

1           **On the early hydration of cubic ye'elinite: new insights from**  
2                           **time-resolved *in situ* MAS NMR spectroscopy**

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1 **Abstract:**

2 Two polymorphs of ye'elinite are known to exist in calcium sulfoaluminate cements, namely,  
3 orthorhombic (iron free),  $C_4A_3\$$  and cubic/pseudo-cubic (iron incorporated),  $C_4A_{3-x}F_x\$$  forms.  
4 The very early hydration behaviour of cubic ye'elinite (nominal composition:  
5  $Ca_{3.8}Na_{0.2}Al_{5.6}Fe_{0.2}Si_{0.2}O_{12}SO_4$ ) has been investigated using a time-resolved *in situ* multi-  
6 nuclear ( $^1H$ ,  $^{27}Al$ ,  $^{23}Na$  and  $^{29}Si$ ) MAS NMR spectroscopic approach. The study shows that the  
7 reaction pathway and the intermediate species formed are substantially different from those  
8 that are observed during the hydration of orthorhombic ye'elinite, and the rate as well as the  
9 nature of hydration products are dictated by the presence or the absence of limestone ( $CaCO_3$ ).  
10 Furthermore, the detection of diverse transient species as well as the uncovering of different  
11 kinetic behaviour during the early hydration of cubic ye'elinite illustrate the advantages of  
12 time-resolved *in situ* MAS NMR experimental approach for fingerprinting hydrated phases.

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14 **Keywords:**

15 Cubic ye'elinite, hydration, ettringite, monosulfate, time-resolved *in situ* NMR

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17 **1. Introduction**

18 Recently developed eco-friendly and low carbon footprint binders such as calcium  
19 sulfoaluminate (CSA), sulfobelitic, belite-ye'elinite-ferrite (BYF) and ternesite based cements  
20 have ye'elinite as a key constituent in them.[1–2] Ye'elinite based cements are also known  
21 for their high early strength, fast setting, rapid hardening, as well as excellent chemical  
22 resistance and reduced shrinkage.[3,4] CSA clinker, is produced by burning a mixture of  
23 bauxite, limestone and gypsum in a temperature range 1250 – 1350 °C resulting in a ye'elinite  
24 ( $C_4A_3\$$ ) rich binder.[2] However, the partial substitution of expensive bauxite by an iron  
25 containing mineral results in the development of iron-rich ye'elinite ( $C_4A_{3-x}F_x\$$ ) based clinker.  
26 While the iron-free ye'elinite crystallizes in orthorhombic form (o-ye'elinite), iron  
27 incorporated ye'elinite exist in cubic/pseudo-cubic polymorphic form (c-ye'elinite).[5]  
28 Development of iron-rich ye'elinite based binders such as ferritic calcium sulfoaluminate  
29 based cements and BYF cements are gaining momentum due to the scarcity and expensiveness  
30 of bauxite.[6]

31 Solid-state NMR spectroscopy is a unique tool for the investigation of hydration kinetics due  
32 to its unparalleled ability to probe molecular level transformations and to equally detect and  
33 quantify crystalline, amorphous and surface species. A recently developed time-resolved *in situ*  
34 multinuclear MAS NMR approach has the ability to detect transient species and fingerprint the  
35 critical and rapid mineralogical changes on the time scale of seconds.[7] *In situ*  $^1H$  MAS NMR  
36 spectroscopy can fingerprint all the hydrated proton bearing phases while  $^{27}Al$  MAS NMR can  
37 easily distinguished the anhydrous and hydrated aluminate phases.

