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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 characterization of the structural changes upon calcination with XRD, ICP-MS, FT-IR, 27Al-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, 27Al-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 (CaCO₃) and montmorillonite was observed.
Key words: pozzolan, cement, coccolith, Mössbauer spectroscopy

Highlights:

- Calcination of raw calcerous montmorillonite can provide a reactive pozzolanic source for environmentally friendly binders with improved compressive strength.
- Oxidation of Fe$^{2+}$ to Fe$^{3+}$ in montmorillonite leads to structural disordering and thus to a higher pozzolanic reactivity.
- Finely intermixed coccoliths in montmorillonite enable the formation of a reactive glass.
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$_2$ 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 600-800°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 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-NNR) 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 SO₃. Under the SEM the pyrite distribution appeared only very localised in form of pyrite framboids (Figure 10). The non-homogeneous distribution of pyrite in Clay B might be a reason why SO₃ 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. 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 700-800°C as the highest pozzolanic reactivity of calcined kaolinite can be expected in this temperature range. Clay B was calcined at temperatures between 700-1000°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 \( d_{50} = 1 \) mm. The
finish grinding to a \( d_{50} < 10 \) 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 \( \leq 2 \) µm fraction (clay fraction) was separated from the bulk sample by means of sedimentation. The \( \leq 2 \) 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 2-65° 2\( \theta \) using a step size of 0.0170° 2\( \theta \) and a step time of 20 sec. 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 NS-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 40x40x160 mm molds and stored in a cabinet for 24 hours at 23 ± 2°C and 90% relative humidity (RH). After 24 hours, the mortar prisms were removed from the molds and stored in saturated CH water to avoid leaching, for 28 days. After 28 days storage, the compressive strength was determined according to the Norwegian Standard NS-EN 196-1.

3.5. Specific surface area (BET)

BET specific surface area was measured with a Tristar 3000 Surface Area & Porosity Analyzer apparatus from Micromeritics. Prior to analysis the samples were degassed with a SmartPrep degasser (VacPrep 061) to remove adsorbed contaminants from the surface and pores of the samples.

3.6. X-ray Powder diffraction (XRD)

Powders of calcined Clay A and B were prepared for XRD measurements using the front loading technique. The samples were measured with a D8 Focus diffractometer from Bruker equipped with a Lynx Eye detector and a Cu-K<alpha> X-ray source. A fixed divergence slit of 0.2 mm was used. Measurements were taken from 5-65° 2θ with a step size of 0.2° 2θ and a step time of 1 sec. Data was collected at 40 kV and 30 mA.

3.7. Fourier transformed infrared spectroscopy (FT-IR)

FT-IR spectra were taken in the transmittance mode in the middle-IR (MIR) region. Samples of 2 mg were dispersed in 200 mg of KBr and pressed to pellets of 13 mm diameter using a
mechanical hand press. Measurements were performed using a Bruker IFS 66v FTIR spectrometer equipped with an IR source, KBr beam splitter, and DTGS KBr detector. For each sample, 200 scans in the 400 – 4000 cm⁻¹ (MIR) spectral range were recorded with a resolution of 2 cm⁻¹. A spectrum of the atmosphere was recorded for background corrections of the samples.

3.8. Nuclear magnetic resonance spectroscopy (²⁷Al-MAS-NMR)

The ²⁷Al MAS-NMR spectra have been recorded at 14.1 T, using a 4 mm CP/MAS NMR probe, a spinning speed of νR = 13.0 kHz, a 0.5 µs excitation pulse (~ 11° pulse) (Garg and Skibsted, 2016), a 2 s relaxation delay, ¹H decoupling during acquisition, and in between 6560 and 50300 scans.

3.9. Mössbauer spectroscopy

The Mössbauer measurements were carried out at room temperature on a spectrometer with a constant acceleration type of vibrator and a ⁵⁷Co/Rh source. The samples were ground, mixed with BN (boron nitride) and spread out to form absorbers. Calibration spectra were recorded using natural iron foil at room temperature as a reference absorber. Spectra obtained were folded and analysed using the least-squares Mössbauer fitting program Recoil.

