



HAL
open science

Calcined palygorskite and smectite bearing marlstones as supplementary cementitious materials

Victor Poussardin, Michael Paris, William Wilson, Arezki Tagnit-Hamou,
Dimitri Deneele

► **To cite this version:**

Victor Poussardin, Michael Paris, William Wilson, Arezki Tagnit-Hamou, Dimitri Deneele. Calcined palygorskite and smectite bearing marlstones as supplementary cementitious materials. *Materials and structures*, 2022, 55 (8), pp.224. 10.1617/s11527-022-02053-0 . hal-03833458

HAL Id: hal-03833458

<https://hal.science/hal-03833458v1>

Submitted on 19 Dec 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

[Click here to view linked References](#)

1 **Calcined palygorskite and smectite bearing marlstones as** 2 **supplementary cementitious materials**

3 Victor Poussardin^{1,2,3}, Michael Paris², William Wilson³, Arezki Tagnit-Hamou³, Dimitri
4 Deneele^{1,2*}

5 ¹*GERS-GIE, Univ Gustave Eiffel, IFSTTAR, F-44344 Bouguenais, France*

6 ²*Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000*
7 *Nantes, France*

8 ³*Université de Sherbrooke, Sherbrooke, QC, Canada*

9 *corresponding author: dimitri.deneele@univ-eiffel.fr

11 **Highlights**

- 12 • Palygorskite-bearing marlstone is suitable for a use as a SCM
- 13 • Palygorskite-bearing marlstone exhibits a higher dihydroxylation (²⁷Al MAS NMR),
14 self-reactivity in water and compressive strength in cementitious media than smectite-
15 bearing marlstone.
- 16 • Pouzzolanic reactivity was significantly higher for systems with calcined palygorskite
17 than calcined smectite only, as shown both by portlandite consumption (XRD) and C-
18 (A)-S-H formation (²⁹Si MAS NMR).

26 **Abstract**

1
2 27
3
4 28 This article focuses on the use of two calcined marlstones as supplementary cementitious
5
6 29 materials, one with palygorskite and smectite (MS1) as clay phases and the other with smectite
7
8 30 only (MS2). The calcination and the reactivity of these two materials were first analysed by X-
9
10
11 31 ray diffraction (XRD) and Magic Angle Spinning Solid State Nuclear Magnetic Resonance
12
13 32 (MAS NMR). The two calcined marlstones were combined with Portland cement to produce
14
15
16 33 mortars and measure compressive strength. The XRD and ²⁷Al MAS NMR results showed that
17
18 34 800°C is an optimal calcination temperature and that both calcined marlstones can be used as
19
20
21 35 supplementary cementitious materials. The reactivity of MS1 was found to be higher than that
22
23 36 of MS2. This was confirmed with compressive strength measurements which showed superior
24
25
26 37 performance for mortars blended with calcined MS1 rather than calcined MS2. This difference
27
28 38 between MS1 and MS2 is due to the presence of palygorskite in MS1, which greatly improves
29
30
31 39 the reactivity and final mechanical performances. Therefore, palygorskite bearing marlstones
32
33 40 are suitable for a use as SCM and this suggests that palygorskite exhibits a significant
34
35
36 41 pozzolanic reactivity.

37
38
39 42
40 43 **Keywords:** Palygorskite, marlstone, SCMs, MAS NMR, calcined clay, dolomite
41
42 44
43
44 45
45
46 46
47
48 47
49
50 48
51
52 49
53
54 50
55
56 51
57
58 52
59
60
61
62
63
64
65

1. INTRODUCTION

In order to comply with the Paris climate agreements, and to limit the global temperature increase below 1.5°C compared to pre-industrial levels, the most polluting industrial sectors need to reduce significantly their greenhouse gas emissions (may their CO₂ emissions). It is estimated that 5 to 8% of global anthropogenic CO₂ emissions comes from the cement industry [1]. In this context, cement producers are seeking to reduce their carbon footprint.

The use of Supplementary Cementitious Materials (SCMs) to replace part of the clinker is now seen as one of the major solutions to reduce the environmental footprint of the cement industry [2]. Blast furnace slag [3, 4] and power plant fly ash [5–7] are the main examples of SCMs used today that reduce the environmental footprint of cement. However, blast furnace slag resources remain limited, preventing large-scale deployment of this technology, and fly ash reserves from coal combustion will continue to decline in the coming years as the energy transition legitimately limits their availability [2].

Among alternative SCMs, calcined clays are gaining in popularity. The resources of clays potentially viable as SCMs after calcination are abundant and well distributed around the world, especially in developing countries where the demand for cement is constantly growing [2]. The numerous studies carried out on the subject have shown that metakaolin (from the calcination of kaolin) has the highest reactivity in cementitious media [8–11], whereas calcined smectites [12–14] and illites [15–17] are much less reactive. These results led to a growing interest in the use of calcined kaolins (rock composed of kaolinite, quartz and minor accessory minerals) as SCMs, and to the development of Limestone Calcined Clay Cements (LC3) [18, 19].

Only few studies have looked at other types of clays than kaolinites, smectites and illites [20, 21], mainly because of industrial competition (which leads to higher prices) and lower availability. Furthermore, the majority of studies focused on relatively "pure" samples, which

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

78 are mainly composed of clay minerals, quartz and other accessory minor minerals. Yet it is
79 common to find clay minerals associated with other compounds, especially carbonates. If the
80 proportion of carbonates is high, this mixture of clay minerals and carbonates is named
81 marlstone.

82 Marlstones are often neglected by manufacturers of fired clay materials such as bricks because
83 of their high content of calcium carbonate. They are considered as waste by many industries
84 and supplies are increasing [22]. However, these materials contain a significant proportion of
85 clay minerals, which can become pozzolans upon calcination. The use of marlstones as SCMs
86 could therefore make it possible to recover mining wastes (and/or overburdens) while reducing
87 the environmental footprint of cement production. Numerous studies looked at the use of
88 marlstones as SCMs [23–27] , but the great variability of this type of material limits the
89 possibility of global analyses. For each type of marlstones considered as a potential SCM, it is
90 imperative to understand the evolution of each phase (clay minerals and carbonates) composing
91 the marlstones during its calcination, as well as its influence on the reactivity and the final
92 mechanical performances of calcined marlstone-cement blends.

93 This study focuses on the use as SCMs of two marlstones considered as waste by the mining
94 industry. The first objective is to determine whether these materials can be used as SCMs. The
95 second objective is to study the physico-chemical changes taking place during the calcination
96 and the reaction of these new pozzolans and to correlate this information with the final
97 mechanical performances. The last objective is to determine how palygorskite (an
98 unconventional clay contained in one of the two materials) contributes to the pozzolanic
99 reactivity.

100

101

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

The materials studied (MS1 and MS2) are two marlstones considered as waste by the mining industry. The samples were received as loose blocks and mechanically crushed before analysis. Table 1 shows the results of the chemical analysis (performed by X-Ray Fluorescence (XRF)). The proportions of each element are expressed in weight percent.

Table 1. Chemical analysis of MS1 and MS2.

	Element	O	Ca	Si	Mg	Al	Fe	K	P	Na	Ti	V
MS1	wt. %	55.5	14.2	15.6	6.0	4.7	1.5	1.0	0.6	0.2	0.2	0.1
MS2	wt. %	56.0	16.4	16.2	5.5	3.8	1.2	0.2	0.2	0.2	0.2	0

MS1 and MS2 have a very close chemical composition, especially regarding the proportions of silicon, calcium, magnesium and aluminium. These similarities in the chemistry of MS1 and MS2 are not surprising as both materials originate from the same sedimentary deposit. X-ray diffraction analysis (XRD) was performed to highlight the mineralogical composition MS1 and MS2 and the different phases were quantified using the Rietveld refinement technique (see supporting information). Table 2 shows the results of the quantitative phases analysis for MS1 and MS2.

Table 2. wt.% of the crystalline phases of MS1 and MS2.

	Phase	Dolomite	Palygorskite	Smectite	Biotite	Hydroxylapatite	Quartz
MS1	wt.%	54	17	16	2	3	8
MS2	wt.%	59		27	1	2	11

119 MS1 and MS2 have a relatively close mineralogy, they are both mainly composed of dolomite
1 associated with clay phases (smectite and biotite), quartz and hydroxylapatite. The main
2 difference is the occurrence of palygorskite in MS1, which replaces part of the smectite.
3
4
5
6
7
8
9

122

123 **2.2. Marlstone calcination**

124 MS1 and MS2 were calcined at 600, 800 and 900°C in alumina crucibles using a laboratory
15 furnace. The choice of these temperatures was made in accordance with the first study on
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

130 **2.3. Hydration of calcined marlstones**

131 The calcination and hydration of MS1 have already been the subject of two previous studies
132 [29, 30] which demonstrated the formation of several reactive phases after calcination, notably
133 CaO. As MS2 has a very close mineralogy to MS1, it is very likely to have the same reactive
134 phases formed. Therefore, the pozzolanic activity of calcined MS1 and MS2 could not be
135 measured using the classical pozzolanic activity tests (Chapelle test [31] and R³ [32]), which
136 requires the material tested not to contain free calcium. It was therefore decided to characterise
137 the reactivity of these calcined materials by carrying out hydration tests.

