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# 1           **Extraction of Tricalcium Aluminate for Research Applications by Selective**

## 2                           **Dissolution of Portland Cement Clinker**

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### 17   **Abstract**

18   Tricalcium aluminate ( $C_3A$ ) is the most reactive phase in Portland clinker. In the study of the  $C_3A$   
19   hydration process, the use of synthetic samples is often preferred over clinker-sourced samples due  
20   to the absence of traces of other elements in synthetic  $C_3A$ . However, the reproduction of results  
21   from synthetic samples using clinker-sourced  $C_3A$  samples is challenging due to the difficulty of  
22   complete extraction of aluminate phases from clinker without damaging their structure. Salicylic and  
23   maleic acid/methanol solutions were used in the past to isolate  $C_3A$ , but complete extraction has not  
24   been observed. Thus, it was necessary to modify the selective dissolution method. Possible processes  
25   were tested with white and ordinary portland clinkers. A modified process with maleic acid/methanol  
26   solution was developed and the samples were analyzed by X-ray diffraction (XRD),  
27   thermogravimetric analysis (TGA) and Raman spectroscopy. compared with synthetic  $C_3A$  samples.  
28   The modified selective dissolution process with maleic acid/methanol solution proposed in this work  
29   was effective in achieving complete isolation of aluminate-based phases, and can be used for further  
30   studies of the hydration process of clinker-sourced  $C_3A$  samples to improve the understanding and  
31   quality of Portland cement clinkers.

32 **Keywords:** selective dissolution; cubic tricalcium aluminate; orthorhombic tricalcium aluminate;  
33 clinker Portland; X-ray diffraction; Raman spectroscopy  
34

## 35 **Introduction**

36 Portland cement clinker is a multiphase material, where each of the mineral components  
37 reacts simultaneously but at very different rates during its hydration, to form a hardened  
38 cement paste. Among the four major mineral phases in Portland cement, tricalcium  
39 aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$  or  $\text{C}_3\text{A}$  in abbreviated cement chemistry nomenclature) is the most  
40 reactive. The reaction of this phase with water is very rapid, releasing large amounts of heat  
41 ( $\sim 1260$  J/g) (Bullard et al. 2011), and causing undesirable flash setting of cement if this is  
42 not moderated through the addition of a retarding agent such as calcium sulfate. The  
43 reactions involving  $\text{C}_3\text{A}$  are responsible for much of the initial stiffening and solidification  
44 of Portland cement (Bullard et al. 2011) .

45 The theoretical crystalline structure of  $\text{C}_3\text{A}$  is cubic with a lattice constant of  $15.263 \text{ \AA}$ , built  
46 up of hollow rings of six corner-sharing  $\text{AlO}_4$  tetrahedra, held together by  $\text{Ca}^{2+}$  ions (Odler  
47 1998; Taylor 1997; Takeuchi et al. 1980). The presence of minor elements (mainly  $\text{Na}^+$  and  
48  $\text{K}^+$ ) in the clinkerization process can modify the structure of  $\text{C}_3\text{A}$  from cubic to  
49 orthorhombic, as these cations substitute for  $\text{Ca}^{2+}$ . The orthorhombic  $\text{C}_3\text{A}$  structure is  
50 generally doped with  $\text{Na}_2\text{O}$  at a concentration between 4.6 to 5.7 wt.% ( $\text{Na}_{2x}\text{Ca}_{3-x}\text{Al}_2\text{O}_6$ )  
51 (Odler 1998; Ostrowski and Żelazny 2004; Y. and F.M. 1980). The content of minor  
52 elements in the cement kiln, derived from raw materials and fuels, is crucial for this  
53 modification. Different clinkers can have their aluminate phase constituents influenced by  
54 the use of different fuels (oil, coal, petroleum coke, among others) even with the same raw  
55 materials, producing orthorhombic  $\text{C}_3\text{A}$  phases doped with Na and/or K (Gobbo et al. 2004).  
56 Previous reports have shown that the hydration processes of cubic  $\text{C}_3\text{A}$  and alkali-doped  $\text{C}_3\text{A}$   
57 proceed in markedly different ways (Boikova et al. 1977; Juenger and Jennings 2001;  
58 Kirchheim et al. 2009, 2011; Stephan and Wistuba 2006; Wistuba et al. 2007). Some studies  
59 have reported a higher reactivity for orthorhombic than cubic  $\text{C}_3\text{A}$  in the absence of sulfate

60 (Glasser and Marinho 1984; Pauri and Collepardi 1987), while others found exactly the  
61 opposite (Boikova et al. 1977; Kirchheim et al. 2009, 2011; Myers et al. 2017; Rheinheimer  
62 et al. 2016; Stephan and Wistuba 2006).