3.10. Electron probe micro analysis (EPMA)

All samples were cast in epoxy resin, plane polished in iso-propanol and coated with carbon. For analyses, a JEOL JXA-8500F EPMA equipped with 5 wavelength dispersive X-ray spectrometers (WDS) and an energy dispersive X-ray spectrometer (EDS) was used. All samples were investigated in the backscattered electron imaging (BEI) mode with an
accelerating voltage of 15 kV. All results from WDX measurements are given in atomic percent (at%).

3.11. Inductively coupled plasma mass spectrometry (ICP-MS)

Dispersions of Clay A and B and alkaline solution were prepared in a ratio of 1:30. 3 g of clay were added to 90 mL solution and constantly rotated in a plastic bottle for 3 days. After 3 days the plastic bottle was standing still to enable the clay to settle down on the bottom of the bottle. About 15 mL of the clear solution were taken off with a pipette for ICP-MS analysis. The same was done with a reference sample, composed of only alkaline solution. HR-ICP-MS analysis was performed using a Thermo Finnigan model Element 2 instrument. The samples were introduced using a SC-Fast autosampler with a peristaltic pump. The instrument was equipped with a concentric PFA-ST nebulizer connected to a Scott PFA spray chamber, aluminium sample and skimmer cones, a demountable torch and a quartz injector.

4. Results and discussion

4.1. Compressive strength of mortars

Figure 1 shows the 28 day compressive strength of mortars with 20% replacement of cement by calcined Clay A (left) and calcined Clay B (right). The black line is showing the compressive strength of the reference mortar without cement replacement. The compressive strength of the reference mortar was about 55 MPa. Clay A seemed to be very reactive within the calcination temperature range between 700-800°C. Within the whole temperature range, 20% replacement of cement with calcined Clay A resulted in compressive strength up to about 8 MPa higher than what was achieved with the reference mortar. Calcined Clay B showed a narrower reactivity window. The reactivity with regard to compressive strength development increased from 700-800°C followed by a decrease from 800-1000°C. 20% replacement of cement by Clay B
calcined at 800°C resulted in 7 MPa higher 28 day compressive strength compared to the reference mortar. Higher replacement levels of cement up to 50% were tested for Clay A and B at a calcination temperature of 800°C (Danner et al., 2015; Danner et al., 2012a; Danner et al., 2013). It could be shown that even with 50% cement replacement, higher or equal 28 day compressive strength was achieved compared to the reference mortar.

4.2. BET specific surface area

Table 3 shows the measured BET surface area of Clay A and B, raw, and calcined at 700 and 800°C. While the BET specific surface area of the montmorillonite rich Clay B decreased with increasing temperature, the kaolinite rich Clay A showed no change. When calcined to 700°C the specific surface of Clay B fell from 71.3 to 54.1 m²/g. This is a result of a first collapse of the montmorillonite layers through dehydration of the interlayer spaces reducing the d-spacing of the mineral structure. This was confirmed with XRD presented in section 4.3. Upon further heating to 800°C, the specific surface dropped significantly to 15.1 m²/g. The complete dehydroxylation caused a further decrease of the inner surfaces. Recrystallization was not observed with XRD for Clay B at 800°C. The specific surface of Clay A did not change from 100 to 800°C within the error of the measurement. Quartz and orthoclase do not undergo any significant changes when heated to these temperatures. Even the transformation of kaolinite to metakaolinite has only a minor impact on the specific surface (Fernandez et al., 2011; He et al., 1995).

XRD
Figure 1: 28 day Compressive strength of mortars with 20% replacement of cement by calcined Clay A (left) and calcined Clay B (right).

Figure 2 shows the XRD diffractograms of Clay A, raw and calcined at 700 and 800°C. When calcined at 700°C, the kaolinite reflections disappeared due to dehydroxylation of the kaolinite structure, i.e. transformation of kaolinite to X-ray amorphous metakaolinite. This is visible in the increased background of the diffractograms from Clay A calcined at 700 and 800°C. Quartz and orthoclase minerals were not affected by the heat treatment. Muscovite reflections were...
still visible at a calcination temperature of 800°C. The dihydroxylation of muscovite takes place between 850°C and 900°C (2003; Meyers and Speyer, 2003). The phase assemblage as visible in the XRD diffractograms did not change between 700-800°C. There is no recrystallization to expect in kaolin when burned at such relatively low temperatures. At temperatures above 1100°C, the formation of mullite may occur (Mota et al., 2009; Sperinck et al., 2011). The good pozzolanic reactivity of Clay A calcined at 700 and 800°C in mortar tests is coherent with the identical XRD diffractograms at 700 and 800°C. Already at 700°C, the transformation to metakaolin is complete and the pozzolanic reactivity does not increase further.

