

Recent progress in solid-state NMR of quadrupolar nuclei. Application to the characterization of hydration and sulfate attack products.

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1 INTRODUCTION

Sulfates and hydrates chemistry and reactivity are among the key elements needed for understanding the hydration, setting and durability of cementitious materials. Consequently, it is often necessary to probe by spectroscopic means the molecular structures of hydrates and sulfates formed inside a cement matrix. In this respect, the potential of solid-state Nuclear Magnetic Resonance (NMR) has been extensively explored and exploited for the study of cement-based systems, taking advantage of its unique ability to scrutinize disorganized and poorly organized systems in a non-invasive manner, and this independently of the nature of the matrix. The resonances of ²⁹Si, ²⁷Al and ¹H have been particularly useful for NMR studies of cement since the late eighties. Beyond the well-established traditional magic-angle spinning NMR, sophisticated multiple-pulse techniques are now available. Nevertheless, several serious obstacles have remained when acquiring and interpreting the NMR spectra of quadrupolar nuclei, especially those of low gyromagnetic ratio.

However, the past three years have seen significant technological and theoretical advances in the field of solid-state NMR of quadrupolar nuclei. Among them, DFT-based calculations of the EFG and estimation of its distribution within the GIM model now allows for a quantitative and unambiguous interpretation of structure and disorder at a molecular scale. We will show how this improves the analysis of the ²⁷Al NMR spectra of cement pastes. Another significant progress is a generalizing access to very high magnetic fields (above 17 T) which permits the study at natural abundance of previously unreachable nuclei such as ³³S.

2 MATERIALS AND METHOD

2.1 Materials

A class G cement (courtesy of the French Petroleum Institute) was hydrated following published procedures [1]. Monocarboaluminate AFm was prepared according to [2].

MgSO₄ was purchased from Aldrich. Mineral technical grade gypsum (CaSO₄·2H₂O) was courtesy of Soletanche-Bachy (France). Ettringite

($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) was courtesy of Dr. Divet (LCPC, France). The samples were ground to powder when necessary and used as such.

2.2 MAS NMR

Magic angle spinning nuclear magnetic resonance (MAS NMR) one-pulse experiments were performed at 11.7 T (^{27}Al) at the ESPCI in Paris (France) and at 19.6 T (^{33}S) at the NHMFL in Tallahassee (USA) in 4 mm zirconia rotors. The pulse lengths corresponded to a tilt angle of less than $\pi/(2I+1)$. The chemical shift was referred to neat CS_2 (^{33}S) and $\text{Al}^{3+}_{\text{aq}}$ (^{27}Al). The central bands of the one-pulse spectra were fitted using the DMFIT program [3].

3 ANALYSIS OF SOLID-STATE NMR SPECTRA OF DISORDERED MATERIALS

The NMR response of single nucleus with a spin number $I=1/2$ such as ^1H or ^{29}Si can be discussed solely on the basis of one transition ($-1/2 \leftrightarrow +1/2$) perturbed by chemical shift and dipolar interactions. Oppositely, nuclei with $I>1/2$ exhibit several transitions: central ($-1/2 \leftrightarrow +1/2$), and satellites ($m \neq \pm 1/2$, $m \leftrightarrow m-1$). Furthermore, they have an electrical quadrupole moment which couples with the electrical field gradient (EFG) created by its surrounding charges (the lattice). The Zeeman interaction (H_Z) with the applied magnetic field which dominates the NMR response is thus perturbed by the resulting quadrupolar interaction (H_Q) (Figure 1).

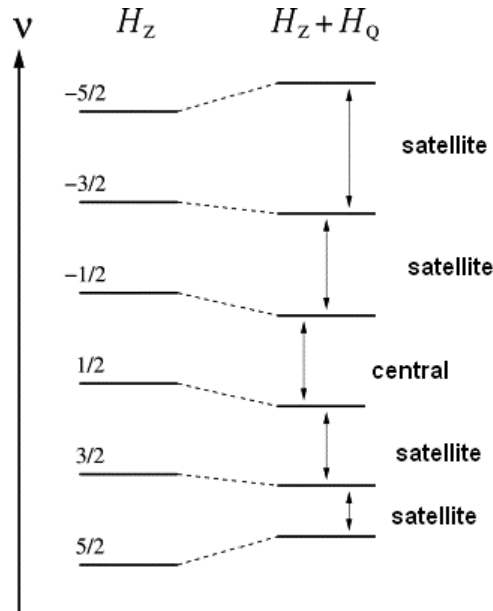


Figure 1: Schematic representation of the NMR transitions perturbed by the quadrupolar interaction.

