Investigating the use of Fly Ash and Nanomaterials for Sustainable Concrete Infrastructure

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***Abstract*— Sustainable infrastructure addresses many concerns, such as limiting pollution, minimizing the use of natural resources, and reducing energy consumption and greenhouse emissions. The benefits of using fly ash in concrete are widely known, but fly ash mixes are typically limited to 25% or less by mass in practice. Incorporating nanomaterials, such as nanoalumina and nanoclay, into high-volume fly ash (HVFA) mixes can rework the structure and improve the properties of fly ash typically used in concrete. The main objective of the study was to determine the maximum amount of Portland cement that could be replaced by fly ash and nanomaterials in concrete without sacrificing overall strength and durability. Fresh properties, hardened properties, and durability tests of HVFA with nanomaterials-based concrete mixes were investigated and compared to a control (Portland cement-based concrete). 80 wt% (by cementitious materials) fly ash and 5 wt% (by cementitious materials) nanomaterials (nanoalumina and nanoclay) were used. Compressive, flexural, and tensile strength tests were conducted in addition to freeze-thaw durability. The compressive and flexural strengths of HVFA (80% fly ash) with nanomaterials were slightly lower than the control. In addition, the freeze-thaw durability of HVFA with nanomaterials-based concrete was lower than that of the control. HVFA with nanomaterials-based concrete mixes can be used in specialized applications that are not exposed to significant freeze-thaw cycles, perhaps in warmer climates. Scanning electron microscope (SEM) morphology shows nanomaterials serve as a filler in Portland cement-fly ash mixtures.**

Keywords—fly ash, nanomaterials, concrete infrastructure, sustainability.

I. INTRODUCTION

The main criteria for sustainable infrastructure are minimizing impact on and the use of natural resources; reducing energy consumption; reducing greenhouse gas emissions; limiting pollution (air, water, earth, and noise); improving health, safety, and risk prevention; and ensuring high levels of user comfort and safety. Use of fly ash as supplementary cementitious materials (SCMs) in concrete helps to reduce cost, conserve energy and resources, improve durability, reduce environmental impact, and enhance workability [1]. One drawback of using high volumes of fly ash (HVFA) is a resulting delay in initial setting time due to drastically slow hydration, which reduces the early strength of concrete. However, the ability of nanomaterials to accelerate the rate of hydration of ordinary Portland cement/SCMs blends opens the possibility of significantly lowering the level of cement in concrete [2-4], potentially removing this roadblock to reducing greenhouse gas production in the construction industry.

Nanomaterials may improve concrete infrastructure sustainability through improving the efficient use of existing materials, either by reworking them or changing their structures, to ensure that materials' properties are improved to provide a longer life. Nanomaterials improve cementitious properties through two mechanisms: by increasing the rate of the pozzolanic reaction due to their higher surface areas and by acting as centers of nucleation to improve the microstructure. The great reactivity and the pozzolanic nature of nanomaterials further increase the reaction rate by reducing the amount of calcium ions in the hydration water [5-14].

A. Problem Statement

Ordinary Portland cement demand is expected to increase almost 200% from 2010 levels by 2050, reaching 6,000 million tons/year globally. There is a critical need to investigate the use of fly ash and nanomaterials-based concrete for sustainable concrete infrastructure.

The benefits of using fly ash in concrete are widely known, but fly ash mixes are limited in practice. Incorporating nanomaterials, such as nanoalumina and nanoclay, into HVFA mixes may rework the structure and improve the properties of fly ash typically used in concrete.

B. Objectives

This study tested the hypothesis that all or a majority of ordinary Portland cement can be replaced by fly ash and nanomaterials in concrete. Nanomaterials can accelerate the rate of the hydration reaction of fly ash in concrete and improve its desirable properties [6]. There were four specific objectives for this study:

- To determine the fresh properties of fly ash and nanomaterials-based concrete as compared to the control (Portland cement-based concrete);
- To determine the mechanical properties of fly ash and nanomaterials-based concrete as compared to the control;
- To measure the nanostructural properties of fly ash and nanomaterials-based concrete as compared to the control; and
- To investigate the freeze-thaw resistance of fly ash and nanomaterials-based concrete as compared to the control.

II. MATERIALS AND METHODS

A. Material Properties

The properties of the fine and coarse aggregates, fly ash, and nanomaterials used in this study are described briefly in this section.

1) Aggregates: Physical properties and gradation of aggregates were determined following ASTM standards. Table 1 shows the physical properties of the aggregates used in this study. The physical properties were used to design concrete mix. Aggregate gradations were within the lower limit and upper limit.