In Figure 3, the phase changes during the calcination of Clay B between 700-1000°C are presented. Raw Clay B was dried at 100°C so that the interlayer space of montmorillonite decreased due to dehydration. This caused a shift of the 001 montmorillonite reflection from about 6° 2θ to 9° 2θ resulting in an overlapping with the illite reflection at 8.9° 2θ. At a calcination temperature of 700°C the kaolinite reflection at 12.4° 2θ disappeared due to transformation to metakaolin. Calcite was not completely decomposed until 850°C. Montmorillonite was visible until 800°C. It appeared from the background of the diffractograms that the highest amount of amorphous phases was present between 800-850°C. The main phases detected at temperatures above 850°C were anorthite (CaAl$_2$Si$_2$O$_8$), wollastonite (CaSiO$_3$) and diopside (CaMgSi$_2$O$_6$). Gehlenite (Ca$_2$Al$_2$SiO$_7$) appeared as an intermediate phase at 850 and 900°C. When coexisting with quartz or other SiO$_2$ minerals, gehlenite becomes unstable and reacts further to anorthite and wollastonite (Duminuco et al., 1998; Rathossi et al., 2004; Trindade et al., 2009). With regard to the compressive strength results obtained in the mortar tests, the beginning recrystallization of new stable and unreactive phases at 850°C explains the decreasing reactivity of Clay B at temperatures above that and hence the decrease in compressive strength of the mortars.
4.3. FT-IR spectroscopy

The FT-IR spectra of the raw and calcined Clay A are shown in Figure 4. Kaolinite showed four OH stretching bands at 3696, 3670, 3670, 3620 cm\(^{-1}\) (Chakchouk et al., 2009; Madejova and Komadel, 2001; Tironi et al., 2012). Additionally, three well-resolved Si-O stretching bands at 1114, 1032, 1008 cm\(^{-1}\), typical for kaolinite were observed. The absorption band at 696 cm\(^{-1}\) was assigned to Si-O stretching of kaolinite or quartz. The absorption band observed at 912 cm\(^{-1}\), is related to the Al-O-H deformation band of the octahedral sheet in the structure. Absorption bands observed at 538 and 469 cm\(^{-1}\) are attributed to Al-O-Si and Si-O-Si deformation bands respectively. The first describing the connection of octahedral and tetrahedral sheet in the kaolinite structure and the second reflecting the bonding of tetrahedra in the tetrahedral sheet. These signals were also visible in Clay B (Figure 5). Quartz and orthoclase was detected in the absorption bands at 795 and 755 cm\(^{-1}\) respectively.

Calcination at 700°C resulted in the disappearing of the OH stretching bands between 3600-3700 cm\(^{-1}\) and the Al-O-H deformation band at 912 cm\(^{-1}\). This indicates complete dehydroxylation of kaolinite. All samples appeared to adsorb water from the atmosphere visible in the bands at 3400 cm\(^{-1}\) and 1635 cm\(^{-1}\). The well-resolved Si-O stretching bands transformed into one wide peak with a maximum at about 1080 cm\(^{-1}\) upon calcination. This was explained with the formation of a 3 dimensional amorphous silica network (Madejová, 2003). The disappearing of the Al-O-Si deformation band at 538 cm\(^{-1}\) and the shifting of the Si-O-Si deformation band at 469 to a higher wavenumber has been observed by several authors (Madejová, 2003; Tironi et al., 2012). Additionally, new absorption bands appeared at 570 and 870 cm\(^{-1}\). These can most likely be ascribed to the amorphous metakaolinite structure. Especially the disappearance of the Al-O-Si deformation band and the shift and broadening in the Si-O-Si deformation band potentially imply significant structural changes in the local
environment of the Al and Si atoms in the octahedral and tetrahedral sheet. Increasing the calcination temperature from 700 to 800°C did not result in a change of the FT-IR spectra. The higher intensities of most of bands at a calcination temperature of 800°C, are explained by a potential higher sample saturation in the KBr disk.