Relevant examples for cement are ^{27}Al ($I=5/2$), ^{17}O ($I=5/2$), ^{33}S ($I=3/2$) and ^{43}Ca ($I=7/2$). Because the EFG is tensorial in nature, so is the quadrupolar

interaction which therefore depends on the orientation of the crystallite with respect to the applied magnetic field. Upon, as is customary, magic-angle spinning of the sample, the frequency shift associated to the quadrupolar interaction for each transition and each orientation reduces to second-order to

$$\nu_{(m,m-1)}^{(2)} = \frac{1}{3} \frac{\nu_Q^2}{\nu_0} [I(I+1) - 3m^2] \left(1 + \frac{h^2}{3} \right) - \frac{\nu_Q^2}{\nu_0} [6I(I+1) - 3m^2 - 3] f_1(a, b, h)$$

Derivation of this rather formidable looking equation, exact definition of terms and expression of the function f_1 is given in [4]. ν_Q represents the strength of the EFG and of the resulting quadrupolar interaction, η its asymmetry, ν_0 the Larmor frequency, and (α, β) the angles defining the relative orientation of the EFG tensor principal axis relative to a frame aligned with the spinning axis.

In a material where all crystallites are randomly oriented such as in a cement paste, the full NMR response of the sample will be obtained by integration over all possible transitions (m) and orientations (α, β) . This integral has no analytical solution so the NMR spectra are usually interpreted by numerical fitting of the experimental spectrum using freeware such as DMFIT [3]. Alternative methods include full analysis of the spinning sidebands pattern as in the SATRAS experiment [5]. This method is more accurate but also more complex and consequently has not been applied to cements. In conclusion, the resonance position and lineshape of a quadrupolar nucleus in a polycrystalline sample cannot be simplified to a Lorentzian or Gaussian lineshape without error. This is exemplified in Figure 2 on the ^{27}Al MAS NMR spectrum of a monophasic polycrystalline sample of monocarboaluminate (AFm). The quantitative error when using a Gaussian-Lorentzian lineshape as in [6] remains however small in this case, about 10 %, since the crystal structure is highly symmetric.

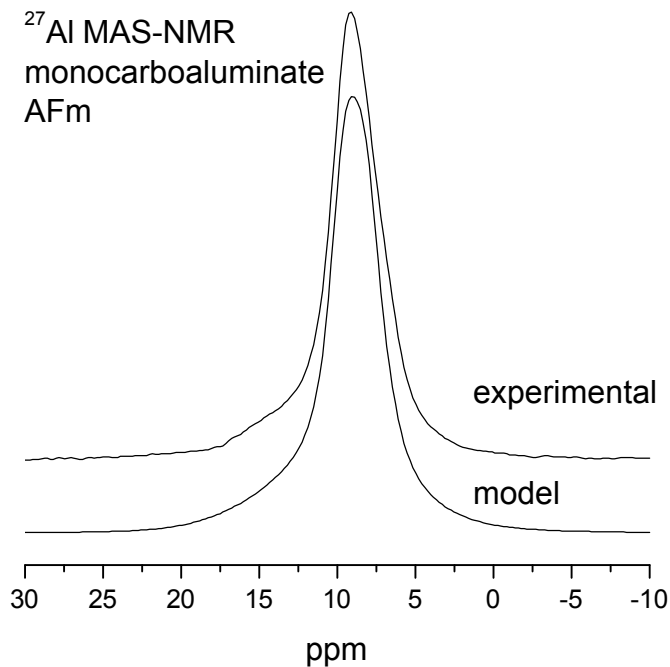


Figure 2: ^{27}Al MAS NMR spectrum of a monophasic polycrystalline sample of monocarboaluminate (AFm). The resonance is slightly asymmetric due to the superposition of the central and satellite transitions and to a small distribution of the EFG. It can be satisfactorily modeled using the following parameters: average $C_Q = 2.2$ MHz, $\delta = 10.4$ ppm.