63 This contradiction is also observed in the presence of calcium sulfate sources, but it is notable  
64 that the studies that reported a higher reactivity during hydration for cubic than orthorhombic  
65  $C_3A$  used samples whose composition (and thus reaction) may have been influenced by the  
66 presence of other phases (Mortureux et al. 1980). There is therefore identified a strong  
67 influence from using clinker-sourced aluminates rather than pure isolated aluminate phases  
68 (Odler and Wonneman 1983; Samet and Sarkar 1997). Studies with pure synthetic  $C_3A$   
69 samples showed a higher reactivity of orthorhombic Na-doped  $C_3A$  in the presence of  
70 gypsum (Kirchheim et al. 2011; Myers et al. 2017; Stephan and Wistuba 2006). However,  
71 the use of laboratory-synthesized phases rather than materials processed in a clinkerization  
72 process may introduce deviations from the “real” behaviour of the aluminate phases within  
73 Portland cement, as additional substitutions (such as Fe) can be introduced in the industrial  
74 process, and the particle size distributions of the synthetic and industrial products are often  
75 very different. The hydration of  $C_3A$ -gypsum systems is strongly affected by the presence  
76 of other soluble clinker phases, such as alite ( $C_3S$ ). The dissolution of  $C_3A$  is increased in  
77 the presence of alite as the sulfate ions are partially absorbed by the C-S-H derived from  
78 alite hydration and then desorbed to form ettringite. Therefore, the rate of formation of  
79 monosulfate is also reduced (Quennoz and Scrivener 2013).

80 In this sense, the application of a selective dissolution process to extract and isolate  $C_3A$   
81 from the other clinker phases could be an opportunity to resolve important open questions.  
82 If successful, selective dissolution could enable the isolation of the industrially produced  
83  $C_3A$  from among the multi-phase clinker, meaning that this can be analyzed directly and  
84 without interference from the other clinker constituents.

85 Since the first application of selective dissolution to Portland cement in the 1950s with  
86 Takashima's experiments to develop the extraction protocol using an organic acid-methanol  
87 solution (Gutteridge 1979; Odler 1998; Puligilla and Mondal 2015), various studies have  
88 focused on C<sub>3</sub>A extraction. This procedure is challenging considering the low content (<10  
89 wt.%) of C<sub>3</sub>A within the clinker, as well as its high reactivity. Therefore, the extraction of  
90 C<sub>3</sub>A from the silicate and ferrite constituents of the clinker is not straightforward. Gutteridge  
91 (1979) assessed the effectiveness of a dissolution processes based on salicylic acid and  
92 methanol, while Cabrera and Plowman (1988) extracted the calcium aluminate phases using  
93 a method based on maleic acid and methanol.

94 Cabrera and Plowman (1988) showed that when using maleic acid/methanol solution to  
95 extract interstitial phases (C<sub>3</sub>A and tetracalcium aluminoferrite (Ca<sub>2</sub>AlFeO<sub>5</sub> or abbreviated  
96 C<sub>4</sub>AF)) from Portland clinkers, a low molecular weight calcium silicate complex formed a  
97 protective layer around C<sub>3</sub>A grains, preventing further hydration. This layer could be  
98 removed by applying a thermal treatment at 800 °C to the extracted sample to ensure the  
99 reactivity of the aluminate phases.

100 In addition, the studies performed by Gutteridge (1979) and Cabrera and Plowman (1988)  
101 showed that the degree of dissolution of tricalcium silicate (alite; Ca<sub>3</sub>SiO<sub>5</sub> or abbreviated  
102 C<sub>3</sub>S) was higher than that of dicalcium silicate (belite; Ca<sub>2</sub>SiO<sub>4</sub> or abbreviated C<sub>2</sub>S), and that  
103 a longer reaction time was required for complete dissolution of both silicate phases. The  
104 maleic acid/methanol solution needed 15 minutes to complete the reaction, while the  
105 salicylic acid/methanol solution needed 2 hours.

