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1 **Calcareous Smectite Clay as a Pozzolanic Alternative to Kaolin**

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25 **Calcareous Smectite Clay as a Pozzolanic Alternative to Kaolin**

26

27 The hydration of cement pastes with addition of a kaolinite rich clay (Clay A) and a calcareous
28 smectite rich clay (Clay B) was investigated with isothermal calorimetry, in-situ XRD, PXRD,
29 TGA and EPMA. Portland cement was replaced by 20, 35 and 50 weight% calcined clay in
30 cement pastes and mortars. Both clays showed good pozzolanic reactivity. However, clay A
31 having a higher amount of metakaolin and higher specific surface was more reactive in terms
32 of CH consumption and mortar strength development. 50% replacement of PC by calcined Clay
33 A resulted in increased 28 day compressive strength while mortars with 50% calcined Clay B
34 showed almost equal 28 day compressive strength compared to the reference. With increasing
35 addition of calcined clay, the second aluminate reaction (formation of AFm phase) of cement
36 hydration was accelerated and the cement pastes became under sulphated. This resulted in a
37 stronger and earlier sulphate depletion peak, especially in pastes with calcined Clay A. Due to
38 3% calcite in the used cement the main hydration product found was carboaluminate hydrate.
39 The favoured formation of carboaluminate hydrate stabilised ettringite in the cement pastes.

40

41 **Keywords:** Pozzolana; cement; hydration; in-situ XRD, compressive strength

42

43 **1 Introduction**

44 Taking into account all steps from raw material mining to the final product, cement production
45 is a highly energy intensive process, contributing 5-7% of the worldwide carbon dioxide
46 emissions (Ernst Worrell, Lynn Price, Nathan Martin, Chris Hendriks, & Meida, 2001; Mehta,
47 1999). The most effective way of reducing CO₂ emissions in the short and long term is the
48 replacement of parts of the clinker content with supplementary cementitious materials (SCMs)
49 (Damtoft, Lukasik, Herfort, Sorrentino, & Gartner, 2008; Ernst Worrell, et al., 2001; Schneider,
50 Romer, Tschudin, & Bolio, 2011). In the long term, large enough availability and sufficient
51 reactivity, will determine the choice of suitable SCM sources (Gartner, 2004). The availability
52 of the most common used SCM's, i.e. slag and fly ash, is limited compared to the production
53 of cement and might decrease further in the future. Due to the widespread availability of
54 calcined natural clays, this type of SCM has high potential to serve the cement industry
55 sufficiently for a more sustainable future (K Scrivener, 2015).

56 In dependence of the clay mineralogy, calcination between 600-800°C, leads to the
57 formation of amorphous or disordered metastable phases with high pozzolanic activity
58 (Fernandez, Martirena, & Scrivener, 2011). Among the different clay minerals, kaolinite is
59 proven to have the highest pozzolanic reactivity when calcined at the optimum temperature.
60 Therefore, the pozzolanic reactivity of metakaolin was subject of detailed studies e.g.
61 (Ambroise, Maximilien, & Pera, 1994; F. Avet and Scrivener, 2018b; De Silva and Glasser,
62 1992; El-Diadamony, Amer, Sokkary, & El-Hoseny, 2016; Frías and Cabrera, 2001; Jones,
63 2002; Mlinárik and Kopecskó, 2013; Sabir, Wild, & Bai, 2001; Siddique and Klaus, 2009;
64 Tironi et al., 2014; Tironi, Scian, & Irassar, 2015; Tironi, Trezza, Scian, & Irassar, 2012).
65 Kaolin clays with high purity are scarcely available and at the same time important raw
66 materials for other industries. Consequently, there is a regaining interest in investigating poly-
67 mineral clays containing different clay and non-clay minerals. With growing interest of using

68 calcined natural clays in the construction industry, the evaluation of the pozzolanic potential of
69 local impure clays is getting more attention (Al-Rawas, Hago, Al-Lawati, & Al-Battashi, 2001;
70 Almenares Reyes, Díaz, Rodríguez, Rodríguez, & Hernández, 2018; Alujas, Almenares,
71 Betancourt, & Leyva, 2015; Aras, Albayrak, Arikan, & Sobolev, 2007; Berriel et al., 2016;
72 Beuntner and Thienel, 2015; Chakchouk, Samet, & Mnif, 2006; Huenger, Gerasch, Sander, &
73 Brigzinsky, 2018; Pöllmann, Da Costa, & Angelica, 2015; Shayma'a, Malath, Dalya Kh, Firas,
74 & Abdul Wahab, 2012; Tironi, et al., 2012). It was shown that low grade kaolinitic clays with
75 only 40% kaolinite content and high amounts of impurities of non-clay minerals like quartz
76 and feldspars, can have sufficient pozzolanic reactivity (Alujas, et al., 2015; Aras, et al., 2007;
77 François Avet, Snellings, Alujas Diaz, Ben Haha, & Scrivener, 2016; Tironi, et al., 2012). The
78 pozzolanic reactivity of calcined natural clays was shown to increase with increasing amount
79 of kaolinite (François Avet, et al., 2016; Chakchouk, et al., 2006). The coupled substitution of
80 cement with calcined clay and limestone was also investigated (Antoni, Rossen, Martirena, &
81 Scrivener, 2012; F. Avet and Scrivener, 2018a, 2018b; Bishnoi and Maity, 2018; Cancio Díaz
82 et al., 2017; Favier, Zunino, Katrantzis, & Scrivener, 2018; Kunther, Dai, & Skibsted, 2015;
83 Nied, Stabler, & Zajac, 2015; Karen Scrivener, Martirena, Bishnoi, & Maity, 2017; Tironi, et
84 al., 2015). It was found that up to 45% substitution of cement with a 2:1 blend of metakaolin
85 and limestone gave better compressive strength than the pure reference cement system (Antoni,
86 et al., 2012). The good performance was explained by a strong synergistic effect between
87 calcined clay and limestone (Antoni, et al., 2012; Nied, et al., 2015).

88 Only few studies covered investigations on natural clays already containing high
89 amounts of calcium carbonate. Calcareous clay is not suitable for production of burnt clay
90 products (e.g. bricks and light weight aggregate) due to the decomposition of CaCO_3 to CaO
91 after burning. During service CaO may react with moisture to form Ca(OH)_2 which can result

92 in so called “pop outs“. Thus, these types of clays are not yet exploited by other industries and
93 can serve as a large SCM resource to produce blended cements.

94 A recent study showed that marl (47% calcium carbonate in the raw material) can be a
95 good pozzolanic material when calcined between 400-800 °C (Rakhimov, Rakhimova,
96 Gaifullin, & Morozov, 2017). The present authors have previously published extensive studies
97 on the pozzolanic activity of smectite rich clay containing 20-25% calcium carbonate, for
98 simplicity called calcined "marl". (Danner, Justnes, Norden, & Østnor, 2015; Danner, Justnes,
99 & Ostnor, 2012; Danner, Østnor, & Justnes, 2013; Justnes and Østnor, 2014; Østnor, Justnes,
100 & Danner, 2015).

101 In this paper, the hydration of cement pastes with addition of two natural clays is
102 investigated. Cement hydration of pastes with a kaolinite rich clay is compared to pastes with
103 a calcareous smectite rich clay. Most smectite rich clays are known to have lower pozzolanic
104 reactivity compared to kaolinite rich clays (Fernandez, et al., 2011). This paper shows that
105 smectite rich clays containing calcium carbonate can be an effective pozzolanic material,
106 comparable to natural kaolin, which enables pozzolanic cements with up to 55% clinker
107 replacement (CEM IV/B) considering the 28 days compressive strength in mortars.

