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Influence of nano-sized highly purified magnesium alumino silicate clay on thixotropic behavior of fresh cement pastes

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HIGHLIGHTS

- Small amount of nanoclay addition increases the rate of structural rebuilding.
- Higher than 1.3% of nanoclay addition decreases the rate of structural rebuilding.
- There is a strong relationship between the flow percent and rheological properties.
- Higher rate of heat of hydration generation corresponded with faster rebuilding rate.

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ABSTRACT

Thixotropic behavior of cementitious materials is attracting much attention due to its important applications in concrete practice, such as formwork pressure, multi-lift casting, slip form paving, pumping and segregation. This study investigates the influences of nano-sized highly purified magnesium alumino silicate clay (3 nm in diameter, called nanoclay) on thixotropic behavior, particularly, the structural rebuilding of fresh cement pastes. In this study, rheological properties (yield stress, viscosity and thixotropy) of cementitious pastes, with and without nanoclay, were measured at every 15 min after the pastes were mixed. Flow table tests were conducted, and the results were compared with those measured from the rheology tests. Statistical methods were utilized to determine the rates of changes in thixotropy with time. The results indicate that a small amount of nanoclay addition (0.5–1% by mass of cement) significantly facilitates particle re-flocculation or structural rebuilding, and effectively enhances the thixotropy of cement pastes.

1. Introduction

Over the past decades, much research has been focused on flow properties of concrete, which has led to further development and extended applications of a new generation of concrete, such as high performance concrete and self-consolidating concrete (SCC).

Under a steady state flow condition, the concrete flow behavior is often simply described by a yield stress and viscosity model, such as the Bingham or Hershel–Bulkley models [1]. However, due to its thixotropic behavior, the yield stress and viscosity of concrete actually always change with time [2–4]. Such thixotropic behavior is beneficial for controlling concrete formwork pressure, multi-lift casting, slip form construction, pumping, and segregation, where timely increases in concrete yield stress and viscosity are necessary to facilitate the construction speed and achieve quality products [5,6].

Thixotropic behavior is a common rheological phenomenon in the field of colloid science. It illustrates the decrease of viscosity of a colloidal suspension at a constant or increasing shear rate and the recovery of the viscosity when the material is at rest [7]. Thixotropic behavior in heterogeneous materials, such as a cement suspension, results from particle interactions of the material with time. Once the cement is mixed with water, flocs form rapidly with time due to particle contact, thus forming a three-dimensional networked internal structure [8]. When subjected to shearing, the flocs are broken due to the rupture of the inter-particle links, and the viscosity of the cement paste is reduced. At rest, the internal structure of the cement paste tends to rebuild with time. In other words, thixotropic behavior of a cement paste results from the reversible behavior of coagulation, separation and re-coagulation with time when external shearing is applied and removed [2].

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Recently, researchers demonstrated that small addition of nanometer-sized clay (called nanoclay) particles can effectively improve the shape stability of semi-flowable self-consolidating concrete for slip-form paving [9–11]. Such shape stability is attributed to the improved thixotropy of the concrete mixtures containing nanoclay [12]. Nanoclays may contribute to concrete thixotropy in many different ways: firstly, most clay particle surfaces and edges are charged, by which they can attach with each other to form a more stable microstructure, and therefore creating a higher viscosity. Under shearing, the charged clay particles tend to rearrange or re-orientate, thereby lowering viscosity during flow. Yildiz [12] indicated that with addition of electrolyte, the thixotropy of some clay (such as sodium silicate) almost disappears. Secondly, some clay particles have irregular microstructure which effectively builds up a strong networking microstructure with a higher viscosity [13]. Thirdly, some nanoclays with much smaller particle size and higher specific surface area have ability to play a role of nano-fillers which can effectively fill the gaps between cement particles [14], by which more contacting points effectively build up into an interlocking microstructure.

Lately, many attempts have been conducted to build models that can simulate the thixotropy of cement or concrete with different mineral additions and use of superplasticizers [15–17]. Some researchers measured the change in thixotropy of cement pastes with time [18], which has provided useful information on the rate at which the structure of a cementitious material rebuild. Ferron et al. [14] investigated the structural rebuilding of cement pastes of SCC based on their thixotropy variation with time, and they studied the effects of different alkali and fly ash content and superplasticizers. Tregger et al. [10] quantified the effects of clay addition on the strength and microstructure of concrete using shear and compressive rheology methods. However, the study of the effects of clay on thixotropy of cementitious materials is still very limited.

The objective of this study is to investigate effects of highly purified magnesium alumino silicate nanoclay on thixotropy of fresh cement pastes. Nanoclay was added to cementitious pastes at increasing dosage, up to 3% of cement mass. Hysteresis loop test was used to measure the cementitious paste thixotropy at increasing resting times to study the structural rebuilding rate of cement paste. The flow table test was used to correlate the rheological results with a standard approach. Isothermal calorimeter tests were also performed to investigate how nanoclay content influences both cement hydration and the structural rebuilding rate. The results indicate that the nanoclay have a significant role to play to increase or improve the thixotropic rebuilding of cement paste.