106 The effectiveness of a selective dissolution process must be assured if it is to give meaningful  
107 results: it is essential that this process does not modify the C<sub>3</sub>A crystal structure or reactivity,  
108 beside the difficulty of the extraction of interstitial phases by dissolving the main silicate  
109 phases alite and belite. Christensen et al. (2004) used selective dissolution of clinkers to

110 extract aluminate phases, obtaining in their dissolution residues a high content of these  
111 phases (67.7% cubic C<sub>3</sub>A, 0.1% orthorhombic C<sub>3</sub>A and 2.2% C<sub>4</sub>AF). However, the calcium  
112 silicate phases (19.4% alite, 10.6% belite) were still present. Gobbo et al. (2004) used  
113 aluminate phase extraction using salicylic acid/organic acid solutions in order to quantify  
114 the interstitial phase, but only white (C<sub>4</sub>AF-free) Portland cement clinkers were used.

115 It is evident that further improvements in the selective dissolution protocols are necessary  
116 for complete extraction of each phase from Portland cement clinker. Thus, the complete  
117 extraction of aluminate phases from any Portland cement clinker might be an opportunity to  
118 fill the gaps in the understanding of C<sub>3</sub>A reactivity using industrially-synthesized phases in  
119 the absence and presence of calcium sulfate sources, clarifying the relevance and findings of  
120 previous work with synthetic samples.

121 This paper focuses on the use of selective dissolution to isolate calcium aluminate phases  
122 from Portland cement clinkers using maleic acid/methanol solution and salicylic  
123 acid/methanol solutions, to quantify the effectiveness of these methods and determine the  
124 structural features of the phases extracted. Complementary to this, the extracted aluminate  
125 phases were compared to synthetic samples by Raman spectroscopy and X-ray diffraction  
126 (XRD) analysis.

127

## 128 **Experimental Program**

### 129 **Materials**

130 This study was conducted using ordinary Portland clinker (OPC) and white Portland clinker  
131 (WPC), both commercially produced in Brazil. The chemical composition of each clinker as  
132 measured by a Philips PW2440 X-ray fluorescence spectrometer is shown in Table 1. The  
133 clinker pellets were mechanically ground for 3 hours using a ball mill, and their particle size

134 distribution data are shown in Figure 1. Particle size distributions were measured in a  
135 Malvern Mastersizer 3000 PSA. The lower size limit of this equipment was 40 nm, and the  
136 Mie approximation was applied in the analysis of the granulometry data.

137 Cubic (pure) and orthorhombic (Na-doped)  $C_3A$  were supplied by Mineral Research  
138 Processing Cie, Meyzieu (France). XRD and Rietveld analysis were used to verify the phase  
139 compositions, and determined that the cubic  $C_3A$  (Inorganic Crystal Structure Database,  
140 ICSD, code 94742) was 99 wt.% pure with GOF (goodness of fit) of 2.1, and Na-doped  $C_3A$   
141 (ICSD code 1880) was 100 wt.% pure with GOF of 1.9; both GOF parameters were lower  
142 than 5 which indicates good description of the phases (Post and Bish 1989). Specific surface  
143 area (Brunauer-Emmett-Teller (BET),  $N_2$ ) of the materials and particle size distributions of  
144 the pure  $C_3A$  phases are presented in Figure 2.

145 Methanol ( $CH_3OH$  – purity of 99.99% - anhydrous) and maleic acid ( $C_4H_4O_4$ ), supplied by  
146 RF Química, were used for the selective dissolution methods.

147

#### 148 **Selective dissolution (SD)**

149 Two selective dissolution methods: Maleic acid/methanol (MAM) solution as described by  
150 Cabrera and Plowman (1988), and salicylic acid/methanol (SAM) solution as described by  
151 Gutteridge (Gutteridge 1979), were tested. The acids used are classified as hazardous by the  
152 2012 OSH Hazard Communication Standard (29CFR1910.1200); they can be harmful if  
153 swallowed, and can cause serious eye damage, skin irritation, and other effects. Therefore,  
154 appropriate protective gloves and eye protection were used during the experiments. The  
155 resulting extracted phases were analysed by X-ray diffraction (XRD), Rietveld analysis  
156 (Rietveld 1969) and particle size distribution.