108 **2 Materials and Experiments**

109 **2.1 Materials**

110 Table 1 and Table 2 show the bulk mineralogy of crystalline phases of raw Clay A and Clay B
111 determined with Rietveld analysis, and the chemical composition of the clays calcined at
112 800°C. The main mineral phases of Clay A are kaolinite, quartz and feldspar. Clay B is a
113 smectite rich clay, with 25% calcite and 8% kaolinite. Norcem standard cement (CEM I 42.5
114 R) was used for mixing pastes of cement and calcined clay. The chemical composition is given
115 in Table 2. The used cement contained 3% limestone. Pyrite was detected with XRD in Clay
116 B, however, the chemical composition showed no SO₃. Under the SEM pyrite framboids were
117 found in the raw clay indicating very localised distribution of pyrite (Danner, Norden, &
118 Justnes, 2018). The sulphur from pyrite might have been removed during the calcination
119 process. Heating of pyrite between 600-1000°C with the addition of air results in decomposition
120 of pyrite and the formation of iron oxides and sulphur dioxide gas (Runkel and Sturm, 2009).
121 A detailed characterisation of both clays in the raw and calcined state, including the XRD
122 spectra of the starting clay, can be found in (Danner, et al., 2018).

123

124 Table 1 and Table 2

125

126 **2.2 Production of calcined Clays**

127 The calcination of Clay A and B was performed in a direct natural gas heated rotary kiln at
128 IBU-tec advanced materials AG (Weimar, Germany). The kiln is designed for a continuous
129 thermal treatment and was used to simulate trials under industrial conditions. The feed rate was
130 30 kg/h and the residence time in the kiln was 45 min. The clays were calcined at different
131 temperatures between 600-1100°C and their pozzolanic reactivity was investigated in
132 dependence of the temperature (Danner, et al., 2018). Clay B showed highest pozzolanic

133 reactivity at 800°C. Clay A already showed high pozzolanic reactivity when burned at 700°C.
134 However, the pozzolanic reactivity was relatively constant between 700 to 800°C (Danner, et
135 al., 2018). Therefore, this paper, compares results for both clays burned at 800°C. Changes in
136 microstructure and phase assemblage upon calcination of the clays are reported in detail in
137 (Danner, et al., 2018).

138 The calcined clay lumps were milled down with a discontinuous drum mill to a $d_{50} <$
139 $10 \mu\text{m}$ at UVR-FIA GmbH (Freiberg, Germany).

140

141 ***2.3 Quantitative mineralogical analysis of the raw clays using X-Ray Diffraction (XRD)***

142 Bulk mineralogy of natural Clay A and B was performed with XRD on dried and ground
143 samples using the back-loading sample preparation technique. The $\leq 2 \mu\text{m}$ fraction (clay
144 fraction) was separated from the bulk sample by means of sedimentation, smeared on a glass
145 plate and dried in air. The clay fraction was investigated under three different conditions (a-c);
146 a: untreated, b: after treatment with ethylene glycol vapours in a desiccator for 24 h at 60°C, c:
147 after heating at 500°C for 1 h. For analysis, a PAN Analytical X'Pert Pro MPD equipped with
148 a X'Celerator RTMS detector, an automatic divergence slit and a Cu-K α X-ray source was
149 used. The samples were measured from 2-65° 2 θ using a step size of 0.0170° 2 θ and a step
150 time of 20 sec. Data was collected at 45 kV and 40 mA. More details on the procedure of
151 quantitative mineralogical analysis can be found in (Nielsen, 1994; Nielsen, Cremer, Stein,
152 Thiébault, & Zimmermann, 1989).

153

154 ***2.4 X-Ray Fluorescence (XRF)***

155 XRF analysis was performed with a Bruker AXS S8 Tiger WDXRF equipped with a 4 kW
156 generator. Dried and powdered clay samples were ignited at 850°C. Dried clay sample (0,5 g)

157 was added to a 2:1 mix of lithium- tetraborate and metaborate (5 g) and lithium iodide (60 μ g).
158 The mixture was fused in a platinum crucible and moulded to a glass disk.

159

160 ***2.5 Mixing of Pastes***

161 Portland cement (PC) was dry mixed with 20, 35 and 50 weight% calcined clay and
162 homogenized by hand. Deionized water was added, and the paste was mixed for 1 minute by
163 hand with a plastic spatula. The water to binder ratio was 0.5 and the pastes were hydrated for
164 28 days at 20°C. The hydration was stopped by washing the pastes with ethanol, crushing by
165 hand and drying the samples in a desiccator above saturated CaCl₂-solution (RH about 33%).

166

167 ***2.6 Isothermal Calorimetry***

168 Isothermal calorimetry of cement pastes was carried out at 20°C using a TAM Air (TA
169 Instruments). About 6 g of paste were weighed accurately and used for each measurement.
170 Mixing was performed outside the calorimeter by hand with a plastic spatula for 1 min. The
171 cumulative heat of cement pastes was determined with an accuracy of ± 0.5 J/g.

172

173 ***2.7 In situ XRD***

174 In-situ XRD was performed using a Bruker D8 Advance, equipped with Cu-K α radiation and
175 a Vantec-1 position sensitive detector. The cement pastes were smeared in the sample holder
176 and the sample surface was flattened by stripping off the excess material with a glass plate.
177 About 1 g of paste was used for each measurement. The sample was then placed in an MRI
178 Physikalische Geräte GmbH sample chamber, and data was collected at room temperature
179 (20°C) and constant relative humidity of 96%. The measurements started about 3 ± 1 min after
180 mixing. One scan took about 13 min, and a total of 110 scans were collected during 24 h.

181 Results are shown in form of 2-D level plots where intensities of appearing phases are
182 visualized by a colour gradient (Danner, Justnes, Geiker, & Lauten, 2015).

183

184 **2.8 Powder X-Ray diffraction (PXRD)**

185 Dried samples of hydrated cement paste were finely ground with a hand mortar and prepared
186 for XRD measurements using the front loading technique. The samples were measured with a
187 D8 Focus diffractometer from Bruker equipped with a Lynx Eye detector and a Cu-K α X-Ray
188 source. A fixed divergence slit of 0.2 mm was used. Measurements were taken from 5-65° 2 θ
189 with a step size of 0.2° 2 θ and a step time of 1 sec.

190

191 **2.9 Thermogravimetry (TG/DTG)**

192 Thermogravimetric analysis was performed with a Mettler Toledo TGA/SDTA 851. Dried
193 powdered samples of cement paste were analysed with a heating rate of 10°C/min between 40
194 – 1100°C in nitrogen atmosphere (30 ml/min flow rate). Prior to analysis, all samples were
195 dried additionally for 2 h at 40°C inside the TGA apparatus to remove adsorbed water. The
196 Ca(OH)₂ consumption after 28 days of hydration was calculated from the weight loss in the
197 temperature interval of Ca(OH)₂ decomposition. The exact boundaries for the temperature
198 interval of Ca(OH)₂ are read from the 1st derivative curve (DTG). The weight loss calculated
199 from the difference of the horizontal tangents in the TGA signal is multiplied with the molar
200 ratio 74/18 to obtain Ca(OH)₂ from H₂O mass loss at about 500°C.

201

202 **2.10 Electron Probe Micro Analysis (EPMA)**

203 For EPMA analysis, hydrated paste samples were cast in epoxy resin, plane polished in iso-
204 propanol and coated with carbon. The instrument used was a JEOL JXA-8500F Electron Probe
205 Micro Analyser (EPMA). The JEOL JXA-8500F instrument is equipped with 5 wavelength

206 dispersive X-ray spectrometers (WDS) and an energy dispersive X-ray spectrometer (EDS).
207 All samples were investigated in the backscattered electron imaging (BEI) modus with an
208 accelerating voltage of 15 kV.

