



Chloride induced corrosion durability of high volume fly ash concretes containing nano particles



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HIGHLIGHTS

- Nano silica improved the compressive strength of high volume fly ash concretes.
- Nano CaCO₃ improved the compressive strength of high volume fly ash concretes.
- Nano silica improved the durability of high volume fly ash concretes.
- Nano silica improved the corrosion resistance of high volume fly ash concretes.
- Nano CaCO₃ improved the compressive strength of high volume fly ash concretes.

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ABSTRACT

This paper presents experimental results on chloride induced corrosion and related durability properties such as chloride permeability, water sorptivity, chloride diffusion and porosity of ordinary concrete and high volume fly ash (HVFA) concretes containing nano silica (NS) and nano calcium carbonate (NC) particles as partial replacement of cement. The NS and NC are used as 2% and 1%, respectively by wt. of cement in the above concretes. Results show that the addition of NS and NC significantly improved the corrosion resistance of ordinary concrete and HVFA concretes in terms of lower corrosion currents, lower steel loss and longer time require to create corrosion induced crack. Sorptivity, chloride diffusivity and chloride permeability of above concretes also reduced significantly due to the addition of NS and NC, which correlate well with the corrosion tests. The addition of NS and NC also significantly reduced the capillary pores and gel pores of above concretes and also shifted the pore concentration towards the medium capillary pores. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of above concretes also confirms the reduction of calcium hydroxide (CH) in the concretes containing nano particles, thus the formation of additional calcium–silicate–hydrate (CSH) gel in the system.

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1. Introduction

The wide spread use of ordinary Portland cement (OPC) concrete in construction industry in the world is due to its lower cost and better durability than structural steel. However, still reinforced concrete (RC) structures possesses durability problems and one of the most important durability problem is the chloride induced corrosion of steel in RC. Concrete industry is also blamed to contribute global CO₂ gas emission into atmosphere between 5% and 7% due to the use of OPC in the production of concrete. Worldwide there is an overwhelming consensus in concrete industry to reduce the carbon footprint of concrete through reducing the bulk portion of cement in the concrete. The use of supplementary cementitious

materials to improve the durability and mechanical properties of concrete is a common practice now-a-days. Pozzolanic materials such as silica fume, fly ash, blast furnace slag and metakaolin are commonly used due to unique characteristics of each material in improving the properties of cement concrete.

Fly ash which is the by-product of coal fired power station is used as partial replacement of cement in concrete for many years. In year 2012, the utilisation of fly ash for construction application has achieved 55.79% and become a commercial product which is available in bulk quantities [1]. Fly ash has pozzolanic activity which is attributed to the presence of SiO₂ and Al₂O₃. It reacts with calcium hydroxide during cement hydration, to form additional calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) which are effective in forming denser matrix leading to higher strength [2–4]. In practice, the quantity of fly ash to replace cement is limited to 15–25% by mass of the total cementitious

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material [2]. Use of high fly ash contents as partial replacement of cement in concrete commonly known as high volume fly ash (HVFA) concrete is also researched [5,6]. However, the HVFA concrete exhibits lower early age strength than ordinary concrete. Several micro size cementitious materials, which are highly reactive pozzolan such as silica fume, rice husk ash, etc. are added to HVFA concrete to address the low early age strength gain and durability properties. In recent years, the use of nano materials has received particular interest in construction materials especially in cement mortar and concrete. Nano material is defined as a very small particle with size under a scale of 10^{-9} m, produced from the modification of atoms and molecules in order to produce large scale material [7]. Materials with nano-scale structure could help to influence the strength development and enhance the durability properties. It is due to the high surface area of nanoparticles which reduced the calcium hydroxide to form additional calcium silicate hydrate (C–S–H) within the hydration products. Moreover, nanoparticles improve the structure of aggregate which results in better bond between aggregates and cement paste. Among many nano materials, the use of nano silica (NS) in concrete and mortar has recently been researched [8–18].