Figure 5 shows the FT-IR spectra of the raw and calcined Clay B. The band observed at 3620 cm⁻¹ is typical for dioctahedral montmorillonites with a high amount of aluminium in the octahedra (Madejová, 2003). The absorption band at 3699 cm⁻¹ reflects the presence of kaolinite. The OH stretching band of H₂O molecules at 3439 cm⁻¹ is found in almost all clay minerals, especially when smectite is dominating. Common for all smectites is the broad complex Si-O stretching band at 1030 cm⁻¹ (Madejová, 2003). Within this broad band a shoulder was observed at around 1100 cm⁻¹ which can be assigned to kaolinite. The Al-O-H deformation band observed at 911 cm⁻¹ is typical for dioctahedral smectite minerals (Madejová, 2003). Calcium carbonate absorption bands were found at 713, 874, 1428 and 2514 cm⁻¹. The absorption band at 1799 cm⁻¹ is typical for several carbonate minerals and could potentially be due to the small amounts of siderite found in Clay B (Table 1). The presence of quartz was visible in the Si-O stretching bands at 796 cm⁻¹ and 696 cm⁻¹. Small amounts of organic material showed bands at 2877 cm⁻¹ and many smaller peaks at higher frequencies.

When calcined at 700°C the OH stretching band of kaolinite at 3699 cm⁻¹ disappeared while the OH stretching band of the montmorillonite at 3621 cm⁻¹ was still visible. At 800°C montmorillonite became dehydroxylated as well, also visible by the disappearing of the Al-O-H deformation band at 911 cm⁻¹. With increasing calcination temperature, the Si-O stretching bands around 1030 cm⁻¹ broadened indicating the presence of amorphous silica (Madejová, 2003). Potential distortion in the montmorillonite layers and modified bonding of the bridging oxygen atoms was visible in the diminishing intensities of the Al-O-Si and Si-O-Si deformation bands at 534 and 469 cm⁻¹. The Si-O-Si band broadened, decreased in intensity and shifted to
higher frequencies. This confirms a lower crystallinity in the tetrahedral sheet and distortions in the arrangement of the tetrahedra. The completely disappearing Al-O-Si deformation band might reflect a decreasing content of octahedral cations (Madejová, 2003). The disappearance of the band at 534 cm⁻¹ and the displacement of Si-O-Si band at 469 cm⁻¹ was confirmed for kaolinite to metakaolinite transformation in several papers as a sign for the presence of an amorphous reactive phase (Chakchouk et al., 2009; Tironi et al., 2012). Calcium carbonate was not completely decomposed at 800°C confirming results from XRD. The partly decomposition of calcite was reflected in a peak broadening and a decreasing intensity of the band at 1428 cm⁻¹. The higher intensities of some absorption bands in the sample calcined at 700°C are explained by a potential higher sample saturation in the KBr disk.

4.4. ²⁷Al MAS NMR

Figure 6 shows the ²⁷Al MAS NMR spectra of the raw and calcined Clay A. Spinning side bands are marked with asterisks. The chemical shifts at 71.4 ppm and 56.9 ppm originate from Al in tetrahedral coordination, and are typical for Al sites in layered clay mineral structures (70.8 ppm) and fully condensed Al(OSi)₄ sites (59.3 ppm) (Brown et al., 1987b; Drachman et al., 1997; Fernandez et al., 2011; Jeans and Bergaya, 2008; Skibsted, 2011). Al in tetrahedral coordination might represent the substitution of Al for Si in the tetrahedral sheet of muscovite. However, orthoclase present in Clay A also contains Al entirely in tetrahedral coordination and exhibits a chemical shift in the same region between 56-60 ppm (Zhou et al., 1997). The most intense chemical shift observed at 4.9 ppm reflects Al in octahedral coordination, i.e. octahedral sheets in kaolinite. The relative intensities were 2.6% (71.4 ppm), 11.9% (56.9 ppm) and 85.5% (4.9 ppm), confirming that most of the aluminium was present in octahedral sheets of the kaolinite structure.
The $^{27}$Al MAS NMR spectrum of Clay A calcined at 800°C showed chemical shifts for Al in tetrahedral (57.2 ppm), five-fold (29 ppm) and octahedral (4.2 ppm) coordination (Fernandez et al., 2011; Rocha and Klinowski, 1990). An estimation of the relative intensities for the different sites, by spectral integration, gave relative intensities of 37.3% (57.2 ppm), 40.3% (29 ppm), and 22.4% (4.2 ppm). This indicates that Al was mainly present in 4 and 5-fold coordination in Clay A, calcined at 800°C. 4-fold coordinated Al was observed before in calcined kaolinite (Fernandez et al., 2011) but it cannot be excluded that a significant amount of the intensity of this peak derives from the orthoclase. The change in coordination and especially the presence of 5-coordinated Al clearly indicates a disordering and loss of crystallinity of the structure.