209

210 ***2.11 Compressive Strength***

211 Mortars were prepared by substituting Portland cement (PC) with 20, 35 and 50 weight%
212 calcined clay. The mixing procedure was according to the Norwegian Standard NS-EN 196-1
213 ("Standard CEN - EN 196-1 Methods of testing cement Part1: Determination of strength,"
214 2005). The water to binder ratio (w/b) was held constant at 0.5 in all mortar mixes by using
215 superplasticizer. The amount of superplasticizer used increased with increasing amount of
216 cement replacement by calcined clay. In mixes containing 50% calcined Clay A and B, 1.5 and
217 1% superplasticizer by weight of binder was added. The consistency of fresh mortar was
218 determined using a flow table and the flow of mortars containing calcined clay was within \pm
219 5% of the reference mortar. The mortar mixes were cast in three 40x40x160 mm moulds and
220 stored in a cabinet for 24 hours at $23 \pm 2^\circ\text{C}$ and 90% relative humidity (RH). After 24 hours,
221 the mortar prisms were removed from the moulds and stored in saturated CH water to avoid
222 leaching. The compressive strength was determined after 1, 3, 7 and 28 days according to the
223 Norwegian Standard NS-EN 196-1.

224

225 **3 Results and Discussion**

226 **3.1 Isothermal Calorimetry**

227 The curves of thermal power and cumulative heat development up to 35 hours of hydration of
228 the cement pastes blended with Clay A and Clay B are shown in Figure 1 and Figure 2,
229 respectively.

230 The thermal power curve (i.e. heat of hydration rate evolution) of PC without calcined
231 clay showed the typical behaviour for cement hydration. After the induction period, which
232 ended between 3-4 hours, two exothermic peaks related to the acceleration period appeared.
233 The first maximum after 9-10 hours is associated to the silicate reaction, i.e. the formation of
234 C-S-H and CH from hydration of C₃S and C₂S. The second maximum in the acceleration period
235 appeared after about 15 hours and is associated to the aluminate reaction, i.e. a combination of
236 renewed ettringite formation and the conversion of Aft (ettringite) to AFm (mono-sulphate)
237 phases (Taylor, 1997). The second maximum in the acceleration period is also referred to as
238 the sulphate depletion peak (Jansen, Goetz-Neunhoeffer, Lothenbach, & Neubauer, 2012).
239 When PC was blended with Clay A or B the two maxima in the acceleration period appeared
240 stronger and earlier with increased substitution of cement by calcined clay. The time between
241 the two maxima in the acceleration period seemed also to decrease with increasing replacement
242 level of PC. The effect was more pronounced for cement pastes mixed with Clay A. The times
243 of appearance of the second maxima (t_{\max} = time of maximum thermal power) in the
244 acceleration period are given in Table 3 for the different cement pastes.

245 A similar change in kinetics was observed in literature for cements blended with
246 metakaolin, silica fume or calcined marl (Antoni, et al., 2012; Fernandez Lopez, 2009; Ng and
247 Justnes, 2015a, 2015b; Rahhal and Talero, 2008; Rossen, Lothenbach, & Scrivener, 2015;
248 Talero and Rahhal, 2009). The substitution of cement by calcined clay mainly affects the
249 aluminate reaction. The high specific surface area of calcined clays significantly modifies the

250 reactivity of the aluminate phases. Additionally, with increasing levels of calcined clay, the
251 systems get under sulphated which also causes the sulphate depletion peak to shift to earlier
252 times. The higher the content of metakaolin the earlier and more distinct is the sulphate
253 depletion peak (Antoni et al., 2012). Clay A contains 47% metakaolin compared to 8% in Clay
254 B explaining the increased acceleration of nucleation in pastes with Clay A (Antoni et al.,
255 2012). Besides 8% metakaolin, Clay B also contains about 50% meta-smectite which
256 contributes to reactivity, however, less than metakaolin. Metakaolin contains more reactive
257 alumina compared to meta-smectite which is why cement pastes with Clay A appear
258 considerably more under-sulphated than pastes with Clay B. Antoni et al., 2012 observed that
259 at very high levels of PC replacement, the sulphate depletion peak might occur before the main
260 silicate reaction. Sulphate optimisation by adding additional sulphates to the system could
261 move the sulphate depletion peak back to later times (Antoni et al., 2012). It was also shown
262 that the higher heat flow and enhanced aluminate reaction can be related to the so called filler
263 effect (Lothenbach, Scrivener, & Hooton, 2011). The calcined clays act as nucleation sites and
264 promote the nucleation of the hydrates forming. Besides the higher kaolinite content and thus
265 the higher amount of reactive alumina, Clay A contains a higher amount of inert phases (e.g.
266 quartz and feldspar) compared to Clay B (Table 1 and Table 2). Clay B calcined at 800°C
267 contains only about 5% calcite compared to 25% in the raw clay before calcination (Danner et
268 al., 2018). The inert phases of clay A do not change upon calcination. Consequently, calcined
269 Clay A contains about 50% filler minerals compared to about 10% in calcined Clay B.

270

271 *3.2 In-situ XRD*

272 **Error! Reference source not found.** shows the in-situ XRD level plot of the pure PC paste
273 hydrated for 24 h. Partly dissolution of the clinker grains C_3S/C_2S and C_3A is visible in the
274 decreasing intensities between $29-42^\circ 2\theta$. Continuous ettringite (AFt) formation can be

275 observed at 9.1, 15.7 and 22.9° 2 θ from the first minutes. After about 11 h, the formation of
276 crystalline portlandite (CH) was detected. The time of portlandite detection correlated with the
277 time of the start of the sulphate depletion peak in isothermal calorimetry (Figure 1 and Figure
278 2).

279 Figure 4 shows the in-situ XRD level plot of hydration of cement paste blended with
280 20% Clay A, together with the thermal power curve. At 10.8° 2 θ the formation of an AFm
281 phase was detectable after about 12.5 h. The peak positions (10.8 and 21.7° 2 θ) indicate the
282 presence of hemi-carboaluminate hydrate. In the pure PC paste the formation of hemi-
283 carboaluminate hydrate was not detected during the first 24 hours of hydration. The time of
284 hemi-carboaluminate detection was associated with the peak of the sulphate depletion in the
285 acceleration period of the thermal power curve. In the cement pastes blended with calcined
286 clay the aluminate reaction, here the formation of hemi-carboaluminate hydrate appeared to be
287 accelerated. Ettringite did not disappear with the formation of hemi-carboaluminate hydrate.
288 Ettringite stabilization by favoured formation of carboaluminate hydrate AFm phases in
289 systems containing limestone is a well-known effect (De Weerd, Kjellsen, Sellevold, &
290 Justnes, 2011). As mentioned earlier, the cement used in this study contained about 3%
291 limestone which enabled the formation of carboaluminate hydrate phases even in the system
292 with Clay A. In the cement paste containing 20% calcined Clay A the precipitation of CH was
293 accelerated by about 2 h compared to the pure PC paste. The time of first detection of CH was
294 again associated with the start of the sulphate depletion peak in the thermal power curve. The
295 results show that the silicate and aluminate reaction of cement hydration were accelerated.

296 Sections of the in-situ XRD level plots of cement pastes blended with 20, 35 and 50%
297 Clay A hydrated for 24 h, are given in Figure 5. The formation of hemi-carboaluminate hydrate
298 was accelerated with increased amount of calcined clay in the cement paste. The time of first
299 detection of hemi-carboaluminate was after about 9 and 7 h in cement pastes with 35 and 50 %

300 Clay A, respectively. This was again in good agreement with the peak time of the sulphate
301 depletion peak in the thermal power as given in Table 3.

302 Cement pastes blended with Clay B showed a similar behaviour as cement pastes
303 blended with Clay A, however, not to the same extent. As mentioned above this can be
304 explained by the lower amount of metakaolin, and hence the lower amount of reactive alumina.
305 The main precipitation of hemi-carboaluminate was associated to the sulphate depletion peak
306 in the acceleration period. Additionally, in all cement pastes with calcined Clay B, the
307 formation of CH correlated with the start of the sulphate depletion peak. Again, both the
308 aluminate and silicate reaction appeared to be accelerated with increasing amount of calcined
309 clay in the paste.

