



# Quantitative analysis of pure triclinic tricalcium silicate and C–S–H gels by $^{29}\text{Si}$ NMR longitudinal relaxation time



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## HIGHLIGHTS

- The  $^{29}\text{Si}$  longitudinal relaxation time ( $T_1$ ) for the anhydrous  $\text{C}_3\text{S}$  was studied.
- The  $T_1$  for the remnant  $\text{C}_3\text{S}$  in hydrated pastes and C–S–H was also studied.
- The anhydrous  $\text{C}_3\text{S}$  has considerably long  $T_1$ .
- The remnant  $\text{C}_3\text{S}$  in hydrated pastes has considerably shorter  $^{29}\text{Si}$   $T_1$  than the anhydrous  $\text{C}_3\text{S}$ .
- The  $T_1$  of the signals of the remnant  $\text{C}_3\text{S}$  and C–S–H gel in hydrated pastes are considerably similar.

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## ABSTRACT

$^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance ( $^{29}\text{Si}$  MAS NMR) has been commonly used to monitor the hydration degree of tricalcium silicate ( $\text{C}_3\text{S}$ ) and the structure of the calcium silicate hydrate known as C–S–H gel generated during their hydration, which is responsible for the strength and durability of cement pastes. The present study is aimed to measure the longitudinal relaxation times ( $T_1$ ) for the different types of Si in the structure of anhydrous triclinic  $\text{C}_3\text{S}$ , the remnant  $\text{C}_3\text{S}$  in pastes after a number of hydration days and the hydrated product (C–S–H gel). Results showed that the longitudinal relaxation times of the  $^{29}\text{Si}$  signals of  $\text{C}_3\text{S}$  remaining after hydration are considerably shorter than the anhydrous  $\text{C}_3\text{S}$  phase of the starting material; an effect that was interpreted as an extra contribution of  $^{29}\text{Si}$ – $^1\text{H}$  dipolar relaxation provided by the surrounding water molecules. Interestingly, the shorter  $T_1$  of the remaining non-hydrated  $\text{C}_3\text{S}$  which is comparable to the C–S–H gel permits a much faster acquisition of quantitative  $^{29}\text{Si}$  MAS spectra.

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## 1. Introduction

$\text{C}_3\text{S}$  synthesized from a stoichiometric mix of silica gel and calcium oxide (originated from calcined calcium carbonate) at 1450 °C following rapid cooling to ambient temperature leads to triclinic  $T_1$  polymorph. Hydrated tricalcium silicate ( $T_1$ ) forms portlandite  $\text{Ca}(\text{OH})_2$  and a calcium silicate hydrate known as C–S–H gel,

*Abbreviations:* FT, Fourier transform; MAS, magic angle spinning; NMR, nuclear magnetic resonance; FID, free induction decay;  $T_1$ , longitudinal or spin–lattice relaxation time;  $d_1$ , inter-scan relaxation delay;  $d_1^{\text{min}}$ , minimum required inter-scan relaxation delay; LB, line-broadening factor used for the apodization of the FID with an exponential function.

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the substance primarily responsible for the mechanical strength of cement. Since the gel is amorphous or scantily crystalline, the technique most commonly used in these hydration studies is  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance (MAS NMR).

Substantial information regarding the characterization of the C–S–H gels has been obtained by  $^{29}\text{Si}$  MAS NMR in hydrated samples of ordinary Portland cement (OPC), white Portland cement (WPC) or tricalcium silicate ( $\text{C}_3\text{S}$ ) [1–7]. However, very few studies have addressed the  $^{29}\text{Si}$  longitudinal relaxation in silicate phases because some solid silicates or alumino-silicates have long relaxation times (typically >30 min for samples depleted of paramagnetics [8]). Knowing the longitudinal (or spin–lattice) relaxation time of each  $^{29}\text{Si}$  signal ( $T_1$ ) in the  $^{29}\text{Si}$  MAS spectrum is crucial to establishing a suitable value of the scan duration, which is

approximately expressed by the parameter  $d_1$  (the FID acquisition time is typically  $\sim 40$  ms and is negligible compared to  $d_1$  in this type of samples), that guarantee a quantitative NMR spectrum [9]. Thus, a better understanding of the relaxation mechanisms would be of considerable interest to ensure that the scan duration ( $d_1$ ) in the experiment is long enough to obtain quantitative evaluation of the spectra and insights into specific framework interactions. The scan duration in a  $^{29}\text{Si}$  MAS spectrum and other NMR experiment relying in direct polarization and detection of the nucleus, should be at least three to five times longer than the  $T_1$  of the signal to ensure that after several scans of the experiment, its integral (area) is quantitative (i.e. proportional to the number of nuclei generating the resonance and its concentration or abundance in the sample).

