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Research paper

Characterization of Florida kaolin clays using multiple-technique approach

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ABSTRACT

Kaolinite content of 10 raw Florida clays examined in this study was determined to be in the range of 70 to 90 mass %. This kaolinite content is sufficiently high for production of a potentially reactive pozzolanic material. The majority of the clays were at least partially disordered, which also indicates good pozzolanic activity of these materials after calcination. A good fit of the collected X-ray diffractograms during Rietveld refinement was obtained by using a combination of kaolinite, nacrite and dickite structures to allow modeling of stacking faults in kaolinite, adjusting for Fe^{3+} substitution and refining atomic coordinates. The results of kaolinite quantification were similar to those obtained by thermogravimetric analysis, which validates the proposed approach. Stoichiometric calculation also provided comparable results for all the clays, except for one sample where large overestimation of kaolinite content compared to X-ray diffraction and thermogravimetric analysis was observed. It was concluded that Florida clays present a promising potential source of supplementary cementitious materials for production of sustainable concrete.

1. Introduction

As a number of articles pointed out, the demand for concrete around the world is growing, and so does the pressure on the concrete industry to reduce CO_2 emissions and make concrete more eco-friendly (Cancio Díaz et al., 2017; Patel and Martirena Hernández, 2013; Sánchez Berriel et al., 2016; Scrivener, 2014; Zhou et al., 2017). While the supply of by-products that can be used as supplementary cementitious materials (SCM) is globally limited, kaolin is an abundant resource that can potentially be used as an SCM (Scrivener, 2014). The use of metakaolin (MK) obtained from the calcination of high-purity kaolins has been shown to be very effective in improving concrete strength and durability (Al-Akhras, 2006; Ambroise et al., 1994; Aquino et al., 2001; Batis et al., 2005; Coleman and Page, 1997; Courard et al., 2003; He et al., 1994; Poon et al., 2001; Ramlochan et al., 2000). However, since deposits of high-purity kaolin are rare, the cost of MK is high due to additional separation and processing requirements. Recently, there has been a lot of interest in using calcined naturally occurring lower kaolinite content (lower purity) clays as SCM. A number of studies have been conducted at various locations around the world on the suitability of local raw clays for SCM production (Almenares Reyes et al., 2018; Bediako et al., 2017; Chakchouk et al., 2006; Singh and Garg, 2006; Souri et al., 2015; Tironi et al., 2014a). However, the potential for utilization of low-purity kaolins in the United States has not been widely explored. The goal of this study was to characterize the raw kaolins in Central Florida in order to determine if they may be suitable for calcination and potential use as SCM.

Several parameters have been reported to affect the reactivity of calcined low-kaolinite content clays. The pozzolanic reactivity is known to be affected by the chemical and mineralogical characteristics of the raw clay and the calcination process. Raw clay's properties include kaolinite content and kaolinite degree of order/disorder while the calcination process controls the degree of dehydroxylation and particle size distribution (Bich et al., 2009; Granizo et al., 2000; Hollanders et al., 2016; Kakali et al., 2001; Krishnan and Bishnoi, 2015; Murat, 1983; Tironi et al., 2012). Commonly used techniques for the determination of the structural disorder are Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), while thermogravimetric analysis (TGA) or stoichiometric calculations using chemical oxide composition are typically used for kaolinite content quantification (Avet et al., 2016; Bich, 2005; Tironi et al., 2014b; Tironi et al., 2012). Both TGA and stoichiometric calculation rely on an ideal chemical formula for kaolinite and are not able to quantify all the phases present in the sample. Several researchers have noted that the presence of other minerals, besides kaolinite, can affect the reactivity of the calcined material (Ghorbel and Samet, 2013; Haldar et al., 2018; Zunino and Scrivener, 2018). While XRD is commonly used for identification of minerals present in raw clays prior to calcination, the majority of the studies do not utilize XRD with Rietveld refinement for mineral quantification, and those that do, regard the results of Rietveld

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analysis as semi-quantitative (Claverie et al., 2015). XRD analysis is more comprehensive, but is known to be challenging because of the variable degree of disorder that can be present in kaolinite. This raises a question of how kaolinite quantification results compare between these techniques.

Rietveld refinement has been shown to provide reliable quantitative results for anhydrous and hydrated cement as well as SCM (Aranda et al., 2012; Le Saoût et al., 2011; Singh and Subramaniam, 2016; R. Snellings et al., 2014a; Snellings et al., 2014b; Stetsko et al., 2017; Wilson et al., 2014). However, refinement and quantification of raw clays is more complicated due to the varying degree of disorder of the kaolin-group minerals. As the degree of disorder increases, reflections observed in the XRD diffractogram of kaolinite become broader and more asymmetric (Brigatti et al., 2006), making it increasingly challenging to obtain a good fitting through Rietveld refinement.

This disorder can arise from the presence of isomorphous substitutions or the existence of stacking faults in the kaolinite structure (Brigatti et al., 2006). Kaolinite can have a variable amount of Al^{3+} substitution in its crystal structure by Fe^{3+}, Mg^{2+}, Ti^{4+}, and V^{3+} (Brigatti et al., 2006), which causes a departure from the ideal chemical formula of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) thus affecting its quantification (Prandel et al., 2017; Prandel et al., 2015; Rengasamy et al., 1975). In terms of the effect of isomorphous substitutions on the degree of disorder, Brindley et al. (1986) reported a general trend between the total Fe_2O_3 content in Georgia kaolins and their crystallinity. The degree of kaolinite disorder increased with increasing Fe_2O_3 content. Prandel et al. (2017) also pointed out that substitution of Fe^{3+} for Al^{3+} results in an increase in the unit cell volume of kaolinite.