157 The selective extraction processes followed by Cabrera and Plowman (Cabrera and  
158 Plowman 1988; Plowman and Cabrera 1984) and Gutteridge (1979), showed limitations that  
159 meant that it was not possible to achieve full aluminate extraction. As a third and  
160 complementary form of analysis, the MAM method from Cabrera and Plowman (1988) was  
161 slightly modified (as is shown in Table 2) to enable better assessment of the aluminate  
162 phases. This new modified method is denoted as MAM\*. The extracted phases from the  
163 modified method (MAM\*) were handled under N<sub>2</sub> gas to avoid carbonation and stored under  
164 vacuum in glass containers with silica gel. The samples were characterized by XRD, Raman  
165 spectroscopy, and thermogravimetric analyses (TGA). The dry powder samples were ground  
166 by hand in an agate mortar to reduce agglomeration, and then homogeneously loaded into  
167 the corresponding sample holder. The extracted phases were compared to synthetic phases.

#### 168 **Thermogravimetric analysis (TGA)**

169 Thermogravimetric analysis was performed using a Universal Thermobalance V4.2E TA  
170 from Mettler Toledo. Samples of approximately 40 mg were heated under a N<sub>2</sub> (40 mL/min)  
171 atmosphere at a rate of 10 °C/min, from 30 to 995 °C.

#### 172 **X-ray diffractometry (XRD) and Rietveld analysis**

173 X-ray diffractometry was conducted in a Siemens D5000 diffractometer with a broad focus  
174 CuK $\alpha$  tube anode applying 40 kV and 40 mA, a 2 $\theta$  range of 5-70°, and a step size of 0.01°/s.  
175 Data sets were refined by the Rietveld method using the PANalytical X'Pert Plus software.  
176 The database used for Rietveld refinement and phase identification was the PDF-4 file of the  
177 International Centre for Diffraction Data (ICSD). The refinements were also adjusted to  
178 achieve a residue value (R<sub>WP</sub>) lower than 12 and GOF lower than 3 (Post and Bish 1989).  
179 The background was fitted with a Chebyshev function with 4 terms, and phases described  
180 by pseudo-Voigt peak shapes fitted to minimise the residue R<sub>y</sub> (x).

181 **Raman spectroscopy**

182 Raman spectroscopy was used to analyze the clinkers before and after selective dissolution,  
183 and the pure C<sub>3</sub>A samples. The tests were performed using a Renishaw in Via Raman  
184 Microscope with an integral optical microscope (Olympus BH2 system). The excitation  
185 source was a 514.0 nm (25 mW) Ar laser. A maximum power of 4–5 mW was possible at  
186 the sample with approximately 5 μm spot diameter, via a standard ×50 ultra long working  
187 distance, ULWD, microscope objective. The Raman shift was calibrated prior to each  
188 experiment against the 520 cm<sup>-1</sup> peak of silicon. For analysis, the sample was placed on a  
189 glass slip and placed under the microscope. A randomly chosen area was brought into focus  
190 with the ×50 ULWD objective lens. Raman spectra were recorded in triplicate. Each analysis  
191 was performed for 200–1700 cm<sup>-1</sup>, 10 second exposure, 3 accumulations.

192

193 **Results and discussion**

194 **Selective dissolution (SD) processes for the original maleic acid/methanol (MAM) and**  
195 **salicylic acid/methanol (SAM) methods.**

196 Figure 3 and Table 3 show the particle size distribution of the clinker samples, and their  
197 Brunauer-Emmett-Teller (BET) specific surface areas, after each selective dissolution  
198 process. The mean particle size of the clinkers was significantly reduced after the selective  
199 dissolution process, where a reduction up to 49% was identified. It is possible to observe in  
200 Figure 3 a displacement between the particle size curves after each selective dissolution, and  
201 an increase in the BET values in Table 3. However, the displacement between the curves  
202 and the difference in the BET values were higher when applying SAM (up to 63%) in  
203 comparison to the MAM (up to 36%) solution regardless of the type of clinker, which is  
204 attributed to the difference in time that the samples were exposed during each procedure: 5

205 and 20 minutes for original methods of MAM and SAM, respectively. Among the clinkers  
206 tested, OPC had a larger difference (up to 63%) than WPC when applying the SAM solution.

207

208 Cabrera and Plowman (1988) also reported a rise in the particle size distribution when using  
209 the MAM method, although this process was described as broadly providing satisfactory  
210 results. Gutteridge (1979) postulated the importance of using a nominal particle size smaller  
211 than 5  $\mu\text{m}$  in selective dissolution processes, although this was not the case in the current  
212 work.

