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Quantitative ^{29}Si MAS NMR spectroscopy of cement and silica fume containing paramagnetic impurities

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Abstract

The low natural abundance and the long spin lattice relaxation time of ^{29}Si lead to long measurement times and/or low signal-to-noise ratios using ^{29}Si magic angle spinning NMR spectroscopy. By contrast, samples containing paramagnetic iron ions have much shorter relaxation times, making measurements up to seven times more efficient, but at the same time making quantitative analysis unreliable. To solve the problem, the spin-lattice relaxation times of ordinary Portland cement (opc) and silica fume with and without iron content has been determined with inversion recovery experiments. The effect of varying the spectrum repetition time on the quantitative analysis is demonstrated for mixtures of opc with silica fume. For opc and silica fume with iron impurities repetition times as short as 5 s has permitted accurate quantitative analysis of the silicates present in these materials.

Keywords: Cement; ^{29}Si MAS NMR spectroscopy; Silica fume

1. Introduction

^{29}Si magic angle spinning (MAS) NMR spectroscopy has proven to be a valuable tool for the characterization and quantitative analysis of both anhydrous and hydrated calcium silicates in Portland cements [1,2]. Nevertheless, two problems must be solved: First, the low receptivity of the nucleus ^{29}Si entails a signal-to-noise (S/N) ratio, which is 2874 times lower than that of protons [3]. Second, the spin-lattice relaxation time, T_1, of ^{29}Si of most silicon-containing minerals is long [4], because nuclear spins like those of ^{1}H and ^{19}F adjacent to ^{29}Si are missing so that the spin-dipolar relaxation mechanism is not efficient. It follows that the time for recording repetitive spectra is also long. So, if one chooses to cure the low-receptivity problem of ^{29}Si by data accumulation, this leads to long spectrometer times, and optimisation of the experiment is desirable. We are aware of only two systematic studies, where this has been done by measuring T_1 prior to the quantitative analysis of the silicate phases [5,6], while in other cases T_1 might have been checked, without mention in the papers [7].

Nuclear relaxation is accelerated considerably if it is mediated by unpaired electron spins, because their magnetic dipole moment is 658 times bigger than that of protons [8]. This can be put to good use by incorporating paramagnetic transition metal ions into the silicate lattice, and olivine is a striking example. Thus, Grimmer et al. [9] have shown that upon increasing the content of Fe^{2+} ions in synthetic olivine up to 10% the ^{29}Si NMR signal is broadened considerably and eventually disappears in the baseline. Paramagnetic ions, mostly Fe^{3+} and Fe^{2+} in weak ligand fields are often met in various components of cement. This would render quantitative ^{29}Si MAS NMR analysis incorrect, because the silicon atoms may be influenced differently. In what follows we demonstrate that this can be overcome by considering relaxation.

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2. Experimental

2.1. Materials and sample preparation

The cement used was an ordinary German Portland cement CEM I 42.5 R (opc), the two silica fumes used (SF and SF(Fe)) were industrial products. The chemical compositions are shown in Table 1, analysed with X-ray fluorescence.

The samples measured by NMR spectroscopy were prepared by mixing Portland cement under dry conditions with 20 wt.% of SF or SF(Fe), respectively. The mixtures, opc/SF and opc/SF(Fe), were stored under nitrogen in closed bottles.

2.2. Solid state NMR spectroscopy

Solid state NMR experiments were performed with a Bruker Avance 300 spectrometer (magnetic field strength 7.0455 T, resonance frequency of ^{29}Si is 59.63 MHz). The samples were packed in 7 mm zirconia rotors and spun at 5 kHz under an angle of 54°44'. The chemical shifts were recorded relative to external tetramethylsilane (TMS).

The spin-lattice relaxation times, T_1, were determined by the inversion recovery experiment [10]. The waiting time, τ, was varied in 0.25-s steps from 0 to 5 s for the samples opc and SF(Fe), and in 2-s steps up to 20 s for the sample SF. The waiting time for zero-intensity response, τ_0, is related with T_1 through $\tau_0 = T_1 \ln 2$.