$^{27}$Al MAS NMR spectra of the raw and calcined Clay B (800°C) are shown in Figure 7. The spectrum of the raw Clay B showed three chemical shifts at 70.8 ppm, 59.3 ppm, and 4.3 ppm with the following relative intensities 5.4%, 16.0%, and 78.7%, respectively. As expected, Al was mainly present in the octahedral sheet of the montmorillonite. The spinning sidebands closest to the central-transition region are marked by asterisks.

The $^{27}$Al NMR spectrum of Clay B calcined at 800°C showed two chemical shifts at 59.6 ppm and 3.7 ppm with the relative centre-band intensities of 95.1% and 4.9%, respectively. Octahedral Al in the raw montmorillonite has been almost completely converted to Al in tetrahedral coordination. The signal at 3.7 ppm in the calcined sample might represent residual octahedrally coordinated aluminium from montmorillonite (Drachman et al., 1997) or from kaolinite and illite (Fernandez et al., 2011). The dehydroxylation accompanied with the change in coordination for Al must result in significant structural alterations. The reorganizing octahedral sheet will induce distortions in the tetrahedral silicon sheet as well, from changing bond lengths and angles up to a complete separation (Drachman et al., 1997). This was
confirmed with FT-IR spectroscopy where a disappearing Al-O-Si band was observed upon calcination.

**4.5. Mössbauer spectroscopy**

Mössbauer spectroscopy was only used to study Clay B. The iron content of Clay A was too low to be studied by this method. Representative Mössbauer spectra of the raw and calcined Clay B are shown in Figure 8. Data points and fitting are marked with crosses and black lines, respectively. The individual red and blue lines correspond to the absorption of the Fe$^{2+}$ and Fe$^{3+}$ components, respectively. The lines marked black in Figure 8a are the inner lines of the six-line patterns emanating from the magnetic part. In the fitting procedure, both Fe$^{2+}$ and Fe$^{3+}$ are represented by two absorption lines with equal intensities (doublets). The isomer shift ($\delta$) taken as the centre of the doublet, is referred to $\alpha$-Fe as standard absorber. The electric quadrupole splitting ($\Delta$), is the splitting of the doublet. In the fitting, the isomer shift, quadrupole splitting, doublet intensity (I) and the line width ($\Gamma$) were kept as varying parameters. Both spectra showed strong resonances at around 0 - 2 mm/s as it is typical for clay minerals (Murad and Wagner, 1998). The calcined Clay B showed furthermore resonances at higher velocities (Figure 8b). These resonances are parts of six-line patterns originating from a magnetic part of the sample. These outer lines representing the magnetic phases are rather symmetric. The isomer shift ($\delta$) was 0.36 (1) mm/s and the quadrupole coupling constant ($\varepsilon$) was about - 0.11 (3) mm/s. The high fields are representative for hematite ($\alpha$-Fe$_2$O$_3$). The field distribution potentially derives from solid solutions of corundum-hematite ($\alpha$-Fe$_{2-x}$Al$_x$O$_3$) (Brown et al., 1987a; Majzlan et al., 2002). The substitution of Fe with Al would result in a lowering of the field. With this interpretation, the whole magnetic signal comes from Fe$^{3+}$. The intensities of these magnetic patterns showed, within error, 30 mass% of Fe in the calcined sample to be present in the magnetic part.
The analysis of spectra, recorded with lower velocity scale, (Figure 8a) were performed with varying number of quadrupole split doublets. The spectrum of the raw montmorillonite consisted mainly of a slightly split doublet and wider doublets (marked blue in the figure). From the fitting of the doublets in the raw montmorillonite, Fe$^{3+}$ and Fe$^{2+}$ were detected. In Table 4 averaged hyperfine interaction values for the ferric and ferrous patterns of raw and calcined Clay B are given. The isomer shifts and quadrupole splitting’s found are characteristic for clay minerals, like kaolinite, illite and montmorillonite (Murad and Cashion, 2011). The values for the isomer shift of Fe$^{3+}$ and Fe$^{2+}$ indicated octahedral coordination for both (Takeda et al., 1979). Fe$^{3+}$ and Fe$^{2+}$ were thus substituted for Al$^{3+}$ and Mg$^{2+}$ in the octahedral layer of montmorillonite. All changes recorded for the iron species are therefore representative for any change in the octahedral layer of the structure, i.e. the Al environment. The allowed quadrupole splitting versus isomer shift combinations for $^{57}$Fe were investigated in (Murad and Cashion, 2011). Different combinations result in different coordination for Fe$^{3+}$ and Fe$^{2+}$. The coordination of Fe$^{3+}$ seemed to change towards 5 and 6 upon calcination as the quadrupole splitting increased. Increasing quadrupole splitting may also be due to changes in the ligand structure for Fe caused by dehydroxylation. The isomer shift of Fe$^{2+}$ decreased from the raw to the calcined Clay B and so did the quadrupole splitting, indicating a change in coordination towards 4. The values obtained for isomer shift and quadrupole splitting are in agreement with literature and were interpreted as the result of strong distortions in the octahedral layer of calcined clay mineral structures (MacKenzie and Rogers, 1977; Takeda et al., 1979).