213 Table 4 shows the phase proportions in the clinker samples before and after each selective  
214 dissolution, determined by applying Rietveld-based quantitative phase analysis. The belite  
215 phase was not completely removed by SAM extraction of the WPC sample, with 0.9% of  
216 this phase remaining. In the OPC-SAM tests, alite was found in all samples but in quantities  
217 that did not exceed 6.2%. The SAM solution left higher residual alite contents than MAM  
218 for both OPC and WPC samples. Periclase was found at concentrations of 3.6% and 3.3%  
219 in the OPC-MAM and OPC-SAM samples, respectively.

220 In terms of hydrate products, 1.2% and 0.6% portlandite was found in WPC-MAM and  
221 WPC-SAM samples, respectively. The main phase related to hydration and carbonation of  
222 the  $\text{C}_3\text{A}$  ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$  – calcium monocarboaluminate hydrate (“AFm”  
223 structure family)) was identified in all samples, but a higher content of this phase was found  
224 in WPC-MAM (1.2%).

225 Table 4 correlates the phases identified in each clinker sample before and after each selective  
226 dissolution process. The ratios shown in the table are remarkably constant: aluminate to  
227  $\text{C}_4\text{AF}$ , periclase to aluminate, and cubic to orthorhombic  $\text{C}_3\text{A}$  phase ratios were essentially  
228 unchanged by the removal of the alite and belite from the clinkers, indicating a high degree

229 of selectivity. The values of GOF obtained in Rietveld-based quantitative phase analysis  
230 indicated a good correlation between the obtained and calculated XRD patterns (Post and  
231 Bish 1989), indicating that the selective dissolution procedures did not introduce a large  
232 quantity of disordered or amorphous material into the residues that were isolated.

233 Figure 4 shows the XRD data, highlighting the main peaks related to the extracted  
234 aluminates, with visible remnant peaks of alite (with  $d$ -spacings of 2.770 Å and 2.602 Å in  
235 the  $\{\bar{6}06\}$  and  $\{\bar{8}22\}$  directions, respectively (De la Torre et al. 2002)). The cubic  $C_3A$  was  
236 identified mainly through the single peak at 2.6987 Å corresponding to the [400] direction,  
237 and the orthorhombic by the peaks located in the  $2\theta$  axis at 32.9, 33.0 and 33.2°. The  $C_4AF$   
238 (characteristic peaks at 2.6581 Å and 1.8263 along the  $\{141\}$  and  $\{080\}$  directions (Colville  
239 and Geller 1971)) and periclase (identifiable at 2.432 Å and 1.4895 Å along the  $\{111\}$  and  
240  $\{200\}$  directions, respectively (Tsirel'son et al. 1998)) were not able to be extracted  
241 completely, as expected. Minor phases related to hydration (portlandite) and carbonation  
242 were also found, probably due to handling and storage of the samples before and during the  
243 analysis.

244 The results obtained by Christensen et al. (2004) also showed that the complete removal of  
245 Si-rich phases (alite and belite) was not possible using SAM solution. A residual value of  
246 19.4% alite and 10.6% belite were observed in their samples, preventing further aluminate  
247 hydration studies.

248

## 249 **Results from the modified maleic acid methanol (MAM\*) process**

### 250 **X-ray diffraction analysis**

251 Figure 5 shows XRD patterns for WPC and OPC samples before and after the modified  
252 selective dissolution process (as shown in Table 2), denoted MAM\*. The modification of

253 the method enabled the complete removal of alite and belite, as well as portlandite and the  
254 carbonated AFm phase that were identified in the SAM procedure.

255 Peaks attributed to cubic  $C_3A$ , orthorhombic K-doped  $C_3A$ ,  $C_4AF$  and periclase were  
256 observed by XRD in the WPC and OPC samples after selective dissolution. The selective  
257 dissolution was similarly effective for both clinkers, independent of their phase content.

258 Figures 6 and 7 show the XRD patterns of extracted samples obtained from the modified  
259 MAM\* process (OPC-MAM\* and WPC-MAM\*) and synthetic samples (ort. Na- $C_3A$  and  
260 cubic  $C_3A$ ) in the  $2\theta$  ranges between  $30-35^\circ$  and  $45-50^\circ$   $2\theta$ , respectively. The extracted  
261 samples showed broader peaks due to the key aluminate phases than did the synthetic phases,  
262 especially at higher  $2\theta$  angles. It was also possible to confirm in the WPC-MAM\* sample  
263 (Figure 6) a single peak at  $33.4^\circ$   $2\theta$  related to cubic  $C_3A$ , and a double peak in the OPC-  
264 MAM\* sample (Figure 6) at  $33.2$  and  $33.4^\circ$  related to orthorhombic K-doped  $C_3A$ . The peaks  
265 related to orthorhombic  $C_3A$  doped with Na (ort. Na- $C_3A$  – synthetic sample) and with K  
266 (OPC-MAM\* – extracted sample) showed a small displacement due to the different  
267 interstitial ions leading to different lattice distortions.

