Research paper

Calcined kaolinite–bentonite clay blends as supplementary cementitious materials

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A B S T R A C T

In an effort to limit the environmental impact of concrete materials, there is increasing interest in the development and use of a wider range of minerals as acceptable supplementary cementitious materials (SCMs). This study investigated calcined blended clays of kaolinite and bentonite, with impurities, to assess their feasibility as SCMs. The combined use of Rietveld quantitative x-ray diffraction (RQXRD) and thermogravimetric analysis (TGA) techniques proved useful in initially gauging amorphous content post-calcination, lending insight into the relationship between calcination temperature and pozzolanic reactivity. The results demonstrated that for the calcined blended clays, as the amorphous content increased, the SCM consumed more portlandite and the compressive strength of cement-SCM mortars increased. Blends of kaolinite–bentonite clays, containing initially 35 wt.% crystalline kaolinite prior to calcination, achieved roughly 10% increase in compressive strength over samples containing 100 wt.% cement, at 90 days. Blended kaolinite SCMs may offer significant advantages as a low-cost alternative binder or cement replacement material, with the ability to maintain or enhance mechanical strength.

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1. Introduction

In an effort to limit the environmental impact of concrete materials, there is increasing interest in the development and use of supplementary cementitious materials (SCMs) (Lothenbach et al., 2011; Juenger et al., 2012). SCMs replace a portion of the cement, altering the manufacturing emissions associated with concrete (Mehta, 1998; Juenger et al., 2012). Additionally, with the cost of cement having increased by more than 150% over the past 10 years (Ahmad et al., 2011), the necessity for low-cost SCMs is warranted. Recent research has addressed the development of the pozzolanic properties of non-kaolin calcined clays, such as bentonite and illite shale, as inexpensive SCMs (He et al., 1995; Chakchouk et al., 2006; Sakizci et al., 2009; Fernandez et al., 2011; Taylor-Lange, 2013; Tironi et al., 2013; Taylor-Lange et al., 2014), with results highlighting some initial shortcomings associated with clays containing solely or primarily bentonite or illite. Calcined kaolinite is an excellent SCM, but the elimination of impurities during the manufacturing of metakaolin requires a wet beneficiation treatment, drying and grinding, all of which consume energy, produce waste, and increase the cost of the SCM. Clay deposits naturally contain a variety

of clay minerals such as kaolinite, illite, and montmorillonite and non-clay impurities such as quartz, feldspars, mica, rutile, hematite, cristobalite and calcite (Habert et al., 2008; Tironi et al., 2012). Therefore, in an effort to minimize the purification processing of clay minerals prior to use as SCMs and to enable a wider range of materials to be accepted for SCM use, this study focused on the investigation of blended clays of kaolinite and bentonite with impurities in the final product.

The kaolinite used to make metakaolin is a non-swelling, naturally hydrated, aluminosilicate, classified with a 1:1 layered structure consisting of aluminum atoms coordinated in octahedral sheets and silica atoms coordinated in tetrahedral sheets linked by oxygen and hydroxyl groups (Lombardi et al., 2002; Vejmelková et al., 2010). Bentonite clays are composed of mostly montmorillonite with companion minerals including feldspars, cristobalite and crystalline quartz. Montmorillonite is classified as 2:1 layered aluminosilicate and consists ideally of one alumina octahedral sheet placed between two silica tetrahedral sheets (Paluszkiewicz et al., 2008; Sakizci et al., 2009). Unlike kaolinite, swelling abilities of bentonite are due to isomorphous substitutions of mainly magnesium, iron, or aluminum, with hydrated sodium or calcium cations occurring in the interlayer positions (Murray, 1999; Mirza et al., 2009; Alver and Alver, 2012). The predominant cation is used in the classification of high-swelling (sodium) bentonite or low-swelling (calcium) bentonite (Mirza et al., 2009). Calcined bentonite is known to be a late-reacting pozzolan resulting in strength gain and improved

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microstructure of cement-based materials (Müller, 2001; Fernandez et al., 2011; Wong et al., 2013; Taylor-Lange et al., 2014).

