



Performance Characteristics of Mineral Admixtures in Cement Mortars: Hydration Kinetics, Flow Rheology, and Pore Structure Refinement

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ABSTRACT

Partial replacement of Portland cement with industrial byproducts remains standard practice for reducing clinker consumption and associated emissions. Yet, questions remain on how disparate mineral additions interact across the fresh, hardening, and microstructural stages. This paper synthesizes empirical findings across recent experimental work evaluating fly ash (FA), ground granulated blast furnace slag (GGBFS), condensed silica fume (SF), limestone powder (LP), and natural pozzolan (NP) in cementitious mortars and pastes. Fresh mix evaluations show that while raw fly ash and porous natural pozzolans delay setting and increase water demand, supplementary blast furnace slag and limestone powder maintain paste lubricity and respond cleanly to polycarboxylate ether dispersants. At the microscale, mechanical pulverization of fly ash below a median size of roughly 6 μ m accelerates pozzolanic reactions, shifting hydration peaks and yielding compressive strengths equal to or exceeding pure cement specimens between 28 and 56 days. Parallel findings for silica fume show that despite early dilution troughs, refined capillary systems drop water absorption down to 6.6%. The collected findings confirm that adjusting replacement dosages alongside particle fineness controls the compromise between initial workability and long-term matrix durability.

1. INTRODUCTION

Concrete and cement-based composites represent the backbone of global infrastructure, serving as the foundational building material for transportation corridors, residential construction, hydraulic structures, and industrial assets worldwide. Ordinary Portland cement operates as the primary cohesive binder holding aggregates together, providing structural stability and compressive resistance. However, this extensive reliance on traditional clinker comes at an unsustainable ecological price. The thermal decomposition of calcium carbonate during kiln calcination, paired with the burning of fossil fuels required to reach sinter temperatures around 1450°C, releases tremendous volumes of greenhouse gases into the atmosphere. Conservative industry surveys indicate that every ton of clinker manufactured generates nearly an equivalent weight of carbon dioxide, contributing between 5% and 8% of all anthropogenic carbon emissions worldwide. Consequently, civil engineers face a critical mandate: developing durable, economically feasible binder blends that substantially lower clinker consumption without sacrificing mechanical performance or service life.

The widespread adoption of supplementary cementitious materials offers an effective technical strategy to achieve industrial decarbonization. By incorporating byproducts from thermal power generation, steel manufacturing, and metallurgical silicon refining—principally coal fly ash, ground granulated blast furnace slag, and silica fume—practitioners can divert massive solid waste streams from disposal facilities into productive building systems. However, substituting unprocessed mineral byproducts directly for cement clinker introduces complicated physical and chemical challenges on the job site. Unground supplementary binders typically impede early strength gain, as secondary pozzolanic reactions cannot commence until primary tricalcium silicate phases hydrate to release sufficient free calcium hydroxide into pore solutions. In fresh mixtures, irregular grain morphology and residual porous fractions alter workability, creating erratic water demands and disrupting polymer adsorption when dosing polycarboxylate-based superplasticizers.

Resolving these engineering trade-offs requires an integrated understanding of binder fineness, replacement ratios, and hydration mechanisms. Mechanical pulverization increases surface area, enhances particle packing, and exposes reactive glassy silica phases. This review examines five benchmark experimental studies to synthesize how varying mineral types, substitution levels, and milling intensities dictate fresh-state rheology, early thermal kinetics, compressive resistance, and capillary pore refinement. By connecting laboratory microscale observations with macroscopic performance, this synthesis establishes practical guidelines for designing high-performance, low-carbon blended mortars.

2. LITERATURE REVIEW

The collected experimental work falls naturally into three central themes: fresh paste workability and setting responses, early-to-late hydration and strength gain, and microstructural densification alongside moisture resistance.