268 Table 5 shows the results of Rietveld analysis for WPC-MAM\* and OPC-MAM\*, including  
269 GOF and the phase ratios of  $C_3A/C_4AF$ , periclase/aluminate, and cubic/orthorhombic  $C_3A$   
270 ratios obtained in Rietveld analysis of the samples before and after the modified MAM\*  
271 procedure. The presence in OPC-MAM\* of  $C_4AF$  and periclase must be considered in any  
272 further study of aluminate hydration (Stephan and Wistuba 2006). A content of 96.5% cubic  
273  $C_3A$  and 3.5%  $C_4AF$  was isolated from the WPC through the MAM\* method, as this clinker  
274 was originally free of periclase (Table 4). This difference between OPC-MAM\* and WPC-  
275 MAM\* was expected when compared with the clinkers before the application of the selective  
276 dissolution process, but it was necessary to analyze the phase ratios before and after SD  
277 process to confirm the effectiveness and selectivity of the extraction.

278 As for the SAM method above, the phase ratios between aluminates and periclase were  
279 largely unchanged by the MAM\* selective dissolution process, and the GOF values less than  
280 5.0 indicated a good fit between the observed and calculated diffractograms, indicating the  
281 absence of any newly formed disordered/amorphous phase (Post and Bish 1989).

## 282 **Thermogravimetry**

283 The thermogravimetric results (Figures 8) confirmed the difference between unhydrated  
284 samples before and after the modified MAM\* process. Derivative thermogravimetry (DTG)  
285 peaks related to adsorbed humidity at 100 °C and decarbonation at 550-700 °C (Scrivener et  
286 al. 2016) were minimal after selective dissolution of both clinker samples. The final mass  
287 loss values for both of the extracted residues WPC-MAM\* and OPC-MAM\* were below  
288 0.5%.

289 The sample denoted OPC-MAM<sup>CARB</sup> (Figure 8a) were stored for 3 weeks in the same  
290 conditions as the clinker samples (in glass containers with silica gel under controlled  
291 vacuum), to identify any possibility of changes or pre-hydration in storage. The results  
292 showed peaks related to adsorbed humidity at ~100 °C, hydrated aluminate phases at 254-  
293 268 °C, and decarbonation at 652-707 °C (Scrivener et al. 2016). The time of storage when  
294 using extracted samples from Portland clinker must evidently be minimized to avoid  
295 prehydration and carbonation, even in controlled environments (Dubina et al. 2014, 2015).  
296 This process would be critical when studying hydration processes using extracted samples.  
297 It is known that both cubic and orthorhombic C<sub>3</sub>A show the formation of hydroxy-AFm  
298 (C<sub>4</sub>AH<sub>13</sub>) on their surfaces during prehydration in absence of CO<sub>2</sub>, and that this is more  
299 pronounced in orthorhombic C<sub>3</sub>A (Dubina et al. 2015). Both polymorphs of C<sub>3</sub>A can produce  
300 on their surfaces monocarboaluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·11H<sub>2</sub>O) when exposed to a  
301 carbonated environment (Dubina et al. 2015).

## 302 **Raman spectroscopy**

303 Table 6 summarises the Raman shifts identified by previous authors, and in this work, for  
304 synthetic aluminate phases and cubic  $C_3A$ , orthorhombic Na-doped  $C_3A$ , and  $C_4AF$  derived  
305 from clinkers. The differences observed in Table 6 are mainly attributed to differences in  
306 equipment configurations.

307 Figure 9 shows the Raman spectra of clinker, synthetic and extracted samples from the  
308 MAM\* process. The Raman bands of clinker samples (WPC and OPC) proved to be difficult  
309 to analyse due to the phase multiplicity, which led to peaks overlapping. The peaks may also  
310 have been broadened due to pre-hydration and carbonation as observed in the XRD Rietveld  
311 analysis. However, Raman bands were observed for cubic  $C_3A$  at  $758\text{ cm}^{-1}$  (Bensted 1976)  
312 and orthorhombic K-doped  $C_3A$  at  $718\text{ cm}^{-1}$ .

