



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: [www.elsevier.com/locate/clay](http://www.elsevier.com/locate/clay)

Research paper

## Pozzolanic reactivity of pure calcined clays

Sofie Hollanders<sup>a,\*</sup>, Rieko Adriaens<sup>a</sup>, Jørgen Skibsted<sup>b</sup>, Özlem Cizer<sup>c</sup>, Jan Elsen<sup>a</sup><sup>a</sup> Division Geology, Department of Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E, 3001 Leuven, Belgium<sup>b</sup> Department of Chemistry, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark<sup>c</sup> Building Materials and Building Technology, Department of Civil Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium

### ARTICLE INFO

#### Article history:

Received 3 April 2016

Received in revised form 1 August 2016

Accepted 1 August 2016

Available online xxxx

#### Keywords:

Calcined clay

Metakaolin

Amorphous material

Pozzolanic reactivity

Supplementary cementitious materials

### ABSTRACT

Eight reference clay samples, 4 kaolinitic, 3 smectitic and 1 illitic clay, were purified and thermally treated in order to determine their pozzolanic reactivity in cementitious materials. The clays were calcined in a fixed-bed electrical furnace at temperatures ranging between 500 °C and 900 °C. Both raw and calcined clays were characterized by ICP-OES, XRD and BET techniques. Their pozzolanic reactivity was evaluated with clay-lime pastes after 3, 7, 14, 28, 56 and 90 days using thermogravimetry (TGA). The results indicate that all kaolinitic clays are highly reactive at a broad range of firing temperatures (500–900 °C). The degree of ordering of the raw kaolinite influences the optimal activation temperature and the rate of the calcined clay-lime reaction. The smectitic clays possess a clear optimal calcination temperature of 800 °C. Ca-rich smectites are proven to be somewhat more reactive than Na-rich smectites. However, even at 800 °C, its reactivity is significantly smaller compared to kaolinite. Hectorite and illite calcined at an optimal temperature of 800 and 900 °C, respectively, exhibit poor pozzolanic reactivity.

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## 1. Introduction

Portland cement-based materials such as concrete are nowadays the most widely used construction materials. Due to a global production of cement of 4.2 Bt/y and enormous quantities of concrete produced and consumed globally (20–35 Bt annually), the cement industry accounts for around 4% of the total global greenhouse gas emissions and up to 8% of the total global anthropogenic CO<sub>2</sub> emissions (Barcelo et al., 2013; Damtoft et al., 2008). Blending cement with supplementary cementitious materials (SCMs) is considered to be one of the most effective ways of reducing the environmental impact of the cement industry (Gartner, 2004; Juenger and Siddique, 2015; Lothenbach et al., 2011). Conventional and high-quality SCMs like granulated blast furnace slag from iron production and fly ash from coal combustion of electricity production are being utilized completely (Snellings et al., 2012). Nevertheless, there is a shift and interest to search for alternative SCM sources due to supply-and-demand concerns in the future. One of the most promising alternative sources are calcined clays since they have not yet reached their full potential as cement replacement and clay is an abundant and widespread material which can lower transportation costs (Schneider et al., 2011). The production process of calcined clay is less energy intensive due to lower firing temperatures and the absence of a decarbonation reaction. The calcination of clays occurs in the temperature range of 600 and 850 °C, and results in the

dehydroxylation of the clay whereby an amorphous phase is formed. The Si and Al in this phase can chemically react at ambient temperatures with Ca(OH)<sub>2</sub> (portlandite), which is formed during cement hydration, in the presence of water to form compounds that possess cementitious properties.

Several studies have already demonstrated the effectiveness of calcined clays, particularly for kaolinitic clays to produce metakaolin with increased pozzolanicity, i.e. reactivity with portlandite (Al-Rawas and Hago, 2006; Fernandez et al., 2011; He et al., 1994; Sabir et al., 2001; Tironi et al., 2012). However, calcined clays other than metakaolin are hardly used as SCMs due to the complexity of clay minerals and ignorance of the underlying reaction mechanisms. Hence this study investigates the potential use of calcined clays from a mineralogical point of view by linking the characteristics of the untreated clays to the pozzolanic reactivity of the calcined clays. Since it is of key importance to understand the origin of the pozzolanic reactivity and determine the main parameters that influence the reactivity, pure reference clays (kaolinitic, smectitic, illitic) with differences in degree of ordering are used to avoid interference of impurities. Eight clays were selected to have an optimal range of clay minerals, variable degree of ordering and differences in the predominant cations.

