The effect of zinc oxide additions on the performance of calcined sodium montmorillonite and illite shale supplementary cementitious materials

Sarah C. Taylor-Lange [a,*], Fahad Rajabali [a], Natalie A. Holsomback [a], Kyle Riding [b], Maria C.G. Juenger [a]

[a] Department of Civil, Architectural, and Environmental Engineering, 1 University Station C1748, The University of Texas at Austin, Austin, TX 78712, USA
[b] Department of Civil Engineering, 2107 Fiedler Hall, Kansas State University, Manhattan, KS 66506, USA

ABSTRACT

The objectives of this study were to use activation treatments on sodium montmorillonite and illite shale, to alter early hydration or later pozzolanic reactivity when used as supplementary cementitious materials (SCMs). For comparison purposes, treatment methods were also applied to the highly reactive pozzolan, metakaolin, and the inert filler, quartz. Activation treatment strategies included the addition of 0.15 wt% zinc oxide and the use of thermal treatments to the SCMs at temperatures of 650 °C, 830 °C and 930 °C. The use of zinc oxide additions increased the early hydration rate of SCM-containing pastes, yet introduced a chemical retardation and negatively impacted early compressive strengths. Moreover, the results suggest that retardation was inversely correlated with the pozzolanic reactivity of the SCM used. Thermal treatment methods were effective at influencing the SCM pozzolanic reactivity, with montmorillonite calcined at 830 °C and illite calcined at 930 °C behaving as late-reacting pozzolans. SCMs calcined at these temperatures resulted in higher 90 day compressive strengths compared to mortars containing the quartz filler. Overall, this study provides insight into different strategies that maybe used to enhance the reactivity of impure calcined clays in order to facilitate their acceptance into the concrete industry.

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1. Introduction

General use of the calcined clay, metakaolin, as a supplementary cementitious material (SCM) in concrete is limited by regional availability and high cost relative to cement. To overcome these limitations, there is increasing interest in implementing non-kaolinite minerals, such as bentonite and shale, as inexpensive alternatives [1]. Despite widespread abundance [2], these inexpensive alternative calcined clay minerals as SCMs are not commonly used in the concrete industry due to poor early reactivity, poor pozzolanic reactivity and a subsequent reduction in mechanical performance at early and late ages [1,3]. The objectives of this study were to use activation treatment methods on sodium montmorillonite and illite shale to alter early hydration or later pozzolanic reactivity when used as SCMs.

The most active period of cement hydration is roughly from 3 h to 72 h, where cement exothermically reacts with water resulting in the formation of the following primary hydration products: (i) a non-stoichiometrically defined calcium-silicate-hydrate (abbreviated C-S–H), (ii) calcium hydroxide, (iii) ettringite and other hydration products [4]. During this primary reaction, the calcined clay SCM is relatively inert, thus a replacement of 15 wt% SCM would reduce the heat release, similar to a Class F fly ash [5]. The total cumulative heat released during this reaction can be roughly correlated with early compressive strength [6]. Therefore, using calcined clay SCMs can decrease the early strength of cement-based materials and it is of interest to combat this problem [7].

Previous research has shown that the treatment method of specific metal oxide additives can successfully alter the behavior and properties of metakaolin and cement–metakaolin blends [8–10]. Kuechler [8] used cone fusion to show that the addition of titanium dioxide and iron oxide prior to calcination lowered the refractoriness of calcined kaolinite (i.e. thermal resistance). Chatterji et al. [9] demonstrated that zinc oxide additions of 0.001 wt%, 0.01 wt% and 0.1 wt% changed the reactivity of kaolinite measured by lime reactivity tests. Taylor-Lange et al. [10] demonstrated that the addition of zinc oxide to metakaolin cement pastes increased the early cement hydration rate. However, the use of zinc oxide with cement alone has been shown to greatly retard hydration, increasing the induction period, altering the rate of heat evolution

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* Corresponding author. Tel.: +1 (310) 499 3924; fax: +1 (512) 471 4555.
  E-mail address: taylorlanges@utexas.edu (S.C. Taylor-Lange).

and decreasing the early compressive strength [11–13]. Taylor-Lange et al. [10] demonstrated that the use of the metakaolin with cement buffered the severity of retardation caused by the zinc oxide, while providing an increase in the cumulative heat released. Therefore, this study expanded upon this finding, investigating the use of zinc oxide treatment methods as a potential strategy to enhance the early hydration kinetics of cement combined with sodium montmorillonite and illite shale, to facilitate the acceptance of these SCMs in industry by combatting the problem of early strength loss.

In addition to early hydration reactivity, use of the zinc oxide and thermal treatment methods on the pozzolanic reactivity of the clays, was also investigated. Heat treatment of the clay materials in a kiln, a process known as calcination, is the most common method to influence the mineral's pozzolanic reactivity [14,15]. Calcination functionally removes the hydroxyl groups that maintain the layered crystal structure, creating a metastable amorphous silica source [4,16,17]. This amorphous silica may consume one of the primary cement hydration products, calcium hydroxide (portlandite), during the secondary pozzolanic reaction [18]. This secondary reaction often leads to increased mechanical strength of the material due to the production of the binding phase (calcium silicate hydrate) at the expense of portlandite and porosity [19–22]. Sodium montmorillonite and illite shale have a repeating triple layer structure (tetrahedral-central octahedral–tetrahedral) and contain fewer hydroxyl groups relative to the kaolinite mineral, making structural collapse due to thermal treatment less efficient [23,24], thereby reducing pozzolanic reactivity [1,25]. Therefore, this study investigated the use of thermal treatments conducted on the aforementioned SCMs at temperatures of 650 °C, 830 °C and 930 °C, coupled with the zinc oxide treatments, to enhance their pozzolanic reactivity.

