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Mixtures of silicon and aluminum oxides to optimize the performance of nanoporous thin films in concrete

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ABSTRACT

This study explored the effect of two combinations of silicon and aluminum oxides, nanosilica–nanoboehmite and nanosilica–gibbsite, on the hydration reaction of cement and the porosity of the interfacial transition zone (ITZ). The influence of sols on the cement hydration reaction was investigated using isothermal calorimetry while their effect on the porosity of the aggregate–paste interface was validated using scanning electron microscopy. The nanosilica–nanoboehmite mixtures were found to accelerate the hydration reaction to a higher degree than the individual components, nanosilica and nanoboehmite. Further, the effect was also found to be dependent on the stoichiometry of the mixture of nanoparticles. The nanosilica–gibbsite combinations not only accelerated the reaction but also increased the cumulative heat of hydration. In this case, the enhancement is attributed to the seeding effect of the gibbsite particles, being more prominent at the smaller particle sizes. Lastly, when these materials were applied as nanoporous thin films on the aggregates, all sol mixtures not only helped to decrease the overall porosity but also contributed to refinement of the porosity in the cement paste adjacent to the aggregate. These effects were observed up to 250 μm away from the surface of the aggregate thus not restricted to the typical length of the interfacial transition zone in concrete (40–50 μm).

1. Introduction

The interface between the aggregates and the cement paste, referred as the interfacial transition zone (ITZ), is one of the most vulnerable areas in concrete. It is a preferential area for the nucleation of cracks [1–3]. The surface of the aggregates can act as vectors for the ingress of deleterious microfines (particles < 75 μm) as aggregate coatings during the mixing process, mostly certain types of clay minerals, or as starting point of degradation mechanisms such as alkali–silica reaction (ASR) or freezing and thawing deterioration. A wide range of factors controls the microstructure in the ITZ. Water to cement ratio [4] and low packing efficiency of cement particles in the vicinity of the aggregates [5–7] are one of the most influential factors. At high water to cement ratios, the ITZ develops a distinctive microstructure when compared to the bulk areas [4]. The combination of these two factors creates a distinctive microstructure in the ITZ characterized by high porosity and presence of large portlandite crystals. Details on this hypothesis have been extensively discussed elsewhere [5,8–12]. One of the approaches used in the past to strengthen this area was to coat the surface of the aggregate with different components, particularly supplementary cementitious materials (SCMs). These materials tend to benefit the ITZ in two ways, acting as fillers and reducing the portlandite concentration due to their pozzolanic nature [13–17].

The deposition of certain metallic oxide nanoparticles, as nanoporous thin films (NPTF), on the surface of the aggregates has been shown to be a promising technique to engineer the ITZ [18]. Small quantities of silica introduced, as NPTF, are capable of modifying the ITZ and therefore improving the early mechanical properties of mortar specimens. The principal benefit of adding nanosilica to concrete materials is the capacity of this type of particles to serve as nucleating sites for the hydration reaction and to promote the formation of calcium silicate hydrate (C–S–H). However, less attention has been directed towards studying the combination of both silica and boehmite to promote the formation of calcium aluminate silicate hydrates (C–A–S–H) over C–S–H. The incorporation of aluminum into the C–S–H in has been the subject of previous research work [19–21]. The investigation with synthetic gels and computer models indicate that the aluminum can replace the silicon in the silica chains in the structure of C–S–H. These silica chains get stabilized by binding to calcium oxide layers forming a silica–calcium layer. The interlayer between silica–calcium layers

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is occupied by free calcium ions and water molecules. The aluminum replaces silica in specific positions of the original silica chain. These substitutions result in several changes in the chemo-mechanical properties of the hydrated gel such as higher capacity of the gel to bind alkalis [20,22]. Additionally, the aluminum can also replace calcium in the interlayer spacing and then bind itself to silica chains creating a variety of dimensional linkages ultimately resulting in enhanced integrity and stability of the overall gel structures [20]. The consequences of this linkage are an increase in the strength and elastic response of the C–A–S–H [20].

These changes could be of great interest to engineer the ITZ of concrete. It is hypothesized that the microstructure of the ITZ can be benefited by high concentrations of C–A–S–H rather than C–S–H, in particular if the former hydration gel displays higher strength and elastic response in addition to the capacity to immobilize alkali cations to prevent ASR reactions. In this sense, specific NPTF can be used to promote nucleation of C–A–S–H near the ITZ. At a later stage of the hydration, the aluminum necessary for the further grow of C–A–S–H gel can be supplied by traditional SCMs added in the bulk.

The use of NPTFs over the surface of the aggregate as additives to specifically improve the ITZ is a novel approach. This way of introducing the nanoparticles has the potential to reinforce the microstructure of the ITZ as well as to modify the surface chemistry of the aggregates used in concrete. This technology can have a positive impact in locations with restricted access to quality aggregate sources. For example, the NPTF can be used to improved performance of currently marginal aggregates, such as natural aggregate with significant contents of clay minerals strongly adhered to their surface [23], and improve the poor performance of concrete made with recycled concrete aggregates due to weak ITZ [24].

