Communication

Applicability of natural abundance [33]S solid-state NMR to cement chemistry

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Abstract

With the development of high-magnetic field spectrometers, [33]S solid-state NMR is now clearly feasible but remains complex, especially considering the low sensitivity of [33]S NMR. This communication briefly explores the potential of [33]S NMR in the field of cement chemistry. Based on a few significant examples such as the one of ettringite, whose sulfur NMR spectrum is reported here for the first time, it appears that [33]S solid-state NMR might be able to distinguish between the sulphates present in a cement paste taking advantage of both the chemical shift and the quadrupolar interaction.

1. Introduction

Sulphate solubility, chemistry, and reactivity are among the key elements needed for understanding the durability of cementicious materials. Several processes of the deterioration of cement matrices, such as delayed ettringite formation, can be interpreted in terms of sulphate-phase stability and sulphate ions' interactions with hydrates. Consequently, the development of spectroscopies able to probe quantitatively the local environment of sulphates inside a cement matrix appear as desirable experimental complements to theoretical attempts to model the evolution of cementitious materials with temperature and time. In particular, Raman spectroscopy has recently received attention as a tool able to distinguish the sulphate species according to the split and shift of the sulphate group vibration modes [1]. However, Raman spectroscopy of cement samples remains difficult to operate in a quantitative manner

due to strong absorption and fluorescence at the Raman frequency range by the matrix. Moreover, significant overlap can be expected in complex hydrated materials. By comparison, NMR has the potential to provide quantitative information on the local environment of chemical groups regardless of the crystallinity and the nature of the matrix (provided it is diamagnetic). For this reason ^{29}Si and ^{27}Al NMR have been extensively used to study cement pastes. However, except for a few remarkable studies [2,3], until recently, the literature has remained silent on sulfur NMR. Indeed, [33]S NMR appeared out of reach in the solid state, mainly because of its low resonance frequency and reduced sensitivity due to its low gyromagnetic ratio (γ) (2.055×10^7 rad T^{-1} s^{-1}, that is less than 10% of the one of proton) and low natural abundance (0.76%) [4]. As high-field (>17 T) spectrometers are now being serviced worldwide, the limitations associated with the low γ are expected to vanish, and it has been recognized that it is now time to revisit the potential of [33]S NMR to identify local structures of sulphides [5], sulphites [6], and sulphates [6,7]. Nevertheless, solid-state [33]S NMR is still clearly in its infancy as only one published study has gone beyond demonstrating feasibility and has actually applied the technique [6]. In order to explore more

specifically this new potential in chemical systems relevant to cement science, we thus report and discuss here the feasibility of one-pulse, natural abundance ^{33}S solid-state MAS NMR spectra obtained at 63.6 MHz (19.6 T) for three bulk compounds representative of sulphate speciation in cement paste: magnesium sulphate, gypsum, and ettringite.

2. Materials and methods

2.1. Materials

Cs$_2$SO$_4$ and MgSO$_4$ were purchased from Aldrich. Three gypsum (CaSO$_4$·2H$_2$O) samples were studied. Synthetic 90%+ enriched ^{33}S CaSO$_4$·2H$_2$O was precipitated from an enriched sulphate solution obtained by the oxidation of elemental ^{33}S with bromine. Reagent grade synthetic natural abundance ^{33}S CaSO$_4$·2H$_2$O was purchased from Aldrich. Mineral technical grade was courtesy of Soletanche-Bachy (France). Ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O) was courtesy of Dr. Divet (LCPC, France). The samples were ground to powder when necessary and used as such. XRD patterns were verified prior to NMR using a Philips X'Pert MPD diffractometer at the Cu K$_\alpha$ radiation.
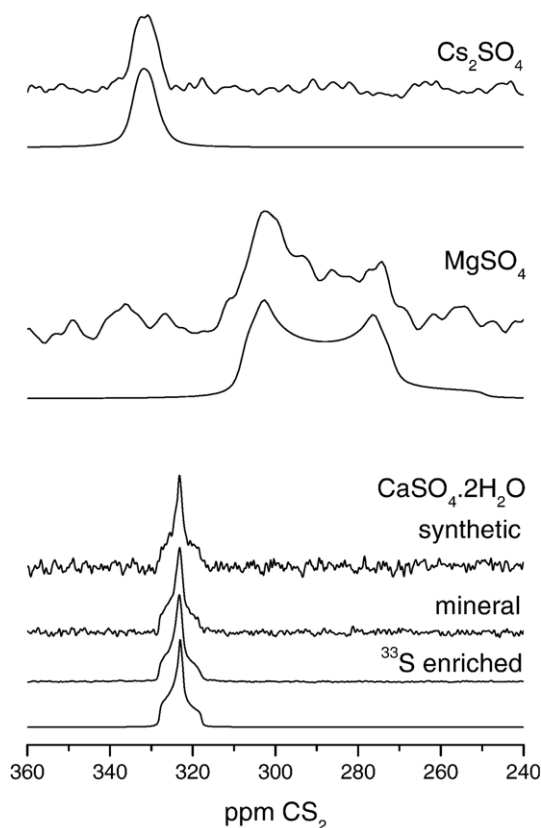

