

## Supporting information for

# Investigating the hydration of C<sub>3</sub>A and the evolution of AFm phases in the combined presence of anhydrite and limestone using solid-state NMR, XRD and TG techniques

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## <sup>27</sup>Al MAS NMR

Aluminium is a fundamental building block for various types of minerals formed during the hydration of cement that contribute to the durability of concrete. There are a few aspects of aluminium that makes it a favourable NMR active nucleus for the spectroscopic study of cements and its NMR properties are given in Table S1. <sup>27</sup>Al is naturally 100% isotopically abundant and has a very high gyromagnetic ratio as well as very short relaxation time, therefore, routine observation is easy and fast (of the order of few minutes in oxides).

Table S1: NMR properties of <sup>27</sup>Al nucleus

| Properties   | Magnitude (unit)  |
|--|---|
| Spin number ( <i>I</i> )   | 5/2   |
| Nuclear magnetic moment ( <i>μ</i> )                               | 4.30869 μN  |
| Gyromagnetic ratio ( <i>γ</i> )                                    | 6.976 × 10 <sup>7</sup> rad T <sup>-1</sup> s <sup>-1</sup> |
| Resonance frequency (at 11.75 T)                                   | 130.32 MHz  |
| Quadrupole moment ( <i>Q</i> )                                     | 148.2 mb  |
| Isotopic natural abundance   | 100 %   |
| Receptivity (relative to <sup>13</sup> C)                          | 1.22×10 <sup>3</sup>  |
| Isotropic chemical shift ( <i>δ<sub>iso</sub></i> ) range (oxides) | +100 - -20 ppm  |
| Quadrupole coupling constant ( <i>C<sub>Q</sub></i> )              | 0 - 20 MHz  |
| Asymmetry parameter ( <i>η<sub>Q</sub></i> )                       | 0 - 1   |
| Relaxation times ( <i>T<sub>1</sub></i> )                          | < 5 s   |
| Experimental approaches  | Static, MAS, CPMAS, MQMAS, REDOR, STMAS                     |

<sup>27</sup>Al nucleus in oxides generally has a large chemical shift range, with respect to the shift scale of proton, thereby making it an attractive nucleus for solid-state NMR. Aluminate minerals observed in cements usually resonate within the 100 to -20 ppm scale with distinguishable chemical shift ranges for the potentially coexisting AlO<sub>4</sub>, AlO<sub>5</sub> and AlO<sub>6</sub> polyhedra with often sufficient resolution for quantification. The <sup>27</sup>Al NMR investigations on cement pastes showed different contributions in the range 50-100, 25-45 and -10-20 ppm, respectively, due to tetra-, penta- and octa-coordinated aluminium environments, respectively.

Although, crystalline and amorphous aluminate phases in hydrated cements can be equally detected and quantified by <sup>27</sup>Al NMR techniques, inherently low spectral resolution from quadrupolar broadening and chemical shift distribution due to the presence of disordered phases makes it challenging for the detailed interpretation, especially for species that appear in the octahedral region (-10 to 20 ppm). However, parameters such as quadrupolar coupling constant and asymmetry parameter can provide significant information that can help in identifying the structurally different Al sites [S1]. Owing to the importance

of chemical shift, most NMR studies of quadrupolar nuclide report isotropic chemical shift ( $\delta_{iso}$ ) along with quadrupolar coupling constant ( $C_Q$ ) and asymmetry parameter ( $\eta_Q$ ).

As stated in the previous section, amongst the  $C_3A$  hydration products such as hydrogarnet, ettringite and the various AFm phases,  $^{27}Al$  appear in octahedral coordination and resonate in the narrow chemical shift range of 8.5 to 13.5 ppm. Especially, when multiple AFm phases and/or their solid-solutions exist simultaneously it can be challenging to distinguish the individual phases from their isotropic chemical shift values. In such cases, sometimes it is useful to detect peaks based on centre-of-gravity peak ( $\delta_{CG}$ ) position of the central transition which is related to isotropic chemical shift ( $\delta_{iso}$ ) according to the following equation.