310

311 ***3.3 Powder X-ray diffraction of hydrated Cement Pastes (PXRD)***

312 Figure 6 shows the diffractograms of cement pastes with 0, 20, 35 and 50% replacement of
313 cement by calcined Clay A (left) and calcined Clay B (right) hydrated for 28 days at 20°C. The
314 hydration products formed in cement pastes blended with calcined Clay A were ettringite,
315 carboaluminate hydrates and strätlingite. Strätlingite was first formed in the paste containing
316 35% calcined clay. At least 30% of PC have to be replaced by metakaolin to form crystalline
317 strätlingite (Ambroise, et al., 1994) because strätlingite is not stable in presence of calcium
318 hydroxide (Okoronkwo and Glasser, 2016). Carboaluminate hydrates formed due to a reaction
319 of AFm phases with the limestone contained in the cement. Besides the decreasing level of
320 limestone in the pastes with higher addition of calcined Clay A, the amount of hemi-
321 carboaluminate hydrate increased with increasing level of cement replacement. Increased
322 addition of calcined Clay A results in an increased amount of metakaolin and thus an increased
323 amount of reactive alumina to form AFm phases. The in total higher amount of AFm phases in
324 the system can react with the limestone, consequently forming a higher amount of hemi-

325 carboaluminate hydrate. Thus, the formation of carboaluminate hydrate is limited by the
326 amount of reactive alumina more than the availability of limestone. Still, due to the limiting
327 amount of limestone at high replacement levels a favoured formation of hemi-carboaluminate
328 occurred. With 50% calcined clay, almost all calcium hydroxide was consumed after 28 days.
329 Moreover, with increasing clay content a new peak at $8.9^\circ 2\theta$, to the left side of ettringite,
330 appeared. This peak could possibly be assigned to muscovite present in Clay A. The mineral
331 structure of muscovite is not much affected by the heat treatment at 800°C and becomes more
332 and more visible with increasing clay content in the pastes. However, the peak intensities do
333 not increase proportionate from 20 to 35% cement replacement. At present, it is not clear to
334 which phase the peak belongs to.

335 The crystalline hydration products observed in cement pastes blended with calcined
336 Clay B after hydration for 28 days at 20°C were similar to the phases detected in pastes with
337 Clay A, with the exception that strätlingite did not form. With 20% addition of calcined Clay
338 B the amount of carboaluminate hydrates increased. Further increase of calcined Clay B
339 appeared to result only in a minor increase of the amount of carboaluminate hydrates.
340 Compared to Clay A, Clay B contains less reactive alumina and thus forms in total less AFm
341 phases. In pastes with calcined Clay B, higher amounts of mono-carboaluminate formed
342 relative to hemi-carboaluminate as observed in pastes with calcined Clay A. The favoured
343 formation of mono-carboaluminate in pastes with Clay B can be explained by the additional
344 content of limestone in Clay B. Due to the pozzolanic reaction, the CH content decreased as
345 the amount of carboaluminate hydrates increased, but CH was not depleted even with an
346 addition of 50% Clay B. Ettringite was still stable after 28 days of hydration and no conversion
347 to monosulphate phases was found. As mentioned earlier the favoured formation of
348 carboaluminate hydrates in systems with limestone results in a stabilization of ettringite (De
349 Weerd, et al., 2011; Lothenbach, Le Saout, Gallucci, & Scrivener, 2008).

350

351 **3.4 Thermogravimetry (TG/DTG)**

352 The DTG curves of cement pastes blended with Clay A and Clay B after hydration for 28 days
353 at 20°C are shown in Figure 7. Both systems showed four major peaks at around 130, 190, 490
354 & 700-800°C. These peaks are associated with the decomposition of ettringite and C-S-H
355 (130°C), carboaluminate hydrate (190°C), calcium hydroxide (490°C) and calcite (700-
356 800°C). In addition, both systems showed a small shoulder around 250°C and a small peak
357 around 370°C. These signals are typically observed in hydrating cementitious systems and are
358 commonly associated with the decomposition of AFm phases like carboaluminate hydrates
359 (Lothenbach, Durdzinski, & De Weerd, 2015; Ramachandran, 1988). It can be seen, that the
360 amount of formed carboaluminate increased with increasing clay content in the cement pastes
361 while the amount of ettringite appeared rather stable. The CH content was significantly reduced
362 after 28 days of hydration in the cement pastes containing calcined clays. Pastes containing
363 calcined Clay A produced a higher amount of carboaluminate hydrate compared to pastes with
364 Clay B. It can also be seen that calcined Clay A consumed more CH than calcined Clay B due
365 to the higher amount of reactive material (metakaolin). The amount of CH after 28 days of
366 hydration at 20°C was calculated from the TG curves and is given in Table 4. Pure PC produced
367 about 16% CH after hydration for 28 days at 20°C. With increased amount of calcined clay the
368 amount of CH after 28 days was reduced. It is shown that Clay A consumed more CH in the
369 cement paste compared to Clay B at similar levels of addition. With 50% calcined Clay A only
370 about 2% CH were left in the paste after 28 days of hydration at 20°C, assuming that no other
371 hydrates decompose in the CH range. As comparison about 5% CH was left in pastes with 50%
372 calcined Clay B. The results show that both clays are very effective pozzolanic materials

373

374 **3.5 Electron Probe Micro Analysis (EPMA)**

375 Figure 8 and Figure 9 show backscattered electron (BSE) images of the cement pastes blended
376 with 20, 35 and 50% calcined Clay A and Clay B, respectively, after hydration for 28 days at
377 20°C. Point analysis was performed in different locations marked with numbers 1-8. The WDX
378 compositions measured in these points is given in atomic% in Table 5. The microstructure of
379 all pastes appeared very dense. Larger grains of quartz and feldspars from the clays and grains
380 of more or less hydrated clinker phases were found in a matrix of finer crystalline hydration
381 products. With increasing amount of calcined clay in the pastes, the amount of CH observed
382 was decreasing. In pastes with Clay A, strätlingite was the main hydration product to be
383 detected. At higher replacement levels (Figure 8c) cross sections of strätlingite platelets were
384 found all over the matrix. In the cement paste blended with 20% Clay A strätlingite could be
385 found in voids but seemed to be less crystalline (Figure 8a). The average composition of Points
386 1, 3, 4 & 5 was Ca = 11.9, Al = 9.9 and Si = 5.9. The ratio of Ca/Al=1.2 and Ca/Si=2.0 correlates
387 well with the composition of strätlingite.

388 The long needles visible in pastes with calcined Clay B (Figure 9a) might represent
389 ettringite from the cement hydration. The needles were too thin to be analysed with WDX. In
390 voids of the matrix, crystalline Ca-Al hydrates were detected (Figure 9a-c). The measured
391 composition of points 6-8 is given in Table 5 The Ca/Al ratio varies from 1.9 in point 6 to 2.8
392 in point 8. Point 6 and 7 most likely represent carboaluminate AFm phases with iron and
393 silicon substitution in the structure, while point 8 might be assigned to Fe-substituted ettringite
394 (Danner, 2013).

395

396 **3.6 Compressive Strength**

397 Figure 10 shows the compressive strength development of standard mortars from 1 to 28 days,
398 with 20, 35 and 50% replacement of PC by calcined Clay A. The error of compressive strength
399 results from mortar tests was about ± 1 MPa. At 1 day curing the compressive strength of the

400 mortars was reduced with increasing replacement level of PC. Still, already after 3 days the
401 mortar with 20% replacement of PC by calcined Clay A achieved a similar compressive
402 strength than the reference. After 7 days, mortars with 20 and 35% calcined Clay A showed
403 26% and 9% higher compressive strength than the reference. After 28 days curing, even the
404 mortar mix containing 50% calcined Clay A had a higher strength than the reference. The 28
405 day compressive strength was increased by 23, 15 and 9% respectively, when PC was replaced
406 with 20, 35 and 50 calcined Clay A (Table 6).