Another important advantage of using NPTF for industrial solutions is that its deposition is done through sols, defined as water suspension of nanoparticles. The sols are used to coat the aggregates by dip- or spray-coating methods. This unique method of applying nanoparticles in concrete has several advantages over the traditional addition of nanoparticles as dry powder additives [18]. The technology necessary to apply this material in aggregates is already available in the market. Water spraying of aggregates is a common practice among certain blast furnace slag aggregate producers. The required amount of NPTF to obtain a significant benefit is lower when compared to disperse dry powder nanoparticles thus reducing the cost involved. The sol–gel method used for synthesizing the nanoparticles opens the door for tailoring the chemistry of the nanoparticles according to specific chemical characteristics of the components in the cement paste or the surface of the aggregate. Finally, the use of sols to apply nanoparticles is a safer application method since the risk of inhaling these tiny particles by operators is eliminated. It is important to remember that currently, the research on NPTF is in an early stage. Additional research work is needed to fully evaluate their impact on mechanical performance and durability of cementitious materials before considering technology for deployment.

The objective of this work was to explore the potential of incorporating different combinations of nanosilica and aluminum oxides to modify the ITZ of concrete materials when applied as NPTF. The effect of the nano-additives in the hydration reaction of cement and porosity in the ITZ was analyzed by isothermal calorimetry and by scanning electron microscopy (SEM), respectively. Two approaches were taken to create the mixtures of silica and aluminum oxides: the combination of nanosilica (SiO_2) and nanoboehmite [AlO(OH)] to promote the formation of C–A–S–H over C–S–H, and enhancement of the seeding effect near the ITZ by combining nanosilica with gibbsite [$Al(OH)_3$] particles of different coarseness. A micro-size range of the $Al(OH)_3$ particles were chosen to minimize their dispersion away from the surface of the aggregate.

2. Materials and experimental methods

2.1. Materials

The following reagent grade chemicals were used in the preparation of the sols: aluminum-tri-sec-butoxide (ATSB), tetraethyl orthosilicate (TEOS), sec-butyl alcohol ($C_4H_{10}O$), nitric acid (HNO_3), ammonium hydroxide (NH_4OH), aluminum nitrate [$Al(NO_3)_3$] and deionized water (18.2 MΩ cm). The Bogue phase composition of the portland cement, based on the manufacturer, is 62% C_3S, 11% C_2S, 7% C_3A, and 11% C_4AF by mass.

2.2. Preparation of sols

All the nanoparticles were synthesized following standard sol–gel processes where the hydrolysis and later condensation of the corresponding alkoxide were catalyzed under acid or basic pH.

The acid and basic nanosilica sols were prepared by mixing TEOS with deionized water (1.47 L of water per mol of TEOS) previously acidified to pH 3 with nitric acid or basified to pH 8 with ammonium hydroxide, respectively. The mixtures were then stirred for 24 h at 25 °C [25]. The nanoboehmite sol was prepared by dissolving a mole of ATSB into 2.6 mol of sec-butyl alcohol. The alkoxide–alcohol solution was added to 2.031 L of deionized water previously heated up to 85 °C and acidified with 44.51 mL of 1.6 M nitric acid solution. The resulting aqueous solution was stirred for 24 h [26]. The size of the aluminum hydroxide particles in the basic nanoparticle sol was determined by the initial concentration of $Al(NO_3)_3$ added in the alkaline solution prior to the addition of the TEOS. The $Al(NO_3)_3$ concentrations used were 0.1, 0.05 and 0.025 M, which precipitated $Al(OH)_3$ particles with D50 values of 21, 15 and 5 μm, respectively.

The nanosilica–nanoboehmite nanoparticle mixtures were prepared by mixing different volumetric proportions of acidic sols of nanosilica and nanoboehmite, respectively. Prior to use, all the sols were dialyzed to eliminate side impurities and their concentrations were determined. The dialysis process was carried out by filling a Spectrum Spectra/Por 3 RC membrane tubing with 250 ml of sol and immersing the membrane in 4L liters of deionized water acidified to pH 3 with nitric acid for acid nanosilica and boehmite, or basified to pH 8 with ammonium hydroxide for basic nanosilica and gibbsite combination. The dialysis process lasted 24 h.

Following the synthesis of the sols, a thorough material characterization was performed on the nanoparticles to determine their principal mineralogical and physical characteristics. An Empyrean Series 2 X-ray Diffraction System manufactured by Panalytical was used to examine the mineralogy of the xerogels. The size range and the Brunauer, Emmett and Teller (BET) surface area was determined with a Zeta Potential Analyzer ZETA PLUS manufactured by Brookhaven Instruments and by nitrogen absorption with an ASAP 2020 – Physisorption Analyzer manufactured by Micromeritics, respectively. The BET surface area measurements were done according to the standard DIN ISO 9277 as proposed elsewhere [27]. The degasification of the samples was performed at 200 °C. The specific surface area was calculated using relative pressures data ranging from 0.05 to 0.30. The XRD diffractograms along with the mineralogical information are illustrated in Fig. 1, while the physical data is summarized in Table 1.

2.3. Specimen preparation

The above sols were used to deposit NPTFs on the surface of siliceous limestone particles, which were subsequently covered with