313 The peaks found for the extracted samples (WPC-MAM\* and OPC-MAM\*) had smaller  
314 intensities and a more broad and rounded peak shape in comparison to the synthetic samples.  
315 The main Raman bands for the extracted cubic  $C_3A$  phase were observed at  $508\text{ cm}^{-1}$  and  
316  $758\text{ cm}^{-1}$ . In the extracted OPC residue it was not possible to observe a clear peak attributable  
317 to the orthorhombic K-doped  $C_3A$  phase.

318 The  $C_3A$  synthetic phases with cubic ( $505\text{ cm}^{-1}$  (Black et al. 2006) and  $754\text{ cm}^{-1}$  (Black et  
319 al. 2006)) and orthorhombic Na-doped ( $511\text{ cm}^{-1}$  and  $761\text{ cm}^{-1}$  (Bonen et al. 1994))  
320 crystalline structures showed sharp and well-defined Raman bands.

321

## 322 **Conclusions**

323 Previously proposed selective dissolution methods using salicylic acid-methanol (SAM) and  
324 maleic acid-methanol (MAM) solutions were not completely effective in extraction of  
325 aluminate phases from white and grey Portland cement clinkers. Rietveld analysis of the

326 extracted residues showed incomplete extraction, with alite and belite phases remaining in  
327 the samples. Furthermore, the particle size distribution analysis showed an important  
328 modification of the sample particle size. Among the two methods, MAM solution gave better  
329 results related to a higher dissolution of the silicate phases (range of 97.5-98% extraction of  
330 alite into MAM solution, compared to 92-96% for SAM solution) and a smaller difference  
331 in particle size distribution and BET surface area, in relation to the SAM solution.

332 However, the modified selective dissolution method proposed here, denoted MAM\*, gave  
333 complete removal of the silicate phases when applied to two different Portland clinkers,  
334 while retaining the original ratios between  $C_3A$  polymorphs, and between the aluminate,  
335 ferrite and periclase phases present in the clinkers. The samples analyzed by XRD with  
336 Rietveld analysis showed only aluminate (cubic and orthorhombic  $C_3A$  and  $C_4AF$ ) and  
337 periclase peaks in their XRD diffractograms. To avoid interference by  $C_4AF$ , which is very  
338 difficult to remove, the authors suggest using white Portland clinker for future studies.  
339 Broader peaks were observed for the extracted samples in comparison to synthetic  $C_3A$   
340 samples when analysed by XRD and by Raman spectroscopy, indicating the need for further  
341 studies on the relative degrees of disorder in the industrial vs synthetic phases, and its  
342 influence on the hydration process, to apply this selective dissolution method to the  
343 generation of a deeper understanding of aluminate hydration in Portland cements.

344

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356

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- 468

469 Figure Caption List:

470 **Fig. 1.** Particle size distribution of Portland clinkers.

471 **Fig. 2.** Particle size distribution and BET of synthetic cubic and orthorhombic Na-C<sub>3</sub>A  
472 samples.

473 **Fig. 3.** Particle size distribution of samples before and after MAM and SAM.

474 **Fig. 4.** XRD pattern of extracted samples –  $2\theta$  10-70°.

475 **Fig. 5.** XRD diffractograms of WPC and OPC, before and after MAM\*.

476 **Fig. 6.** XRD diffractograms from Fig. 5 expanded in the region 30-35°  $2\theta$ .

477 **Fig. 7.** XRD diffractograms from Fig. 5 expanded in the region 45-50°  $2\theta$ .

478 **Fig. 8.** Thermogravimetric analysis (A) OPC, OPC-MAM\* and OPC-MAM<sup>CARB</sup> samples;  
479 (B) WPC, WPC-MAM\*.

480 **Fig. 9.** Raman bands of OPC, WPC and pure synthetic C<sub>3</sub>A samples between 470-800 cm<sup>-1</sup>.  
481 <sup>1</sup>.

482

483 **Table 1** Chemical composition and loss on ignition of clinkers as determined by X-ray  
 484 fluorescence (wt.%).

Clinker	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Loss on ignition
WPC	68.3	23.3	0.3	4.3	0.4	0.1	0.2	2.9
OPC	65.8	20.4	3.6	5.1	1.4	1.7	0.4	1.8

485

486 **Table 2** Stages of the modified maleic acid (MAM\*) process for selective dissolution.