407 Figure 11 shows the compressive strength development of standard mortars from 1 to
408 28 days, with 20, 35 and 50% replacement of PC by calcined Clay B. It should be noted that
409 the strength of the reference mortar with 100% PC was higher than for the tests made with Clay
410 A. The reason for this is that the tests were performed at different times, and thus, different
411 batches of the same cement were used. Consequently, when comparing the strength
412 development of mortars with Clay A to mortars with Clay B, the relative strength development
413 should be compared. After curing for 1 and 3 days, the compressive strength of the mortars
414 was reduced the higher the replacement level of PC by calcined clay. Nevertheless, the 1 day
415 strength of the mortar with 50% replacement by Clay B was about 10 MPa, which is sufficient
416 for removing formwork of concrete in practice. After 7 days curing, the compressive strength
417 of mortars with 20 and 35% replacement was 95 and 92% of the reference strength. At 28 days,
418 the mortars with 20 and 35% addition of calcined Clay B had a 7 and 6% higher compressive
419 strength than the reference. With 50% replacement of PC by calcined Clay B the strength was
420 with 95% almost equal to the reference.

421 Table 6 and Table 7 show the relative strength of mortars with 20, 35 and 50%
422 replacement of PC by calcined Clay A and calcined Clay B after 1, 3, 7 and 28 days of curing.
423 As described before, the systems are under-sulphated at high replacement levels which might
424 reduce the early age strength of the mortars. Sulphate optimisation could increase the early age

425 strength. In a different study, it was shown that 1 day compressive strength of systems with
426 45% cement replacement by a metakaolin and limestone blend can be increased by adding extra
427 calcium sulphate (Antoni, et al., 2012). Comparing the relative strength of the mortars after
428 1day curing, there seems to be no significant difference between the strength development of
429 mortars with Clay A and mortars with Clay B. From 3-28 days the mortars containing 20 and
430 35% calcined Clay A had a considerable higher relative compressive strength than the mortars
431 containing 20 and 35% calcined Clay B. This can be explained by the higher reactivity of
432 calcined Clay A containing a higher amount of metakaolin. Calcined Clay B has a total higher
433 amount of clay minerals with 53% smectite and 8% kaolin. Due to this, calcined Clay B showed
434 also pozzolanic reactivity. However, the meta-smectite in calcined Clay B is less reactive than
435 metakaolin which seems to slow down the reactions compared to Clay A. At high replacement
436 levels of 50% the early compressive strength (1-7 days) is reduced. With decreased level of
437 cement the amount of CH produced and being available for reaction with the calcined clays is
438 reduced. Furthermore, besides increasing the amount of reactive clay minerals, the amount of
439 inert phases is increased with increased addition of calcined clay.

440

441

442 **4 Conclusions**

443 The hydration of cement pastes with addition of a kaolinite rich clay (Clay A) and a calcareous
444 smectite rich clay (Clay B) was investigated with isothermal calorimetry, in-situ XRD, PXRD,
445 TGA and EPMA. Portland cement was replaced by 20, 35 and 50 weight% calcined clay in
446 cement pastes and mortar tests.

447 The following conclusions can be drawn.

- 448 • Due to the higher amount of metakaolin and the higher specific surface, calcined Clay
449 A showed highest pozzolanic reactivity in terms of CH consumption and mortar
450 strength development. Mortars with 20, 35 and 50% PC replacement by calcined Clay
451 A showed higher 28 day compressive strength compared to the reference.
- 452 • The calcareous smectite rich Clay B demonstrated good pozzolanic activity but
453 appeared to react slower than Clay A. Considering the 28 days strength and sufficient
454 early strength of mortars, calcareous smectite clays may enable pozzolanic cements
455 with up to 55% clinker replacement (CEM IV/B).
- 456 • With increasing addition of calcined clay the second aluminate reaction (formation of
457 AFm phase) of cement hydration was accelerated and the cement pastes became under
458 sulphated. This resulted in a stronger and earlier sulphate depletion peak, especially for
459 pastes with calcined Clay A.
- 460 • Due to 3% calcite in the used cement the main hydration product found in pastes with
461 calcined Clay A was hemi-carboaluminate hydrate. Due to additional calcite in calcined
462 Clay B, the formation of mono-carboaluminate hydrate was favoured in pastes with
463 high additions of calcined Clay B. The favoured formation of carboaluminate hydrate
464 stabilised ettringite in the cement pastes.

465

466

467

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475

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680

681 Table 1: Mineralogical composition of the raw clays (Clay A and Clay B)

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

682

683

684 Table 2: Chemical composition and BET specific surface area of Clay A and B calcined at
685 800°C and the cement used in pastes.

Oxide (%)	A	B	Cement
SiO₂	60.6	48.7	19.9
Al₂O₃	30.0	17.8	4.8
Fe₂O₃	3.4	10.4	3.3
CaO	0.1	13.8	61.9
K₂O	3.2	2.4	1.0
Na₂O	—	0.7	0.5
MgO	0.4	2.8	2.7
MnO	0.0	0.2	
P₂O₅	0.1	0.2	0.2
TiO₂	0.4	1.0	
SO₃			3.3
Total	98.2	98.0	97.6
LOI	1.8	2.0	2.4
BET (m²/g)	19	15	2

686

687 Table 3: Times of maximum thermal power (t_{max}) from the hydration of cement pastes with
688 20, 35 and 50 wt% calcined Clay A and B

PC + Clay A		PC + Clay B	
	t _{max} (h)		t _{max} (h)
PC	15.3	PC	15.3
20% A	12.5	20% B	16.5
35% A	9.3	35% B	15.1
50% A	7.3	50% B	13.8

689

690

691

692 Table 4: Amount of CH (measured from TG curves) in the pastes after 28 days of hydration

PC + Clay A		PC + Clay B	
	CH _{28d} (%)		CH _{28d} (%)
PC	16	PC	16
20% Clay A	10	20% Clay B	12
35% Clay A	5	35% Clay B	8
50% Clay A	2	50% Clay B	5

693

694 Table 5: WDX composition in atomic percent of points 1-8 indicated in Figure 11 and 12.

WDX_No.	Ca	Al	Si	Fe	K	O
1	12.9	9.4	5.3	0.8	0.3	70.8
2	16.5	8.9	1.1	0.5	0.1	72.1
3	11.3	9.4	5.9	0.6	0.2	72.5
4	11.5	10.1	6.7	0.5	0.2	70.9
5	11.7	10.6	5.5	0.5	0.1	71.4
6	16.9	9.1	0.8	1.5	0.1	71.1
7	16.7	6.9	2.8	0.5	0.3	72.2
8	16.1	5.8	0.9	1.6	0.0	75.2

695

696

697 Table 6: Relative strength of mortars containing calcined Clay A

Relative compressive strength (%)				
Time	REF	20%	35%	50%
1 day	100	82	56	34
3 day	100	99	80	55
7 days	100	126	109	71
28 days	100	122	115	109

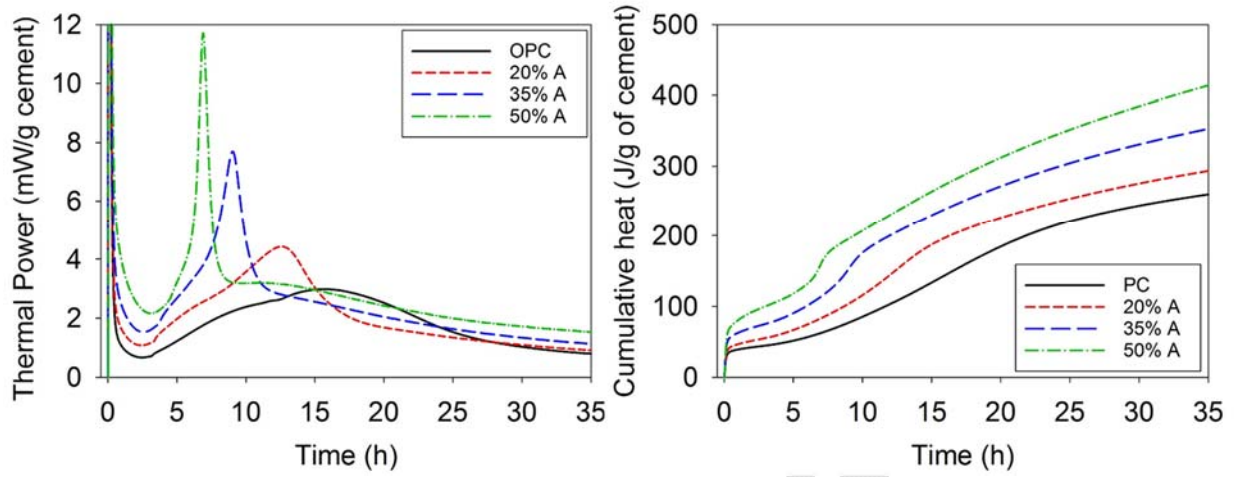
698

699

700 Table 7: Relative strength of mortars containing calcined Clay B

Relative compressive strength (%)				
Time	REF	20%	35%	50%
1 day	100	81	64	43
3 day	100	88	77	58
7 days	100	95	92	84
28 days	100	107	106	95