Heat treatment is used to make a calcined clay pozzolan. During the heat treatment of kaolinite to form metakaolin, two hydroxyl groups, from the hydroxyl surface, join to form a water molecule leaving the once bonded oxygen as a superoxide anion (Pampuch, 1971; Maiti and Freund, 1981; Brindley and Lemaitre, 1987; Frost and Vassallo, 1996). The instabilities caused by the anion imbalance result in crystal structure collapse forming metastable, anhydrous aluminum silicates. For clays containing mostly kaolinite this mechanism leads to almost complete dehydroxylation, typically resulting in a highly reactive pozzolan. This pozzolanic reaction is such that the portlandite in hydrated cement reacts with anhydrous aluminum silicates to form calcium silicate hydrate or calcium aluminate silicate hydrate gel, strätlingite, tetracalcium aluminate hydrate, cubic hydrogarnet, among other compounds (Pera et al., 1998; Wild et al., 1998; Cabrera and Rojas, 2001; Darweesh and Nagieb, 2007; Siddique and Klaus, 2009). By proportioning the amount of SCM, which limits the strätlingite formation limit, the pozzolanic reaction can result in improved cement-based material properties including an increase in compressive strength, a decrease in material porosity and a subsequent increase in material durability and service life (Caldarone et al., 1994; Coleman and Page, 1997; Dali Bondar et al., 2011; Samet et al., 2007; Taylor-Lange et al., 2013).

Unlike kaolinite, which has a well-defined mechanism for dehydroxylation, the dehydroxylation for non-kaolinite minerals is less well known, with findings suggesting both differences (Holdridge and Vaughan, 1957; Ataie and Riding, 2013) and similarities (Brindley and Wan, 1978; Zemenova et al., 2014). Impure calcined clay behavior is complex and contingent upon the initial clay composition and each mineral's sensitivity to a given temperature. Mineralogy, low, medium or high crystal order (Ambroise et al., 1992; Bich et al., 2009), the mineral surface conditions (Frost and Vassallo, 1996), and quantity and composition of impurities also influence dehydroxylation. Therefore, clay mineral blends present a scenario where only a fraction of the total quantity may dehydroxylate, providing less amorphous content and, therefore, a less reactive pozzolan. For blended clays, selection of a suitable calcination temperature for creating a pozzolanic material becomes more challenging as the temperature interval between structural disorganization and recrystallization narrows (Habert et al., 2009).

This study is part of a larger effort to develop new, sustainable, low cost calcined clay material options, containing less kaolinite and utilize alternative minerals to expand resource selection. Two clay blends, kaolinite–calcium bentonite and kaolinite–sodium bentonite were calcined at temperatures of 650 °C, 830 °C and 930 °C, and compared with both a reactive pozzolan and a non-reactive quartz filler. Rietveld quantitative x-ray diffraction and thermogravimetric analysis (RQXRD-TGA) were used as methods to assess the effectiveness of a specific temperature at reducing clay crystallinity. RQXRD provided valuable information including the clay composition and total amorphous content following calcination. TGA provided a means to determine the degree of dehydroxylation from which the total amorphous content could be determined as a check for RQXRD. RQXRD-TGA results allowed for a suitable calcination temperature to be selected for each clay sample, validated through testing for pozzolanic behavior and compressive strength when used as SCMs. The findings will allow for a better understanding of the influence of thermal treatment on impure clay minerals and aid in the utilization of available clayey soils as potential SCMs.

2. Materials and methods

2.1. Materials and calcination

In this study, two kaolinite–bentonite clays were tested as SCMs (i) a Texas kaolinite–calcium bentonite from the Southern Clay Products quarry (Distributor: Southern Clay Products, Inc.), and (ii) a 50:50 (by

Table 1
Chemical composition and physical characteristics of the materials.

