

Journal of Engineering Research and Reports

Volume 26, Issue 8, Page 269-277, 2024; Article no.JERR.120927 ISSN: 2582-2926

Enhancing Concrete with Ultrafine Fly Ash: Mechanical Strength and Frost Resistance

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Article Information

DOI:<https://doi.org/10.9734/jerr/2024/v26i81244>

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/120927>

Review Article

Received: 27/05/2024 Accepted: 30/07/2024 Published: 06/08/2024

ABSTRACT

Fly ash, a byproduct collected from the flue gas of coal combustion, serves as an effective additive in concrete. It offers environmental benefits by converting waste into a valuable resource, thus promoting energy conservation, emission reduction, and waste utilization. Additionally, fly ash enhances the mechanical properties and frost durability of concrete. Commonly used as a partial substitute for cement, it helps conserve resources. However, its use may compromise early strength and durability, which limits its applications. The transformation of raw fly ash into ultrafine fly ash through mechanical grinding increases its fineness and specific surface area, thereby boosting its reactivity and micro-aggregate effects. This process produces denser C-S-H gel and optimizes the concrete microstructure. Research shows that although ultrafine fly ash may slightly reduce early concrete strength, it significantly enhances long-term strength, with a 10% substitution improving early compressive strength by 20.2% and later strength by 13.7%. However, excessive fly ash content can reduce frost resistance, with an optimal substitution level at 25% significantly

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Cite as: Zhang, Yuqi. 2024. "Enhancing Concrete With Ultrafine Fly Ash: Mechanical Strength and Frost Resistance". Journal of Engineering Research and Reports 26 (8):269-77. https://doi.org/10.9734/jerr/2024/v26i81244.

enhancing this property compared to standard concrete. Blending ultrafine fly ash with other mineral admixtures further boosts mechanical properties and frost durability. Challenges include increased processing costs and early strength deficiencies, along with the necessity to control heavy metal content for environmental and health safety. Future research should aim to optimize fly ash particle distribution and reactivity, develop cost-effective production methods, and blend fly ash with other minerals to improve concrete's mechanical and frost resistance properties, thus expanding its potential applications.

Keywords: Ultrafine fly ash; mechanical properties; frost resistance; microstructure.

1. INTRODUCTION

Fly ash, a by-product of coal-fired power plants, is predominantly composed of spherical or hollow particles [1]. Its ineffective utilization poses risks to human health and production processes. As a mineral admixture for concrete, fly ash can partially replace cement, thereby contributing to energy savings and emission reductions. The latent activity of fly ash enhances the workability, durability, and physical-mechanical properties of concrete, reduces the required amount of cement, and lowers concrete production costs [2]. Additionally, fly ash exhibits three primary effects: morphological effect, activity effect, and micro-aggregate effect [3]. However, the reactivity of conventional fly ash is limited, leading to minimal improvements in the mechanical properties and durability of concrete. This necessitates further research and analysis into the application of ultrafine fly ash.

Ultrafine fly ash is produced through ultrafine grinding of fly ash, resulting in sub-micron, spherical microbeads with a finer fineness than ordinary fly ash. The average particle size is generally less than 10 μm, and the specific surface area exceeds 600 m²/kg. Its morphology differs from that of ordinary fly ash [4], characterized by smooth surfaces and regular spherical shapes, which confer a higher specific surface area and enhanced morphology and activity. It has a low water demand and exhibits higher early activity compared to ordinary fly ash, making it more valuable for practical applications [5]. Ultrafine fly ash is considered a high-quality additive, providing better particle gradation in cementitious materials. Additionally, it fully utilizes the three main effects of fly ash [6].

The fineness of fly ash is a critical factor influencing its performance. Li Hui [7] discovered that the activity of ultrafine fly ash increases with its fineness. This enhancement is attributed to the increased specific surface area of the

spherical particles, which boosts the likelihood of contact with the smooth surface of cement particles, thereby improving its activity [8]. Wang Wusuo and colleagues [9] compared the effects of ultrafine fly ash and ordinary fly ash on concrete performance, finding that ultrafine fly ash significantly enhances the mechanical properties of concrete. This improvement is due to the secondary hydration reaction of ultrafine fly ash particles in the highly alkaline environment of the paste, which increases its pozzolanic activity. Additionally, ultrafine fly ash can better exert the micro-aggregate effect [10].