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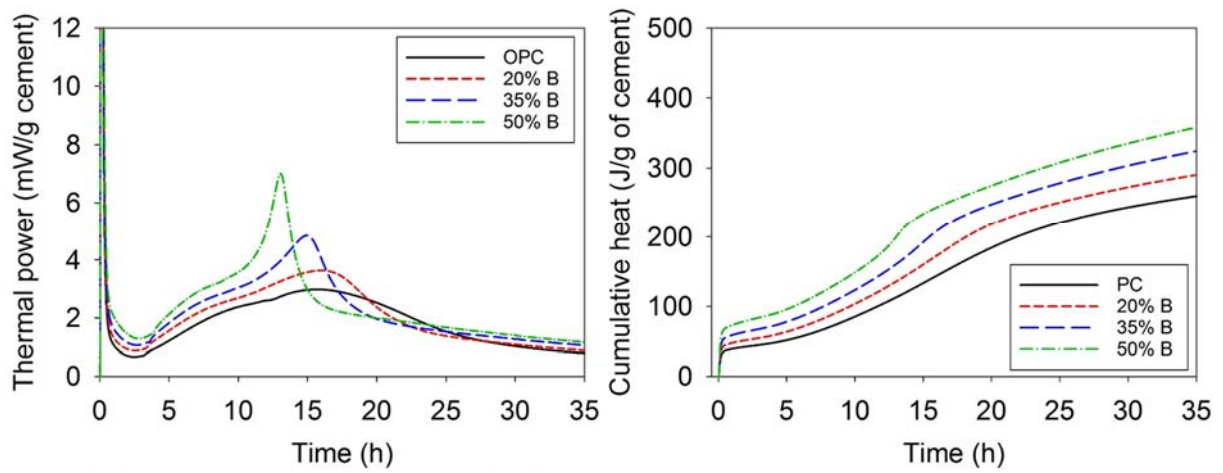


702

703 Figure 1: Thermal Power (left) and cumulative heat (right) of pastes of PC and 20, 35, 50 wt%

704 calcined Clay A

705



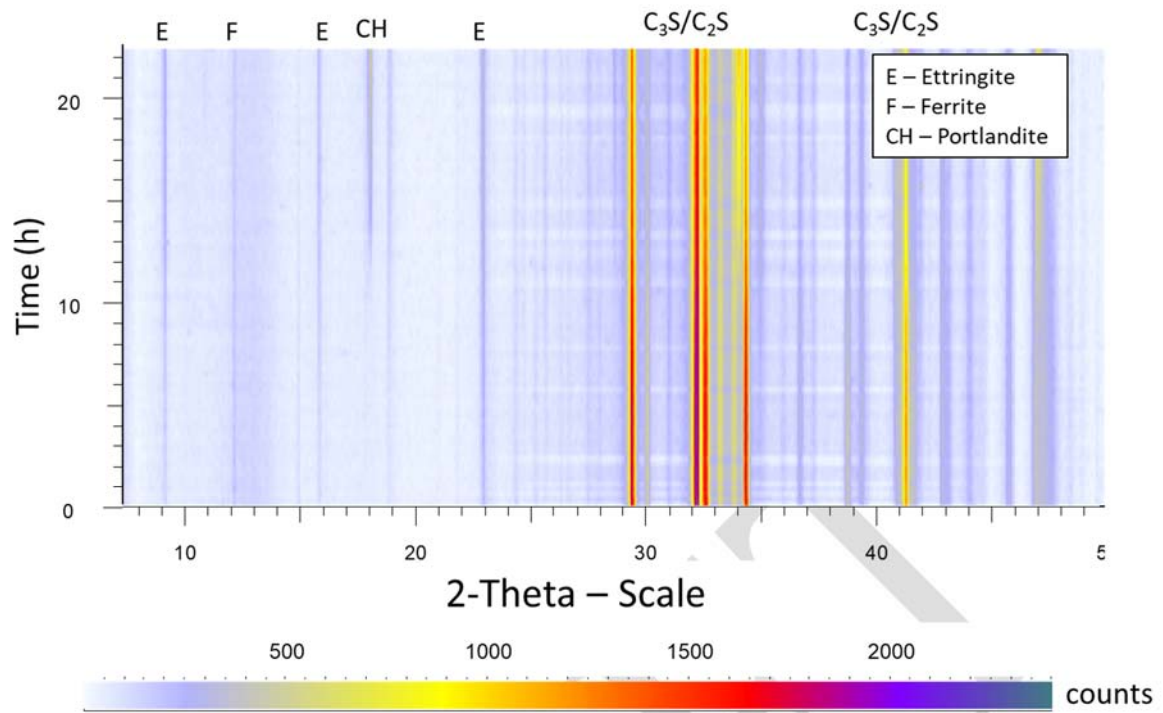
706

707 Figure 2: Thermal Power (left) and cumulative heat (right) of pastes of PC and 20, 35, 50 wt%

708 calcined Clay B

709

710

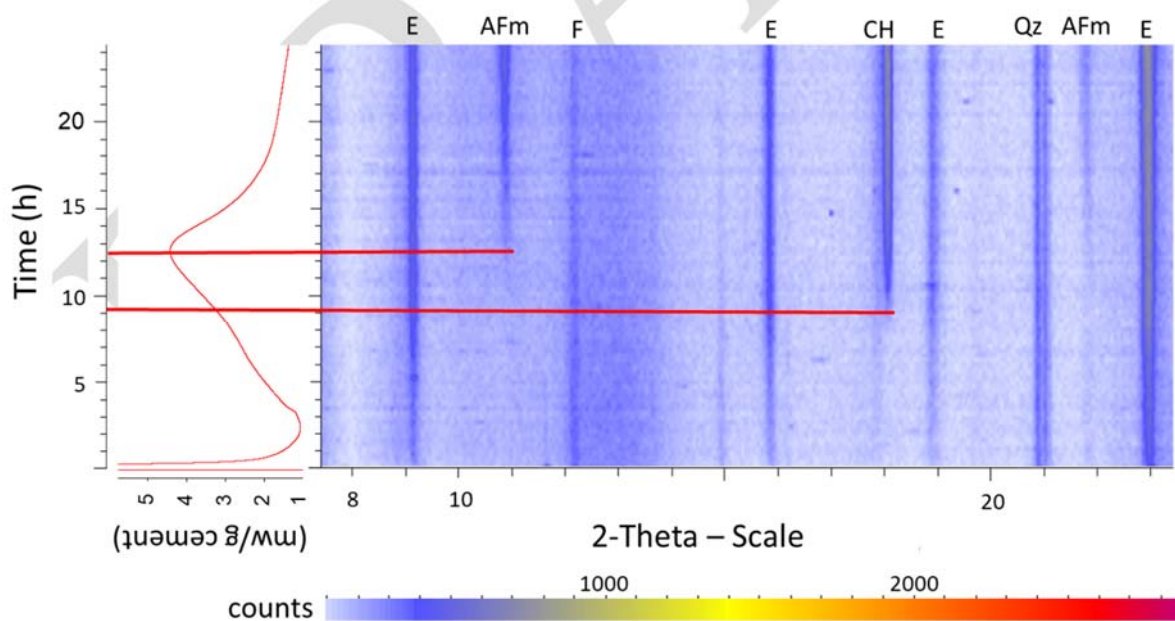


711

712 Figure 3: in-situ XRD level plot of hydrating PC paste during the first 24 h of hydration.

713 (E=ettringite; F=ferrite phase C₄AF; CH=portlandite)