Table 1. Aggregate physical properties

Property	Coarse	Fine
Bulk specific gravity	2.684	2.673
Saturated surface dry specific gravity	2.708	2.685
Apparent specific gravity	2.749	2.705
Absorption (%)	0.88	0.43
Fineness Modulus (FM)	-	2.68
Soundness (MgSO4 for 5 cycles)	0.9	3.5
Abrasion Loss (%)	23	-

2) Fly ash: The physical and chemical analysis of fly ash used in this study was completed by Headwaters Resources following ASTM standards. ASTM and/or AASHTO limits for chemical and physical analysis of fly ash were met for Type C. Energy dispersive x-ray spectroscopy (EDS) was also used to determine the amounts of individual elements in fly ash. Scanning electron microscopy (SEM) was also used to observe the surface topography of fly ash.

3) Nanomaterials: Due to exponential population growth and limited availability of virgin materials, extensive scientific research has been carried out to identify other raw materials that can be utilized as SCMs [6, 11, 15]. It has been found that readily available raw minerals, such as clay and silica, have huge potential for use in the construction industry [16]. Two different nanomaterials were selected for use in this study based on their performance and availability: nanoalumina and nanoclay.

Nanoalumina can be used as a reactive agent to increase the hydraulic activity of slowly reactive materials, such as fly ash, and to refine the microstructure of paste, leading to the improvement of mechanical strength at early ages [6].

Nanoclays have shown promise in enhancing mechanical performance, resistance to chloride penetration, and self-compacting properties of concrete, while also reducing permeability [17-20]. The nanoclay used in this study was Cloisite 20.

B. Mix Design

In order to determine the maximum amount of fly ash plus nanomaterials that could replace cement, several trial batches were mixed. Throughout this process, varying levels of cement and fly ash were used. After replacing 100% of the cement with fly ash, the cylinders were not strong enough after removing the mold. As the research team began adding cement in 5% intervals, mix stability increased. Fly ash levels, therefore, were set at 80% by mass of cementitious materials. Overall, the ratio of fly ash, cement, and nanomaterials used in the HVFA mixes was 80/15/5 wt% for this study. The three mix designs were 80/15/5 wt% nanoalumina, 80/15/5 wt% nanoclay, and a control (Portland cement-based concrete).

In this study, a 28-day compressive strength of 4,000 psi was used for each mix. Higher volumes of fly ash (80%) acted as water reducers and did not require as much water to achieve the same slump as the control. Water was reduced by 15-20% due to HVFA. It should be noted that the amount of fine aggregate was reduced to accommodate the additional volume of fly ash; this is due to the lighter mass of fly ash. Table 2 shows all three mix design proportions in this study.

Table 3. Mix design proportions and properties

	Control	80/15/5 wt% Nanolumina	80/15/5 wt% Nanoclay
Cement (kg/m^3)	430	65	65
Fly Ash (kg/m^3)	0	0	0
Coarse Aggregate (kg/m^3)	0	344	344
Fine Aggregate (kg/m^3)	0	0	0
Water (l/m^3)	1055	1055	1055
Entrained Air (ml/m^3)	0	0	0
Expected Air Content (%)	604	516	516
w/c Ratio	0	0	0

C. Mixing

Effective dispersion of nanomaterials is critical to achieving the full benefits in cementitious systems. Self-aggregation, especially at high dosages of nanomaterials, is a common concern (Qing et al. 2006, Sobolev et al. 2006, Veras-Agulho et al. 2009, Ozyildirim and Zegetosky 2010, Sanchez and Sobolev 2010), which sometimes leads to nonhomogeneous microstructure development and poor performance. High-speed mixing was found to be effective in the proper dispersion of nanomaterials (Sobolev et al. 2006, Flores et al., 2010). Thus, high-speed mixing was used in this study for maximum dispersion.

D. Testing

1) Fresh Properties: Fresh property tests included unit mass, air content, slump, and temperature. Air-entraining admixture was added in order to achieve the required air content for durability. The pressure method was used to measure air content following ASTM C231M. The density of fresh concrete was measured following ASTM C138M. Slump was measured according to ASTM C143M.

2) Hardened Properties: Mechanical properties tested include compressive strength (ASTM C39M), flexural strength (ASTM C293), and tensile strength (ASTM C496M). Mechanical properties of concrete specimens were measured using a Universal Testing Machine (UTM) after proper curing. Addition of nanomaterialss improves the compressive strength of ordinary Portland cement mortar and concrete (Sobolev et al. 2006, Chang et al. 2007, Gaitero et al. 2008, Sobolev et al. 2008, Gaitero et al. 2009, , Morsy et al. 2009, Sobolev et al. 2009, Flores et al. 2010, Gaitero et al. 2010, Nazari and Riahi 2012, Gonzalez et al. 2013). Addition of nanoalumina has had a limited effect on the compressive strength of concrete (Li et al. 2006). Incorporation of nanoclay was reported to enhance the tensile strength in a cement composite (Morsy et al. 2010).