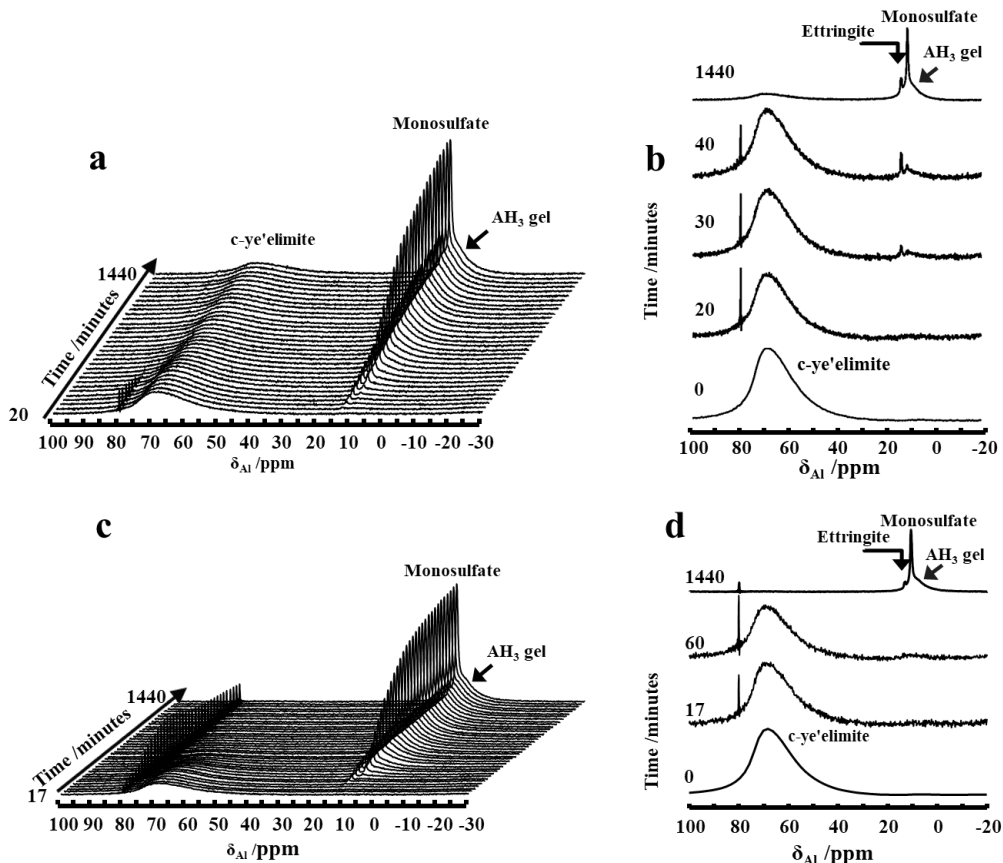
38 In the present work, we have investigated the very early hydration behaviour of cubic  
39 ye'elinite (nominal composition:  $Ca_{3.8}Na_{0.2}Al_{5.6}Fe_{0.2}Si_{0.2}O_{12}SO_4$ ) using a time-resolved *in situ*

1 multi-nuclear ( $^1\text{H}$ ,  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  and  $^{29}\text{Si}$ ) MAS NMR spectroscopic approach. We have also  
 2 studied the role of water to solid ratio and the addition of calcium carbonate on the hydration  
 3 mechanism of cubic ye'elimite.

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## 5 2. Results and Discussion

6 The details of sample preparation and the preliminary characterization are given in the  
 7 supplementary information. In Fig. 1a, we show the time-resolved *in situ*  $^{27}\text{Al}$  MAS NMR  
 8 spectra recorded on a cubic ye'elimite paste prepared with a w/s of 0.5. The first  $^{27}\text{Al}$  spectrum  
 9 of the *in situ* data recorded at 20 minutes (Fig. 1b) revealed a short dormant period where no  
 10 hydrated octahedral aluminate phases are detected. However, a very sharp peak appeared in the  
 11 tetrahedral region at 80 ppm and is due to hydrated aluminate species. The very narrow line  
 12 width indicate that the  $[\text{Al}(\text{OH})_4]^-$  species is highly mobile as in liquid-state confirming the  
 13 commencing of the dissolution of cubic ye'elimite. As the hydration progressed, the tetrahedral  
 14 aluminate species in solution transformed into octahedral species in the solid. At about 30  
 15 minutes, two peaks started to emerge in the octahedral region, one sharp peak at 13.3 ppm and  
 16 a broad resonance in the range 5 – 15 ppm. The former is due to the precipitation of crystalline  
 17 ettringite,  $[\text{Ca}_6\text{Al}_2(\text{OH})_{12}](\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$  and the latter is due to amorphous aluminium  
 18 hydroxide gel,  $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ . [7] After 40 minutes, further changes are seen in the octahedral  
 19 region of the spectrum with the growth of an additional resonance at about 10.8 ppm, and is  
 20 due to an AFm phase, monosulfate,  $[\text{Ca}_4\text{Al}_2(\text{OH})_{12}](\text{SO}_4) \cdot x\text{H}_2\text{O}$  with  $x = 5, 6,$  and  $7.5$ . [7]