714



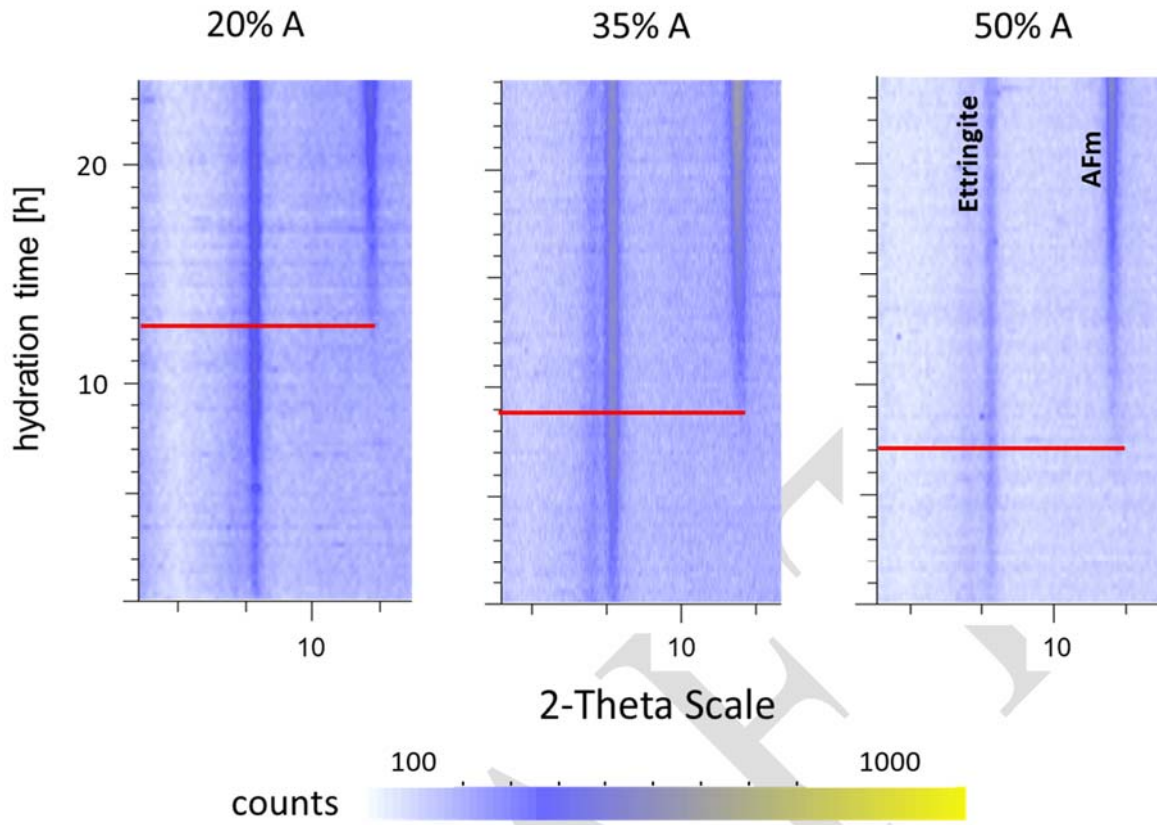
715

716 Figure 4: in-situ XRD level plot and thermal power curve of cement paste with 20 wt% calcined

717 Clay A hydrated for 24 h. (E=ettringite; AFm=hemi-carboaluminate; F=Ferrite phase C₄AF;

718 CH=portlandite; Qz=Quartz)

719

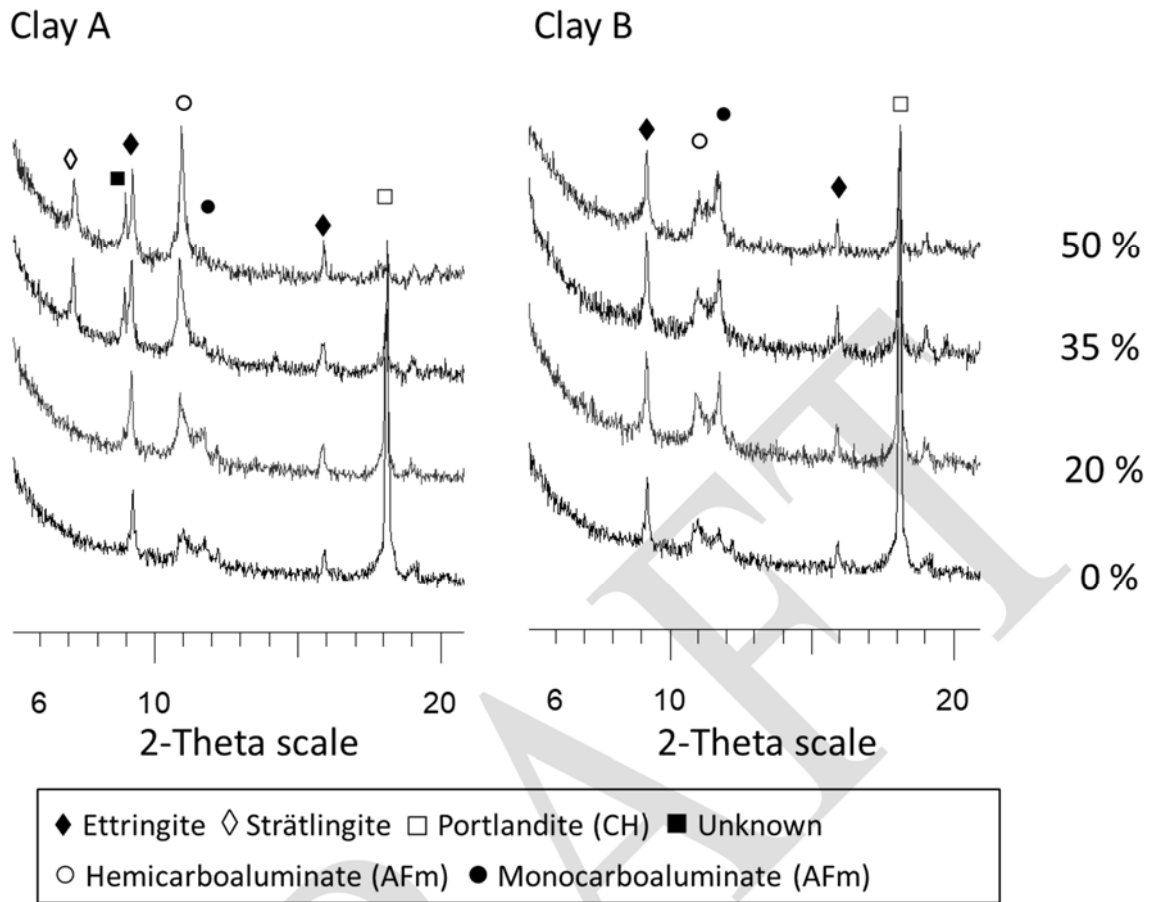


720

721 Figure 5: in-situ XRD levelplot of PC pastes with 20, 35 and 50 wt% Calcined Clay A hydrated
 722 for 24 h at 20 °C. AFm = hemi-carboaluminate