To the best of our knowledge, no studies have investigated the effect of zinc oxide additions to calcined montmorillonite and illite minerals to enhance the early cement hydration kinetics or their later pozzolanic reactivity. Successful enhancement of the reactivity of non-kaolinite calcined clays and subsequent performance enhancement would enable impure, blended clay materials to become competitive SCMs for use in concrete. With widespread availability and lower cost compared to pure kaolinite, clays containing montmorillonite and illite minerals may become a competitive, more sustainable building material option. Therefore it is of great interest to investigate methods to improve the reactivity of montmorillonite and illite minerals for use as SCMs.

2. Materials and methods

2.1. Material characterization

The clay minerals used in this study include sodium montmorillonite clay (Wards Natural Science Establishment, Inc.), labeled 'M' and illite shale (Wards Natural Science Establishment, Inc.), labeled 'I'. To compare montmorillonite and illite behavior, quartz labeled 'Q' (Old Hickory, Clay World) was used as inert filler material and kaolinite, labeled 'K' (Wards Natural Science Establishment, Inc.) was used as a highly reactive pozzolan [1]. Zinc oxide (Acrōs Organics, 99%) was added to the SCMs after calcination. ASTM C150 [26] Type I Portland cement (Texas Lehigh Cement Co., processed November 2011), ASTM C109 [27] Ottawa Silica Sand (Humboldt) and deionized water were used in making pastes and mortars. Control pastes and mortars consisted of no SCM, and with or without the metal oxide addition.

The oxide composition and loss on ignition (750 °C) of the montmorillonite, illite and Portland cement, tested on a dry basis, are presented in Table 1, obtained by X-ray florescence (XRF) using

Table 1
The oxide composition of the cement, sodium montmorillonite and illite shale (mass%).

Oxide	Cement	Montmorillonite	Illite
SiO_2	20.47	62.54	63.30
Al_2O_3	5.48	19.86	17.09
Fe_2O_3	2.54	4.36	5.20
CaO	65.30	1.52	1.07
MgO	1.22	2.43	2.25
Na_2O	0.15	2.25	0.24
K_2O	0.92	0.63	5.50
TiO_2	0.24	0.18	0.81
Mn_2O_3	0.07	0.05	0.05
P_2O_5	0.23	0.06	0.13
SrO	0.08	0.04	0.01
BaO	0.04	0.02	0.05
SO_3	3.26	0.54	0.35
LOI	3.07	5.52	3.95
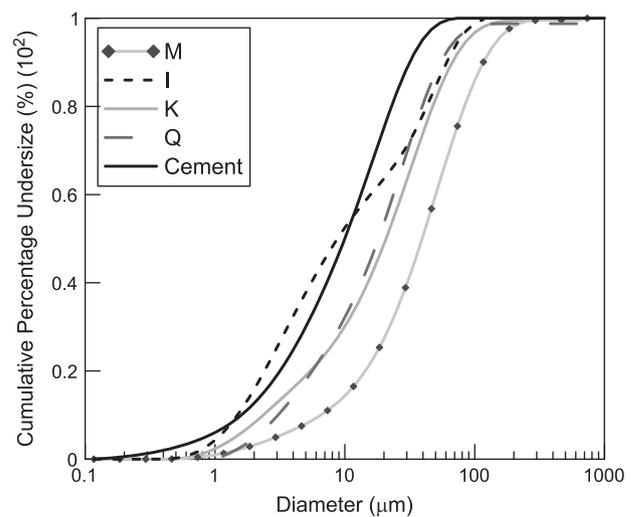
Fig. 1. The particle size distribution for montmorillonite (M), illite (I), kaolinite (K), prior to heat treatment, quartz (Q), and cement samples as a function of particle diameter.

a 1 kW Wavelength Dispersive S4 Explorer (Bruker-AXS) and following ASTM C311 [28]. XRF was performed by Wyoming Analytical Laboratories.[1]

The particle size distributions of the clay minerals, quartz, and cement were determined using a Spraytec particle size analyzer (Malvern Instruments, Inc.). Prior to testing, the illite shale was ground using an aggregate grinder (Barun Chipmunk VD67) to pass sieve No. 4 (4.75 mm diameter), then pulverized using a sand grinder (Bico Inc. Burbank, California). The resulting powder was sieved to pass 200 mesh (0.074 mm). The other constituents were purchased in powder form. Fig. 1 shows the cumulative percent undersize for montmorillonite, illite, kaolinite, quartz and cement samples. The average particle diameter (d_{50}) for the zinc oxide was 1.1 μm. The surface areas of the montmorillonite, illite, and kaolinite minerals were determined using a Micromeritics BET 2020-Analyzer as 21.07 m^2/g, 15.19 m^2/g and 29.84 m^2/g, respectively. These BET surface area results fell within the general range for kaolinite and smectite clays [29,30].

2.2. Calcination and zinc oxide treatment methods

The calcination temperatures for the montmorillonite and illite were chosen according to He et al. [25] to be 830 °C and 930 °C,

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