Against this background, this paper summarizes the characteristics of ultrafine fly ash and its impact on concrete. Experimental tests and analyses by previous scholars have evaluated the mechanical properties and frost resistance of ultrafine fly ash concrete. These research findings are crucial for promoting the application and development of ultrafine fly ash concrete, thereby advancing the realization of green buildings.

2. CHARACTERISTICS OF ULTRAFINE FLY ASH

2.1 Physical Properties and Chemical Composition of Ultrafine Fly Ash

Fly ash comprises fine, powdery particles that are predominantly spherical and mostly glassy. The color of fly ash can range from brownish to gray to black, contingent upon the unburned carbon content present [11]. Typically, the specific gravity of fly ash falls within the range of 2.1 to 3.0, while its specific surface area can vary from 170 to 1000 m²/kg. The average particle size measures less than 20 μm, with a corresponding specific surface area typically ranging from 300 to 500 m²/kg; the specific surface area of fly ash is influenced by factors such as surface roughness and porosity, where a higher specific surface area indicates greater porosity [12].

Ultrafine fly ash is produced by grinding raw fly ash, which exhibits higher reactivity compared to its raw form. Post-grinding, it forms uniform, small-sized particles with minimal variance. Typically, solid glass spheres within fly ash remain intact but surface scratched during grinding, facilitating chemical reactions and particle bonding [13]. Mechanical grinding destroys larger hollow particles while leaving smaller particles unaffected, thus creating additional active surface sites. Although small particles may not break during grinding, their inert surface layer is compromised, heightening surface activity and enhancing fly ash reactivity [14]. Research indicates that ultrafine fly ash obtained post-grinding possesses particles smaller than 10 um and a specific surface area of 600 m²/kg. Ultrafine fly ash exhibits small particle size, high specific surface area, and significant agglomeration effects [15]. Zhou Zhou et al. [16] observed that incorporating fly ash reduces internal structure defects in concrete, promoting uniform slurry and notably decreasing dry concrete density. However, excessive usage can reduce early concrete mechanical properties. Additionally, ultrafine fly ash's lower density enhances workability and performance. Ultrafine fly ash particles, due to their minuscule size, pose a considerable risk to air quality when present in the atmosphere for extended periods. These particles can penetrate the human body via the respiratory and digestive systems, potentially leading to respiratory ailments and other health issues.

The chemical properties of fly ash are significantly influenced by the type of coal combusted. According to the American ASTM C618-80 standard, fly ash is categorized into anthracite, bituminous, sub-bituminous, and lignite types. The major constituents of fly ash are oxides such as $SiO₂$, $Al₂O₃$, $Fe₂O₃$, and CaO, with $SiO₂$ and $Al₂O₃$ constituting over 60% of its total mass. Li Qiao et al. [17] observed that fly ash comprises a blend of crystalline and amorphous minerals, displaying substantial variability in mineral composition. Crystalline minerals typically include quartz, mullite, iron oxide, magnesium oxide, lime, and anhydrite, while amorphous minerals appear glassy. The chemical composition of fly ash particles varies, leading to distinct phases during production. Even within the same type of fly ash, both chemical and mineral compositions differ with particle size. XRD phase analysis indicates that as particle size decreases, the concentration of metallic elements increases, suggesting higher

enrichment in smaller particles. Fine particle fly ash exhibits lower crystallinity compared to coarser particles, thereby reducing its reactivity. Furthermore, fine particle fly ash contains active components like calcium sulfate and potassium aluminosilicate, underscoring the significant influence of particle size on composition distribution and reactivity, consistent with findings from other researchers [18-19]. Due to the high concentrations of heavy metals in fly ash, including As, Pb, Cd, Zn, Cu, and Ni, there is a significant risk of heavy metal accumulation. This accumulation can result in the contamination of soil and air, posing serious threats to human health. Consequently, the potential toxicity of fly ash and its adverse effects on human health must be carefully considered and addressed.