^{29}Si MAS NMR spectra of the mixtures were recorded with single pulse technique. The repetition time was varied in the range of 0.1 to 30 s, while the post-pulse delay was set to 7 μs, which was found to be the lowest possible value for avoiding pulse break-through. The signal patterns of the spectra were deconvoluted with the Bruker WINNMR software, and the resulting integrals were calculated relative to the content of cement and silica fume.

3. Results and discussion

The inversion recovery experiments are shown in Fig. 1, while the numerical results are collected in Table 2. When comparison is made with the data in Table 1, it turns out that T_1 decreases with increasing content of iron ions. Interestingly, for the cement sample different spin-lattice relaxation times were determined for the signals of C_3S (0.14 s) and C_2S (0.60 s), respectively. While these T_1 values are in good agreement with previous results [5] we may now conclude that the iron ions are more abundant in the C_2S phase than in the C_3S phase of the cement. Dobson et al. [6] have reported T_1 values of C_3S to be a function of the content of iron ions. From this we conclude that in our case C_3S contains 0.5 wt.% iron ions. Extending the concept to C_2S gives an iron ion content of 0.15 wt.%.

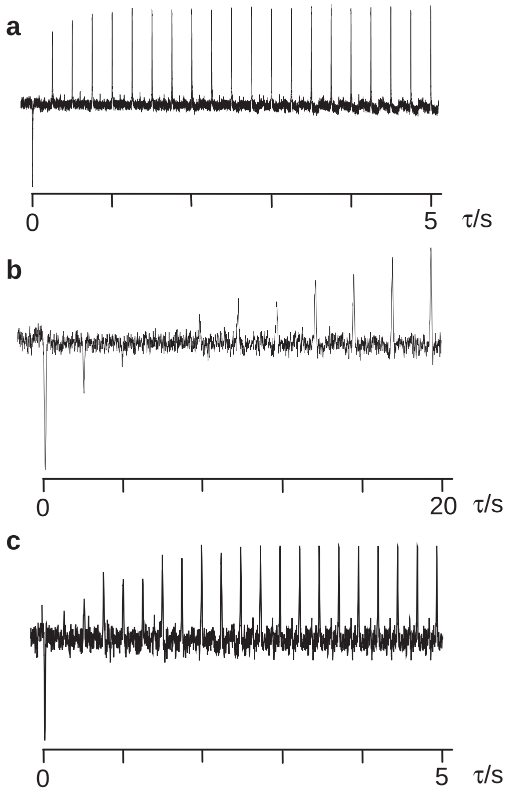

Fig. 1. Inversion recovery experiment: a — cement; b — silica fume; c — silca fume containing iron.

The variation of T_1 has important consequences for obtaining quantitative results from ^{29}Si NMR spectra, because spectrum accumulation must be applied for a good S/N ratio. Consequently, the repetition time, T_R, i.e., the time after which the subsequent spectrum can be recorded, depends on T_1 so that a given T_R might be suitable for one of the signals, whereas for others it would be too short or too long thereby leading to incorrect integrals or a waste of spectrometer time, respectively. If full relaxation of the sample is chosen, a satisfactory quantitative result is obtained for $T_R \sim 5\ T_1$. Thus, a cycle time of 3 s would be

Table 1
Chemical composition of the materials used [weight%]

	opc	SF	SF(Fe)
SiO_2	19.9	98.0	92.4
Al_2O_3	5.58	0.30	0.76
Fe_2O_3	3.48	0.05	1.70
CaO	61.2	0.3	0.3

Table 2
Results of the inversion recovery experiments

Sample	τ_0 [s]	T_1 [s]
opc	0.1/0.4	0.15/0.60
SF	6.0	8.7
SF (Fe)	0.2	0.3

sufficient for the NMR spectrum of the cement sample. The ^{29}Si NMR signal of the iron-free silica fume has a T_1 of 8.7 s, and $T_R \sim 45$ s would be the minimum necessary for a quantitative investigation. In contrast, the signal of the iron-containing silica fume SF(Fe) has a relaxation time of 0.2 s, which corresponds to the relaxation times of the cement signals. It follows that for the investigation of a mixture of cement with SF(Fe) $T_R \sim 3$ s would be appropriate, because the sample component with the longest T_1 is decisive.