138 For both MS1 and MS2, 1g of 800°C calcined material was manually mixed with water
139 according to the chosen water to binder ratios (w/b = 0.8; 1; 2 and 4). The mixtures were left to
140 react in sealed conditions for 7, 14, 28 and 180 days. At the end of each time period, the
141 hydration was stopped by freezing at -24°C during 24h and freeze-drying during 48h under

142 vacuum. The dried materials were crushed and analysed by X-ray diffraction (XRD) and solid
143 state nuclear magnetic resonance (MAS NMR). As the result analysis did not reveal any
144 significant differences between the different w/b, only the hydration results for w/b = 0.8 are
145 reported.

147 **2.4. X-ray diffraction analysis (XRD)**

148 Measurements were made with a Bruker D8 diffractometer using a Bragg-Brentano geometry
149 with a copper anode tube X-ray source (40 kV/40 mA) emitting Cu K α radiation. The
150 acquisitions of the diffractograms were made between 4° and 60° 2 θ with a step size of 0.017°
151 2 θ and a measurement time of 1s per step. The Rietveld quantification of MS1 and MS2 was
152 performed using the Profex Rietveld refinement program [33].

154 **2.5. Solid state nuclear magnetic resonance (MAS NMR)**

155 ²⁷Al MAS NMR spectra were acquired in a 2.5 mm MAS probe using a Bruker Avance III 500
156 MHz spectrometer with the following parameters : MAS frequency of 30 kHz, excitation pulse
157 length of $\pi/13$, radio frequency field of 11 kHz and repetition time of 1s.

158 ²⁹Si MAS NMR spectra were acquired in a 7 mm MAS probe using a Bruker NEO 300 MHz
159 spectrometer with the following parameters : MAS frequency of 5 kHz, excitation pulse length
160 of $\pi/2$ and repetition time of 10s. The chosen 10s repetition time is too short to obtain a
161 quantitative signal from the quartz, but as quartz is unreactive shorter repetition time can be
162 used to save spectrometer time.

163 All the acquisitions were performed with ¹H decoupling. An aqueous solution of Al(NO₃)₃ was
164 used to referenced ²⁷Al spectra while ²⁹Si spectra were referenced against TMS

165 (Tetramethylsilane). The Dmfit software [34] was used to perform the spectral decompositions
166 (see supporting information).

167 **2.6. Calcined marlstone-cement blends and compressive strength measurements**

168 The compressive strength was assessed on mortar cubes (50 x 50 x 50 mm³) made with graded
169 standard (supports ASTM C109) sand (sand to cement ratio = 2.75) and a constant water to
170 binder ratio (w/b = 0.484). Blended cement was obtained by mixing 80 wt.% of general use
171 Portland cement (GU) with 20 wt.% of 800°C calcined MS1 (for M-MS1 mortar) or MS2 (for
172 M-MS2 mortar). The particle size distributions of the GU cement and MS1 and MS2 (before
173 and after calcination) are shown in Table 3. The d-values indicate the maximal particle size
174 diameter that includes 10% (d10), 50% (d50) and 90% (d90) of the particles (volume-weighted
175 basis).

176 Table 3. Particle size distributions of GU cement and marlstones (MS1 and MS2) before and
177 after calcination at 800°C.

Label	d10 (µm)	d50 (µm)	d90 (µm)
MS1	3.5	19.5	64.1
800°C-MS1	4.0	24.5	91.6
MS2	2.4	14.8	53.1
800°C-MS2	3.6	28.2	66.3
GU cement	3.5	20.5	59.7

178
179 Both 800°C-MS1 and 800°C-MS2 have a particle size distribution close to that of GU cement,
180 which ensures homogeneous blends.

181 Control mortars cubes (labelled M-Ref) were prepared using 100% GU cement. A
182 polycarboxylate (PC) superplasticizer (0.6% by total weight of binder) was used to obtain a
183 flow equivalent to that of the control mixture (± 5 mm). Table 4 shows the proportions of the
184 investigated mortars.

186 Table 4. Mix proportions of mortars

Label	Cement (g)	Pozzolan (g)	Sand (g)	Water (g)
M-Ref	500	0	1375	242
M-MS1	400	100	1375	242
M-MS2	400	100	1375	242

187
188 Mortars were mixed and specimens were molded according to the standard procedure ASTM
189 C109 [35]. After molding, the specimens were placed in plastic bags for 20-24h until
190 demolding. The demolded mortar cubes were stored in saturated lime water until testing. At 7
191 and 28 days the compressive strength was assessed according to the ASTM C109 loading
192 procedure [35].

194 3. RESULTS AND DISCUSSION

195 3.1. Calcination

196 Fig. 1. displays the evolution of MS1 (Fig. 1.A) and MS2 (Fig. 1.B) X-ray diffractograms as a
197 function of the calcination temperature.

C2S = Ca_2SiO_4	Bio = Biotite $\text{K}(\text{Mg,Fe})_3(\text{OH,F})_2(\text{Si}_3\text{AlO}_{10})$
Dol = Dolomite $\text{CaMg}(\text{CO}_3)_2$	Pal = Palygorskite $(\text{Mg,Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$
Pe = Periclase MgO	Li = Lime CaO
Qz = Quartz SiO_2	Sm = Smectite $(\text{Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
Dehy Sm = Dehydrated Smectite	Hy = Hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
Au = Augite	Ak = Akermanite

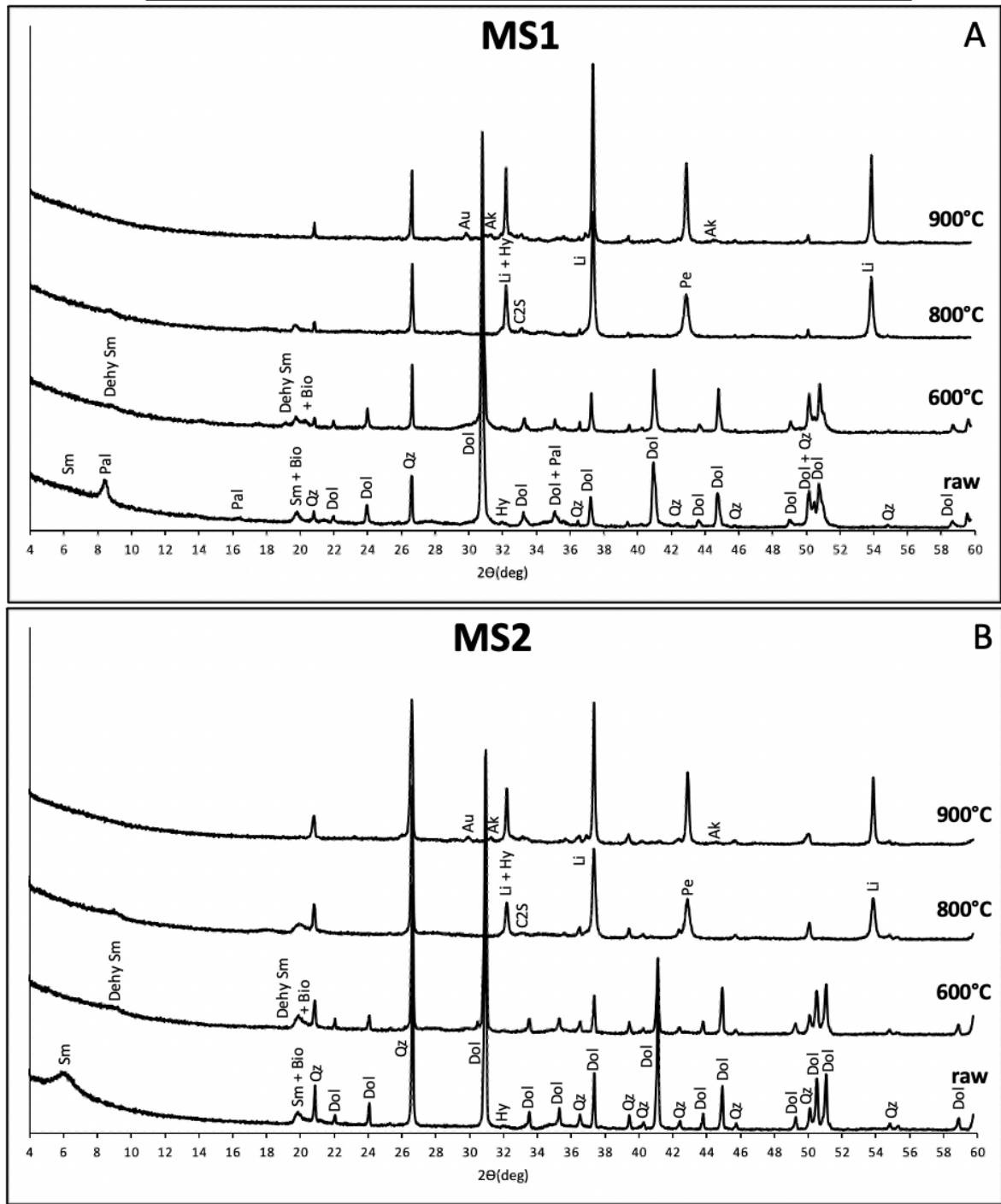


Fig. 1. Evolution of the X-ray diffractograms of MS1 (A) and MS2 (B) as a function of the calcination temperature.