The traditional approach of adjusting numerically the quadrupolar interaction however desperately fails in the case of amorphous materials. For instance, it has been previously impossible to accurately account for the so-called third aluminum hydrate (TAH) formed during hydration of Portland cement. It has been attributed following an extensive NMR characterization [7] to a disordered aluminate hydroxide or calcium aluminate. Indeed, in disordered material, distribution of charges results in a distribution of the EFG. A further average over the resulting distribution of quadrupolar parameters ν_Q and η is thus necessary to compute the lineshape. It has been generally assumed that the asymmetric broadline of ^{27}Al resonances in amorphous materials reflected this continuous distribution of quadrupolar parameters $P(\nu_Q, \eta)$. This distribution remained nevertheless unknown. It has been recently drawn to the attention of the NMR community that this issue has been addressed successfully within the context of Mossbauer spectroscopy [8]. Assuming statistical isotropy, from a random distribution of electric charges (Gaussian isotropic model) Czjzek [9] had derived an analytical expression for the bivariate distribution:

$$P(n_{\sigma}, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) \exp\left(-\frac{n_{\sigma}^2(1+h^2-3)}{2\sigma^2}\right)$$

σ characterizes the strength of the quadrupolar interaction and d is the number of independent random parameters (equals five for symmetrical environments). Since, this approach has been used to successfully model and interpret the NMR spectra of glasses [10-12]. We suggest applying it to disordered hydrates such as TAH as well. As can be seen on Figure 3, the asymmetric lineshape of the TAH is satisfactorily reproduced.

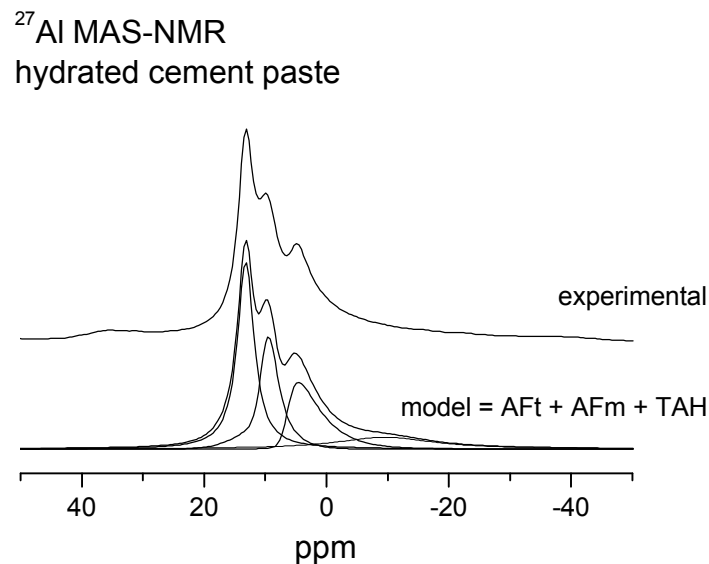


Figure 3: Octahedral coordination range of the ²⁷Al MAS NMR spectrum of a class G cement hydrated 28 days with a water to cement weight ratio of 0.39. Use of the Czjzek model allows to model and accurately separate the contributions due to trisulfoaluminate (AFt), monosulfoaluminate (AFm), and the third aluminum hydrate (TAH). The asymmetry of the lineshapes relate to the respective symmetry and crystallinity of the phases. A small contribution due to pentahedral aluminum is also present around 35 ppm.

Having a theoretical basis for the lineshape has obvious advantages compared to empirical decompositions. Quantitative analysis is considerably improved as it is possible to discriminate between the expected lineshape and spurious baseline artifacts. It is also possible to differentiate unambiguously between a superposition of species (unresolved overlapping resonance of several chemical species with different environments, i.e. mixture of phase) and a single amorphous environment (single resonance of one species with a distribution of

environment, i.e. one amorphous phase). Finally, it becomes possible to relate the lineshape to physically meaning terms such as for example the extent of disorder in the phase. Presently, we have successfully used the Czjzek distribution to follow the hydration reactions of cement/polymer composites [13].