To show the consequences of different relaxation times for the application of ^{29}Si MAS NMR spectroscopy, the mixtures opc/SF and opc/SF(Fe) were measured with varying repetition times. The chemical shifts of the NMR signals of the two mixtures were identical (Fig. 2), and a change of the signals was not observed.

The effect of the repetition time on the quantitative results is shown in Fig. 3. In the case of the mixture opc/SF(Fe) the ^{29}Si MAS NMR spectrum gives the expected content of 20% SF/(Fe) for $T_R = 5$ s. When applying short T_R values to the mixture opc/SF, saturation effects of the ^{29}Si MAS NMR signal are obvious. Thus, at the above value of $T_R = 5$ s the SF content is 8%, which is far below the admixed content of 20%. Even at T_R as big as 30 s the measured SF content is still too low (17% versus 20%, respectively). Note that at $T_R = 45$ s, the necessary value derived from T_1 above, the expected SF content was indeed obtained.

4. Conclusions

^{29}Si MAS NMR spectroscopy is a useful tool for the quantitative investigation of silicate phases in cement-based materials if some requirements are considered. Low natural abundance and the long relaxation time of ^{29}Si usually lead to long measurement times. However, paramagnetic iron impurities can considerably shorten the relaxation time. In the present work this has been exploited for recording the spectra of silica fume. For an iron content of 1.7% the relaxation time and hence the spectrum repetition time were much shorter so that for a given signal-to-noise ratio the overall measuring time could be decreased by a factor of about 7 as compared with a silica fume where iron was virtually absent. These findings are expected to be generally applicable for the investigation of cement-based materials. The measurement of ^{29}Si relaxation times has been shown to be essential for reliably determining the content of mixed silicate phases. In this way the hydration of Portland cement with different additives (silica fume, quartz meal, fly ash) has been studied [11] and further work is in progress.

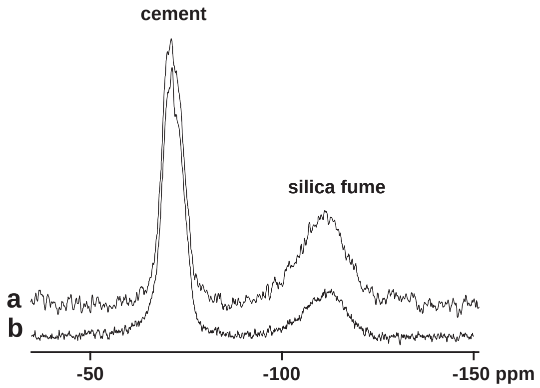

Fig. 2. ^{29}Si MAS NMR spectra of the mixtures a — opc/SF (Fe), b — opc/SF, $T_R = 5$s.

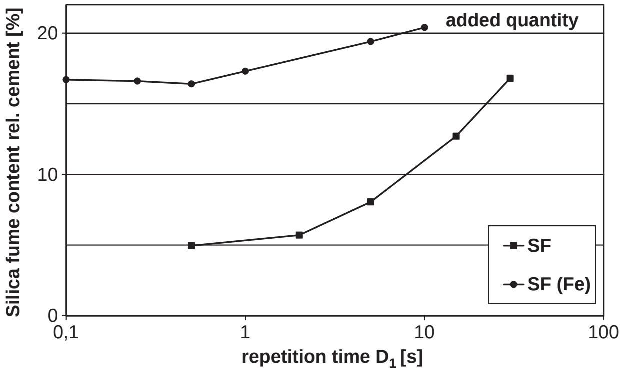

Fig. 3. Dependence of the quantitative results of the NMR spectra on the repetition time.

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