



# Agglomeration and reactivity of nanoparticles of SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and clays in cement pastes and effects on compressive strength at ambient and elevated temperatures

Yonathan Reches, Kate Thomson, Marne Helbing, David S. Kosson, Florence Sanchez\*

Department of Civil and Environment Engineering, Vanderbilt University, PMB 351831, 2301 Vanderbilt Place, Nashville, TN 37235-1831, USA

## HIGHLIGHTS

- Instability of SiO<sub>2</sub> and TiO<sub>2</sub> NP suspensions in alkaline environment.
- NPs formed microscale agglomerates in the cement matrix.
- NP agglomeration state in water not indicative of final state in cement matrix.
- TiO<sub>2</sub>, bentonite, and halloysite NPs increased compressive strength at 200 °C.

## ARTICLE INFO

### Article history:

Received 27 July 2017

Received in revised form 29 January 2018

Accepted 6 February 2018

### Keywords:

Nanoparticles

Cement

Agglomeration

Reactivity

Mechanical properties

Thermal durability

## ABSTRACT

The agglomeration state of SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, bentonite, and halloysite nanoparticles (NPs) in solutions, including simulated cement environments, and their agglomeration and reactivity within the cement paste were evaluated. In water, all NPs formed agglomerates, while sonication and addition of polycarboxylate-based, high range water reducer generally decreased the agglomerate size. Agglomeration of NPs was observed in the chemical environment of hydrating cement paste. The bridging role of Ca<sup>2+</sup>, charge balancing, screening by K<sup>+</sup>, and pH were identified as factors controlling agglomeration. TiO<sub>2</sub>, bentonite, and halloysite NPs enhanced the cement paste residual compressive strength after exposure to elevated temperature.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nano-particles (NPs) of silicon dioxide (SiO<sub>2</sub>), titanium dioxide (TiO<sub>2</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), and clays (e.g. montmorillonite/bentonite and halloysite) have been observed to improve the performance and durability of cement-based materials and, as such, have been the focus of extensive research in recent years [1–5]. However, widely differing effects and high variability in mechanical properties have been reported with the addition of the same NPs as well as different types of NPs. For example, the addition of SiO<sub>2</sub> NPs to mortar at a content of 0.25% per mass of cement was observed to change the 90 day compressive strength relative to the control by –7% and +13% [6]. Similarly, the replacement of 10% of the mass of ordinary Portland cement (OPC) in mortar with SiO<sub>2</sub> NPs has been shown to increase the compressive

strength at 28 days by 34% [7] to 160% [8], for similar mix compositions and particle size of SiO<sub>2</sub> NPs. The replacement of 2.5% of the mass of OPC in mortar with SiO<sub>2</sub> NPs (12 nm), Al<sub>2</sub>O<sub>3</sub> NPs (13 nm), and Fe<sub>2</sub>O<sub>3</sub> NPs (20–60 nm) has been observed to change the 28 day strength by –43%, +6%, and +12%, respectively [9]. The micro-scale mechanisms, which might explain these differences, have not yet been clarified. Understanding the agglomeration and reactivity of NPs in the cement matrix may be an important element explaining the wide range of effects observed. Common approaches to reducing the agglomeration of NPs in aqueous media and cement pastes has been through sonication [10–14] and use of surface modifiers and surfactants [15–19]. While it has been commonly assumed [5,8,20–31] that NPs are well-dispersed in the cement system, it has been observed that NPs tend to agglomerate in aqueous media [10,32], particularly in the presence of salts [33,34], such as found in the hydrating cement environment [35]. Yet, the agglomeration state of NPs in the resultant hydrated cement paste has not been studied extensively. Table S1 provides a summary of NP

\* Corresponding author.

E-mail address: [florence.sanchez@vanderbilt.edu](mailto:florence.sanchez@vanderbilt.edu) (F. Sanchez).

dispersion/agglomeration conditions from prior work in the literature on NPs in cement-based materials. In addition, the degree of agglomeration of NPs has been shown to affect their reactivity [36]. While SiO<sub>2</sub> NPs and clays NPs have been reported to react pozzolanically with calcium hydroxide (Ca(OH)<sub>2</sub>) during cement hydration to form binding phases [20,37–39] and similar reactions have been suggested as possible for other NPs, such as anatase-TiO<sub>2</sub> NPs [40], limited information on NP interactions with the cement paste is available.

This paper evaluates the extent of agglomeration and chemical reactivity of SiO<sub>2</sub>, TiO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, bentonite (i.e., montmorillonite), and halloysite NPs during cement paste preparation and hydration and aims at helping to understand the influence of NPs on the properties of cement pastes at ambient and elevated temperatures. Sonication and use of a polycarboxylate-based, high range water reducer (P-HRWR) were investigated as methods to decrease the extent of agglomeration in water and hydrated cement pastes. The extent of NP agglomeration, as determined based on agglomerate size, was studied in water and in the chemical environment of hydrating cement paste. The chemical reactivity of the NPs was investigated *ex-situ* by determining their reactivity with a solution of Ca(OH)<sub>2</sub> based on mass gain and characterization of the reaction products through chemical analysis. The effect of NP addition on the change in cement paste unconfined compressive strength and modulus of elasticity at ambient temperature after 28 days and 91 days of curing and also after 91 days of curing followed by exposure to 200 °C and 400 °C was evaluated. The present investigation is part of a project related to concrete dry casks for storage of spent nuclear fuel, where sustained temperatures may approach 400 °C [41].