A typical problem to set the NMR quantitative scan conditions in solid silicates is the high variability of their  $^{29}\text{Si}$   $T_1$ . They range from milliseconds to minutes, depending on the chemical environment [10]. For instance, solid silicates depleted of paramagnetic ions have considerably long  $T_1$  and the minimum scan duration typically required to obtain a quantitative spectrum is on the order of minutes. This, together with the large number of experimental repetitions required to record a sufficiently sensitive spectrum (i.e. with good signal to noise ratio), translates into long spectrometer measuring times.

To measure longitudinal relaxation times  $T_1$  three different methods have been proposed, namely inversion-recovery [11], variable delay Bloch decay also known as progressive saturation [9,12,13], and saturation-recovery [13,14]. The three methods have been recently evaluated for its application to  $^{29}\text{Si}$  NMR of cements [13] and concluded that the saturation-recovery offers the best balance of theoretical simplicity and spectral tractability with minimal disadvantage. Besides, it is also the method of choice to measure  $T_1$  for samples with a broad chemical shift range as it occurs for certain spin  $1/2$  heteronuclei such as  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ ,  $^{209}\text{Pb}$  and others, and in general for many quadrupolar nuclei.

The  $T_1$  values of  $^{29}\text{Si}$  have been determined in anhydrous silicate phase, alite (tricalcium silicate) and belite (dicalcium silicate), for different types of commercial Portland cements and milled clinkers. The  $T_1$ 's reported are consistently lower in alite than in belite and the content of paramagnetic ions ( $\text{Fe}_2\text{O}_3$ ,  $\text{NiCl}_2$ ,  $\text{Mn}_2\text{O}_3$ , etc.) can considerably reduce their  $T_1$  [13,15]. Thus, the reported  $T_1$  for alite range from 0.24 to 0.067 s and for belite from 8.2 to 0.54 s [5,16–18]. The  $T_1$  are much higher for white Portland cement (WPC) than ordinary Portland cement (OPC) because the former has a lower content of bulk  $\text{Fe}_2\text{O}_3$ .

To the best of our knowledge there are no studies of the  $^{29}\text{Si}$  longitudinal relaxation time in pure anhydrous triclinic  $\text{C}_3\text{S}$ , and these measurements would be useful to assess quantitative conditions in the  $^{29}\text{Si}$  MAS spectrum. Thus, the present study is aimed to ascertain conditions for fast acquisition and quantitative recording  $^{29}\text{Si}$  MAS spectra by measuring  $^{29}\text{Si}$  longitudinal relaxation times ( $T_1$ ) for the different materials: anhydrous triclinic  $\text{C}_3\text{S}$ , the remnant  $\text{C}_3\text{S}$  in  $\text{C}_3\text{S}$  pastes after a number of days of hydration and the hydrated product (C–S–H gel).

## 2. Experimental

### 2.1. Materials and sample preparation

Synthetic tricalcium silicate ( $\text{C}_3\text{S}$ ) was prepared by solid-state reaction. The synthesised tricalcium silicate has a low BET specific surface,  $0.427 \pm 0.003 \text{ m}^2/\text{g}$ . The DTA, XRD-Rietveld analysis and  $^{29}\text{Si}$  MAS NMR results for the synthesised  $\text{C}_3\text{S}$  (showed elsewhere [19]) confirmed both the purity of the  $\text{C}_3\text{S}$  and its triclinic crystal modification,  $T_1$ .

The  $\text{C}_3\text{S}$  was hand-mixed for 3 min with de-ionized water at a w/s ratio of 0.425 and subsequently cured in containers at  $25^\circ\text{C}$  and a RH of 100% for 28 days (paste A28d). Hydration was stopped with acetone and subsequent vacuum drying for around 1.5 h.

### 2.2. Techniques

#### 2.2.1. $^{29}\text{Si}$ MAS NMR

The experimental conditions for all solid state NMR experiments were as follows: Bruker AVANCE-400 (9.4 T) spectrometer;  $^{29}\text{Si}$  operating frequency was 79.4 MHz; double resonance  $^1\text{H}/\text{X}$  MAS solids probe with 7-mm  $\text{ZrO}_2$  rotors; kaolin as secondary reference for  $^{29}\text{Si}$  chemical shifts ( $\delta = -91.2$  ppm referred to TMS,  $\delta = 0$  ppm); software for spectrum processing and quantitative integration via signal integration was MestRe-C v3.9 [20].