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3) Nanostructural Morphology: The nano-fibrous nature of nanoclays and their filler effect in cement mortar was revealed by morphological studies using SEM. The texture of hydrate products was found to be dense, compact, and had uniform microstructure. SEM tests indicated that the specific surface area of nanoclay is the key factor for denser microstructure of samples (He and Shi 2008, Morsy et al 2009). Nanostructural morphology of fly ash and nanomaterials-based concrete was conducted using SEM.

4) Freeze-thaw Resistance: A durable transportation infrastructure needs to satisfy two requirements: service with minimal required maintenance and sustainability. The durability requirement focuses on the potential perpetual use of the facility with minimum requirement for disruptive maintenance and rehabilitation (Li et al. 2006). All failure mechanisms associated with concrete durability involve fluid transport through the concrete microstructure. The movement of water into and through concrete can contribute to many of the deterioration mechanisms that affect concrete performance. Water itself can result in freeze–thaw damage if a proper air-entraining system is not in place. In northern climates, such as North Dakota, deicing chemicals can adversely affect longevity if the concrete properties are marginal or inadequate. Nanomaterials could greatly increase the life of concrete structures if a method could be developed to make concrete less permeable. This development may pave the way to making concrete freeze–thaw resistant without air entraining (Grove et al. 2010).

One of the problems with using fly ash in concrete is an increased potential for frost damage (Taylor et al. 2007). However, addition of nanomaterials increases durability and service life of concrete by reducing permeability to fluids and by controlling the leaching of calcium (Kroyer et al. 2003, Ji 2005, Sobolev 2005, Cardenas et al.2006, Gaitero et al. 2006, Gaitero et al. 2008, He and Shi 2008, Gaitero et al. 2010, Porro et al. 2010, Nazari and Riahi 2011, Zhang and Li 2011, Nazari and Riahi 2012, Zhang and Wang 2013).

The beams for freeze-thaw resistance testing were prepared following ASTM C215-08 and tested following ASTM C666/C666M-03. Once the beams were exposed to sequences of freeze-thaw cycling, they were tested for fundamental transverse frequency using a sonometer drive and pickup. In order to quantify how the durability of the beams in terms of resistance to freeze-thaw cycles, a frequency test was done. In this test, a supported specimen was forced to vibrate by an electro-mechanical driving unit. The specimen response was monitored by a lightmass pickup unit on the specimen. The driving frequency was varied until the measured specimen response reached a maximum amplitude. The value of the frequency causing maximum response is the resonant frequency of the specimen. Figure 8 shows the actual frequency test setup

III. RESULTS AND DISCUSSIONS

A. Fresh Properties

Table 4 shows measured and/or expected fresh properties for the control and nanomaterials modified HVFA-based concrete. The slump and unit mass of the control mix were lower than the nanomaterials-modified HVFA-based concrete, whereas the air content of the control was higher. This confirms that HVFA reduces the effectiveness of air-entraining admixtures.

Table 4. Fresh properties

Mix Design	Control	80/15/5 wt% Nanoalumina	80/15/5 wt% Nanoclay
Expected Air Content (%)	5	5	5
Measured Air Content (%)	5.6	3.5	4
Measured Slump (in.)	2.5	3.5	4
Measured Unit Mass (lbs/ft^3)	147	161	156

B. Hardened Properties

1) Compressive Strength: Figure 9 shows that compressive strengths of nanomaterials-modified HVFA-based concrete are lower than the control. The HVFA mixes neared a 28-day compressive strength of 3000 psi, as compared to the 4000 psi target strength that the control had achieved. It should be noted that the HVFA mixes exhibited 28-day compressive strengths that were 25% lower than the control while only using about 1/6 of the amount of Portland cement. The compressive strength of HVFA mixes is expected to rise as curing time increases. The compressive strength of nanoclay-modified specimens is higher than those of nanoalumina-modified specimens.