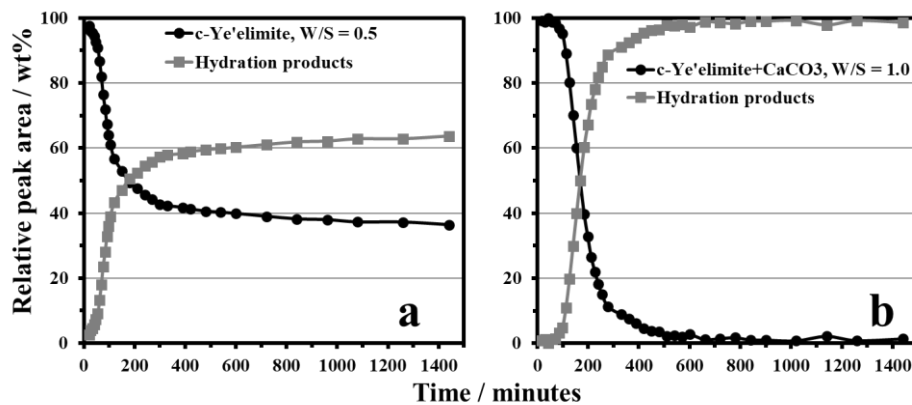
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1 Fig. 1. Stacked plot of time-resolved *in situ*  $^{27}\text{Al}$  MAS NMR spectra of the hydration of cubic ye'elimite alone (a)  
2 and in the presence of  $\text{CaCO}_3$  (c). The  $^{27}\text{Al}$  MAS NMR spectra of selected time intervals corresponding to cubic  
3 ye'elimite hydration alone (b) and in the presence of  $\text{CaCO}_3$  (d).

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5 The peak intensities associated to all the three phases increased as the hydration progressed,  
6 however, the resonances due to monosulfate and amorphous aluminium hydroxide gel grew  
7 comparatively rapidly, consistent with the fast hydrolysis of cubic ye'elimite. After 24 hours  
8 of *in situ* hydration, the phase assemblage consists of ettringite, monosulfate, aluminium  
9 hydroxide and residual anhydrous cubic ye'elimite (Fig. 1b, 1440 minutes). The presence of  
10 anhydrous cubic ye'elimite after 24 hours reveal the lack of water content in the paste for its  
11 complete hydration. Subsequently, we have conducted an experiment with higher w/s ratio in  
12 a combined strategy involving the increase of water content in the paste and with the addition  
13 of a filler,  $\text{CaCO}_3$  in order to study the reaction kinetics of cubic ye'elimite.

14 Fig. 1c shows the *in situ*  $^{27}\text{Al}$  MAS NMR spectra revealing the phase development during the  
15 hydration of cubic ye'elimite together with  $\text{CaCO}_3$  (w/s = 1). Despite a significantly higher  
16 water amount (four times to that of the previous experiment with respect to the ye'elimite  
17 content in the mixture) the main difference from the previous sample is the extended initial  
18 dormant period, lasting about 75 minutes, where no hydration products are detected (Fig. 1d).  
19 After that, ettringite (13.3 ppm) and aluminium hydroxide gel (5 – 15 ppm) started to appear.  
20 When the hydration time reached at about 110 minutes, a new peak started to appear at around  
21 10.8 ppm, steadily grows for the remainder of the experiment and is due to the formation of  
22 monosulfate. Majority of the anhydrous cubic ye'elimite is consumed within 600 minutes  
23 confirming the complete hydration as the amount of water exceeded the stoichiometric content  
24 in this mix.