During the calcination process the Fe$^{2+}$ was expected to be oxidized mostly to Fe$^{3+}$ at 800°C since the calcination takes place in air. The relative amounts (I) of different Fe valences are presented in Table 4 and show that almost all the iron was oxidized in the calcined Clay B. Induced stresses and distortions leading to a highly disorganized calcined montmorillonite
structure due to the oxidation of iron accompanied with increasing quadrupole splitting values was partly confirmed by (Miller et al., 1963; Simopoulos et al., 1975; Tichit et al., 1988).

4.6. SEM

Figure 9a-b shows images of the raw Clay A. In the fine-grained kaolin matrix, larger grains of orthoclase and quartz were observed. Only small kaolinite crystallites with lamellar texture were found in the matrix. The presence of kaolinite was verified by WDX analysis. In contrast to that, large crystallites of muscovite with a size up to 50 µm were found (Figure 9b). When calcined at 700-800°C the kaolinite matrix showed only a slightly modified microstructure (Figure 9c-f). The kaolinites lamellar texture appeared to widen up upon calcination. In point 1 & 2 in Figure 9c-d, the element composition was analysed by WDS (wavelength dispersive spectra). The composition was similar in both points with about 20% Al and 20% Si (both in atomic percent). A composition with Al/Si ratio of 1/1 is typical for metakaolinite with the formula Al$_2$Si$_2$O$_5$. Figure 9e-f show two metakaolinite particles with a size of about 5 µm.

Clay B originates from marine sedimentation and contains calcareous microfossils. The calcium carbonate content in Clay B derives to a large extent from coccoliths, observed all over the raw Clay B (Figure 10a). Coccoliths are the exoskeletons of a group of plant plankton called coccolithophores which belong to the algal division Haptophyta (Young and Henriksen, 2003). Pyrite was found only locally in form of pyrite framboids (Figure 10b) (Lauf et al., 1982). Clay B calcined at 700°C is presented in Figure 10c-d. Coccoliths appeared still stable at this temperature. However, it appeared that the dense matrix widened up. When calcined at 800°C the morphology was altered significantly (Figure 10e-f). The coccoliths were decomposed leaving cavities in the montmorillonite matrix. At the same time the matrix appeared more vitreous (Figure 10e). Moreover, new larger glassy particles were found all over calcined Clay B (Figure 10f). The lower BET specific surface area measured in the calcined Clay B is most
likely the result of these new formed glassy phases. The formation of a liquid phase in calcite bearing clays has also been observed by other authors (Duminuco et al., 1998; Nodari et al., 2007; Trindade et al., 2009). The composition of this new formed phase was measured with WDS analysis. The average composition of 3 particles in atom% was 19% Si, 8% Al, 8% Fe, 5% Ca, 2% Mg, 2% Na+K and 55% O. The result obtained in atom% of the elements was recalculated in weight% of the respective oxides. The calculated oxide composition was similar to the chemical composition measured with XRF of the initial raw Clay B (Danner, 2013). However, the analysis was performed on a limited amount of particles and might not be representative for the whole calcined Clay B. The glassy phase potentially contributes to the good pozzolanic reactivity of the calcined Clay B shown in mortar tests.