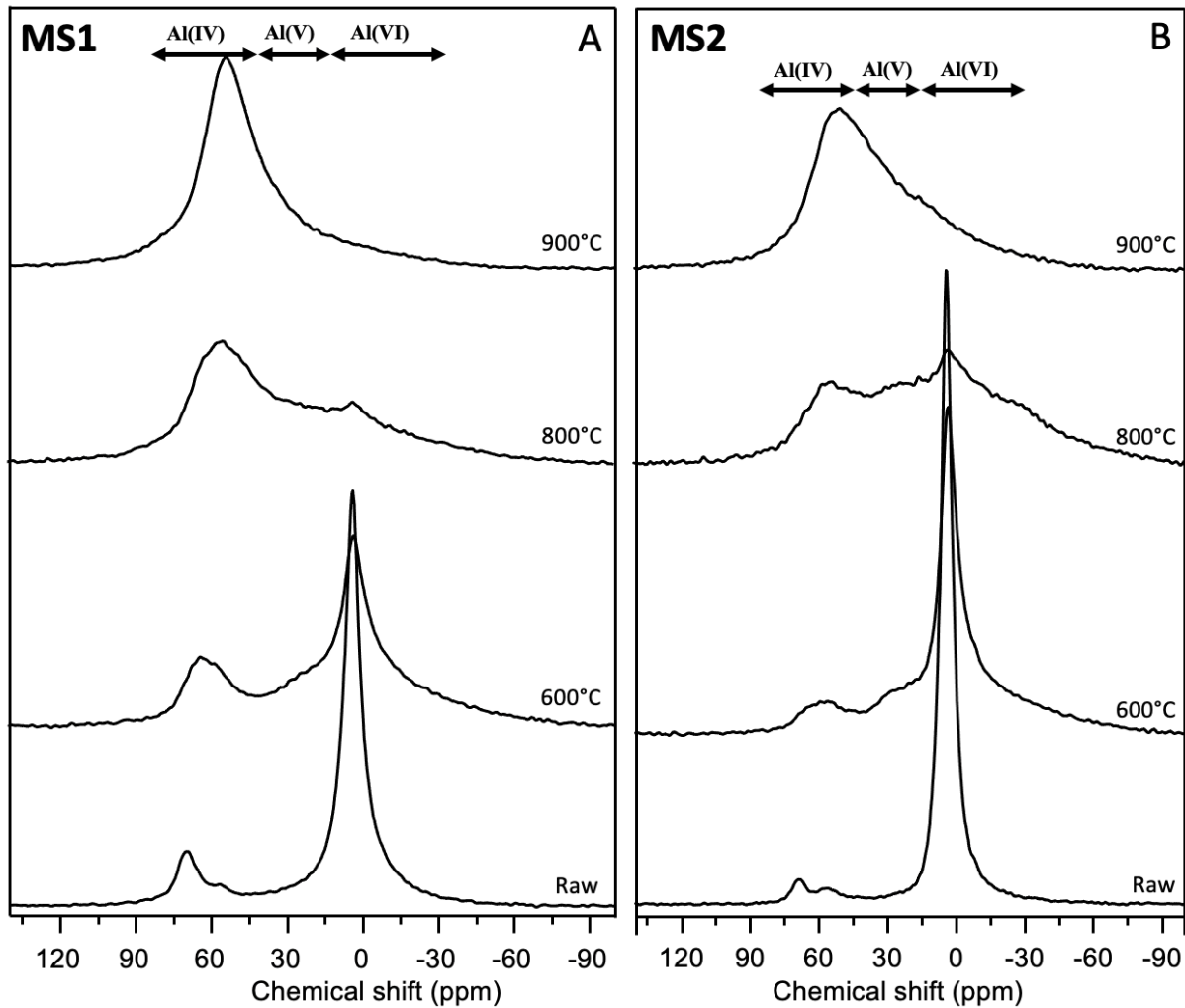
202 At 600°C, for both MS1 and MS2 the 001 peak of smectite (Sm) is shifted from 6.2°(2θ) to
1
2 203 8.75°(2θ). This shift is explained by the dehydration of the smectite during the heat treatment
3
4 204 (the removal of the interlayer water leads to a decrease in d001 basal spacing) [36, 37].
5
6
7 205 Concerning MS1, the characteristic peaks of palygorskite disappears at 600°C, reflecting its
8
9 206 loss of crystallinity.
10

11 207
12
13
14 208 At 800°C, for both MS1 and MS2 the dolomite ($\text{CaMg}(\text{CO}_3)_2$) decarbonates into lime (CaO)
15
16 209 and periclase (MgO) and a peak associated with dicalcium silicate (C_2S) appears. However, the
17
18 210 low intensity of the C_2S peaks (possibly due to low crystallinity of the phase) hinders the
19
20 211 determination of the type of polymorph. The fact that this C_2S is formed at the same temperature
21
22 212 as the lime supports the hypothesis that it results from a recombination phenomenon between
23
24 213 the calcium from the decarbonated dolomite and the silicon from calcined clay phases [38].
25
26
27
28
29 214

30
31 215 At 900°C, for both MS1 and MS2 the characteristic peaks of dehydrated smectite and biotite
32
33 216 disappear, indicating a complete loss of crystallinity of these two phyllosilicates. Quartz and
34
35 217 hydroxylapatite are not sensitive to heat treatment since their peaks remain detectable up to
36
37 218 900°C. Finally, there are recrystallisation phenomena in the form of augite and akermanite at
38
39 219 900°C.
40
41
42
43
44 220

45
46 221 Based on these XRD results, 800°C seems to be a suitable calcination temperature as it allows
47
48 222 the loss of crystallinity of the clay phases without causing recrystallisation phenomena (that
49
50 223 could reduce the reactivity) for both MS1 and MS2.
51
52
53 224
54
55
56 225
57
58 226
59
60
61
62
63
64
65

227 Fig. 2. displays the evolution of the ^{27}Al MAS NMR spectra of MS1 (Fig. 2.A) and MS2 (Fig.
 228 2.B) as a function of the calcination temperature.

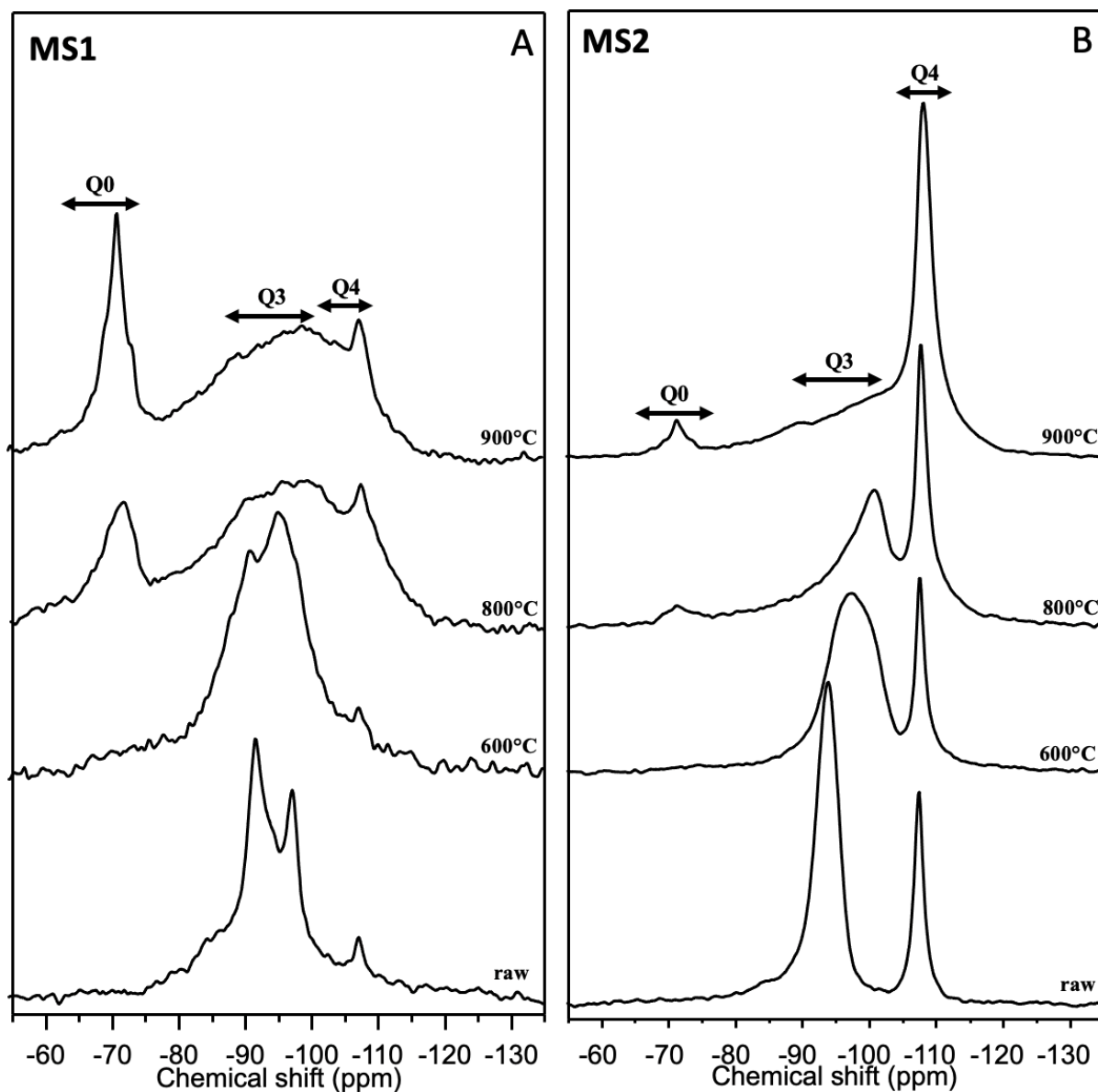


230 **Fig. 2.** Evolution of the ^{27}Al MAS NMR spectra of MS1 (A) and MS2 (B) as function of the
 231 calcination temperature.