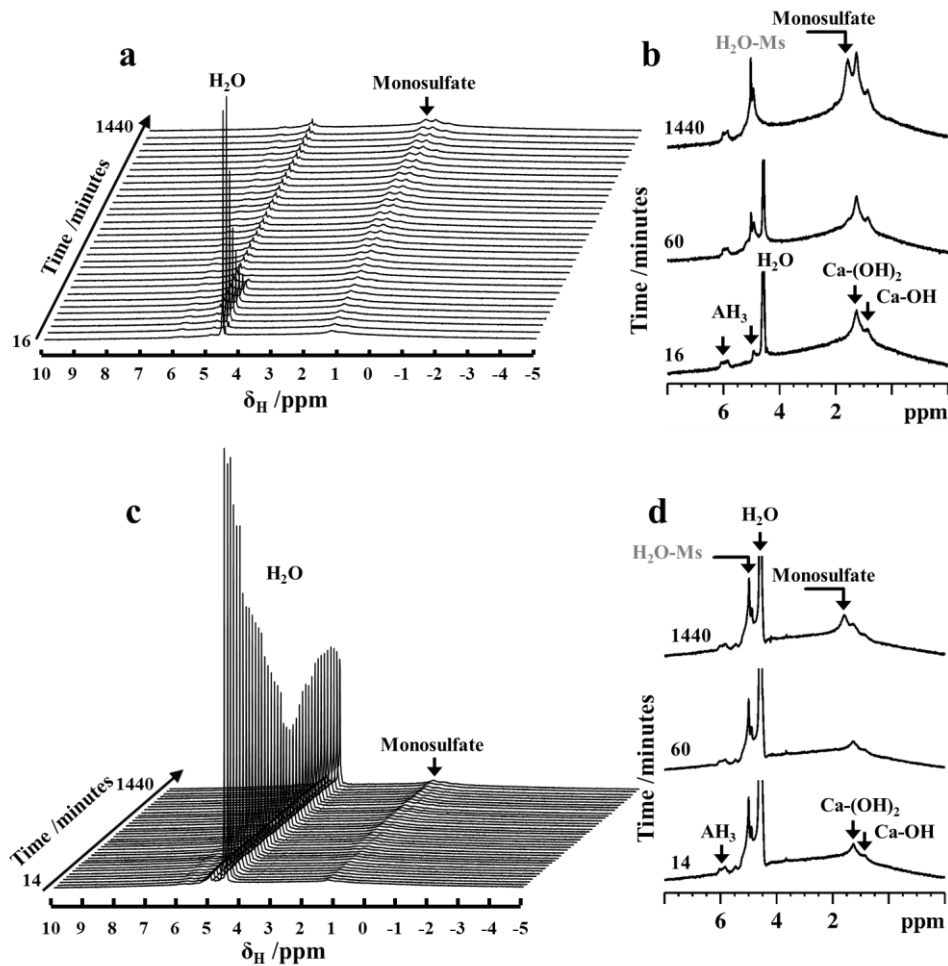


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26 Fig. 2. Time dependence of the peak areas due to reactant (c-ye'elimite) and hydration products (sum of ettringite,  
27 monosulfate and aluminium hydroxide gel) derived from the time-resolved *in situ*  $^{27}\text{Al}$  MAS NMR spectra showing  
28 the variable hydration rate of neat c-ye'elimite (a) and c-ye'elimite/ $\text{CaCO}_3$  mix (b).