$$\delta_{CG} = \delta_{iso} + \delta_{QIS} \quad (S1)$$

where  $\delta_{QIS}$  is the quadrupolar induced chemical shift and for the central transition  $\delta_{QIS}$  is always negative, meaning that  $\delta_{CG}$  peak position will always be lower in ppm value than the isotropic chemical shift value. For a  $^{27}Al$  nucleus residing in an extremely symmetric environment, the quadrupolar interaction becomes negligible and  $\delta_{QIS}$  tends to be zero. Therefore, the maximized peak amplitude of the  $\delta_{CG}$  peak does coincide with the isotropic chemical shift ( $\delta_{iso}$ ) [S1]. However, one must be careful while using  $\delta_{CG}$  peak position for interpretation as it is affected by quadrupolar interactions leading to a field-dependent shift.

Table S2:  $^{27}Al$  MAS NMR data with isotropic chemical shifts ( $\delta_{iso}$ ), centre-of-gravity peak ( $\delta_{CG}$ ), and coordination for various Aluminium sites in hydrated aluminate phases identified in this study.

| Phase   | Site        | Coordination | $\delta_{iso}$ (ppm) <sup>1</sup> | $\delta_{CG}$ (ppm) <sup>2</sup> | Reference |
|---|-------------|--------------|-----------------------------------|----------------------------------|-----------|
| Tricalcium Aluminate ( $C_3A$ )               | $Al^{IV}_1$ | 4            | $80.2 \pm 0.2$                    | -                                | S4        |
|   | $Al^{IV}_2$ | 4            | $78.5 \pm 0.2$                    | -                                |           |
| Hydrogarnet ( $C_3AH_6$ )                     | $Al^{VI}$   | 6            | $12.4 \pm 0.1$                    | $12.4 \pm 0.1$                   | S4        |
| Hydroxy-AFm ( $C_2AH_8$ )                     | $Al^{VI}$   | 6            | $10.3 \pm 0.2$                    | $10.3 \pm 0.2$                   | S6        |
| Hydroxy-AFm ( $C_4AH_{13}$ and $C_4AH_{19}$ ) | $Al^{VI}$   | 6            | $10.2 \pm 0.2$                    | $10.2 \pm 0.2$                   | S4        |
| Ettringite ( $C_6A\bar{S}_3H_{32}$ )          | $Al^{VI}_1$ | 6            | $13.1 \pm 0.1$                    | $13.3 \pm 0.1$                   | S12       |
|   | $Al^{VI}_2$ | 6            | $13.5 \pm 0.1$                    |                                  |           |
| Monosulphate ( $C_4A\bar{S}H_{12}$ )          | $Al^{VI}$   | 6            | $11.1 \pm 0.2$                    | $10.7 \pm 0.2$                   | S12       |

|  |                  |   |            |           |           |
|--|------------------|---|------------|-----------|-----------|
| Monosulphate ( $C_4A\bar{S}H_{10.5}$ )   | Al <sup>VI</sup> | 6 | 10.2 ± 0.2 | 9.7 ± 0.2 | This work |
| Monocarbonate ( $C_4A\bar{C}H_{11}$ )  | Al <sup>VI</sup> | 6 | 10.5 ± 0.2 | 8.6 ± 0.2 | S6        |
| Solid-solutions (OH <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> ) | Al <sup>VI</sup> | 6 | 9.5-11.5   | 9.5-11.5  | This work |

<sup>1</sup>Referenced to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion in 1.0 M AlCl<sub>3</sub> solution at 0.0 ppm, <sup>2</sup>At 11.75 T

<sup>27</sup>Al MAS NMR spectra of C<sub>3</sub>A, ettringite, monosulfate, monocarbonate, C<sub>3</sub>AH<sub>6</sub> and hydroxy-AFm phases, have already been published [S2-S12]. In order to aid the interpretation of the <sup>27</sup>Al NMR spectra and peak assignments, Table S2 summarises the <sup>27</sup>Al chemical shifts observed for aluminate phases identified in this study.