Stages	Sample	Description
1	Clinker/methanol solution	300 mL of methanol and 10 g of clinker; magnetic mixing for 5 min to ensure complete suspension of the particles without raising the temperature (room temperature of 25 °C).
2	Clinker/methanol + maleic acid solution	Add 35 g of maleic acid and mix 25 minutes for the dissolution of portlandite and Si-rich phases (mainly alite and belite).
3	Clinker/methanol + maleic acid solution	Rinse the samples with methanol three times (during 15 minutes) and vacuum filtered (200 mmHg) using quantitative filter paper with slow flow filtration.
4	Retained residue	Dry at 40 °C for 20 min.
5	Retained residue	Thermal treatment at 800 °C for 20 min.
6	Residue	Store the final residue in a sealed container until testing.

487

488 **Table 3** BET values observed after each selective dissolution procedure for each clinker.

	OPC	OPC-MAM	OPC-MAM*	OPC-SAM	WPC	WPC-MAM	WPC-SAM
BET (m <sup>2</sup> /kg)	352	423	542	503	309	405	469

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491

492 **Table 4.** Rietveld-based quantitative phase analysis and phase ratios of samples before and  
 493 after SD.

Phases	OPC	OPC- MAM	OPC- SAM	WPC	WPC- MAM	WPC- SAM
	%					
Alite	75.5	1.5	6.2	73.8	1.9	3.0
Belite	6.9	---	---	12.1	---	0.9
C <sub>3</sub> A	1.8	10.2	9.7	8.3	92.3	91.2
K-C <sub>3</sub> A	2.2	12.6	11.8	---	---	---
C <sub>4</sub> AF	12.0	71.3	68.0	0.3	3.4	3.3
Portlandite	0.5	---	---	4.7	1.2	0.6
Periclase	0.6	3.6	3.3	---	---	---
Calcium carbonate	0.5	0.8	1.0	0.8	1.2	1.0
Aluminates/C <sub>4</sub> AF	0.33	0.32	0.32	27.67	27.15	27.64
Periclase/Aluminates	0.15	0.16	0.15	---	---	---
cub./orth	0.82	0.81	0.82	---	---	---
GOF	3.93	2.85	2.52	4.53	2.60	3.88

494

495 **Table 5.** Rietveld-based quantitative phase analysis after modified MAM\* solution attack  
 496 on WPC and OPC.

Phases	OPC	OPC- MAM*	WPC	WPC- MAM*
	(%)			
C <sub>3</sub> A	1.8	10.9	8.3	96.5
K-C <sub>3</sub> A	2.2	13.3	---	---
C <sub>4</sub> AF	12.0	72.2	0.3	3.5
Periclase	0.6	3.6	---	---
C <sub>3</sub> A/C <sub>4</sub> AF	0.33	0.34	27.67	27.57
periclase/aluminate	0.15	0.15	---	---
Cubic C <sub>3</sub> A /orth. C <sub>3</sub> A	0.82	0.82	---	---
GOF	3.93	3.06	4.53	2.59

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502 **Table 6.** Raman shifts of key aluminate phases.

Phases	Raman bands [ $\text{cm}^{-1}$ ]	Authors	Experimental conditions
Synthetic cubic $\text{C}_3\text{A}$	506   754	(Black et al. 2006)	632.8 nm   He-Ne
	504   753   1083   1525	(Bonen et al. 1994)	1064 $\mu\text{m}$   Nd:YAG*
	508   761	(Conjeaud and Boyer 1980)	514.5 nm   Ar
	1050	(Dyer et al. 1993)	1064 nm
	510   760	(Newman 2005)	1064 nm
(Clinker) cubic $\text{C}_3\text{A}$	505   754	This work	514.0 nm   Ar
	750	(Conjeaud and Boyer 1980)	514.5 nm   Ar
	506   754	(Deng et al. 2002)	632.8 nm   He-Ne
	731	(Martinez-Ramirez et al. 2006)	514.5 nm   Ar
	740   756	(Bensted 1976)	514+632 nm
Synthetic Na doped $\text{C}_3\text{A}$	761	This work	514.0 nm   Ar
	493   521   763   1078	(Bonen et al. 1994)	1.064 $\mu\text{m}$   Nd:YAG
(Clinker) orthorhombic K-doped $\text{C}_3\text{A}$	510   761   1074	This work	514.0 nm   Ar
	718	This work	514.0 nm   Ar
Extracted cubic $\text{C}_3\text{A}$	508   758	This work	514.0 nm   Ar

503 \* neodymium-doped yttrium aluminium garnet