2.2 Fineness of Ultrafine Fly Ash

Mechanical grinding is the predominant method for producing ultrafine fly ash. Throughout the grinding process, particle size primarily decreases through the refinement of larger particles. Initially, fly ash comprises numerous coarse particles that are easily fragmented, thereby optimizing grinding efficiency. However, as the process advances, the accumulation of particle energy state charges impedes further size reduction. This phenomenon diminishes grindability, lowers grinding efficiency, and widens the distribution of particle sizes [20].

Ultrafine fly ash typically refers to fly ash with an average particle size below 10 μm and a specific surface area exceeding 600 m²/kg [21]. Greater fineness enhances its pozzolanic reactivity significantly. Through grinding, the specific surface area of fly ash continues to increase, reducing particle size and enhancing activity. Zhou Shiqiong et al. [22] extensively researched the particle size distribution and morphology of ultrafine fly ash, highlighting its substantial benefits in water reduction and strength enhancement. Initially, ultrafine fly ash enhances strength primarily through dense filling and micro-aggregation. Over approximately 14 days, its inherent pozzolanic properties gradually emerge, further bolstering strength. Xue Yaodong proposed that [23] ball-milled fly ash with fineness ≤12.0% is Grade I, ≤25.0% is Grade II, and ≤45.0% is Grade III. Wang Peiyi observed that [24] finer ultrafine fly ash requires less water and exhibits higher activity. Therefore, incorporating ultrafine fly ash can notably enhance the workability and mechanical properties of concrete, with finer particles yielding more pronounced improvements. Ultrafine fly ash, characterized by particles smaller than 10 um, readily disperses into the air due to its fine size. The ash contains toxic heavy metals that can severely impact soil quality and human health, contributing to resource wastage. These properties make the management of ultrafine fly ash a significant challenge in terms of its storage, disposal, and recycling as solid waste.

3. IMPACT OF ULTRAFINE FLY ASH ON CONCRETE

3.1 Mechanical properties of Ultrafine Fly Ash Concrete

Mechanical properties serve as fundamental indicators to assess concrete performance and are crucial requirements in practical engineering applications, cmpressive strength is one of the most critical factors affecting concrete quality [25]. The strength of concrete exhibits notable variations with varying dosages of ultrafine fly ash [26-31]. Fig. 1 illustrates the compressive strength at 28 days across three studies, each evaluating different levels of ultrafine fly ash content. Fig. 1 shows that for different grades of ultrafine fly ash concrete, the 28-day compressive strength increases when the fly ash content is within 10% comfig pared to concrete without ultrafine fly ash. However, when the fly ash content is between 10% and 20%, the overall compressive strength tends to decrease.

Fly ash is a typical industrial solid waste with significant morphological, activity, and microaggregate effects. It is valuable for optimizing the microstructure and enhancing the strength of concrete [32]. Ultrafine fly ash can further enhance the micro-aggregate filling effect, increase the specific surface area of particles, reduce mineral crystallinity, and significantly boost reactivity and synergistic hydration with cement. The resulting low-alkalinity, high-density C-S-H gel improves the hydrated cementitious material and the microstructure of concrete, thereby enhancing its mechanical properties [8].

With increased ultrafine fly ash content in concrete, its early compressive strength is slightly lower than that of the control group concrete, but its later compressive strength increases significantly. Zhang Yuan and colleagues analyzed that [4], in the early stage, due to the low hydration degree of cement, the hydration reaction of active components in ultrafine fly ash is limited, primarily playing a physical filling role in the paste, leading to a decrease in compressive strength. However, as the age extends, ultrafine fly ash particles start to undergo secondary hydration reactions in the highly alkaline environment within the paste, resulting in an increase in later compressive strength.

Fig. 1. Compressive strength of concrete with different Ultrafine Fly Ash Contents

Pu Daijun [33] conducted compressive strength tests on the effect of different dosages and fineness of fly ash on concrete's compressive performance, showing that concrete strength increases with age when fly ash of the same fineness is added. For fly ash of different fineness, as the fineness increases, concrete strength decreases, indicating a higher practical application value of ultrafine fly ash for highstrength concrete.