## 2. Experimental program

### 2.1. Overview

A staggered experimental approach (Fig. 1) was used in which a series of experiments was first performed to select the appropriate conditions for preparation of the NP suspensions to be employed in the fabrication of the cement pastes for subsequent characterization and mechanical testing at ambient and elevated temperatures. First, the extent of agglomeration resulting from sonication in water for up to 90 min was studied to determine the minimum sonication time required to achieve a steady-state extent of dispersion (Fig. 1a). Second, the effect of NP:water mass ratio on NP agglomeration was investigated over the range of 0.0003–0.03 g NP/g water. Third, to determine the effect of P-HRWR loading on NP agglomeration, P-HRWR was added prior to sonication at mass ratios varying from 0 to 0.33 g P-HRWR/g NP using a NP loading of 0.03 g NP/g water. This NP loading was chosen because it effectively corresponded to a loading of NPs in cement pastes of ca. 0.5% per mass of cement (water to cement ratio of 0.4), which is within the range of typical amounts that have been shown to improve material performance [42]. The agglomeration state of the suspensions was assessed microscopically using dynamic light scattering (DLS) particle size analyses. The zeta potential (ZP) of the suspensions was also measured to provide insights onto the role of surface charge and stability of the suspensions. The set of conditions (i.e., sonication time and P-HRWR:NP mass ratio) that resulted in the smallest extent of agglomeration for a wide range of NPs was then used to study the stability of NP suspensions in the hydrating cement environment and preparation of the cement pastes for subsequent characterization, mechanical, and durability testing.

The changes in agglomeration when NP suspensions are mixed with salt solutions typical of the hydrating cement paste environ-

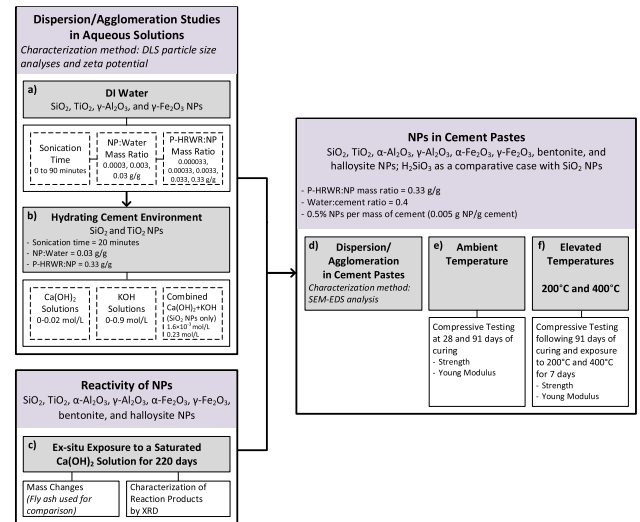


Fig. 1. Staggered experimental approach.

ment were then examined for SiO<sub>2</sub> and TiO<sub>2</sub> NPs to provide insights into changes in NP agglomeration state during a typical cement paste preparation sequence (Fig. 1b). SiO<sub>2</sub> and TiO<sub>2</sub> NPs were used as representative of two different surface charges. Aliquots of sonicated suspensions of NPs prepared with and without P-HRWR were mixed with solutions of Ca(OH)<sub>2</sub> or potassium hydroxide (KOH) to obtain pHs ranging from the initial NP suspension pH (ca. 3–6 depending on the NP type) up to a pH approaching the pH of the hydrating cement paste (12.5 for Ca(OH)<sub>2</sub> and ca. 14 for KOH).

The reactivity of the different NPs in the alkaline cement environment (pH 12–13) was also evaluated (Fig. 1c) via *ex-situ* exposure of each NP to a saturated Ca(OH)<sub>2</sub> solution (pH of 12.5), as a surrogate of the hydrating cement paste environment, for 220 days.

A total of ten (10) different cement paste mixes were prepared: a plain portland cement paste (control), eight (8) portland cement pastes each containing 0.5% per mass of cement (i.e., 0.005 g NP/g cement) of a single type of NP (SiO<sub>2</sub>, TiO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, bentonite, and halloysite NPs), and a Portland cement paste containing silicic acid (H<sub>2</sub>SiO<sub>3</sub>) as a comparative case with SiO<sub>2</sub> NPs. Each cement paste mix was prepared with P-HRWR. A water-to-cement ratio of 0.4 was used. The agglomeration state of NPs within the cement pastes was evaluated microscopically using scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectrometry (EDS) and compared to the agglomeration state in suspensions (Fig. 1d). The response to compressive loading of the different cement pastes as affected by the agglomeration state and reactivity of the NPs in the cement paste was evaluated after 28 days and 91 days of curing (Fig. 1e) and after exposure to 200 °C and 400 °C for 7 days following 91 days of curing (Fig. 1f).

### 2.2. Materials

Type I/II low-alkali OPC (LaFarge, Nashville, TN) conforming with ASTM C150/C150M – 12 was used. A commonly-used P-HRWR, Glenium<sup>®</sup> 7700 (BASF, Ludwigshafen, Germany), was used for workability of the cement pastes and as a dispersing agent to mitigate NP agglomeration. The P-HRWR is a polymer surfactant that works through a dual mechanism of electrostatic repulsion and steric stabilization in which the long molecules of the organic polymer wrap around the particles to prevent their aggregation by

Download English Version:

<https://daneshyari.com/en/article/6715479>

Download Persian Version:

<https://daneshyari.com/article/6715479>

[Daneshyari.com](https://daneshyari.com)