Fig. 1. Powder ^{33}S MAS NMR of sulphates. The one-pulse spectra were obtained at 63.6 MHz (19.6 T). The traces below the spectra are second-order quadrupolar models of the central transition adjusted to the experimental data using DMFIT and the NMR parameters reported in Table 1. Cs$_2$SO$_4$: 752 scans, 10 s recycle time. MgSO$_4$: 30 000 scans, 200 ms recycle time. CaSO$_4$·2H$_2$O natural abundance: 1000 scans, 20 s recycle time. CaSO$_4$·2H$_2$O ^{33}S enriched: 16 scans, 20 s recycle time.

Table 1
^{33}S NMR parameters from lineshape fitting

Compound	C_Q (MHz)	η_Q	δ_{iso} (ppm)	Line broadening (Hz)
Cs$_2$SO$_4$	0.8	0.45	335	200
MgSO$_4$	2.1	0.15	315	200
CaSO$_4$·2H$_2$O	0.7	1.0	328	30
Ca$_6$[Al(OH)$_6$]$_2$(SO$_4$)$_3$·26H$_2$O	0.7	0.45	331	50

2.2. MAS NMR

Magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed at 19.6 T on a Bruker DRX spectrometer in 4 mm zirconia rotors at the NHMFL in Tallahassee (USA). ^{33}S ($I=3/2$) one-pulse experiments were performed at 63.6 MHz, spinning between 6 and 8 kHz. For a quadrupolar nucleus, it was necessary to selectively excite the central transition in order to remain quantitative. This was performed by applying a pulse whose length correspond to a tilt angle of less than $(2I+1)$, namely $\pi/4$ in the case of ^{33}S ($I=3/2$). Consequently, the pulse duration was 2 μs for a radio-frequency magnetic field strength corresponding to a precession frequency of about 45 kHz. The spectral width was 40 kHz with digital filtering. Numbers of acquisitions and recycle times for each sample are indicated in the relevant figure captions. The chemical shift was referred to the resonance of a 1 M Cs$_2$SO$_4$ aqueous solution, taken as a secondary reference at 333 ppm from the primary standard of neat CS$_2$. The central bands of the one-pulse spectra were fitted assuming a central transition second-order quadrupolar line shape using the DMFIT program [8].

