



## Research paper

# Characterisation of calcined raw clays suitable as supplementary cementitious materials



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## ABSTRACT

The potential use of two raw clays (Clay A: kaolin; Clay B: calcareous montmorillonite) as supplementary cementitious material (SCM) in blended cements was investigated. Cement replacement in mortars by 20% calcined Clay A and Clay B resulted in a considerable 28 day compressive strength improvement. The pozzolanic reactivity of Clay A and B is explained by characterisation of the structural changes upon calcination with XRD, ICP-MS, FT-IR, <sup>27</sup>Al NMR, Mössbauer spectroscopy and SEM. At the temperature giving highest pozzolanic reactivity, kaolinite and montmorillonite were completely dehydroxylated, while calcite from Clay B was not completely decomposed. FT-IR, <sup>27</sup>Al NMR and Mössbauer spectroscopy revealed considerable structural deformations of kaolinite in Clay A and montmorillonite in Clay B resulting in an amorphous, reactive state. Oxidation of iron in Clay B during calcination contributed to strong distortions of the octahedral sheet in the montmorillonite structure. Additionally, the formation of a glass phase due to reaction of coccoliths (CaCO<sub>3</sub>) and montmorillonite was observed.

## 1. Introduction

Cement production is a highly energy intensive process, contributing to about 5–7% of the worldwide carbon dioxide emissions (Ernst Worrell et al., 2001; Mehta, 1999). The biggest step towards reducing CO<sub>2</sub> emissions in the short and long term can be achieved by replacing parts of the cement clinker with supplementary cementitious materials (SCMs) (Damtoft et al., 2008; Ernst Worrell et al., 2001; Schneider et al., 2011). In the long run, the right choice of SCM's is mainly a question of availability (Gartner, 2004), as well as pozzolanic reactivity. Natural pozzolans, especially raw clays are widespread and the most promising source of SCM to serve the cement industry sufficiently for a more sustainable future. Since there is a growing interest of applying calcined clays in the construction industry, many countries started to evaluate the pozzolanic potential of local clay deposits (Al-Rawas et al., 2001; Alujas et al., 2015; Aras et al., 2007; Berriel et al., 2016; Beuntner and Thienel, 2015; Chakchouk et al., 2006; Huenger et al., 2018; Shayma'A et al., 2012; Tironi et al., 2012). Calcining raw clays at temperatures between 600 and 800 °C leads to the formation of an active metastable state with high pozzolanic activity (Fernandez et al., 2011). The pozzolanic reaction of calcined clays and calcium hydroxide during cement hydration results in the formation of more

binding phases, reducing the pore space in the cement paste (Davis, 1950; Massazza, 2002; Sabir et al., 2001). This can also lead to improved compressive strength development. The optimum calcination temperature to reach maximum pozzolanic activity depends on the mineralogy of the clays (He et al., 1994, 1996; He et al., 1995). A complete removal of hydroxyl groups upon calcination results in a collapsed and disarranged metastable structure with low crystallinity (Jeans and Bergaya, 2008; Sabir et al., 2001). In a comparative study of calcined illite, montmorillonite and kaolinite using X-Ray diffraction (XRD) and nuclear magnetic resonance spectroscopy (Al NMR), it could be shown that kaolinite undergoes the most significant structural changes upon calcination (Fernandez et al., 2011). Raw clays are often polymineral materials making it difficult to find the optimum calcination temperature. If raw clays are heated at too high temperatures (> 900 °C) recrystallization can take place, resulting in a decreased reactivity.

Ternary blends of cement, metakaolin and limestone have been investigated by many authors (Antoni et al., 2012; Avet and Scrivener, 2018a, b; Bishnoi and Maity, 2018; Cancio Díaz et al., 2017; Favier et al., 2018; Kunther et al., 2015; Nied et al., 2015; Scrivener et al., 2017; Tironi et al., 2015). However, the role of calcium carbonate in raw clays (before calcination) without kaolinite has been paid little

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**Table 1**  
Mineralogical composition of Clay A and B before calcination.

Phase (mass%)	A	B
Kaolinite	47	8
Montmorillonite	—	54
Illite	—	4
Muscovite	2	—
Quartz	18	4
Orthoclase	34	—
Calcite	—	25
Siderite	—	3
Pyrite	—	1

attention to. The present authors have previously published extensive studies (Danner et al., 2015; Danner et al., 2012b, 2013; Justnes et al., 2011; Østnor et al., 2015) of what was called calcined “marl” for simplicity, but actually should be categorized as “calcareous mudstone” being a montmorillonite containing 25% calcium carbonate. It was shown that replacing cement with up to 50% “calcined marl” can lead to higher or equal 28 day compressive strength in mortars.

In this paper, the pozzolanic reactivity of a kaolin is compared to a calcareous montmorillonite. To explain the pozzolanic reactivity, structural changes upon heating were investigated by Fourier transformed infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (Al-NMR) and Mössbauer spectroscopy. Phase changes and microstructural changes were documented by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Additionally, changes in specific surface area (BET), and ion release in an approximated concrete pore water was investigated by inductively coupled plasma mass spectrometry (ICP-MS).