## 2. Materials and methods

Eight fairly pure clays, four kaolinitic clays, with differences in degree of ordering, three smectitic clays and one illitic clay were selected for this study (Table 1). Kaolinite (KGA-1 and KGA-2), Na-

\* Corresponding author.

E-mail address: [sofie.hollanders@kuleuven.be](mailto:sofie.hollanders@kuleuven.be) (S. Hollanders).

**Table 1**  
Characteristics of the clays before and after calcination, Hinckley index (HI), ordering ( $P_0$ ) and BET specific surface area (SSA).

Clay	Ordering HI	Ordering $P_0$	Ordering	SSA (m <sup>2</sup> /g) raw	SSA (m <sup>2</sup> /g) Fired at 800 °C	
K1	Capim	0.85	1.580	High	8.86	9.54
K2	KGA-1	0.74	1.360	High	7.02	7.51
K3	KGA-2	–	0.380	Medium	19.27	19.71
H1	Hal.	–	–	Low	34.38	32.62
S1	SWy-1	–	–	–	23.36	4.19
S2	SAz-1	–	–	–	87.26	4.32
S3	SHCa-1	–	–	–	123.46	1.47
I1	lmt-1	–	–	–	19.91	0.79 (900 °C)

montmorillonite (SWy-1), Ca-montmorillonite (SAz-1), hectorite (SHCa-1) and illite (lmt-1) were obtained from the Clay Minerals Society repository. The kaolinite Capim and halloysite were supplied by an industrial mineral producer. However, these reference clays are natural materials and as such, they are not entirely pure as proven by previous studies (Chipera and Bish, 2001). Impurities of titanium-oxides, quartz, feldspar and calcite may influence the activity of the clay. The smectitic and illitic clays, which contained the highest amount of impurities (5–50%) according to the bulk mineralogical analyses of the raw clays, were therefore first purified according to the Jackson procedure (Jackson, 1975). Afterwards for the smectitic clays the fraction <2 µm was separated by centrifugation to obtain a smectite containing <2% impurities. Since the illitic clay mainly contained coarse illite (>2 µm) the fraction <63 µm was used in order to limit the amount of impurities to 8%.

The mineralogical composition of the unfired (kaolinites, purified illite <63 µm and purified smectites <2 µm) and calcined clays was determined with quantitative X-ray diffraction. The samples were mixed with 10% ZnO as internal standard and wet ground in a McCrone Micronizing mill, following the standard procedure of Środoń et al., 2001. The XRD diffraction spectra were recorded on a Philips PW 1830 diffractometer in Bragg-Brentano  $\theta$ -2 $\theta$  setup equipped with a proportional detector type PW3011/00 and CuK $\alpha$  radiation in the range of 5 to 65° 2 $\theta$  at 40 kV and 20 mA. The step size was 0.02° 2 $\theta$  with a counting time of 2 s. Mineral identification and quantification were performed with X-ray Viewer and QUANTA full-pattern fitting software (© Chevron ETC). Oriented slides of the purified samples <2 µm were prepared by dissolving 160 mg of the extracted clay fraction with 4 ml deionised water, followed by an ultrasonic treatment. The sedimentation slides were recorded under both air-dry and ethylene glycol saturated conditions with step size of 0.02° 2 $\theta$ , counting time of 1 s and a range of 2 to 47° 2 $\theta$ .

To clarify the difference upon calcination between the smectitic clays S1 and S2, the coordination of Si and Al was studied by MAS NMR. The 29Si MAS NMR spectra were recorded on a Varian INOVA-400 spectrometer (9.39 T) equipped with a homebuilt CP/MAS NMR probe for 7 mm outer diameter zirconia (PSZ) rotors. The sample spinning frequency was 6.0 kHz, the pulse width 3.0 µs (~45°), the relaxation delay 15 s, and typically 5600 scans was acquired. The 27Al MAS NMR spectra were obtained on a Varian DirectDrive VNMR-600 (14.09 T) spectrometer using a homebuilt CP/MAS probe for 4 mm outer diameter zirconia (PSZ) rotors. A spinning speed of 13.0 kHz, single-pulse excitation with a pulse width of 0.5 µs a relaxation delay of 2.0 s, and typically 4096 scans were used.