Table S3: Chemical composition of Anhydrite and Limestone.

| Anhydrite                      |      | Limestone                      |       |
|--------------------------------|------|--------------------------------|-------|
| Compound                       | %    | Compound                       | %     |
| LOI                            | 0.7  | LOI                            | 37.99 |
| CaO                            | 44.6 | CaO                            | 49.2  |
| SiO <sub>2</sub>               | 0.1  | SiO <sub>2</sub>               | 7.17  |
| Al <sub>2</sub> O <sub>3</sub> | 0.1  | Al <sub>2</sub> O <sub>3</sub> | 2.47  |
| SO <sub>3</sub>                | 54.3 | Fe <sub>2</sub> O <sub>3</sub> | 0.99  |
| Fe <sub>2</sub> O <sub>3</sub> | --   | SO <sub>3</sub>                | 0.24  |
| MgO                            | 0.1  | Na <sub>2</sub> O              | 0.06  |
| K <sub>2</sub> O               | --   | K <sub>2</sub> O               | 0.76  |
| Ti <sub>2</sub> O              | --   | MgO                            | 0.83  |
| Na <sub>2</sub> O              | --   | Ti <sub>2</sub> O              | 0.1   |
| Minor elements                 | --   | Minor elements                 | 0.19  |

Figure S1: Powder XRD pattern of cubic C<sub>3</sub>A.

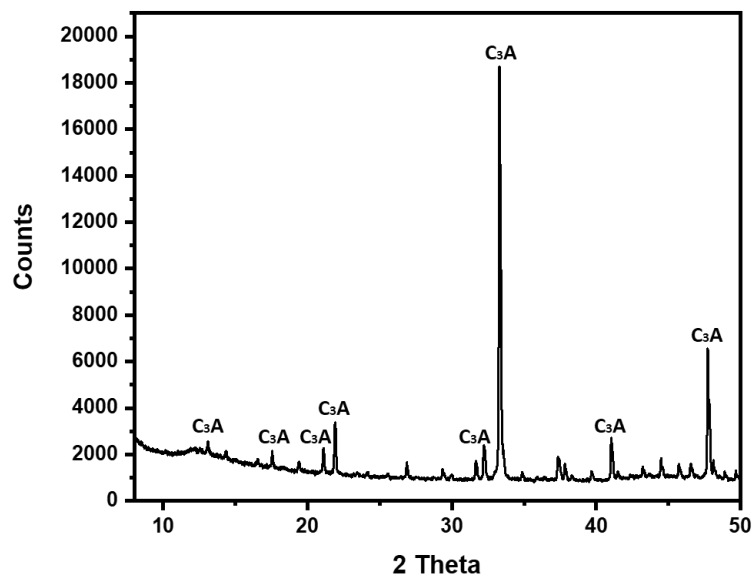
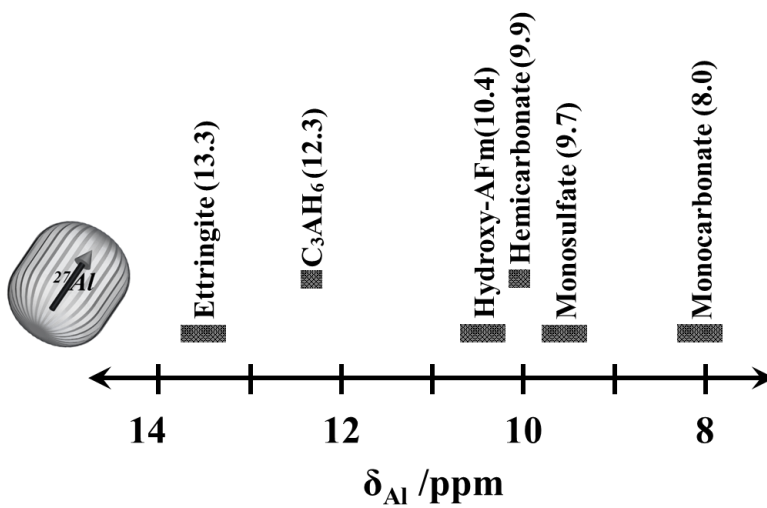


Figure S2: <sup>27</sup>Al NMR chemical shifts of the main AFm phases.



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