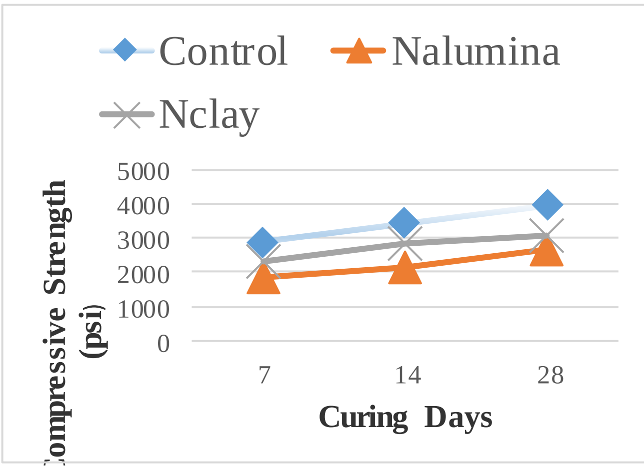

Figure 9. Compressive strength

2) Flexural Strength: Figure 10 shows that the flexural strength of nanomaterials-modified HVFA-based concrete is comparable to the control except at the 28th day of the curing period. The difference in the effect of nanoalumina and nanoclay on flexural strength is not clear since flexural strength slightly changes throughout the curing period.

3) Tensile Strength: Average splitting tensile strengths for nanomaterials modified HVFA-based mixes are lower than the control at all curing days, as shown in Figure 11. Nanoclay has a slightly higher effect on 7-day tensile strength, whereas nanoalumina has slightly higher effect on tensile strength for longer curing periods (14 and 28 days), but the difference is not significant from a practical point of view

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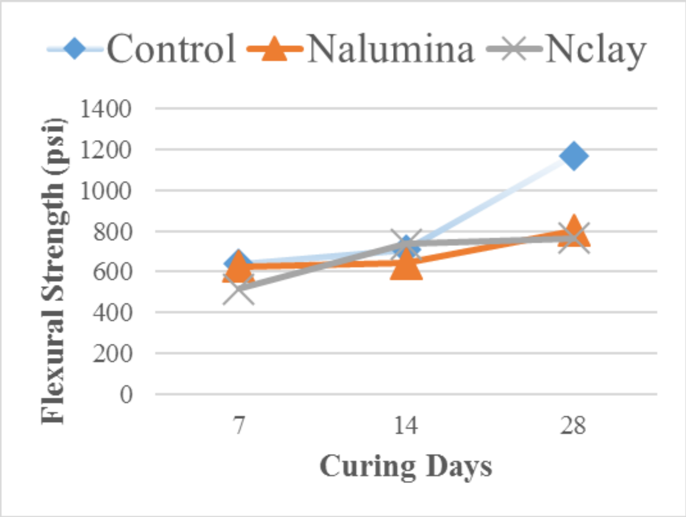

Figure 10. Flexural strength

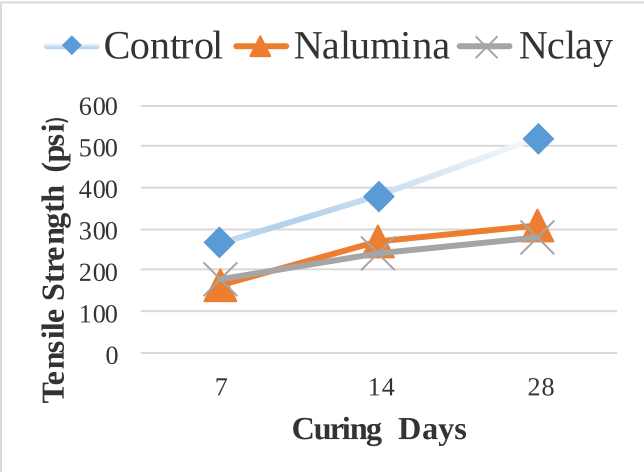

Figure 11. Tensile strength

C. *Nanostructural Morphology*

Figures 12 and 13 show the nanostructural morphology of nanoalumina- and nanoclay-modified HVFA-based concrete, respectively. The figures show that nanomaterials are effective in acting as a filler in between the fly ash and cement.