**2.2.1.1. Measurement of  $^{29}\text{Si}$   $T_1$  relaxation times: 1D  $^{29}\text{Si}$  MAS saturation-recovery experiment.** Longitudinal  $^{29}\text{Si}$  relaxation times ( $T_1$ ) were measured for both the anhydrous  $\text{C}_3\text{S}$  and the A28d samples with the one-dimensional  $^{29}\text{Si}$  MAS saturation-recovery pulse sequence of Fig. 1. The sequence incorporates a saturation-comb that is followed by a variable delay ( $\tau$ ) prior to the excitation pulse of the 1D  $^{29}\text{Si}$  MAS experiment.

To avoid potential errors in the apparent equilibrium magnetization ( $I_0$ ) which are crucial for this experiment, the  $^{29}\text{Si}$  hard  $\pi/2$  pulse was calibrated carefully with the reference kaolin sample. A conveniently short hard  $\pi/2$  pulse of  $7 \mu\text{s}$  was used both for the saturation pulses and the observation pulse of the experiment which covers the full range of spectral signals without significant RF offset effects. The saturation-comb part consisted in a train of 25  $\pi/2$  hard saturation pulses separated by delays of 30 ms (delay  $d_{20}$  in Fig. 1). The delay fulfills the required condition  $T_2 \ll d_{20} < T_1$  for the applicability of the experiment.

For the anhydrous  $\text{C}_3\text{S}$  a series of spectra were obtained with the following values of the variable delay ( $\tau$ ): 1, 2, 4, 6, 10, 20, 40, 60, 100, 150, 200, 250, 300, 350, 400, 450 and 500 s. For the 28 day hydrated paste the values of  $\tau$  were the same as for the  $\text{C}_3\text{S}$  with the exception of the last two listed that were omitted. Each spectrum of the series was acquired with 16 scans and the inter-scan relaxation delay  $d_1$  was set to 60 s to prevent excessive probe and sample heating.

**2.2.1.2. 1D  $^{29}\text{Si}$  MAS study at two inter-scan relaxation delays.** Two one-dimensional  $^{29}\text{Si}$  MAS NMR spectra were acquired for the 28 day hydrated paste of  $\text{C}_3\text{S}$  at  $25^\circ\text{C}$ . Broad-band proton decoupling was applied during the FID (free induction decay) acquisition with the TPPM (Two Pulse Phase Modulation) scheme using a field strength ( $\gamma B_1/2\pi$ ) of 25 kHz. Other conditions were:  $7 \mu\text{s}$  for the  $\pi/2$  excitation pulse; MAS spinning rate of 5 kHz; 128 scans; acquisition time ( $at$ ) of 100 ms; relaxation delay ( $d_1$ ), 60 s for the first spectrum and 615 s for the second.

To simplify the explanation of the optimal conditions for recording quantitative  $^{29}\text{Si}$  spectra in this type of samples, in the following discussion the total scan duration is regarded to be due exclusively to the relaxation delay between scans, symbolised as  $d_1$ . The contribution of other parameters such as pulse duration and FID acquisition time can be assumed to be negligible in comparison.

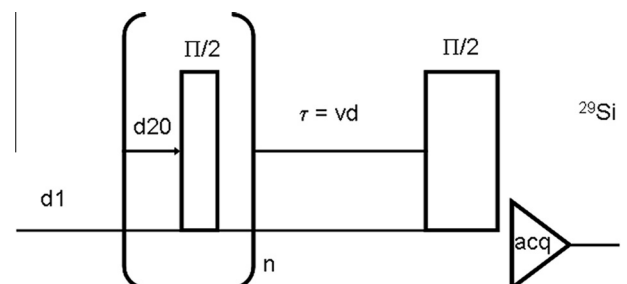
## 3. Results and discussion

### 3.1. Determination of $^{29}\text{Si}$ spin lattice relaxation time, $T_1$ of tricalcium silicate and C–S–H gel

The longitudinal relaxation times ( $T_1$ ) for the  $^{29}\text{Si}$  signals were determined with the 1D saturation-recovery  $^{29}\text{Si}$  MAS experiment. The absolute value of the integral of each signal in the spectrum obtained at a certain value of the delay  $\tau$ ,  $I(\tau)$ , was non-linear fitted to the monoexponential Eq. (1) to determine the  $T_1$  [14].

$$I(\tau) = I_0 \cdot [1 - \exp(-\tau/T_1)] + x_0 \quad (1)$$

where  $x_0$  is an offset due to the experimental difficulty to achieve complete saturation at  $\tau = 0$ .



**Fig. 1.** Pulse sequence of the 1D  $^{29}\text{Si}$  MAS saturation-recovery experiment used to measure longitudinal relaxation times in the cement pastes.

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