With respect to stacking faults, Brigatti et al. (2006) stated that kaolin group minerals have a tendency to form "a wide variety of ordered and disordered polytypes as well as twins," where several types of stacking can be observed in the same material. Russell and Fraser (1994) suggested that disorder could also be due to "small amount of dickite- and/or nacrite-like stacking in the kaolinite structure." Dickite- and nacrite-like stacking in poorly crystalline kaolinites has been reported by Prost et al. (1989).

While commercial software commonly used in the cement industry for Rietveld refinement is able to model substitutions in the kaolinite structure, it is not currently able to model stacking faults. Although several software packages, an overview of which can be found in (Dumon and Van Ranst, 2016), have been developed to deal with the challenges of modeling XRD diffractograms for clay mineral structures, they are not used in the cement industry. Using the idea of Plançon et al. (1989, 1988) that a combination of kaolinite structures is needed for proper fitting of X-ray diffractograms of disordered kaolinites, this study presents the results of mineralogical characterization of raw clays where kaolinite content was quantified with XRD-Rietveld analysis using a combination of kaolinite polytype structures. The results were validated using the conventional TGA and stoichiometric calculations.

2. Materials and methods

Samples of overburden material were obtained from various clay mines in Central Florida for this study. This overburden is typically stockpiled on site and not used, but could be potentially calcined to produce a pozzolanic material. The field samples were dried in a laboratory box furnace, model BF51894C-1, manufactured by Lindberg/MPH at 110 °C until a constant mass was achieved and wet-sieved on the 45 μm sieve to remove the sand fraction. The material finer than 45 μm was used in this study.

The 10 raw clay samples obtained in this manner were oven dried again, after wet-sieving, at 110 °C until constant mass. The elemental oxide composition of the clays was determined using X-ray fluorescence (XRF) according to ASTM C114 (2013). Clay mineralogy was studied using FTIR, XRD with Rietveld analysis and TGA.

A Nicolet iS50 FTIR spectrometer was used to conduct mid-IR spectral scanning of raw clay samples over the range of wavenumbers from 400 to 4000 cm^{-1}. Prior to analysis, samples were lightly ground using a mortar and pestle and sieved again through the 45 μm sieve. This was done to minimize the scattering, distortion and peak broadening of IR radiation due to larger-sized particles that may have resulted from agglomeration during drying. Samples were scanned using the attenuated total reflection (ATR) technique at room temperature using 50 scans per sample with a resolution of 0.241 cm^{-1}.

XRD measurements were conducted in accordance with ASTM C1365 (2016). XRD scans were collected using the Phillips X'Pert PW3040 Pro diffractometer equipped with X'Celerator Scientific detector and a Cu-Kα X-ray source. Tension and current were set to 45 kV and 40 mA respectively; 5 mm divergence and anti-scatter slits were used in the automatic mode. Scans were collected for the 4–70° 2θ angular range, and the sample was rotated at 30 rpm during data collection. The external standard method was selected for determining the amorphous/unidentified content of the raw clay samples. Standard Reference Material 676a (corundum) obtained from the National Institute of Standards and Technology (NIST) was used as the external standard. The mass absorption coefficient (MAC) of corundum was

Table 1
Oxide chemical composition of the clay fraction.

Clay ID	A	B1	B2	B3	B4	C	D	F	E	G
Analyte	mass %									
SiO_2	45.99	42.52	43.32	37.07	41.09	34.05	38.47	42.63	43.67	43.84
Al_2O_3	37.7	35.88	34.33	33.11	33.31	33.13	31.29	34.94	30.08	32.52
Fe_2O_3	0.9	1.63	2.99	10.2	5.35	6.58	8.91	4.55	6.52	5.48
CaO	< 0.01	0.05	< 0.01	0.02	0.17	1.1	0.12	< 0.01	0.37	< 0.01
MgO	0.16	0.39	0.24	0.34	0.33	0.29	0.49	0.21	0.28	0.22
SO_3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.06	< 0.01	< 0.01	0.02	< 0.01
Na_2O	0.05	0.03	0.04	0.05	0.05	0.23	0.05	0.02	0.02	0.02
K_2O	0.24	0.18	0.18	0.15	0.15	0.24	0.23	0.12	0.17	0.3
TiO_2	0.27	1.52	2.52	1.5	1.69	1.05	1.39	1.13	1.76	1.18
P_2O_5	0.05	0.66	0.4	0.77	1.12	5.39	1.26	0.21	0.27	0.81
Mn_2O_3	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	0.01	< 0.01	0.01	0.01
SrO	< 0.01	0.12	0.08	0.12	0.18	0.49	0.16	0.04	0.03	0.23
Cr_2O_3	< 0.01	0.02	0.01	0.03	0.02	0.043	0.03	0.02	0.02	0.01
ZnO	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
BaO	< 0.01	0.07	0.06	0.07	0.1	0.25	0.09	0.01	0.02	0.16
L.O.I (950 °C)	14.17	16.14	15.06	16.52	15.56	16.33	16.6	15.39	15.66	14.41
Total	99.53	99.21	99.23	99.95	99.13	99.23	99.08	99.27	98.9	99.21
$SiO_2 + Al_2O_3 + Fe_2O_3$	85.6	80.0	80.6	80.4	79.8	73.8	78.7	80.3	82.1	81.8
kaolinite content	95.4	90.8	86.8	83.7	84.3	83.8	79.1	76.1	88.4	82.3