4.7. Inductively coupled plasma mass spectroscopy (ICP-MS)

ICP-MS analysis was performed to investigate the release of ions from the raw and calcined Clay A and B in an approximated concrete pore water. Of particular interest was the release of silicon, aluminium and alkalis as these are the main elements contributing to the pozzolanic reaction. The results are given in Table 5. In the raw Clay A, the release of silicon and aluminium was about equal. This can be explained by the mineral structure of kaolinite, having the octahedral and tetrahedral sheet exposed equally. Due to that, the aluminium release of Clay A was considerably higher than for Clay B where montmorillonite dominates. In the layered structure of montmorillonite, the octahedral sheet is located between two tetrahedral sheets. When calcined at 800°C, both the release of silicon and aluminium increased considerably. Calcined Clay A released higher amounts of silicon and aluminium than Clay B, indicating higher pozzolanic reactivity in cementitious binders. In the raw Clay B, the release of silicon was higher than the release of aluminium. As explained above, the tetrahedral sheets of montmorillonite are more exposed to the alkaline solution while the octahedral sheet is
shielded between the tetrahedral sheets. When calcined at 800°C the release of silicon decreased while the release of aluminium increased. This might be explained with structural rearrangement of the metastable structure. The release of calcium from Clay B increased upon calcination. Calcium release in Clay B derives probably from calcite and montmorillonite.

For potassium and sodium, negative values were measured. That means that higher amounts of potassium and sodium were measured in the pure reference solution (alkaline solution without Clay A or Clay B). Reason could be higher alkali ad- and absorption than what was released from Clay A and B. Especially potassium was reduced in much higher magnitude than sodium in the solution. The potassium ion with its ionic radius of about 1.38 Å fits perfectly in the cavity of the pseudo-hexagonal rings of oxygens of the adjacent silica tetrahedral sheet of illite or smectite minerals (Murray, 1999).

5. Conclusions

In this paper the potential use of two raw clays (Clay A: kaolin; Clay B: calcareous montmorillonite) as supplementary cementitious materials in blended cements is investigated. The pozzolanic reactivity of Clay A and B is explained by characterizing the structural changes upon calcination with XRD, FT-IR, Al-NMR, Mössbauer spectroscopy, SEM and ICP-MS. The main conclusions are listed below.

- Compressive strength of mortars with 20% replacement of cement by calcined Clay A and B resulted in more than 10% strength increase after 28 day curing.
- At the temperature of highest pozzolanic reactivity (Clay A: 700-800°C; Clay B: 800°C) kaolinite and montmorillonite were completely dehydroxylated. However, the calcite in Clay B was not completely decomposed.
FT-IR indicated changes in the connectivity of tetrahedral and octahedral sheets of the kaolinite and montmorillonite structure and showed the formation of 3-dimensional amorphous silica networks.

In Clay A, most of the octahedral coordinated Al changed to 5-fold coordination upon calcination. In calcined Clay B, the coordination of Al was changed to tetrahedral coordination.

Oxidation of iron during calcination resulted in strong distortions of the montmorillonite structure in Clay B. The coordination of Fe$^{3+}$ was changing to 5-fold while the coordination of Fe$^{2+}$ was changing towards 4-fold.

Under the SEM, reactive metakaolinite particles were observed in Clay A. In Clay B, the formation of a glass phase due to reaction of coccoliths (CaCO$_3$) and montmorillonite was observed.

When calcined at 800°C, Clay A and B showed increased release of Al in concrete pore water. Clay A did also show increased release of Si. This contributes to the pozzolanic reaction forming more binding phases in cementitious systems.

Acknowledgements:
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References


European Committee for Standardization.


Danner, T., Østnor, T.A., Justnes, H., 2012b. Calcined Marl as a Pozzolan for Sustainable Development of the Cement and Concrete Industry, 12th International Conference on recent Advances in Concrete Technology and Sustainability Issues. American Concrete Institute, Prague.


Skibsted, J., 2011. 27Al MAS NMR investigation of three clay samples. Aarhus University.