FTIR analysis was carried out on KBr-pellets using a Nicolet™ 760 spectrophotometer and a spectral range from 400 to 4000 cm<sup>-1</sup>. A DTGS-KBr detector was used and the resolution was 4 cm<sup>-1</sup> with a co-addition of 100 scans. The bulk chemical analysis of the untreated samples was measured by a Varian 720ES ICP-OES. A lithium metaborate fusion was used as dissolution method. The specific surface area was obtained by the Brunauer-Emmer-Teller (BET) method. The samples were pretreated by heating them to 110 °C for 24 h in a continuous N<sub>2</sub> gas flow. The measurement was performed on a Micrometrics

Tristar 3000 using N<sub>2</sub> as an adsorbate. Raw clays were thermally treated in a laboratory programmable fixed-bed furnace at different temperatures in the range of 500–900 °C. In this process, the heating rate was set at 10 °C/min and a residence time of 2 h was used at the maximum temperature. After gradually cooling, the calcined clays were ground in a McCrone Micronizing mill ® for 5 min to reduce the sintering effect of the calcination process.

The pozzolanic reactivity of the calcined samples was evaluated by means of the chapelle test, based on the French norm (French norm metakaolinite NF-P 18-513, Annexe A) to determine the reactivity of metakaolin, and by thermal analyses of calcined clay-lime mixtures. According to the chapelle test, 1.0 g ground calcined clay is blended with 2.0 g CaO and 250 ml distilled water and heated to 85 °C for 16 h. The non reacted lime was determined by means of sucrose extraction and titration with 0.1 N HCl(aq.). The result is then expressed in mg Ca(OH)<sub>2</sub> fixed by the calcined clay.

The pozzolanic reactivity and the reaction over time have been studied in more detail by preparing calcined clay-lime mixtures. The mixtures of calcined clay and hydrated lime were dry-mixed in a 2:3 weight ratio using a Turbula mixer for 4 h. Distilled water was added to obtain a water/solid ratio of 1:1. The mixtures were stored in sealed containers in a climatized room (20 °C, 90% humidity). After 3, 7, 14, 28, 56 and 90 days the pastes were vacuum dried at 0.03 mbar for 2 h to stop the hydration reactions according to the procedures described in Knäpen et al., 2009. The dried samples were then stored in a desiccator until measurement. The portlandite consumption over time was monitored by thermogravimetric analysis (TGA), by calculating the weight loss in the 350–600 °C range by linear extrapolation. This method, proposed by Taylor, 1997, is expressed relative to the dry weight and is corrected for the background mass loss. For these measurements a Netsch STA 409PC instrument with simultaneous TGA and DSC recordings was used. The sample was heated in Al<sub>2</sub>O<sub>3</sub> crucibles from 25 °C to 1000 °C with a heating rate of 10 °C/min in a N<sub>2</sub> atmosphere with a 60 ml/min flux.

### 3. Results and discussion

#### 3.1. Characterization of clays

##### 3.1.1. Chemical composition

The bulk chemical composition of the unfired clays (kaolinites, purified illite <63 µm and purified smectites <2 µm) is reported in Table 2. Kaolinitic clays contain a high alumina content up to 40 wt.%, with Si/Al ratio of 1.16, calculated based on SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The 2:1 clays S1, S2 and I1 show a higher Si/Al ratio of on average 3 due to the lower amount of alumina present in these clays. Smectitic clay S3 contains only some traces of alumina, since the dominant cation occupying the octahedral position is magnesium, resulting in a clay that contains >20 wt.% Mg.

##### 3.1.2. XRD analysis

XRD patterns of the unfired kaolinites, the purified illite, the smectite clay fraction and of the calcined clays are presented in Fig. 1. The kaolinitic clays, K1 and K2, indicate strong reflections of kaolinite and a poor

**Table 2**  
Bulk chemical composition and Si/Al ratio of the kaolinites, purified illite (<63 µm) and purified smectitic clay fraction, calculated based on SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, of the unfired clays.

% weight	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	LOI	Si/Al
K1	45.82	38.79	0.56	0.01	0.05	0.03	0.20	0.42	14.12	1.18
K2	46.24	40.03	0.27	0.03	0.04	0.03	0.02	1.59	11.76	1.16
K3	44.77	38.45	1.12	0.02	0.06	0.05	0.01	2.23	13.29	1.16
H1	44.85	38.62	0.17	0.04	0.04	n.d.	n.d.	0.01	16.27	1.16
S1	58.03	19.60	4.08	0.02	2.36	0.04	3.04	0.09	12.74	2.96
S2	57.72	16.92	1.49	3.31	5.82	0.03	0.06	0.22	14.41	3.41
S3	52.62	0.46	0.34	2.28	23.67	0.09	0.15	0.02	20.48	/
I1	52.62	22.63	6.64	0.12	2.32	7.72	0.48	0.78	6.68	2.32

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