Workability, Setting Response, and Rheological Mechanics

Fresh mortar fluidity is governed by surface area, morphology, and chemical interactions with dispersants. Adjoudj et al. (2014) evaluated the fresh rheology of mortars prepared with limestone powder, blast furnace slag, and natural pozzolan in the presence of polycarboxylate (PC) superplasticizers. The baseline mortar displayed a yield stress of 12.1 Pa, which dropped to 2.3 Pa once superplasticizer dosage was lifted to 0.4%. When substituting cement, both slag and limestone powder maintained high paste mobility. Slag particles, possessing a broad size spread, improved grain packing and freed up lubricating water, keeping the paste fluid even without admixtures. Limestone powder proved especially compatible with PC polymers; the fine carbonate surfaces exhibited strong polymer adsorption, lowering plastic viscosity without causing mix bleeding.

Natural pozzolan acted in the exact opposite manner in the Adjoudj et al. (2014) trials. Its internal pore network and high moisture affinity sequestered mixing water, pushing yield stress higher and causing slump loss. At 30% natural pozzolan substitution, the plastic viscosity jumped by a factor of 2.6 over control values. Adjoudj et al. captured these conflicting responses through an empirical relationship, $X = X_0 (1 + k_{sp} \cdot \phi) (1 + k_{sl} \cdot \phi) (1 + k_{lp} \cdot \phi)$, confirming positive synergy constants (k_{sl}) for slag and limestone, whereas pozzolanic materials returned negative coefficients due to polymer trapping.

In a related series of trials, Bendezu Romero et al. (2024) studied setting times in ternary and binary systems mixing OPC with fly ash and GGBFS at a water-to-binder ratio of 0.40. Adding unground class F fly ash raised the water required for normal consistency, dragging initial and final sets out. A 50% fly ash replacement pushed the final setting duration to 600 minutes, a heavy delay compared to the 360-minute benchmark of the pure cement sample. Slag mixes proved much more manageable; a 50% slag paste required only 450 minutes to complete its final set. Interestingly, Moghaddam et al. (2019) discovered that mechanical processing mitigates some of these raw fly ash drawbacks. They examined three fly ash variants from the Eraring power station: classified fly ash (CFA, 11.3 μ m), run-of-station ash (RFA, 17.4 μ m), and finely ground run-of-station ash (GRFA, 5.7 μ m). In flow table tests, the ground GRFA and classified CFA improved fresh paste spread (105% to 140%) over neat OPC. Although grinding broke the glassy spheres into more angular fragments, the higher population of fine particles per unit volume created a dynamic roller effect that lowered inter-particle friction.

Hydration Kinetics and Strength Development

Hydration thermal profiles and compressive strength are tied to dilution effects versus secondary pozzolanic activity. Moghaddam et al. (2019) monitored blended pastes across their first 48 hours via isothermal calorimetry. Replacing cement by 20% to 40% fly ash diluted the available tricalcium silicate (C₃S), shrinking early heat output from 258 J/g down to between 164 and 225 J/g. Ash fineness shifted the profile significantly: the ultrafine GRFA paste produced a distinctly higher second hydration peak (3.51 mW/g) than the coarse RFA (3.27 mW/g). It also formed an unexpected third hydration peak around 10 to 12 hours. Because fly ash substitution lowers gypsum concentrations and exposes extra nucleation sites, remaining aluminates phases reactivate, turning early ettringite into monosulfate with renewed heat liberation. Consequently, cubes containing 20% GRFA reached 77 MPa at 28 days—matching 96% of the neat control paste—while coarser RFA mixes reached only 72%.

Hsu et al. (2018) identified similar strength patterns when grinding Class F fly ash into three Blaine fineness grades: 4610 cm²/g (4FA), 5690 cm²/g (5FA), and 6300 cm²/g (6FA) across dosages of 10%, 15%, and 20%. Strength gain was rapid through the initial 14 days and climbed steadily through 56 days. Blends containing 20% 5FA achieved 54.8 MPa at 56 days, an improvement of 24.5% over pure OPC. Yet, grinding fly ash past a critical point brought diminishing returns: the 6FA mixes (6300 cm²/g) gained less strength than the 5FA batches. Scanning electron microscopy showed that excessive grinding caused ultrafine particles to agglomerate into static clusters during mixing, preventing water contact and blunting pozzolanic conversion.