233 Both spectra of raw MS1 and MS2 exhibit two main resonances at 3 and 70 ppm which
 234 correspond to 6-fold and 4-fold aluminium, respectively [39]. The 6-fold aluminium resonance
 235 (3 ppm) can be associated with aluminium in palygorskite, smectite and biotite for MS1 and
 236 with aluminium in smectite and biotite for MS2 [40]. The 4-fold aluminium resonance (70 ppm)
 237 can be associated with the isomorphic substitution of silicon by aluminium atoms into silicate
 238 layers of palygorskite, smectite and biotite structures for MS1 and into smectite and biotite

239 structures for MS2 [40]. A weak resonance at 57 ppm is detected in both MS1 and MS2 spectra,
1
2 240 which corresponds to aluminium in q4(4Si) configuration [41] possibly associated with an
3
4
5 241 additional phase occurring in low quantity and/or with low crystallinity, undetectable by XRD.
6
7
8 242 With the increasing calcination temperature, the 6-fold aluminium resonance intensity
9
10 243 decreases while two new resonances appear at 27 and 59 ppm, which correspond to 5-fold and
11
12 244 4-fold aluminium, respectively [39]. During the calcination of MS1 and MS2, the calcination
13
14
15 245 leads to a departure of hydroxyl groups from the clay phases (the dehydroxylation
16
17 246 phenomenon). The octahedral (6-fold) aluminium atoms to which these hydroxyl groups were
18
19
20 247 bonded have changed their coordination to 5- and 4-fold aluminium atoms. The pozzolanic
21
22 248 activity of a calcined clay could be directly related to the relative proportion of 5- and 4-fold
23
24
25 249 aluminium. These sites, in particular at the 5-fold one, are the starting point of the dissolution
26
27 250 and the initiation of the pozzolanic reaction [15]. For both MS1 and MS2, the highest relative
28
29
30 251 proportion of aluminium 5 and 4 (without recrystallization) is reached at 800°C, which suggests
31
32 252 that this calcination temperature should allow the highest pozzolanic reactivity. By comparing
33
34
35 253 the evolution of MS1 and MS2 it is clear that the dehydroxylation occurs more easily in MS1
36
37 254 (which contains smectite and palygorskite) than in MS2 (which contains only smectite). At
38
39
40 255 800°C, a significantly higher relative proportion of 6-fold aluminium is still remaining in MS2
41
42 256 than in MS1. This difference can be explained by the occurrence of palygorskite in MS1, which
43
44 257 was found to dehydroxylate more efficiently (at lower temperature) than smectite and biotite.
45
46
47
48 258
49
50
51 259
52
53
54 260
55
56
57 261
58
59
60
61
62
63
64
65

262 Fig. 3. displays the evolution of the ^{29}Si MAS NMR spectra of MS1 (Fig. 3.A) and MS2 (Fig.
 263 3.B) as a function of the calcination temperature.



264
 265 **Fig. 3.** Evolution of the ^{29}Si MAS NMR spectra of MS1 (A) and MS2 (B) as function of the
 266 calcination temperature.

267
 268 Both spectra of raw MS1 and MS2 exhibit a resonance at -108 ppm which correspond to Q⁴
 269 silicon atoms and which can be associated with silicon in the quartz structure [42]. For MS1,
 270 the total signal between -84 and -100 ppm is composed of Q³ silicon atoms of smectite (-93
 271 ppm) [12], Q³(1Al) silicon atoms of biotite (-86 ppm) [43], Q² silicon atoms of palygorskite (-

1 272 84 ppm) [44] and two Q³ silicon sites of palygorskite at -98 and -92 ppm which correspond to
2 273 SiO₄ at the edges and at the centre of the ribbons of tetrahedra, respectively [45]. For MS2, the
3
4 274 total signal is only composed of Q³ silicon atoms of smectite and Q³(1Al) silicon atoms of
5
6
7 275 biotite and smectite. For both MS1 and MS2, the increase of the calcination temperature leads
8
9 276 to a broadening of the resonances associated with the Q³ of the clay phases. This broadening is
10
11 277 explained by a distribution of the environments of the silicon atoms and indicate a structural
12
13 278 loss of the clay phases upon calcination [46]. At 800°C a new resonance appears at -71 ppm in
14
15 279 MS1 and MS2 spectra. This new resonance corresponds to Q⁰ silicon atoms and can be
16
17 280 associated with the silicon contained in the C₂S structure [47], in accordance with XRD results.
18
19 281 With increasing the calcination temperature there is a low-frequency shift of the Q³ resonances
20
21 282 for MS2, which is explained by the condensation of the Q³ into Q⁴ silica [17]. By comparing
22
23 283 MS1 and MS2 it is evident that the C₂S formation is facilitated in MS1 compared to MS2 (a
24
25 284 higher relative proportion is observed). This could be explained by the occurrence of
26
27 285 palygorskite as it is the only main difference between both materials. However, this difference
28
29 286 of C₂S formation between MS1 and MS2 is not observable by XRD, meaning that the main part
30
31 287 of this C₂S is amorphous.
32
33
34
35
36
37
38

39 288 Overall, the results of XRD and MAS NMR indicates that 800°C is probably the best
40
41 289 calcination temperature for both MS1 and MS2. Moreover, MS1 seems to be more sensitive to
42
43 290 the calcination, which leads to higher dehydroxylation of the clay phases and to higher relative
44
45 291 amount of C₂S. The major difference between MS1 and MS2 being the occurrence of
46
47 292 palygorskite in MS1, it seems clear that smectite and palygorskite have different responses to
48
49 293 calcination.
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

296 **3.2. Self-reactivity of calcined marlstones in water**

1
2
3 297 The calcination study of MS1 and MS2 revealed the formation of different reactive phases such
4
5 298 as lime, periclase and C₂S as well as the loss of crystallinity of the clay phases. MS1 and MS2
6
7
8 299 were thus hydrated in water in order to study their reactivity, the contribution of each phases,
9
10 300 their evolution and the possible presence of synergies.

11
12
13 301 Fig. 4. displays the evolution of the X-ray diffractograms of MS1 (Fig. 4.A) and MS2 (Fig. 4.B)
14
15
16 302 calcined at 800°C and hydrated in water for 7, 14, 28 and 180 days.

17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

C2S = Ca_2SiO_4	Bio = Biotite $\text{K}(\text{Mg,Fe})_3(\text{OH,F})_2(\text{Si}_3\text{AlO}_{10})$
Pe = Péridase MgO	Li = Lime CaO
Qz = Quartz SiO_2	Br = Brucite $\text{Mg}(\text{OH})_2$
Dehy Sm = Dehydrated Smectite	Hy = Hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$
Ht = Hydrocalcite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$	C = Calcite CaCO_3
Po = Portlandite $\text{Ca}(\text{OH})_2$	