Table 1: Mineralogical composition of Clay A and B before calcination

<table>
<thead>
<tr>
<th>Phase (mass%)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>47</td>
<td>8</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>Illite</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Quartz</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>34</td>
<td>—</td>
</tr>
<tr>
<td>Calcite</td>
<td>—</td>
<td>25</td>
</tr>
<tr>
<td>Siderite</td>
<td>—</td>
<td>3</td>
</tr>
<tr>
<td>Pyrite</td>
<td>—</td>
<td>1</td>
</tr>
</tbody>
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Table 2: Chemical composition of Clay A and B calcined at 800 °C and the cement used in mortar tests

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>A</th>
<th>B</th>
<th>Cement</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>60.6</td>
<td>48.7</td>
<td>19.9</td>
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<tr>
<td>Al₂O₃</td>
<td>30.0</td>
<td>17.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.4</td>
<td>10.4</td>
<td>3.3</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>13.8</td>
<td>61.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.2</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>—</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0</td>
<td>0.2</td>
<td></td>
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<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.4</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>Total</td>
<td>98.2</td>
<td>98.0</td>
<td>97.6</td>
</tr>
<tr>
<td>LOI</td>
<td>1.8</td>
<td>2.0</td>
<td>2.4</td>
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</table>

Table 3: BET specific surface area of raw and calcined Clay A and Clay B

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>raw</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay A</td>
<td>18</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>Clay B</td>
<td>71</td>
<td>54</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 4: Mössbauer averaged results. Isomer shift δ, quadrupole splitting Δ and line width at half maximum Γ are given in mm/s, while the intensities I are given in %. The errors in the parameters are: δ (± 0.01 mm/s), Δ (± 0.05 mm/s), I (± 1%) and Γ (± 0.02 mm/s).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe³⁺</th>
<th>Fe²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ</td>
<td>Δ</td>
</tr>
<tr>
<td>raw Clay B</td>
<td>0.39</td>
<td>0.52</td>
</tr>
<tr>
<td>calcined Clay B</td>
<td>0.33</td>
<td>1.21</td>
</tr>
</tbody>
</table>
### Table 5: Ion release from raw and calcined Clay A and B dissolved in approximated concrete pore water (0.132 M, pH = 13.2, KOH/NaOH = 2/1)

<table>
<thead>
<tr>
<th></th>
<th>Si 30 [mg/L]</th>
<th>Al 27 [mg/L]</th>
<th>Ca 44 [mg/L]</th>
<th>Fe 56 [mg/L]</th>
<th>Na 23 [mg/L]</th>
<th>K 39 [mg/L]</th>
<th>P 31 [mg/L]</th>
<th>Cl 35 [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay A raw</td>
<td>41.9</td>
<td>43.9</td>
<td>1.0</td>
<td>0.0</td>
<td>-158.2</td>
<td>-1302</td>
<td>2.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Clay A 800</td>
<td>106.2</td>
<td>154.1</td>
<td>0.0</td>
<td>0.2</td>
<td>-126.3</td>
<td>-798.3</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Clay B raw</td>
<td>66.7</td>
<td>1.9</td>
<td>2.9</td>
<td>0.0</td>
<td>-13.0</td>
<td>-752.2</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Clay B 800</td>
<td>20.9</td>
<td>29.4</td>
<td>15.7</td>
<td>0.0</td>
<td>-40.7</td>
<td>-165.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 1: 28 day Compressive strength of mortars with 20% replacement of cement by calcined Clay A (left) and calcined Clay B (right).

Figure 2: XRD diffractogram of raw and calcined Clay A
Figure 3: XRD diffractogram of raw and calcined Clay B
Figure 4: FT-IR spectra of raw and calcined (700 and 800°C) Clay A
Figure 5: FT-IR spectra of the raw and calcined (700 and 800°C) Clay B
Figure 6: $^{27}$Al MAS NMR spectra of raw and calcined Clay A

Figure 7: $^{27}$Al MAS NMR spectra of raw and calcined Clay B
Figure 8: Mössbauer spectra of the raw and calcined Clay B sample with low (a) and high (b) velocity scales.
Figure 9: BSI images of the raw Clay A (a-b), calcined at 700 °C (c-d) and calcined at 800°C (e-f). 1 and 2 indicate points for WDS analysis referred to in text.
Figure 10: BSI images of raw Clay B (a-b), calcined at 700°C (c-d) and 800°C (e-f)