ash is capable of performing most effectively and then to select the binder route accordingly.

Second, beneficiation should be treated as part of deployment design rather than as an afterthought. Classification and milling have been shown to increase the intrinsic pozzolanic reactivity of siliceous fly ash by about 57% and 40%, respectively [14]. However, these values should be interpreted as process- and test-specific examples rather than universal gains. The effectiveness of beneficiation depends on the original ash type, glass accessibility, particle-size distribution, residual carbon content, grinding energy, classification method, and the reactivity metric used for evaluation [14,15,26]. For example, classification may improve reactivity by enriching fine and glass-accessible particles or removing coarse/carbon-rich fractions, whereas milling may expose fresh surfaces and increase dissolution kinetics, but excessive grinding can increase water demand or reduce the beneficial spherical morphology. Therefore, beneficiation should be evaluated by route-specific performance tests, such as strength activity, portlandite consumption, heat evolution, dissolution response, or durability-related indicators, rather than by fineness alone.

9. Conclusions

Based on the evidence synthesized in this review, the following conclusions can be drawn:

1. The rational utilization of fly ash is governed primarily by the compatibility between feedstock properties and binder chemistry environments, rather than by replacement ratio alone. Fly ash should therefore be understood not as a generic supplementary material, but as a property-sensitive feedstock whose engineering value depends on how its chemical and physical characteristics match the dominant reaction environment of the target binder [4,5,14].
2. Different binder systems assign fundamentally different functional roles to fly ash. In CH-rich Portland systems, fly ash can evolve from early physical assistance to later pozzolanic contribution [7]. In CSA systems, its role is dominated mainly by filler-driven hydration regulation with limited later reaction [8]. In MKPC systems, fly ash acts primarily as a rheological and microstructural regulator within a phosphate-bonded matrix [9]. In geopolymers, by contrast, fly ash becomes the aluminosilicate precursor itself [10].
3. The suitability criteria of fly ash are therefore system-dependent rather than universal. Fine, low-carbon, glass-rich fly ash with sufficient particle accessibility is generally more suitable for Portland systems; packing-efficient fly ash with limited but useful auxiliary reactivity is more appropriate for CSA systems; physically beneficial fly ash that improves rheology, heat moderation, and matrix stability is more suitable for MKPC systems; and fly ash with high amorphous aluminosilicate content, adequate fineness, and strong activator compatibility is preferred for geopolymer systems [8–10,14,15,27,74].
4. Many of the apparently inconsistent observations reported in the literature can be reinterpreted within a unified framework of system-dependent binder behavior [8–10,12,36,44]. Variations in consistency, setting, workability, strength development, pore refinement, durability, and activator or curing sensitivity should not be viewed as isolated phenomena, but as pathway-specific manifestations of the interaction between fly ash properties and binder chemistry.
5. Dosage-centered comparison alone is insufficient for the rational deployment of fly ash. Testing a single fly ash at different replacement levels within one binder system cannot determine whether that ash has been assigned to its most suitable utilization route. A more informative strategy is to identify the functional role that a given ash can most effectively perform and then select the corresponding binder system accordingly [5,13,14].

6. Beneficiation should be regarded as an integral part of deployment design rather than as a secondary corrective measure. Classification, milling, carbon control, and related upgrading treatments can modify the reactivity, accessibility, and application suitability of fly ash, thereby changing not only its performance within a given route but also the route to which it is most rationally assigned [27].
7. Future research should move from generalized substitution studies toward property-guided deployment strategies. Greater emphasis should be placed on establishing robust links among fly ash descriptors, binder chemistry environments, processing conditions, and target performance, so as to enable more selective, efficient, and scientifically grounded utilization of fly ash across increasingly diverse cementitious systems [1,4,5,14].

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Abbreviations

The following abbreviations are used in this manuscript:

Abbreviations	Full names
FA	Fly ash
SCM	Supplementary cementitious material
OPC	Ordinary Portland cement
CSA	Calcium sulfoaluminate
KDP	Potassium dihydrogen phosphate
MKPC	Magnesium potassium phosphate cement
CH	Calcium hydroxide
LOI	Loss on ignition
SEM	Scanning electron microscopy
XRD	X-ray diffraction
TGA	Thermogravimetric analysis

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