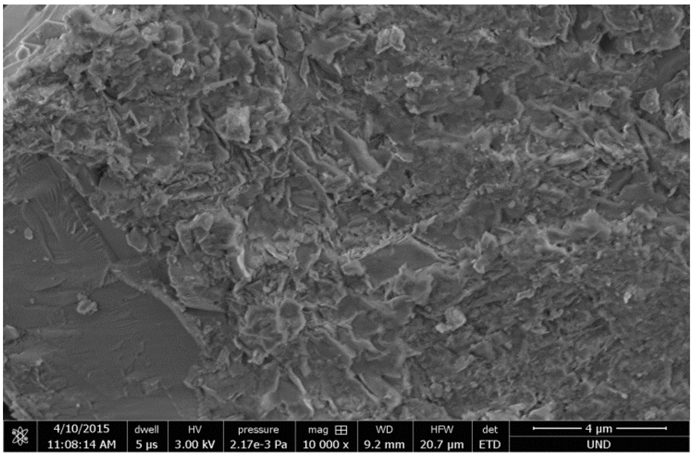

Figure 12. SEM – Nanoalumina modified HVFA-based concrete

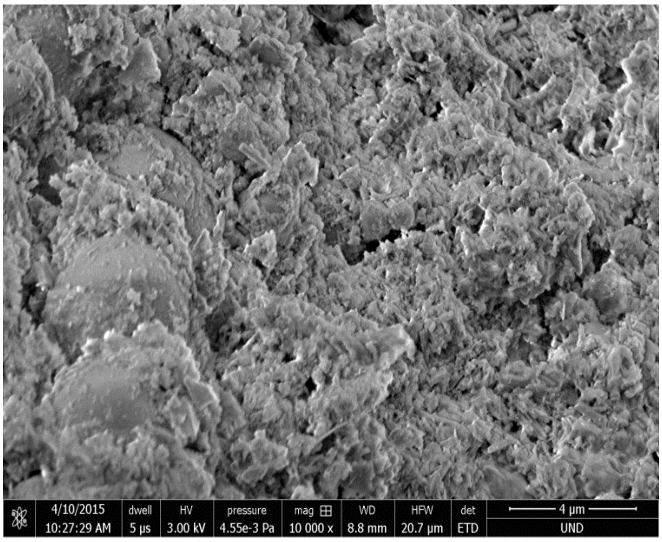

Figure 13. SEM – Nanoclay modified HVFA-based concrete

D. *Freeze-thaw Resistance*

The relative dynamic moduli of elasticity of the nanomaterials-modified HVFA-based concrete are lower than the control, as shown in Figure 14. The difference in relative dynamic moduli may be due to the significant difference in air content of the mixes (control vs. nanomaterials-modified HVFA-based concrete), as shown in Table 4. Relative dynamic moduli of the nanoclay mixes are higher than that of nanoaluminia mixes. Nanoalumina mixes failed early and the test was stopped. Special precautions must be taken with mixes containing HVFA that have high carbon or calcium content. One such study concluded that twice as much air-entrainment admixture needs to be added for mixes replacing more than 50% of cement with fly ash (Crouch et al. 2007). The fly ash used in this experiment contains a significant amount of free lime (CaO), which could account for the air-entraining admixtures' ineffectiveness.

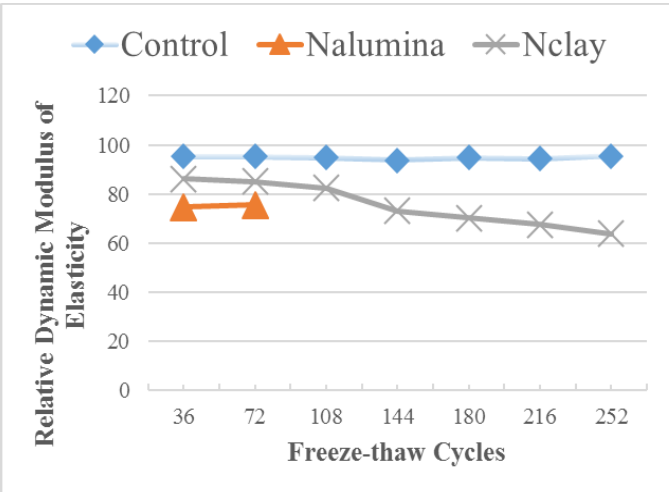

Figure 14. Effect of freeze-thaw cycles on relative dynamic modulus of elasticity

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IV. CONCLUSIONS

Fresh properties, hardened properties, nanostructural morphology of 5% nanomaterials (nanoalumina and nanoclay)-modified HVFA (80%)-based were compared to a control (Portland cement-based concrete). The following conclusions can be drawn based on the study:

- This study confirms that HVFA reduces the effectiveness of air entraining admixture. More air-entraining admixture needs to be added in order to achieve the same air content as the control.
- Compression strengths of the HVFA plus nanomaterials-based concretes were roughly 25% lower than the control. These concretes may be used in applications where strength is not a priority. The nanomaterials help accelerate the hydration process and produce early-age compressive strengths that would not otherwise be possible by only supplementing with fly ash.
- Flexural and tensile strengths of HVFA plus nanomaterials-based concrete were also lower than those of the control.
- Nanostructural morphology using SEM shows that nanomaterials act as fillers in Portland cement and fly ash.
- The durability (freeze-thaw resistance) of HVFA plus nanomaterials-based concrete was lower than that of the control, which is possibly due to the lower air content in HVFA plus nanomaterials-based concrete.

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