3. Results

The natural abundance spectra of caesium [3,6,7], magnesium [7], and calcium sulphates [3,7] have already been reported in the literature and our results are presented here for comparison purpose only (Fig. 1). Our results are in agreement with the ones of Wagler et al. [7]. The fitting of the spectra with second-order quadrupolar line shapes produced a satisfactory estimate of the NMR parameters (Table 1). Of importance to the applicability to cement science, it must be noted that although high fields increase the signal-to-noise ratio due to a simultaneous increase of sensitivity and decrease of the quadrupolar line width, the overall sensitivity remained poor due to the low natural abundance of ^{33}S. The acquisition of the spectrum of bulk gypsum with a signal to noise ratio of 10 took a total of 8 h. Moreover, sulphate groups are about twenty times less abundant in Portland cement than in gypsum. Considering that the signal-to-noise ratio scales with the square of the number of scans, it follows that the acquisition of a signal of same quality in Portland cement would require 133 days. This is obviously impractical. Conversely, the acquisition of the spectrum of the ^{33}S enriched gypsum sample provided a signal to noise over 50 in 5 min. Obviously, ^{33}S NMR is not adapted to the characterization of field samples, and, without isotopic enrichment, would be limited to samples with exceptionally high sulphate contents or to fundamental studies of a chemical sub-system equilibrium.
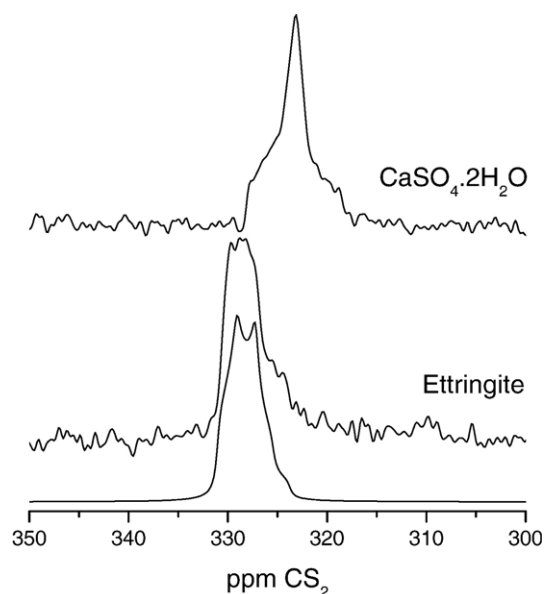
Fig. 2. Comparison of the powder ^{33}S MAS NMR spectra of ettringite (70 000 scans, 1 s recycle time) and gypsum (same as Fig. 1).

Besides sensitivity, to probe the potential of sulphur NMR, it is necessary to address its ability to discriminate between different sulphate speciations. On the one hand, the chemical environment of the sulphur atom in a sulphate group is not expected to vary greatly in one sulphate or another from the expected distorted tetrahedron of the sulphate anion. Indeed, all the sulphates studied here presented similar isotropic chemical shifts within 10 ppm. On the other hand, however, the second-order quadrupolar line shape depends not on the electron density around the nucleus but on the electrical field gradient. It is therefore a very sensitive probe of the electronic symmetry around the nucleus, and thus indirectly of the lattice structure. Thus, for quadrupolar nuclei, the line shape often provides a clearer signature of a particular chemical occurrence than the chemical shift, and it can be related unequivocally to a particular structure through ab initio DFT-based calculations [9]. This conjecture was verified for cement chemical systems by comparing, as an example, the spectrum of the trisulphoalumi-nate ettringite with the one of gypsum (Fig. 2). The line shape of ettringite was significantly distinctive and clearly different from the one of gypsum. In particular, the symmetry of the sulphate group is not as severely distorted in ettringite [10] as in gypsum [11]. This translated in an asymmetry parameter (η) reduced from 1 in gypsum to circa 0.4 in ettringite and thereby in

significantly different line shapes. The two sulphates could thus be distinguished despite having close isotropic chemical shifts: 328 ppm for gypsum and 331 ppm for ettringite. In this case, the quadrupolar interaction spread apart the maxima of each resonance by about 15 ppm in the present field of 19.6 T. There is a thus good prospect that it might be possible to distinguish sulphates in complex cement samples by ^{33}S solid-state NMR at high fields.

4. Conclusion

Despite the low natural abundance of ^{33}S, working at high field provided enough sensitivity to collect spectra in natural abundance for bulk compounds in a reasonable time. It is however clear that dilution of the sulphate in cements (typical values are less than 3% w/w SO_3 in CEM I Portland cement) will have to be compensated by enrichment if one intends to study cementitious matrices.

Despite this limitation, comparison of the gypsum and ettringite ^{33}S MAS NMR line shapes gave strong hope that the ^{33}S signature of sulphate groups will allow quantitative analysis of sulphate mineralogy in cement-related chemical systems. In that case, it might prove a useful complement to XRD or vibrational spectroscopy.

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