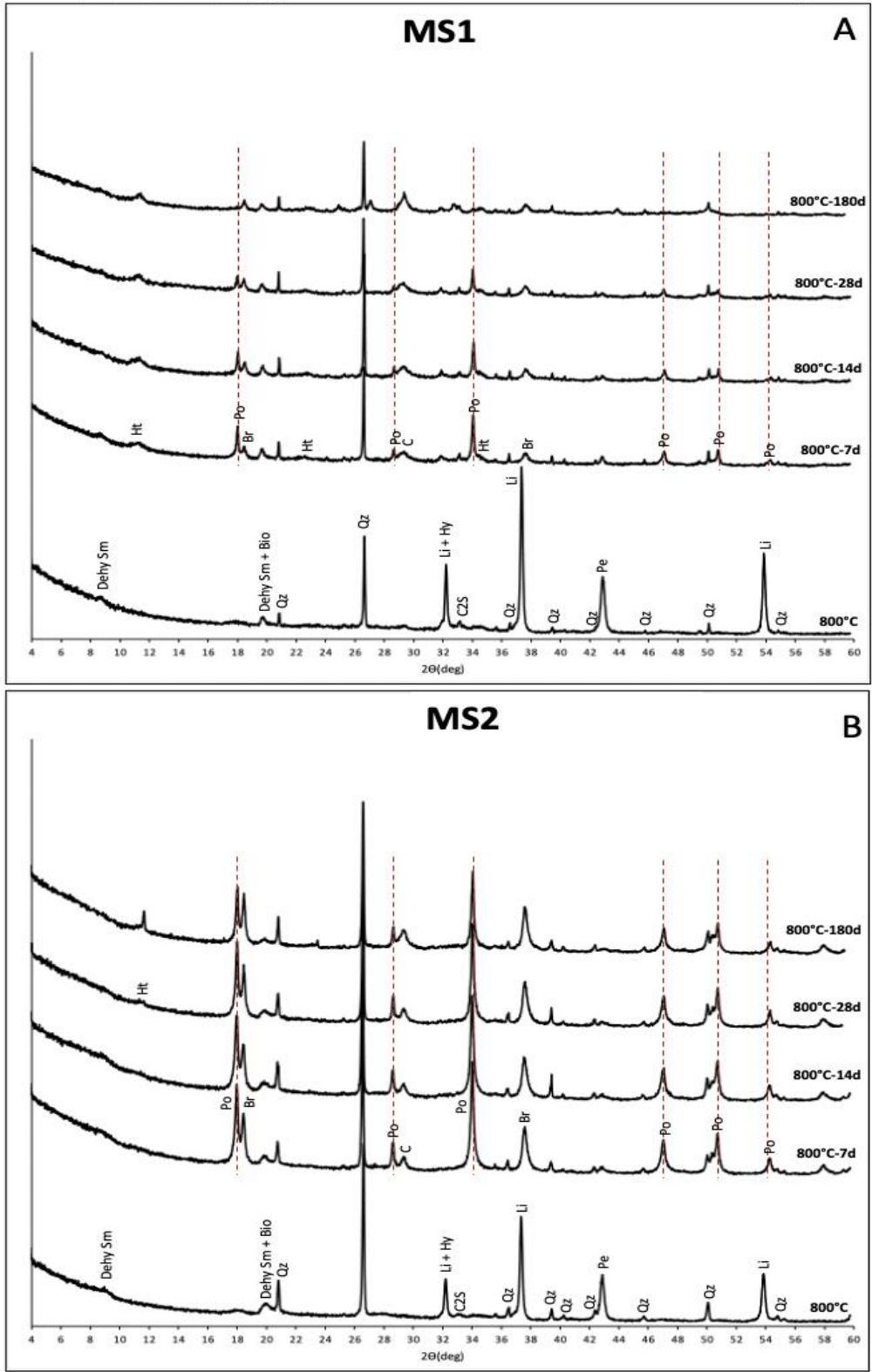


Fig. 4. Evolution of the X-ray diffractograms of MS1 (A) and MS2 (B) calcined at 800°C and hydrated (w/b = 0.8) during 7, 14, 28 and 180 days.

306 After 7 days of hydration, for both MS1 and MS2, diffraction peaks characteristic of portlandite,
307 calcite, hydrotalcite and brucite appear on the diffractograms. The formation of portlandite
308 comes from the hydration of lime and calcite comes from its carbonation. The magnesium from
309 the periclase is incorporated into two phases: brucite and hydrotalcite.

310 The formation of brucite can be problematic in cements. The hydration of periclase into brucite
311 is a phenomenon that has relatively long kinetic compared to the hardening kinetic of cement.
312 This post-hardening swelling can lead to cracking problems and therefore a loss of mechanical
313 performance if there is not enough space available in the matrix [48]. Studies are currently
314 underway to determine whether neoformed brucite leads to cracking in this system. However,
315 there is no post-hardening swelling phenomenon associated with hydrotalcite (the second
316 magnesian phase neoformed in our system) formation in the existing literature and the possible
317 existence of synergies with the cement phases could enhance the formation of hydrotalcite
318 instead of brucite in calcined marlstone-cement system.

319 The amount of neoformed brucite and portlandite is higher for MS2 than for MS1 (larger area
320 under the peaks), therefore it is difficult to compare the evolution of these two phases between
321 MS1 and MS2. With the increasing hydration time, the intensity of the peaks characteristic of
322 portlandite decrease for MS1 and MS2. However, after 180 days of hydration the portlandite
323 diffraction peaks are no longer detectable in MS1. This total consumption of portlandite in MS1
324 could be a first indication of a possible stronger pozzolanic reactivity compared to MS2.
325 However, this apparent consumption of portlandite may also be due to its carbonation into
326 calcite as we observe an increase in the intensity of the peak associated with calcite with
327 increasing hydration time.

328 Fig. 5. shows the evolution of the ^{29}Si MAS NMR spectra of MS1 (Fig. 5.A) and MS2 (Fig.
329 5.B) calcined at 800°C and hydrated in water during 7, 14, 28 and 180 days.

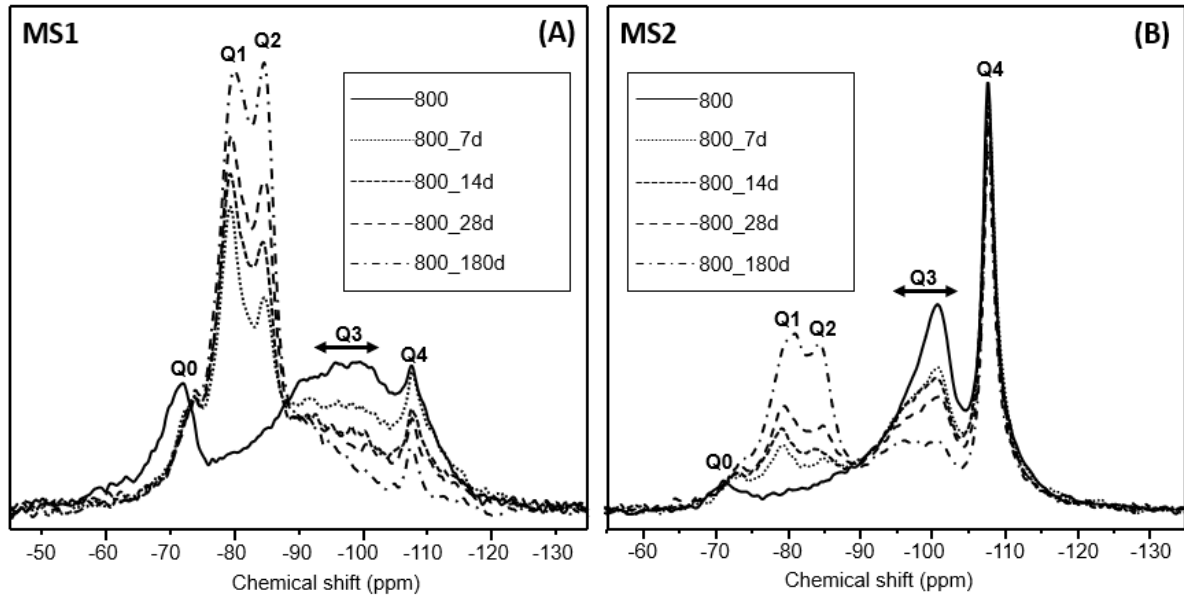


Fig. 5. Evolution of the ^{29}Si MAS NMR spectra of MS1 (A) and MS2 (B) calcined at 800°C and hydrated ($w/b = 0.8$) during 7, 14, 28 and 180 days.

After 7 days of hydration for both MS1 and MS2, a decrease is observed for the intensity of the broad Q^3 resonances previously associated with the calcined clay phases. This decrease is correlated with the appearance of two new resonances at -78 and -85 ppm which correspond to Q^1 and Q^2 silicon atoms, respectively [49]. Q^1 silicon atoms can be associated with pairs of linked silicate tetrahedral (dimers) and/or terminal tetrahedral silicate groups of C-S-H. Q^2 silicon atoms can be associated with C-S-H tetrahedral silicate groups in bridging ($\text{Q}^2\text{-B}$) and/or intermediates ($\text{Q}^2\text{-P}$) configurations [50].

The -71 ppm resonance corresponding to Q^0 atoms (associated previously with C_2S neoformed during calcination) decreases considerably after 7 days of hydration and leaves a resonance at -73 ppm for both MS1 and MS2. This -73 ppm resonance can either be associated with the Q^1 atoms of akermanite/gehlenite and/or Q^0 of non-reactive C_2S . The fact that the C_2S XRD signal remains detectable even after 180 days of hydration supports the hypothesis that some of the C_2S is non-reactive (the crystallised one). However, during the calcination of MS1 and MS2, the formation of akermanite was observed at 900°C (Fig. 1.). The -73 ppm signal can thus also

348 be associated with akermanite which is not yet crystallised enough to be detectable by XRD at
1
2 349 800°C. Finally, several studies have highlighted the formation of gehlenite during the
3
4
5 350 calcination of marlstones [51, 52] and this signal at -73 ppm could therefore be associated with
6
7 351 this phase.

8
9
10 352 After 14 days of hydration, for both MS1 and MS2, the intensity of the Q^3 calcined clay phases
11
12 353 resonances continues to decrease while the intensity of the $Q^1 + Q^2$ resonances associated with
13
14
15 354 C-S-H increases. A new resonance at -81 ppm appears after 14 days for MS1 and 28 days for
16
17 355 MS2, which corresponds to silicon in $Q^{2(1Al)}$ configuration and confirms the incorporation of
18
19
20 356 aluminium into the C-A-S-H structure, which is characteristic of the pozzolanic reaction of
21
22 357 calcined clays. The trend will continue up to 180 days for MS1 and MS2, validating the intrinsic
23
24
25 358 pozzolanic reactivity of these two calcined materials.

26
27
28 359 The comparison of the series of spectra indicates that the formation of C-A-S-H and the
29
30 360 consumption of calcined clay phases are significantly higher for MS1 than MS2. Spectral
31
32
33 361 integration quantification was thus carried out to precisely compare the difference between
34
35 362 MS1 and MS2 in terms of the consumption of calcined clay phases and the formation of C-A-
36
37
38 363 S-H.