Oxides (% mass)	Cement	K	KCaB	KNaB
SiO$_2$	20.47	46.24	62.21	54.39
Al$_2$O$_3$	5.48	37.90	20.07	28.88
Fe$_2$O$_3$	2.54	0.51	3.93	2.44
CaO	65.30	0.14	1.49	0.83
MgO	1.22	0.12	2.51	1.28
Na$_2$O	0.15	0.01	2.20	1.13
K$_2$O	0.92	0.24	0.61	0.44
TiO$_2$	0.24	0.33	0.21	0.26
Mn$_2$O$_3$	0.07	0.00	0.03	0.03
P$_2$O$_5$	0.23	0.17	0.05	0.12
SrO	0.08	0.02	0.04	0.03
BaO	0.04	0.03	0.04	0.03
SO$_3$	3.26	0.06	1.25	0.30
LOI	3.07	14.22	5.38	9.87
D$_{50}$ (μm)	9.80	20.70	20.20	30.00
SSA (m^2/g)	–	21.10	34.90	25.40

mass) laboratory blended kaolinite–sodium bentonite clay, containing Georgia kaolinite and sodium bentonite from South Dakota (Distributers: Wards Natural Science Establishment, Inc.). For comparison, the kaolinite–bentonite clays were compared to a known reactive pozzolan, Georgia kaolinite (Distributer: Wards Natural Science Establishment, Inc.) and an inert filler quartz (Distributer: Clay World, Inc., manufactured at Old Hickory Clay Company). The clay nomenclature used throughout this paper is as follows: Texas kaolinite–calcium bentonite (KCaB), laboratory blended kaolinite–sodium bentonite (KNaB), Georgia kaolinite (K), and quartz (Q). When calcined, the clay name is followed by the selected calcination temperature. For example, the kaolinite–sodium bentonite calcined to 830 °C is labeled, KNaB830. Cement pastes and mortars containing 15 wt.% substitution of the aforementioned SCMs were created when testing the pozzolanic reactivity and compressive strengths. For these samples Type I portland cement (ASTM C150, 2012) (Texas Lehigh Cement Co., processed November 2011), Ottawa Silica Sand (ASTM C109, 2005) (Humboldt) and deionized water were used. In addition, control samples (labeled 'control') were created and included pastes and mortars containing no SCM.

The cement and clay mineral elemental compositions expressed as oxides using x-ray fluorescence (XRF) and loss of ignition (LOI) are presented in Table 1. XRF samples were tested using a 1 kW Wavelength Dispersive S4 Explorer (Bruker-AXS), with the XRF and LOI experiments performed by Wyoming Analytical Laboratories.[1] The particle size distributions for the clays, quartz and cement were determined using laser diffraction of suspended particles in isopropyl alcohol, with a Spraytec particle size analyzer (Malvern Instruments, Inc.) (Table 1). The specific surface areas of the clay samples were determined using a Micromeritics BET 2020-Analyzer (Table 1), with sample outgassing at a temperature of 300 °C and at 666 hPa (500 mm HG) sustained for a 6 hour period. The cement Blaine fineness (ASTM C204, 2007) was tested experimentally using an air permeability apparatus (Humboldt), resulting in an average of 386 m^2/kg.

Heat treatment of clay materials in a kiln, a process known as calcination, is the most common method to influence the mineral's pozzolanic reactivity by functionally removing the hydroxyl groups that maintain the layered structure, creating metastable poorly-crystalline anhydrous aluminum silicates. A review of selected calcination temperatures suggested a temperature range of 600 °C to 850 °C for kaolin and 700 °C to 950 °C for bentonite, as ideal in creating a pozzolan (Rashad, 2013). Based upon this collective review, each clay blend was subjected to calcination at 650 °C, 830 °C and 930 °C. The calcination protocol included: (i) increasing the temperature from 23 °C to the specific calcination temperature at a rate of 5 °C/min, (ii) maintaining the specific