It has been observed that the NS consumed free lime (calcium hydroxide) during cement hydration and formed C–S–H gel due to its high fineness [10]. In addition, the NS with size around 1–100 nm [11] is particularly beneficial in acting as a nucleus to make the cement hydrate dense and improves the interfacial transition zone despite of small amount of replacement. From some conducted experiments, Zhang and Islam [12] and Jo et al. [13] reported better performance of concrete containing NS than that containing silica fume. Li [14] studied the effect of NS (4% by wt.) on compressive strength of HVFA concrete containing 50% fly ash and observed improvement in both short-term and long-term compressive strength of HVFA concrete. Zhang and Islam [12] recently studied the effect of NS on compressive strength and hydration of HVFA mortar and concrete containing 50% fly ash and also reported very similar results that reported by Li [14]. Improved early age compressive strength of HVFA mortars and concretes due to addition of NS are also reported by Hou et al. [15,16] and Shaikh et al. [8], respectively. Research on durability properties of concrete containing nano silica shows that the nano silica has a very reactive performance in making the binding paste matrix denser and improved the water permeability resistant capacity of concrete [17]. Jalal [18] also studied the effect of nano silica and silica fume (SF) on high strength self-compacting concrete. The concretes containing blend of 10% SF and 2% NS showed significant reduction in chloride ion penetration up to 60% compared to the control concrete. It was stated that the nanoparticles not only act as an activator to accelerate cement hydration due to their high activity, but also act as a kernel in cement paste which makes the size of calcium hydroxide crystal smaller and then refines the pore structure of concrete. In a same point of view, He [19] reported that the chloride permeability of Portland cement mortar with nano materials admixed at 1% by weight of cement was markedly reduced, as indicated by the reduced apparent diffusion coefficients of chloride. Additionally, the same conclusion was also reported by Said [20] who investigated the chloride permeability resistance of nano silica concretes based on charged pass and penetration depth of chloride ions. Some authors have also attempted to draw the effect of nano materials on permeability and microstructure improvement [21,19,22].

Another nano material which is currently developed is nano calcium carbonate (NC). Although the use of calcium carbonate was first considered as filler to partially replace cement or gypsum, some studies have shown some advantages of using NC in terms of strength, accelerating effect and economic benefits as compared

to cement and other supplementary cementitious materials. Chemically, the presence of NC leads to increase the rate of hydration reaction of tricalcium aluminate (C_3A) to form a carboaluminate complex thereby increase the total hydration products and consequently strength [23–25]. Moreover, it also reacts with tricalcium silicate (C_3S) and accelerates the setting and early strength development [26]. As a consequence of the formation of a higher volume of hydrates, the increase in hydration degree compensates the dilution effect of the binding material thus develops higher initial strengths [27].

Some studies have suggested a potential benefit of $CaCO_3$ on the development of supplementary cementitious system. Sato and Beaudoin [28] carried out a number of investigations on the incorporation of micro- and nano- $CaCO_3$ materials with high volume of supplementary cementitious materials. In this experiment, cement was replaced with 50% fly ash (series one) and 50% slag (series two) and incorporated 10% and 20% of micro- and nano- $CaCO_3$ by weight of binders. It was found that the replacement of cement with NC accelerated the early hydration of cement and enhanced the early development of modulus of elasticity as the amount of NC increased. The presence of NC has been suggested to have a significant effect on the hydration kinetics of C_3A and C_3S which may cause acceleration of setting and early strength development. On another study, Sato and Diallo [29] reported the seeding effect of NC where the rapid growth of CSH can be obtained by the access of NC on the surface of the C_3S particles. This view is supported by Kawashima et al. [30] who provided a basis for understanding the mechanical properties of high volume fly ash when incorporated with calcium carbonate nanoparticles. It was shown that the 5% nano- $CaCO_3$ with 30% fly ash–cement paste samples tested at 1, 3 and 7 days showed progressive development in the compressive strength compared to typical fly ash–cement paste. It is suggested that fly ash with high aluminate content can introduce addition aluminates to the system thereby decreasing the SO_3/Al_2O_3 ratio and amplifying the impact of the limestone powder on the hydration products [25].

While more experimental results on the effects of NS and NC in ordinary concrete and HVFA concretes have been published, limited research results exist on the effect of nano silica (NS) and nano calcium carbonate (NC) on the durability properties of HVFA concretes, particularly on chloride-induced corrosion durability. Therefore, this study is conducted to investigate the effectiveness of NS and NC on chloride induced corrosion durability properties including water sorptivity, chloride permeability and chloride diffusion of high volume fly ash concretes. The accelerated corrosion test is also conducted to evaluate the corrosion of reinforcing steel in above concretes when exposed to chloride environments. Mercury intrusion porosimetry (MIP) and thermogravimetric analysis (TGA) are also used to characterise the microstructure of paste samples. The results obtained from this study can lead to potential development of highly durable HVFA concrete by incorporation of nano silica and nano calcium carbonate for sustainable RC infrastructure.

2. Experimental details

2.1. Materials

Ordinary Portland Cement Type I (PC) satisfied ASTM C150 [31] standard was used to produce all concretes in this study. Class F Fly ash (FA) in accordance with ASTM C618 [32] was used as partial replacement of cement in HVFA concretes. The powder nano silica (NS) was obtained from Nanostructured and Amorphous Materials, Inc. of USA with average particle diameter of 25 nm. The commercially available powder nano calcium carbonate (NC) with particle size of about 40–50 nm was used (see Figs. 1 and 2). Chemical composition and physical properties of cement, class F fly ash, nano silica and nano calcium carbonate are presented in Table 1.

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