39
40
41 364 Fig. 6. displays the evolution of the relative proportions (from the perspective of silicon content)
42
43 365 of the Q^n (C-A-S-H) and the Q^3 (calcined clay phases) for hydrated 800°C-MS1 (Fig 6.A) and
44
45
46 366 800°C-MS2 (Fig 6.B). Details of this quantification by spectral integration are given in the
47
48 367 supporting information. The Q^4 signal associated with quartz is not quantitative and the Q^0 - Q^1
49
50
51 368 signal associated with C_2S and/or akermanite/gehlenite is constant from 7 days and onward.
52
53 369 Therefore, Fig 6. includes only the evolution of the Q^3 (and Q^3 - Q^4 for MS2) of the calcined clay
54
55
56 370 phases and Q^n of the C-A-S-H.

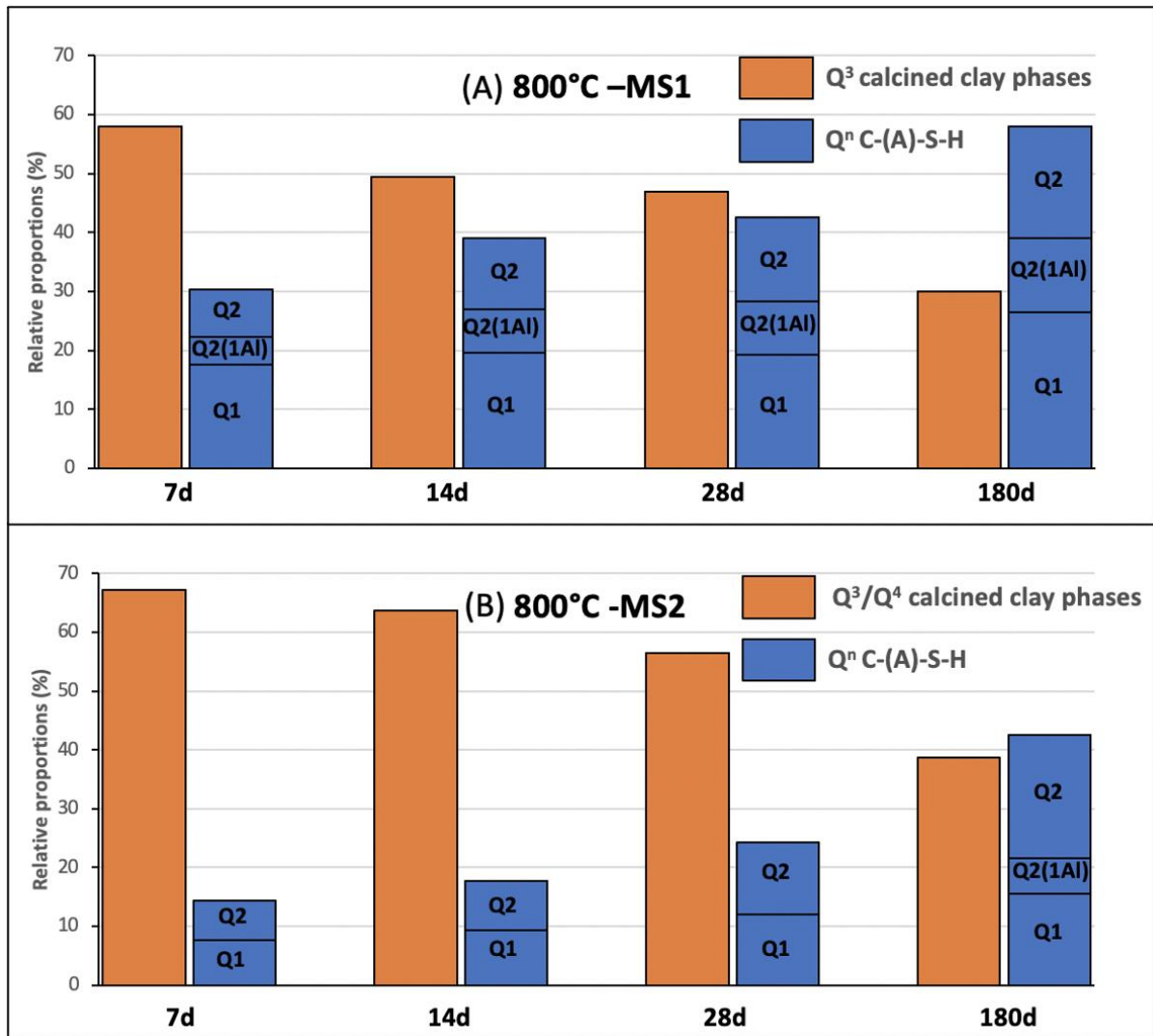


Fig. 6. Relative proportions of silicon-containing phases of MS1 (A) and MS2 (B) calcined at 800°C (from the perspective of silicon content) as function of the hydration time obtained from ²⁹Si MAS NMR spectra.

For MS1, after only 7 days of hydration, the relative proportion of silicon in Qⁿ configuration associated with C-A-S-H is already 30%. From 7 to 180 days of hydration, the relative proportion of silicon in Q³ configuration associated with the calcined clay phases decreases from 58% to 30%. In parallel, the relative proportion of Q¹, Q²(1Al) and Q² silicon associated with the C-(A)-S-H increases from 30% to 58%.

For MS2, after 7 days of hydration, the relative proportion of silicon in Qⁿ configuration associated with C-A-S-H is only 14%, which is much lower than for MS1 (30%). From 7 to

180 days of hydration the relative proportion of silicon in Q³-Q⁴ configuration associated with the calcined clay phases decreases from 67% to 39%. In parallel, the relative proportion Q¹, Q²(1Al) and Q² silicon associated with the C-(A)-S-H increases from 14% to 43%. The consumption of the calcined clay phases, associated with the formation of C-A-S-H and the consumption of portlandite during hydration confirms the pozzolanic reactivity of MS1 and MS2 calcined at 800°C. However, this pozzolanic reactivity is more important for MS1 (which contains palygorskite) than for MS2 ($\frac{Q^n(CASH)}{Q^3} = 1,93$ for MS1 and $\frac{Q^n(CASH)}{Q^3+Q^4} = 1,13$ for MS2 after 180 days of hydration). Compressive strengths were measured on mortars incorporating the two marlstones calcined at 800°C to confirm their different reactivity.

3.3. Calcined marlstone-cement blends

Fig. 7. displays the compressive strength of M-Ref, M-MS1 and M-MS2 after 7 and 28 days of hydration. The error bars indicate the standard deviation for each set of 3 compression measurements.

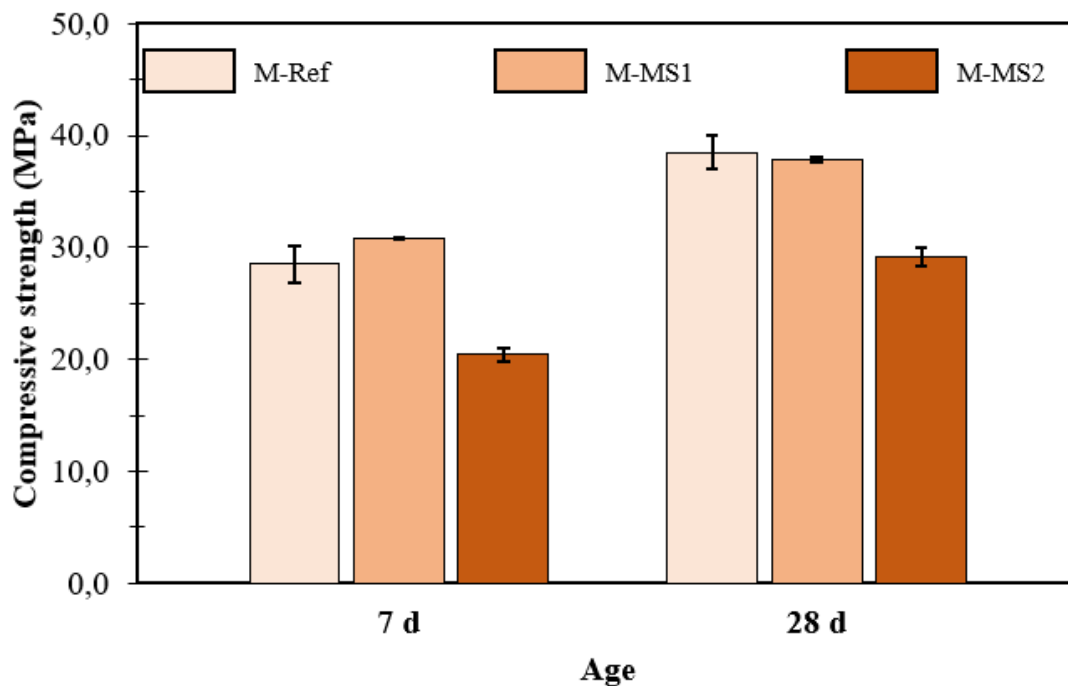


Fig. 7. Compressive strengths at 7 and 28 days of M-Ref, M-MS1 and M-MS2

398 After 7 days M-MS1 shows a compressive strength slightly higher (31 MPa) to that of the
399 reference (29 MPa for M-ref) whereas M-MS2 shows a significant lower strength (20 MPa). At
400 28 days the trend continues for M-MS1 which shows an equivalent compressive strength (38
401 MPa) to that of the reference (39 MPa) whereas M-MS2 still shows significant lower
402 compressive strength (29 MPa).