## 2. Materials

Table 1 shows the phase composition of the Clay A and B and Table 2 shows the chemical composition of Clay A and B calcined at 800 °C. The main mineral phases of Clay A are kaolinite, quartz and orthoclase. Clay B contains high amounts of montmorillonite and 25% calcite. Clay B is a tertiary sediment and was deposited between the middle and late Eocene in a marine depositional environment (Grønbech et al., 2010). The calcite content derives to a large portion from coccoliths (Okkels and Juul, 2008). Pyrite was detected in Clay B, however, the chemical composition showed no SO<sub>3</sub>. Under the SEM the pyrite distribution appeared only very localised in form of pyrite framboids (Fig. 10). The non-homogeneous distribution of pyrite in Clay B might be a reason why SO<sub>3</sub> was not detected with XRF in the analysed sample.

The cement used in mortar tests was Norcem Standard (CEM I 42.5 R) and the chemical composition is given in Table 2.

**Table 2**  
Chemical composition of Clay A and B calcined at 800 °C and the cement used in mortar tests.

Oxide (%)	A	B	Cement
SiO <sub>2</sub>	60.6	48.7	19.9
Al <sub>2</sub> O <sub>3</sub>	30.0	17.8	4.8
Fe <sub>2</sub> O <sub>3</sub>	3.4	10.4	3.3
CaO	0.1	13.8	61.9
K <sub>2</sub> O	3.2	2.4	1.0
Na <sub>2</sub> O	—	0.7	0.5
MgO	0.4	2.8	2.7
MnO	0.0	0.2	—
P <sub>2</sub> O <sub>5</sub>	0.10	0.2	0.2
TiO <sub>2</sub>	0.4	1.0	—
SO <sub>3</sub>	—	—	3.3
Total	98.2	98.0	97.6
LOI	1.8	2.0	2.4

For ICP-MS investigations, an alkaline solution of pH 13.2 and a KOH:NaOH ratio of 2:1 was prepared. The alkaline solution is an approximated pore water based on analyses from the water of fresh paste from CEM I used in Norway. KOH and NaOH was chosen to achieve a pH value > 13, representative for concrete pore solution (Moreno et al., 2004; Williamson and Isgor, 2016).

## 3. Methods

### 3.1. Production of calcined clays

The thermal treatment of Clay A and B was executed at IBU-tec advanced materials AG (Weimar, Germany), using a direct natural gas heated rotary kiln. The kiln is designed for a continuous thermal treatment and was used to simulate trials under industrial conditions. The feed rate was 30 kg/h and the residence time in the kiln was 45 min. Clay A was calcined between 700 and 800 °C as the highest pozzolanic reactivity of calcined kaolinite can be expected in this temperature range. Clay B was calcined at temperatures between 700 and 1000 °C in steps of 50 °C, as the temperature range of highest pozzolanic reactivity was unknown. The milling of the calcined clay lumps produced at IBU-tec was performed at UVR-FIA GmbH (Freiberg, Germany). The material was pre-crushed in a laboratory hammer mill equipped with a 1.6 mm grid applying a circumferential speed of 33 m/s, to obtain a material with d<sub>95</sub> = 1 mm. The finish grinding to a d<sub>50</sub> < 10 µm (determined with laser granulometry) was performed with a discontinuous drum mill.

### 3.2. Quantitative mineralogical analysis of the raw clays by X-ray diffraction (XRD)

Bulk mineralogy of Clay A and B was performed on dried and ground samples using the back-loading technique. Followed by that, the ≤ 2 µm fraction (clay fraction) was separated from the bulk sample by means of sedimentation. The ≤ 2 µm fraction was smeared on a glass plate and dried in air. The clay fraction was investigated under three different conditions (a-c); a: untreated, b: after treatment with ethylene glycol vapours in a desiccator for 24 h at 60 °C, c: after heating at 500 °C for 1 h. For analysis, a PAN Analytical X'Pert Pro MPD equipped with a X'Celerator RTMS detector, an automatic divergence slit and a Cu-K < alpha > X-ray source was used. The samples were measured from 2 to 65° 2θ using a step size of 0.0170° 2θ and a step time of 20 s. Data was collected at 45 kV and 40 mA. More details on the procedure of quantitative mineralogical analysis can be found in (Nielsen, 1994; Nielsen et al., 1989).

### 3.3. X-ray fluorescence analysis (XRF)

XRF analysis was performed with a Bruker AXS S8 Tiger WDXRF equipped with a 4 kW generator. Dried and powdered clay samples were ignited at 850 °C. Then 0.5 g of the dried clay sample was added to 5.0 g of a 2:1 mix of lithium- tetraborate and metaborate and 60 µg of lithium iodide. The mixture was fused in a Pt crucible and moulded to a glass disk.

### 3.4. Compressive strength of mortars

Mortars were prepared by substituting Portland cement (PC) with 20% calcined Clay A and B. The mixing procedure was according to the Norwegian Standard CEN - EN 196-1, (2005). The water to binder ratio (w/b) was held constant at 0.5 in all mortar mixes. In mortars with calcined Clay A and B, this was achieved by adding superplasticizer (Dynamon SP 130, Rescon Mapei) with about 0.3% by dry weight of mortar. The consistency of fresh mortar was determined using a flow table and the flow was within ± 5% of the reference mortar. The mortar mixes were cast in three 40 × 40 × 160 mm molds and stored in

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