723

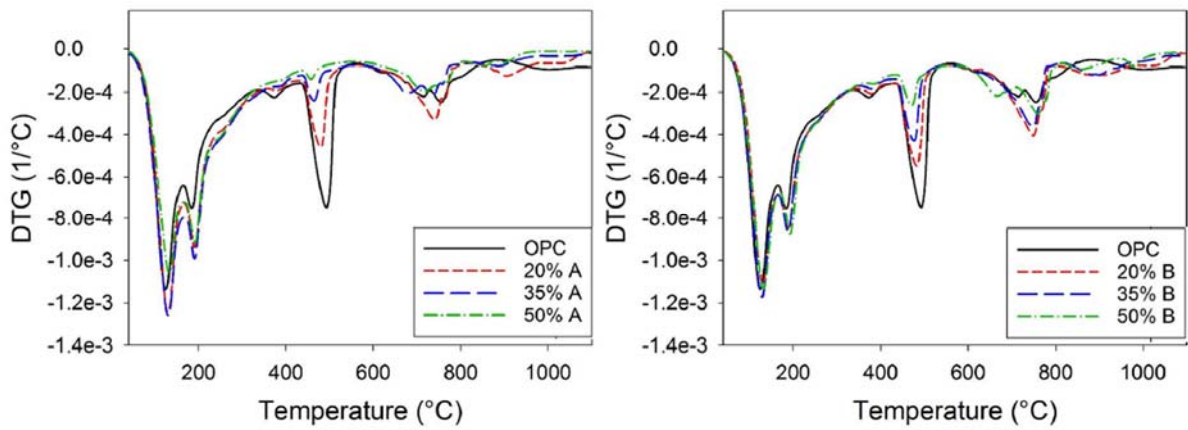
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725

726 Figure 6: XRD diffractograms of cement pastes with 20, 35 and 50 wt% calcined Clay A (left)
727 and calcined Clay B (right) hydrated for 28 days at 20 °C.

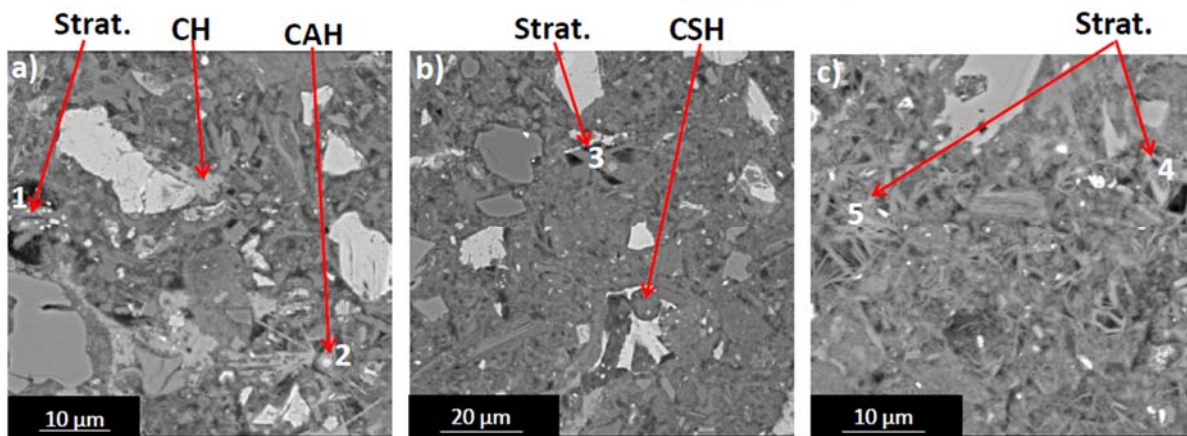
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729

730 Figure 7: DTG of cement pastes with 20, 35 and 50 wt% calcined Clay A (left) and calcined
 731 Clay B (right) hydrated for 28 days at 20°C.

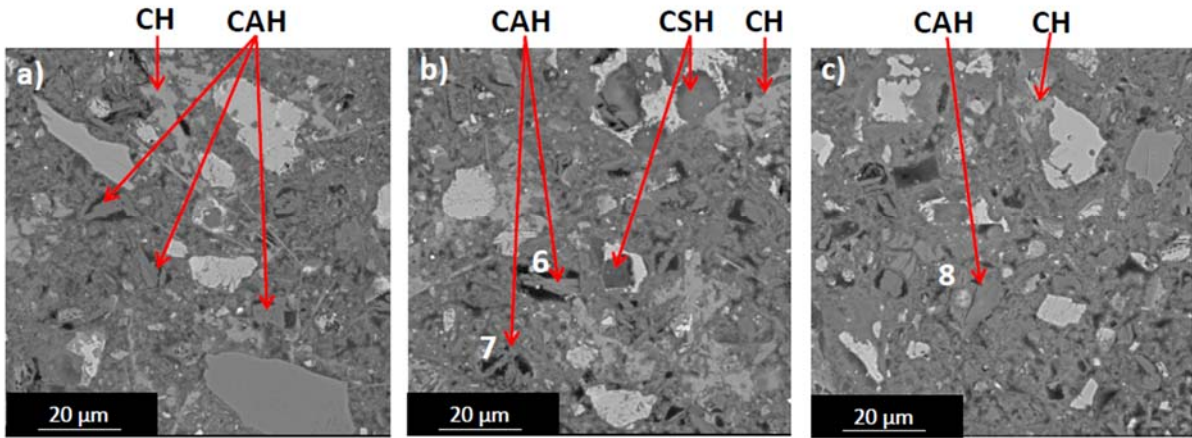
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733

734 Figure 8: BSE images of cement pastes with a) 20, b) 35 and c) 50 wt% calcined Clay A
 735 hydrated for 28 days at 20°C.

736



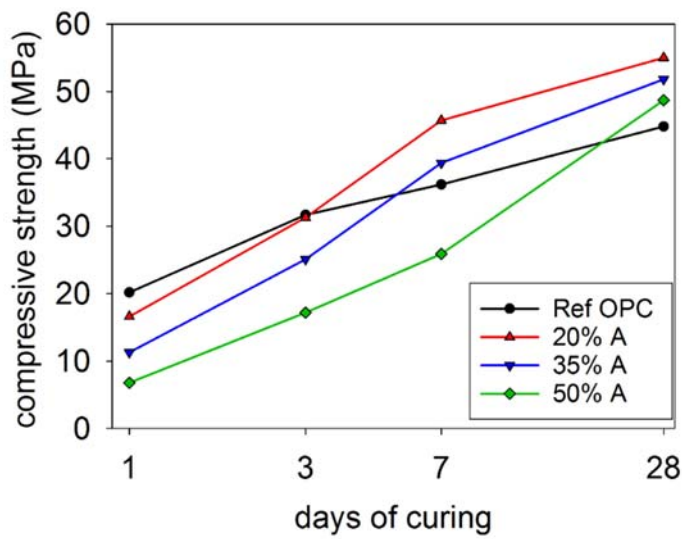
737

738 Figure 9: BSE images of cement pastes with a) 20, b) 35 and c) 50 wt% calcined Clay B
739 hydrated for 28 days at 20°C

740

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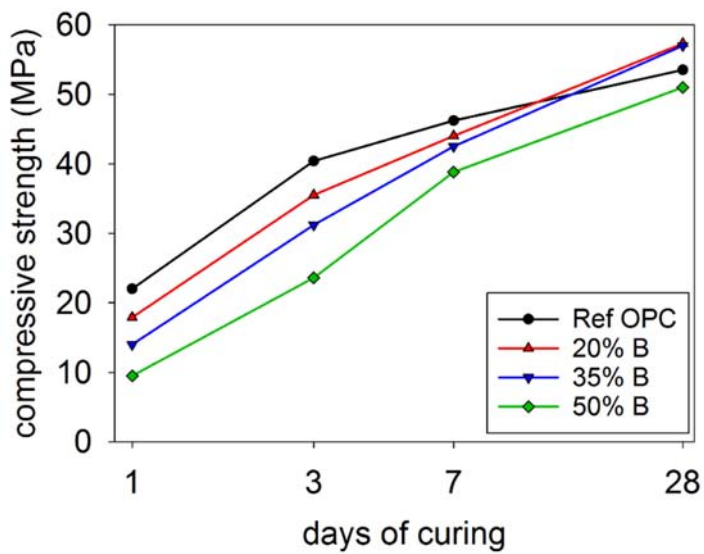
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742

743 Figure 10: Compressive strength of standard mortars with 20, 35, 50 wt% replacement of PC
744 by calcined Clay A

745



746

747 Figure 11: Compressive strength of standard mortars with 20, 35, 50 wt% replacement of PC
748 by Calcined Clay B

749