403 The better mechanical performance of M-MS1 confirms the previous results assessed by ²⁷Al
404 and ²⁹Si MAS NMR. The occurrence of palygorskite in MS1 leads to a higher degree of
405 dehydroxylation at 800°C in comparison to MS2 (Fig. 2.). This enhances the pozzolanic
406 reactivity of 800°C-MS1 in comparison to 800°C-MS2 (Fig. 6.) and results in higher
407 compressive strengths at 7 and 28 days (Fig. 7.). These results suggest that the palygorskite has
408 a higher pozzolanic activity after calcination at 800°C than smectite. To a lesser extent, the
409 higher mechanical performance of M-MS1 compared to M-MS2 could also be attributed to the
410 greater amount of C₂S neofomed during the calcination (facilitated by the occurrence of
411 palygorskite).

412

413 CONCLUSION

414 This paper compares the use of two calcined marlstones as SCMs in terms of calcination, self-
415 reactivity in water and mechanical performance in cementitious blends. The two marlstones
416 differ mainly by the presence of palygorskite (MS1) or not (MS2). Based on the results
417 presented, the following conclusions can be drawn:

418 1. The calcination of MS1 and MS2 leads to the dehydroxylation of the clay phases associated
419 with the formation of lime, periclase and C₂S. A calcination temperature of 800°C resulted in
420 the highest expected reactivity for both MS1 and MS2. The degree of dehydroxylation and the

421 amount of C₂S neoformed are higher for MS1 than MS2, which was attributed to the occurrence
1
2 422 of palygorskite in MS1.
3
4

5 423 2. Both MS1 and MS2 calcined at 800°C exhibit significant self-reactivity in water, mainly
6
7 424 pozzolanic. The comparative study shows that MS1 calcined at 800°C exhibits a higher self-
8
9 425 reactivity than MS2 confirming the results of the calcination analysis.
10
11
12

13 426 3. The comparative study shows that mortars made from cement blended with 20% of MS1
14
15 427 calcined at 800°C have much better compressive strength than those made with MS2 after 7
16
17 428 and 28 days. Once again, this confirms the results of the calcination (higher dehydroxylation of
18
19 429 MS1 than MS2) and self-reactivity in water analysis (higher reactivity of 800°C-MS1 than
20
21 430 800°C-MS2).
22
23
24
25

26 431 4. Calcination, self-reactivity in water and compressive strength results indicate that calcined
27
28 432 palygorskite-bearing marlstones have higher potential use as SCMs in cementitious systems
29
30 433 than calcined smectite-bearing marlstones. These results open up new applications for this type
31
32 434 of marlstones and suggest that palygorskite is a clay that could be used as SCM once calcined.
33
34
35
36

37 435
38
39

40 436 **REFERENCES**

41
42

43 437 1. Huntzinger DN, Eatmon TD (2009) A life-cycle assessment of Portland cement
44 438 manufacturing: comparing the traditional process with alternative technologies. *Journal of Cleaner*
45 439 *Production* 17:668–675. <https://doi.org/10.1016/j.jclepro.2008.04.007>

46 440 2. Scrivener KL, John VM, Gartner EM (2018) Eco-efficient cements: Potential economically
47 441 viable solutions for a low-CO₂ cement-based materials industry. *Cement and Concrete Research*
48 442 114:2–26. <https://doi.org/10.1016/j.cemconres.2018.03.015>

49 443 3. Escalante JI, Gómez LY, Johal KK, et al (2001) Reactivity of blast-furnace slag in Portland
50 444 cement blends hydrated under different conditions. *Cement and Concrete Research* 31:1403–1409.
51 445 [https://doi.org/10.1016/S0008-8846\(01\)00587-7](https://doi.org/10.1016/S0008-8846(01)00587-7)

52 446 4. Yazıcı H, Yardımcı MY, Yiğiter H, et al (2010) Mechanical properties of reactive powder
53 447 concrete containing high volumes of ground granulated blast furnace slag. *Cement and Concrete*
54 448 *Composites* 32:639–648. <https://doi.org/10.1016/j.cemconcomp.2010.07.005>
55
56
57
58
59
60
61
62
63
64
65

- 449 5. Sakai E, Miyahara S, Ohsawa S, et al (2005) Hydration of fly ash cement. *Cement and*
1 450 *Concrete Research* 35:1135–1140. <https://doi.org/10.1016/j.cemconres.2004.09.008>
- 2
3 451 6. Yao ZT, Ji XS, Sarker PK, et al (2015) A comprehensive review on the applications of coal fly
4 452 ash. *Earth-Science Reviews* 141:105–121. <https://doi.org/10.1016/j.earscirev.2014.11.016>
- 5
6 453 7. Hu X, Shi C, Shi Z, Zhang L (2019) Compressive strength, pore structure and chloride
7 454 transport properties of alkali-activated slag/fly ash mortars. *Cement and Concrete Composites*
8 455 104:103392. <https://doi.org/10.1016/j.cemconcomp.2019.103392>
- 9
10 456 8. Alujas A, Fernández R, Quintana R, et al (2015) Pozzolanic reactivity of low grade kaolinitic
11 457 clays: Influence of calcination temperature and impact of calcination products on OPC hydration.
12 458 *Applied Clay Science* 108:94–101. <https://doi.org/10.1016/j.clay.2015.01.028>
- 13
14 459 9. Almenares RS, Vizcaíno LM, Damas S, et al (2017) Industrial calcination of kaolinitic clays
15 460 to make reactive pozzolans. *Case Studies in Construction Materials* 6:225–232.
16 461 <https://doi.org/10.1016/j.cscm.2017.03.005>
- 17
18 462 10. El-Diadamony H, Amer AA, Sokkary TM, El-Hoseny S (2018) Hydration and characteristics
19 463 of metakaolin pozzolanic cement pastes. *HBRC Journal* 14:150–158.
20 464 <https://doi.org/10.1016/j.hbrcj.2015.05.005>
- 21
22 465 11. Zhao D, Khoshnazar R (2020) Microstructure of cement paste incorporating high volume of
23 466 low-grade metakaolin. *Cement and Concrete Composites* 106:103453.
24 467 <https://doi.org/10.1016/j.cemconcomp.2019.103453>
- 25
26 468 12. Brown IW, MacKenzie KJD, Meinhold RH (1987) The thermal reactions of montmorillonite
27 469 studied by high-resolution solid-state ^{29}Si and ^{27}Al NMR
- 28
29 470 13. Garg N, Skibsted J (2014) Thermal Activation of a Pure Montmorillonite Clay and Its
30 471 Reactivity in Cementitious Systems. *The Journal of Physical Chemistry C* 118:11464–11477.
31 472 <https://doi.org/10.1021/jp502529d>
- 32
33 473 14. Kaminskas R, Kubiliute R, Prialgauskaite B (2020) Smectite clay waste as an additive for
34 474 Portland cement. *Cement and Concrete Composites* 113:103710.
35 475 <https://doi.org/10.1016/j.cemconcomp.2020.103710>
- 36
37 476 15. Fernandez R, Martirena F, Scrivener KL (2011) The origin of the pozzolanic activity of
38 477 calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. *Cement and*
39 478 *Concrete Research* 41:113–122. <https://doi.org/10.1016/j.cemconres.2010.09.013>
- 40
41 479 16. Taylor-Lange SC, Rajabali F, Holsomback NA, et al (2014) The effect of zinc oxide additions
42 480 on the performance of calcined sodium montmorillonite and illite shale supplementary cementitious
43 481 materials. *Cement and Concrete Composites* 53:127–135.
44 482 <https://doi.org/10.1016/j.cemconcomp.2014.06.008>
- 45
46 483 17. Garg N, Skibsted J (2016) Pozzolanic reactivity of a calcined interstratified illite/smectite
47 484 (70/30) clay. *Cement and Concrete Research* 79:101–111.
48 485 <https://doi.org/10.1016/j.cemconres.2015.08.006>
- 49
50 486 18. Cancio Díaz Y, Sánchez Berriel S, Heierli U, et al (2017) Limestone calcined clay cement as a
51 487 low-carbon solution to meet expanding cement demand in emerging economies. *Development*
52 488 *Engineering* 2:82–91. <https://doi.org/10.1016/j.deveng.2017.06.001>
- 53
54 489 19. Scrivener K, Martirena F, Bishnoi S, Maity S (2018) Calcined clay limestone cements (LC3).
55 490 *Cement and Concrete Research* 114:49–56. <https://doi.org/10.1016/j.cemconres.2017.08.017>
- 56
57
58
59
60
61
62
63
64
65