Sun Yao [34] designed three dosages of 10%, 20%, and 30% ultrafine fly ash to replace part of the cement, comparing and analyzing the effect of ultrafine fly ash and regular fly ash on the mechanical strength of concrete at 3, 7, 14, and 28 days. The results show that adding ultrafine fly ash effectively improves the early mechanical properties of concrete, with an optimal dosage of 10%. Compared to ordinary concrete, the compressive strength at different ages increased by 20.2%, 15.5%, 13.9%, and 13.7%, respectively. Wang Qun et al. [35] found through orthogonal experiments that when the particle size of ultrafine fly ash is less than $5 \mu m$, concrete with less than 20% ultrafine fly ash content shows better 28-day compressive strength compared to plain concrete. The best mechanical performance is observed with 10%- 20% ultrafine fly ash. Additionally, Faiz U.A. Shaikh et al. [36] discovered that concrete containing 32% fly ash and 8% ultrafine fly ash exhibits superior mechanical properties compared to ordinary concrete made entirely of 100% cement. This finding contrasts with traditional methods of adding fly ash or ultrafine fly ash and offers a new perspective for future research on the impact of ultrafine fly ash on concrete's mechanical properties.

Xiang Xue-Min and colleagues [37] investigated the impact of varying fly ash contents on concrete performance. They used XRD and SEM micro-tests to examine the changes in the concrete microstructure at 28 days with different ultrafine fly ash contents. Active components, such as silicates in ultrafine fly ash, react with $Ca(OH)_2$ in the cementitious system to form new hydration products like calcium silicate hydrate and calcium aluminate hydrate. Fly ash particles effectively fill the voids within the concrete and gradually undergo hydration reactions with increased curing age, producing new hydration products. Consequently, the activity and microaggregate effects of ultrafine fly ash are fully realized, enhancing the mechanical properties of concrete.

Extensive experimental tests and data analysis are often necessary when investigating the mechanical properties of ultrafine fly ash concrete. These tests can be conducted according to international standards to ensure accuracy and reliability. Additionally, numerical simulations can further compare and verify the mechanical behavior of ultrafine fly ash concrete. Finite element modeling is an effective method to analyze the mechanical performance of ultrafine fly ash concrete. This approach allows for a more precise evaluation of key parameters such as the relative dynamic elastic modulus and mass loss of the concrete. Additionally, it offers benefits such as high processing speed and cost reduction [38-39]. Although ultrafine fly ash concrete holds potential in green building, challenges and limitations remain, such as the interface transition zone strength between ultrafine fly ash and the concrete matrix and the feasibility of large-scale application. Ongoing research aims to address these issues, promoting the practical application of ultrafine fly ash concrete. Nevertheless, many unresolved problems and challenges persist, underscoring the importance of continuous research.

3.2 Frost resistance of Ultrafine Fly Ash

The frost resistance durability of concrete reflects its ability to withstand static water pressure, osmotic pressure, and ice swelling pressure caused by phase changes within matrix pores under alternating temperature conditions, especially while in a saturated or humid state for prolonged periods [40]. Freeze-thaw damage in concrete manifests as the continuous generation and expansion of micro- and fine cracks in the matrix, leading to macro-level erosion, cracking, and even sudden failure from the exterior inward [41]. Current research on the mechanisms of freeze-thaw damage in various concretes primarily includes theories of static water pressure, osmotic pressure, and ice swelling pressure. Powers [42] proposed the static water pressure hypothesis for concrete freeze-thaw, suggesting that during cooling, part of the water in the concrete pores freezes and expands, causing the unfrozen water to flow into surrounding pores, thereby generating static water pressure. Powers and others [43] believed that the vapor pressure difference between ice and water drives the unfrozen water to migrate to the freezing zone, known as osmotic pressure, with Powers himself favoring the osmotic pressure theory.