4 NATURAL ABUNDANCE ^{33}S SOLID-STATE NMR OF SULPHATE PHASES IN CEMENT

Except for a few remarkable studies [14, 15], 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) and low natural abundance (0.76%) [16]. 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 sulfides [17], sulfites [18], and sulfates [18-21]. 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 [18]. In order to explore more specifically this new potential in chemical systems relevant to cement science, we thus report 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 sulfate speciation in cement paste: magnesium sulfate, gypsum, and ettringite (Figure 4).

^{33}S MAS-NMR of pure sulfate phases

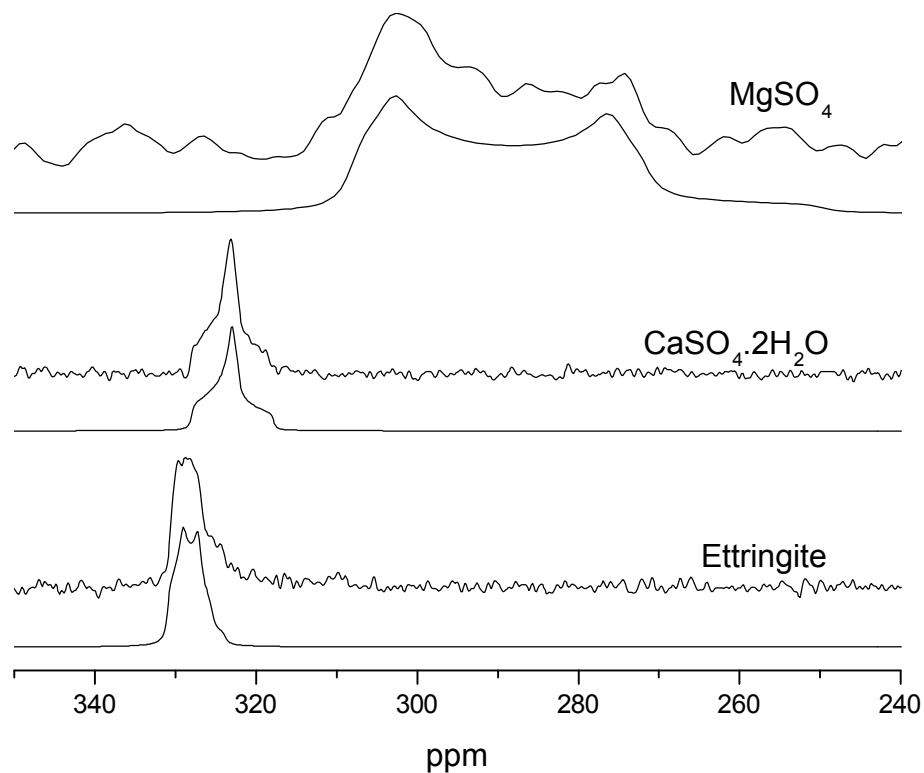


Figure 4: Natural abundance ^{33}S MAS NMR powder spectra of ettringite, gypsum and magnesium sulfate obtained at high magnetic field (19.6 T). The lower traces are the corresponding modeled lineshapes. Acquisition parameters are given in [20].

Working at high field provided enough sensitivity to collect spectra sulfur for bulk compounds. The sulfur NMR fingerprints of each compound were distinctive. Without enrichment, the acquisition time remained relatively long (typically overnight). The dilution of sulfate ions in cements (usually less than 5 % w/w) will probably prevent direct analysis of cement samples by this method. It could nevertheless provide insight into sulfate reactivity and mineralogy by studying sulfate-rich chemical sub-systems of interest to cement.

5 CONCLUSIONS

We have presented two examples of recent advances in solid-state NMR with high potential for improved characterization of cementitious materials by NMR. Building on this rejuvenated potential, we are currently

undertaking studies of the underlying mechanisms of degradation due to sulfate by using ^{33}S NMR together with carefully modeled ^{27}Al data.

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