- 491 20. He C, Makovicky E, Osbæck B (1996) Thermal treatment and pozzolanic activity of sepiolite.
1 492 Applied Clay Science 10:337–349. [https://doi.org/10.1016/0169-1317\(95\)00035-6](https://doi.org/10.1016/0169-1317(95)00035-6)
2
- 3 493 21. He C, Osbaeck B, Makovicky E (1995) Pozzolanic reactions of six principal clay minerals:
4 494 Activation, reactivity assessments and technological effects. Cement and Concrete Research 25:1691–
5 495 1702. [https://doi.org/10.1016/0008-8846\(95\)00165-4](https://doi.org/10.1016/0008-8846(95)00165-4)
6
- 7 496 22. Justnes H, Østnor T, De Weerd K, Vikan H (2021) CALCINED MARL AND CLAY AS
8 497 MINERAL ADDITION FOR MORE SUSTAINABLE CONCRETE STRUCTURES CALCINED
9 498 MARL AND CLAY AS MINERAL ADDITION FOR MORE SUSTAINABLE CONCRETE
10 499 STRUCTURES
- 11
12
13 500 23. Danner T, Norden G, Justnes H (2018) Characterisation of calcined raw clays suitable as
14 501 supplementary cementitious materials. Applied Clay Science 162:391–402.
15 502 <https://doi.org/10.1016/j.clay.2018.06.030>
16
- 17 503 24. Bullerjahn F, Zajac M, Pekarkova J, Nied D (2020) Novel SCM produced by the co-
18 504 calcination of aluminosilicates with dolomite. Cement and Concrete Research 134:106083.
19 505 <https://doi.org/10.1016/j.cemconres.2020.106083>
20
- 21 506 25. Mohammed S, Elhem G, Mekki B (2016) Valorization of pozzolanicity of Algerian clay:
22 507 Optimization of the heat treatment and mechanical characteristics of the involved cement mortars.
23 508 Applied Clay Science 132–133:711–721. <https://doi.org/10.1016/j.clay.2016.08.027>
24
- 25 509 26. Danner T, Norden G, Justnes H (2021) Calcareous smectite clay as a pozzolanic alternative to
26 510 kaolin. European Journal of Environmental and Civil Engineering 25:1647–1664.
27 511 <https://doi.org/10.1080/19648189.2019.1590741>
28
29
- 30 512 27. Bahhou A, Taha Y, Khessaimi YE, et al (2021) Using Calcined Marls as Non-Common
31 513 Supplementary Cementitious Materials—A Critical Review. Minerals 11:517.
32 514 <https://doi.org/10.3390/min11050517>
33
- 34 515 28. Poussardin V, Wilson W, Paris M, et al Calcined palygorskites as supplementary cementitious
35 516 materials
- 36
37 517 29. Poussardin V, Paris M, Tagnit-Hamou A, Deneele D (2020) Potential for calcination of a
38 518 palygorskite-bearing argillaceous carbonate. Applied Clay Science 198:105846.
39 519 <https://doi.org/10.1016/j.clay.2020.105846>
40
- 41 520 30. Poussardin V, Paris M, Wilson W, et al (2022) Self-reactivity of a calcined palygorskite-
42 521 bearing marlstone for potential use as supplementary cementitious material. Applied Clay Science
43 522 216:106372. <https://doi.org/10.1016/j.clay.2021.106372>
44
45
- 46 523 31. Ferraz E, Andrejkovičová S, Hajjaji W, et al (2015) Pozzolanic activity of metakaolins by the
47 524 French standard of the modified Chapelle test: A direct methodology. Acta Geodynamica et
48 525 Geomaterialia 12:289–298. <https://doi.org/10.13168/AGG.2015.0026>
49
- 50 526 32. Avet F, Snellings R, Alujas Diaz A, et al (2016) Development of a new rapid, relevant and
51 527 reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. Cement and
52 528 Concrete Research 85:1–11. <https://doi.org/10.1016/j.cemconres.2016.02.015>
53
- 54 529 33. Doebelin N, Kleeberg R (2015) *Profex*: a graphical user interface for the Rietveld refinement
55 530 program *BGMN*. Journal of Applied Crystallography 48:1573–1580.
56 531 <https://doi.org/10.1107/S1600576715014685>
57
58
- 59 532 34. Massiot D, Fayon F, Capron M, et al (2002) Modelling one- and two-dimensional solid-state
60 533 NMR spectra: Modelling 1D and 2D solid-state NMR spectra. Magn Reson Chem 40:70–76.
61
62
63
64
65

534 <https://doi.org/10.1002/mrc.984>

- 1
2 535 35. C01 Committee Test Method for Compressive Strength of Hydraulic Cement Mortars (Using
3 536 2-in. or [50-mm] Cube Specimens). ASTM International
- 4
5 537 36. Bala P, Samantaray BK, Srivastava SK (2000) Dehydration transformation in Ca-
6 538 montmorillonite. *Bulletin of Materials Science* 23:61–67. <https://doi.org/10.1007/BF02708614>
- 7
8 539 37. Morodome S, Kawamura K (2009) Swelling Behavior of Na- and Ca-Montmorillonite up to
9 540 150°C by in situ X-ray Diffraction Experiments. *Clays and Clay Minerals* 57:150–160.
10 541 <https://doi.org/10.1346/CCMN.2009.0570202>
- 11
12 542 38. Xie J, Chen T, Xing B, et al (2016) The thermochemical activity of dolomite occurred in
13 543 dolomite–palygorskite. *Applied Clay Science* 119:42–48. <https://doi.org/10.1016/j.clay.2015.07.014>
- 14
15 544 39. Maia AÁB, Angélica RS, de Freitas Neves R, et al (2014) Use of 29Si and 27Al MAS NMR
16 545 to study thermal activation of kaolinites from Brazilian Amazon kaolin wastes. *Applied Clay Science*
17 546 87:189–196. <https://doi.org/10.1016/j.clay.2013.10.028>
- 18
19 547 40. Sanz J, Serratos JM (1984) Silicon-29 and aluminum-27 high-resolution MAS-NMR spectra
20 548 of phyllosilicates. *Journal of the American Chemical Society* 106:4790–4793.
21 549 <https://doi.org/10.1021/ja00329a024>
- 22
23 550 41. Muller D, Gessner W, Samoson A, Lippmaa E (1986) Solid-state Aluminium-27 Nuclear
24 551 Magnetic Resonance Chemical Shift and Quadrupole Coupling Data for Condensed AlO₄, Tetrahedra.
25 552 *J Chem Soc Dalton Trans* 5
- 26
27 553 42. Lippmaa E, Maegi M, Samoson A, et al (1980) Structural studies of silicates by solid-state
28 554 high-resolution silicon-29 NMR. *Journal of the American Chemical Society* 102:4889–4893.
29 555 <https://doi.org/10.1021/ja00535a008>
- 30
31 556 43. Mackenzie KJD, Brown IWM, Cardile CM, Meinhold RH (1987) The thermal reactions of
32 557 muscovite studied by high-resolution solid-state 29-Si and 27-Al NMR. *Journal of Materials Science*
33 558 22:2645–2654. <https://doi.org/10.1007/BF01082158>
- 34
35 559 44. Kuang W, Facey GA, Detellier C (2004) Dehydration and rehydration of palygorskite and the
36 560 influence of water on the nanopores. *Clays Clay Miner* 52:635–642.
37 561 <https://doi.org/10.1346/CCMN.2004.0520509>
- 38
39 562 45. Barron PF, Frost RL, Qilil N (1985) Solid state 29Si NMR examination of the 2:1 ribbon
40 563 magnesium silicates, sepiolite and palygorskite. *American Mineralogist* 70:758–766
- 41
42 564 46. MacKenzie KJD, Smith ME *Multinuclear Solid-State NMR of Inorganic Materials*, Pergamon
43 565 *Materials Series*
- 44
45 566 47. Skibsted J, Jakobsen HJ, Hall C (1995) Quantification of calcium silicate phases in Portland
46 567 cements by 29Si MAS NMR spectroscopy. *Journal of the Chemical Society, Faraday Transactions*
47 568 91:4423. <https://doi.org/10.1039/ft9959104423>
- 48
49 569 48. Cherney EA, Hooton RD (1987) Cement Growth Failure Mechanism in Porcelain Suspension
50 570 Insulators. *IEEE Transactions on Power Delivery* 2:249–255.
51 571 <https://doi.org/10.1109/TPWRD.1987.4308096>
- 52
53 572 49. Magi M, Lippmaa E, Samoson A, et al (1984) Solid-state high-resolution silicon-29 chemical
54 573 shifts in silicates. *The Journal of Physical Chemistry* 88:1518–1522.
55 574 <https://doi.org/10.1021/j150652a015>

60
61
62
63
64
65

575 50. Andersen MD, Jakobsen HJ, Skibsted J (2004) Characterization of white Portland cement
1 576 hydration and the C-S-H structure in the presence of sodium aluminate by ^{27}Al and ^{29}Si MAS NMR
2 577 spectroscopy. *Cement and Concrete Research* 34:857–868.
3 578 <https://doi.org/10.1016/j.cemconres.2003.10.009>
4
5 579 51. Shoval S (1988) Mineralogical changes upon heating calcitic and dolomitic marl rocks.
6 580 *Thermochimica Acta* 135:243–252. [https://doi.org/10.1016/0040-6031\(88\)87393-3](https://doi.org/10.1016/0040-6031(88)87393-3)
7
8 581 52. Hughes DC, Jaglin D, Kozłowski R, Mucha D (2009) Roman cements — Belite cements
9 582 calcined at low temperature. *Cement and Concrete Research* 39:77–89.
10 583 <https://doi.org/10.1016/j.cemconres.2008.11.010>
11
12
13 584
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65