Where unground materials are used without mechanical processing, early strength drops are more pronounced. In Bendezu Romero et al. (2024), standard mortars with up to 50% raw slag or fly ash failed to match control strengths within 28 days. Mixes containing 30% fly ash performed best among the blended batches, whereas 50% slag replacement resulted in poor compressive resistance. In silica fume mortars, Uddin et al. (2023) documented severe early strength penalties under saturated surface dry (SSD) conditions; at 3 days, adding 20% silica fume halved the compressive capacity. At 90 days, however, pozzolanic reactions reversed the deficit. At a water-to-binder ratio of 0.40, mortars with 20% silica fume surpassed the control mix by 20% in SSD conditions and 11% in dry tests, establishing 20% as an optimal replacement ceiling.

Microstructural Reorganization, Pore Distribution, and Permeability

Hardened matrix durability depends on closing interconnected capillary networks and consuming free lime. Both Moghaddam et al. (2019) and Hsu et al. (2018) used X-ray diffraction (XRD) to track portlandite [Ca(OH)₂] peaks at 18.0° and 34.1° 2 θ . At 7 days, portlandite peak intensities between blended and pure pastes were largely identical because clinker hydration governed the early phase. By 28 and 56 days, peak heights had dropped substantially in mixes made with fine fly ash. The abundant amorphous silica and alumina consumed Ca(OH)₂ to precipitate secondary calcium silicate hydrate (C-S-H) gels. SEM backscatter images corroborated this phase change: while early paste microstructures displayed smooth unreacted spheres resting in open voids, mature 28-day and 56-day matrices showed fly ash cores encased within fibrous hydration products.

Mercury intrusion porosimetry (MIP) tests reported by Hsu et al. (2018) showed that refining particle size reshapes the capillary structure. In 56-day OPC specimens, cumulative pore intrusion measured 0.0792 mL/g, with primary capillary peaks located near 95 nm and 183 nm. Introducing 20% fine fly ash

(5FA or 6FA) pulled the cumulative volume down to roughly 0.051 mL/g. The shift moved larger capillary voids into sub-10 nm gel pores, reducing overall water absorption from 8.87% (control) to 8.10% (5F20 mix).

Uddin et al. (2023) observed similar pore refinement in silica fume specimens. Owing to an average particle diameter of just 0.15 μm , silica fume acts as an active micro-filler between larger cement grains. At 3 days, water absorption climbed to roughly 24% because the large unreacted surface area demanded moisture. By 90 days, pozzolanic reactions sealed the internal channels, dropping water absorption down to 6.62% in 20% SF mixtures. This coincided with a saturated-to-dry strength ratio of 0.96, proving that pozzolanic densification prevents water infiltration, inhibits chemical ingress, and improves durability in water-retaining structures.

3. CONCLUSION

- Grinding raw fly ash to moderate surface areas (around 5600–5700 cm^2/g , median size $\sim 5.7 \mu\text{m}$) resolves the setting and strength deficits of coarse ash. Over-milling past 6300 cm^2/g causes particle agglomeration, restricting water distribution and limiting pozzolanic reactions.
- For mechanical strength and permeability resistance, optimal cement replacement limits are 20% to 30% for milled fly ash, 20% for silica fume, and 10% to 15% for blast furnace slag. Higher replacement fractions (up to 50%) yield lower raw-material costs and smaller carbon footprints but cause marked drops in early-age strength.
- Slag and limestone powder improve mix lubricity and lower plastic viscosity, maintaining high compatibility with polycarboxylate ether admixtures. Highly porous additions, such as natural pozzolans, pull free water from the mix and require larger superplasticizer dosages to avoid stiffening.
- Secondary C-S-H precipitation combined with physical micro-filling shifts coarse capillary voids into sub-10 nm gel pores. This structural refinement lowers total water absorption to below 7% and yields an SSD-to-dry strength ratio of 0.96, improving matrix durability against moisture and chemical attack.

4. REFERENCES

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