Ultrafine fly ash has potential application value in enhancing the micro- and fine-pore structure of concrete and improving the matrix's resistance to freeze-thaw cycles. When evaluating the freezethaw resistance of concrete, it is commonly represented by changes in macro-physical and mechanical parameters such as mass loss, reduction in dynamic elastic modulus, and decrease in mechanical strength. Additionally, detailed micro-level analysis and evaluation of the freeze-thaw damage behavior of concrete are also crucial, as these macro performances are essentially reflections of the accumulation of micro-damage within the concrete [44]. Hou Tiejun's [45] study on the effect of different fly ash contents on concrete's freeze-thaw resistance revealed that with increasing freezethaw cycles, the dynamic elastic modulus of fly ash concrete gradually decreases, while the mass loss rate significantly increases. Both changes expand, and when the content exceeds 40%, the freeze-thaw resistance of concrete sharply declines, negatively affecting its performance. Similarly, Li Yue and others found that [46] increasing fly ash content exacerbates surface damage and mass loss rate in concrete samples with more freeze-thaw cycles. Under the same freeze-thaw conditions, higher fly ash content leads to a faster increase in mass loss rate and a more significant decrease in the relative dynamic elastic modulus. Wang Chenxia's research indicated that [47] when the fly ash content is less than 30%, mass loss is relatively low and not significantly different. However, when the content exceeds 45%, the mass loss becomes severe. [T](https://www.sci-hub.ee/10.6052/j.issn.1000-4750.2019.12.0770)o address this, some researchers suggest using ultra-fine fly ash instead of ordinary fly ash. Li Yijin and others found that [48] incorporating 25%-30% ultra-fine fly ash improves the concrete's freeze-thaw resistance significantly due to its excellent dispersibility and filling ability, which tightly fills the gaps between cement clinker particles, promotes hydration product formation, and enhances the density and strength of the paste. Qin Li and colleagues [49] pointed out that the pozzolanic reaction of low-dosage fly ash, when coordinated with the cement hydration reaction, generates a denser gel matrix. This process enhances the density of recycled concrete and blocks micro- and fine-pore structures that are detrimental to frost resistance, thereby improving the frost resistance of concrete. Fan and others [50] found that due to the limited activity of fly ash and cement hydration products, excessive fly ash content is detrimental to concrete's frost resistance. However, a fly ash content of 25%

demonstrated good frost resistance. Song Yuhua et al. [51] compared the effects of different fly ash and mineral contents on the freeze-thaw resistance of concrete. The results showed that concrete specimens with a combination of fly ash and mineral powder exhibited superior freezethaw resistance compared to those with a single additive. Additionally, when ultra-fine fly ash and slag were mixed in a 1:1 ratio, the specimens showed the lowest mass loss rate and the best freeze-thaw cycle performance. Similarly, Leng Faguang et al. [52] found that a 45% blended additive showed better freeze-thaw resistance compared to concrete with the same amount of only fly ash.

Therefore, grinding fly ash into ultrafine fly ash increases its specific surface area and reduces mineral crystallinity. This process significantly enhances the micro-aggregate filling effect and pozzolanic activity of fly ash, potentially improving the frost resistance durability of concrete. However, due to the limitations of fly ash itself, it will be necessary in the future to mix ultra-fine fly ash with other mineral materials to further expand the application research of ultra-fine fly ash in the freeze-thaw resistance of concrete. Alternatively, adopting better sorting processes to further enhance the particle distribution and reactivity of fly ash will increase the utilization of this solid waste material.

4. CONCLUSION

Fly ash, a solid waste generated by coal-fired power plants, can be converted into a resource through recycling, resulting in significant energy savings, emission reductions, and environmental benefits. Using mechanical grinding technology, fly ash is processed into ultra-fine fly ash with higher specific surface area and activity, optimizing the microstructure of concrete. Additionally, the morphological effects, activity effects, and micro-filler effects of ultra-fine fly ash can be fully utilized, leading to the formation of a large amount of low-alkali, high-density C-S-H gel. This improves the hydration gel materials and the microstructure of concrete, enhancing the interfacial transition zone strength and thus further improving the mechanical properties and freeze-thaw durability of ultra-fine fly ash concrete. Studies show that incorporating 10% ultra-fine fly ash can increase the early compressive strength of concrete, with significant improvements in freeze-thaw performance at an optimal dosage of 25%. However, excessive use may weaken freeze-thaw resistance. The advantages of ultra-fine fly ash lie in its significant micro-filler effects and activity enhancement, with its fine particles forming dense C-S-H gel in the cement matrix, improving concrete strength and durability, and having strong potential for application. However, challenges such as increased processing costs, insufficient early strength, and potential environmental and health risks from heavy metals must be addressed. Future research should focus on optimizing the distribution and activity of fly ash particles, developing more costeffective production processes, and exploring blending with other mineral admixtures to enhance its mechanical properties and durability, thereby increasing its application potential in green building.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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