2. Materials and experimental methods

2.1. Materials

Type I Portland cement and nanoclay are used in pastes. Their chemical compositions and physical properties are given in Table 1. The nanoclay used is a commercially available highly purified magnesium alumino silicate [19]. Its particles are needle shaped and have a diameter of 3 nm, with lengths varying from 1.5 to 2.0 μm. The needle shaped particles are positively charged at the ends and negatively charged along the axis. When it is at rest, the positively charged particle ends tend to attach to the negative charged particle axis, therefore, a card-house network of microstructure can be expected. However, under shearing, the nanoclay particles arranges into the preferred direction and offset the structural connection between needles. Because of its rearranging characteristics, it has been used for improving thixotropic behavior of cementitious materials.

2.2. Mixing and sample preparation

Paste samples were prepared with a Hobart model N50 mixer. The water-to-cement ratio (w/c) was 0.4. The amount of nanoclay added were 0.5%, 1.0%, 2.0%, and 3.0%, by mass of cement. The sample preparation protocol with incorporating the nanoclay additives is described as follows:

Table 1
Properties of Portland cement and nanoclay.

Portland cement (Type I)		Nanoclay	
Compound	% by mass	Compound	% by mass
CaO	62.8	CaO	1.88
SiO_2	20.6	SiO_2	49.57
Al_2O_3	4.13	Al_2O_3	9.44
Fe_2O_3	2.99	Fe_2O_3	3.31
SO_3	2.56		
MgO	2.99	MgO	8.81
K_2O	0.64	K_2O	0.66
Na_2O	0.10	Na_2O	0.59
L.O.I	2.53	MnO	0.02
C_3S	60	TiO_2	0.42
C_2S	14	P_2O_5	0.68
C_3A	6	CrO_3	0.02
C_4AF	9		
		L.O.I	<0.50
Specific gravity	3.14	Specific gravity	2.62
Specific surface area	452.7 m^2/kg	Specific surface area	150 m^2/g

Step 1: Mix the dry cement and nanoclay at low speed for 1 min;
Step 2: Add water into the blended cement and nanoclay and mix at low speed for 2 min;
Step 3: Stop the mixer for 1 min and scrape down any mixture that had collected on the sides of the bowl;
Step 4: Start mixing at a medium speed for 2.5 min;
Step 5: Stop mixing for 1 min and scrape mixture collected on the sides of the bowl;
Step 6: Start mixing again on a medium speed for another 2.5 min;
Step 7: Place the paste into sample vessels.

2.3. Test methods

Rheometer test: It is challenging to measure change of thixotropy in cementitious materials due to the fact that it experiences different physio-chemical changes and involves irreversible structural build up [14]. No standard method is available for measuring thixotropy of cement paste or concrete. The hysteresis loop, constant shear rate and static yield stress tests had been utilized to describe the thixotropic behavior of cementitious materials [3,20–23]. The portable vane and inclined plate tests had also been proposed for field testing [24,25]. As mentioned previously, the hysteresis loop test, which is most commonly utilized, was used to determine thixotropy of cement paste in the present study.

As shown in Fig. 1, a hysteresis loop is a loop formed by the up-curve and the down-curve during a rheology test. The up-curve is the shear stress curve measured when the tested material is subjected to a range of increasing shear rates, while down-curve is the curve measured while the material is subjected to the same but decreasing shear rates range. The area enclosed by the up- and down-curves relates to the energy needed to break the flocculate structure of the tested material, and can be used to measure thixotropy.

Rheometer tests were ran on six separate samples of the same batch at 0, 15, 30, 45, 60, 75 min after mixing. Three repetitions were conducted for each mixture type. A Brookfield R/S SST2000 rheometer with a single cylinder sample cup and rotating vane was used for determining viscosity, yield stress and thixotropy of cementitious pastes. The diameter of rotating vane was 15 mm and its height was 30 mm. The sample cylinder used was 50 mm in diameter and 100 mm high. The applied loading history shown in Fig. 1a was applied to paste samples to obtain a flow curve shown in Fig. 1b. As shown in Fig. 1a, the shear rate was initially increased from 0 to 100 s^{-1} over 60 s and then immediately ramped down from 100 to 0 s^{-1} over another 60 s. Following a Bingham model, the yield stress was obtained by extending the linear portion of down-curve (20–80 s^{-1}) to the vertical-axis. The viscosity was the slope of linear portion of down curve (20–80 s^{-1}). Thixotropy was measured by calculating the area bounded by the up and down curves at the 20–80 s^{-1} shear rates. The average thixotropy value was plotted versus time. The slope of this line was used for evaluating the structural rebuilding rate of cement paste.

The thixotropy values for each mixture type were analyzed by a statistical software [26]. A regression model estimating effect of time and nanoclay amount was made from the statistical software. A regression equation describing how thixotropy changes with time was given, and the slopes were plotted versus nanoclay amount in order to indicate the structural rebuilding rate with different nanoclay addition.

Flow table test: The standard flow table test was performed according to ASTM C230. Six specimens were prepared for each paste mix. The flow table test was conducted every 15 min, from 0 to 75 min after mixing. Each test had two repetitions. The average flow percentage for each specimen was calculated and then plotted versus time.