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Physical and Chemical Actions of Nano-Mineral Additives on Properties of High-Volume Fly Ash Engineered Cementitious Composites

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Unlike conventional concrete, the material design process for engineered cementitious composites (ECC) involves micromechanics-based design theory, paving the way for the use of high volumes of fly ash (HVFA) as a major component. Using high volumes of fly ash (up to 85% weight fraction of cement) in ECC mixtures enables improved tensile ductility (approximately a 3% increase in long-term tensile strain) with reduced crack widths, although it also leads to significantly reduced early-age compressive and tensile strength and chloride ion resistance. However, nanomineral additives are known to improve mechanical strength and durability of HVFA systems. The study emphasizes the effects of different fly ash (FA)/cement ratios on various properties (hydration and microstructural characteristics, transport and mechanical properties) of ECC mixtures designed with different mineral additives. Experimental results confirm that although different optimum levels can be selected to favor various ECC properties, optimum weight fraction of FA is dependent on the mechanism of nanomodification (that is, type of modifier). The optimum level of fly ash weight fraction that yields the highest rate of improvement through nanomodification of ECC varies for different mechanical and transport properties.

Keywords: chloride ion permeability; engineered cementitious composites; high-volume fly ash; hydration characteristics; mechanical properties; nanomineral additives.

INTRODUCTION

The ingredients and mixture proportions of engineered cementitious composites (ECC) are regularly optimized through micromechanics-based material design theory to satisfy the strength and tensile ductility to attain high tensile ductility in composites.[1] As a result, high amounts of fly ash (FA) have become one of the major components in ECC production. Increasing the weight fraction of FA (up to 85%) in high-volume fly ash (HVFA) ECC tends to improve tensile ductility while retaining a long-term tensile strain of approximately 3%.[2,3] Moreover, with an increase in FA weight fraction, crack width is reduced from approximately 60 to 10 μm (0.0024 to 0.0003 in.), or sometimes even lower, which may benefit the ductility and long-term durability of HVFA-ECC structures.

On the other hand, compared to portland cement, the pozzolanic reaction of FA is a slow process and its contribution to strength can be observed only at later ages. Additionally, the early-age strength of ECC decreases if large amounts of FA are used, which limits the widespread use of HVFA concrete by engineers.[3,4] Therefore, the mixture design of ECC specimens must be carefully optimized to minimize these disadvantages. Apart from the mixture design, a number of factors have been reported to affect the properties of HVFA-ECC. These include uniform dispersion of fiber addition, curing conditions, hydration age, and so on.[5,6] Addition of nanosized mineral modifiers has been widely investigated as a viable alternative to improving the performance of HVFA concrete mixtures, especially at early ages.[7,8] It has been reported that modified HVFA mixtures with $CaCO_3$ show improved properties due to the synergy created between FA and $CaCO_3$ through mechanisms such as C_3S hydration acceleration, ettringite stabilization, and increased compressive strength.[9-11] $CaCO_3$ is known to accelerate formation of hydration products, mainly by promoting C-S-H formation due to seeding effect.[10,12,13] High content of the aluminate phase originating from FA has been shown to increase the effectiveness of $CaCO_3$ and C_3A reactions.[14-17]

The main advantage of using $CaCO_3$ in HVFA systems is higher early-strength values,[10,11] which is a major disadvantage of HVFA-ECC.[18] Microsilica and nanosilica (NS) also provide a seeding surface, accelerating hydration with accelerated pozzolanic activity.[19] However, it is important to note that the mechanism of improvement with $CaCO_3$ and NS use is different. When weight fraction of FA is high, CH becomes critically low at early ages, slowing pozzolanic activity. The pozzolanic reaction of NS further reduces CH levels, which may have a negative effect on properties at later ages.[8,20] In the case of $CaCO_3$, although formation of hemicarboaluminate consumes CH, it is reported to occur at early ages[11,21] when CH levels can be relatively high due to the faster nature of hydration reactions. Consequently, unlike NS, $CaCO_3$ does not pose a CH depletion problem for the HVFA mixtures.

In the studies of HVFA mixtures, it is reported that various factors affect the optimum weight fraction of FA in an HVFA concrete. The general trend is that there is an optimum FA fraction that will yield the highest compressive strength value.[22] However, that optimum weight fraction is dependent on the desired properties of the composite as well as other factors such as water-binder ratio (w/b), chemical and physical properties of components, and curing practices.[5] It is also important to note that higher FA fraction means lower early-strength values, which limits the applicability of HVFA. In a recent paper, the authors of this study investigated the ductility properties of nanomodified ECC mixtures with only a certain FA fraction.[23] However, it is

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