29 Fig. 2 presents the time dependence of peak areas derived from the *in situ*  $^{27}\text{Al}$  MAS NMR  
30 data, which gathered the kinetic information. The sharp growth of products up to 300 minutes  
31 in both samples is clearly evident, however, for longer times the hydration is drastically  
32 retarded in the sample with w/s ratio 0.5. When higher water content was employed, a complete

1 hydration is achieved as shown in Fig. 2b.  $\text{CaCO}_3$  did not participate in the hydration reactions  
 2 as carbonated phases, such as hemi- or mono-carbonate AFm species, are not detected in this  
 3 sample during the *in situ* NMR study, confirming its role as a nonreactive filler. The reaction  
 4 pathway and the kinetics are substantially different from that are observed during the hydration  
 5 of orthorhombic ye'elinite.[7]



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7 Fig. 3. Stacked plot of time-resolved *in situ*  $^1\text{H}$  MAS NMR spectra of the hydration of cubic ye'elinite (a) and  
 8 cubic ye'elinite/ $\text{CaCO}_3$  mix (c). The zoomed spectra of the *in situ*  $^1\text{H}$  NMR data (b and d) highlighting the  
 9 formation of monosulfate (Ms).  $\text{AH}_3$ ; Aluminium hydroxide gel.

10 We have applied the complementary *in situ*  $^1\text{H}$  MAS NMR spectroscopy (Fig. 3a, c) for the  
 11 determination of the hydration products through the speciation of protons within the *in situ*  
 12 cubic ye'elinite hydration experiments.  $^1\text{H}$  NMR studies revealed no marked variations in the  
 13 types of protonic species present in the two samples confirming a similar phase development.  
 14 In the very early hydration period water resonance (4.56 ppm) dominate the spectra, however,  
 15 phases such as calcium hydroxide (1.25 and 0.85 ppm) and aluminium hydroxide gel (4.9 and  
 16 5.9 ppm) are detected (Fig. 3b, d). At about 40 minutes, a sharp peak at around 1.6 ppm started  
 17 to appear in cubic ye'elinite and its intensity kept on increasing and is due to monosulfate, in  
 18 accord with the *in situ*  $^{27}\text{Al}$  MAS NMR data. A similar peak also emerged at the same chemical  
 19 shift at around 110 minutes in c-ye'elinite/ $\text{CaCO}_3$  mix, confirming its identity as monosulfate.  
 20  $^1\text{H}$  resonance due to hydration water is not detected beyond 80 minutes (Fig. 3a) for the cubic

1 ye'elimite paste (as already found when the kinetics of the process was studied – see Figure  
2 2a) while its presence is noted in c-ye'elimite/CaCO<sub>3</sub> mix (Fig. 3c) even after 24 hours of  
3 hydration. However, the hydration dynamics in the latter sample is not straight forward as the  
4 intensity of water resonances decreases up to 400 minutes beyond which it again increases (Fig.  
5 3c). Owing to these data, it can be safely stated that the water content in phases such as  
6 aluminium hydroxide gel and monosulfate is variable, as a consequence the amount of water  
7 available for hydration changes during the hydration process.

### 8 9 **3. Conclusions**

10 This study highlights that the hydration kinetics of cubic ye'elimite strongly depends on the  
11 w/s ratio. Although an initial dormant period was detected, a relatively faster hydration kinetics  
12 is noted for the cubic polymorph of ye'elimite. Thanks to the capability of <sup>27</sup>Al MAS NMR to  
13 allow the quantitative determination of all the species involved in the hydration regardless of  
14 their crystalline or amorphous state, the main hydration products were identified as  
15 monosulfate and aluminium hydroxide, whereas traces of ettringite was also detected,  
16 especially at the beginning of the hydration of cubic ye'elimite. The detection of transient  
17 species such as [Al(OH)<sub>4</sub>]<sup>-</sup> *in situ*, that is precursor to the formation of aluminium hydroxide  
18 gel, suggests that the presence of <sup>23</sup>Na ions predominantly stabilized it during the cubic  
19 ye'elimite hydration. Finally, the employment of calcium carbonate in the blend resulted in a  
20 faster reaction rate and higher product formation, after the dormant period, validating the *in*  
21 *situ* MAS NMR experimental approach developed in this study.

### 22 **4. Acknowledgement**

23 This work was supported by (research grant; P18-RT-720) the Andalusian Regional  
24 Government, Spain.

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