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Quantitative Aspects of ^{27}Al MAS NMR of Calcium Aluminoferrites

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^{27}Al MAS NMR spectra of synthetic calcium aluminoferrites, $Ca_2Al_xFe_{2-x}O_5$ with x = 0.93, 1, 1.33, reveal only a few percent of the expected intensity for the ^{27}Al central transition, indicating that the calcium aluminoferrite phase in Portland cements can barely be observed by ^{27}Al MAS NMR. This result supports the use of ^{27}Al MAS NMR for quantitative analysis of the tricalcium aluminate phase in Portland cements. Advanced Cement Based Materials 1998, 7, 57–59. © *1998 Elsevier Science Ltd.*

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The technique of ^{27}Al magic-angle spinning (MAS) NMR spectroscopy has become an important analytical tool in the characterization of a variety of polycrystalline and amorphous materials from several branches of inorganic chemistry. In recent work on ^{27}Al MAS NMR of Portland cements [1,2], which generally have low aluminum content (2 to 5 wt.% aluminum), we have shown that the technique allows quantification of the calcium aluminate phase ($Ca_3Al_2O_6$) and of the Al guest-ions incorporated into the alite (Ca_3SiO_5) and belite (Ca_2SiO_4) phases of Portland cements [2]. However, Al is also present in the calcium aluminoferrite phase ($Ca_2Al_xFe_{2-x}O_5$, $0 \leq x \lesssim 1.4$), a nonuniform solid solution [3] that typically constitutes 5 to 15 wt.% of Portland cements [4]. Hitherto it has been assumed that the ferrite phase cannot be observed by ^{27}Al NMR methods because of its high concentration of Fe^{3+} ions. In the present report we investigated the validity of this supposition by high speed ^{27}Al MAS NMR of synthetic ferrites with a Fe_2O_3 content in the range of 23 to 35 wt.%.

The problems of quantifying nuclear spins in iron-containing materials by MAS NMR methods have been recognized earlier for ^{27}Al and ^{29}Si in clay minerals and aluminosilicates [5–10]. Oldfield et al. [5] showed that addition of small quantities of ferromagnetic Fe_3O_4 or antiferromagnetic Fe_2O_3 to aluminosilicates causes a significant increase of the intensities and number of spinning sidebands (ssbs) from the ^{27}Al central transition. This is a result of magnetic susceptibility broadening and/or line broadening caused by nuclear–electron dipolar couplings between ^{27}Al and the unpaired electron of Fe^{3+} ions. For clay minerals containing only small quantities of Fe^{3+} ions Jakobsen et al. [7] showed a dramatic improvement of the ^{27}Al and ^{29}Si MAS NMR spectra achieved by high speed spinning ($\nu_r \approx 9$ kHz), while Woessner [8] observed that a reliable quantitation of the ^{27}Al NMR signals could be obtained using $\nu_r \approx 5.3$ kHz in an 11.7-T magnet. Watanabe et al. [9] reported an almost linear relationship between the Fe_2O_3 content and the line width of the ^{29}Si MAS resonance. For clays with somewhat higher bulk Fe_2O_3 contents (1.4 to 5.6 wt.%), Morris et al. [10] observed large discrepancies between the ratios of tetrahedrally and octahedrally coordinated Al determined from ^{27}Al MAS NMR and from compositional analysis. No correlation with the concentration of Fe^{3+} was observed.

The ^{27}Al MAS NMR spectra shown in this report were recorded at room temperature on a Varian UNITY 400 (9.4 T) spectrometer equipped with homemade CP/MAS probes for 4- and 5-mm o.d. Si_3N_4 rotors [11]. To obtain reliable quantitative results [12], single-pulse excitation using a radiofrequency field strength $\gamma B_1/2\pi = 60$ kHz, a 0.7-μs pulse width (15° flip angle), a relaxation delay of 1 s, and weighed samples were used. The synthetic samples of $Ca_3Al_2O_6$ and $Ca_2Al_xFe_{2-x}O_5$; x = 0.93, 1, 1.33 studied were obtained from Construction Technology Laboratories Inc. (Illinois, USA). An earlier investigation of the magnetic properties of calcium aluminoferrites has shown that Fe^{3+}-rich ferrites ($x \lesssim 1.1$) exhibit antiferromagnetic ordering of the Fe^{3+} electron spins, while for $x \gtrsim 1.1$ the ferrites may be in an electronic paramagnetic state at room temperature [13]. Thus, the samples of $Ca_2Al_{0.93}Fe_{1.07}O_5$ and Ca_2AlFeO_5

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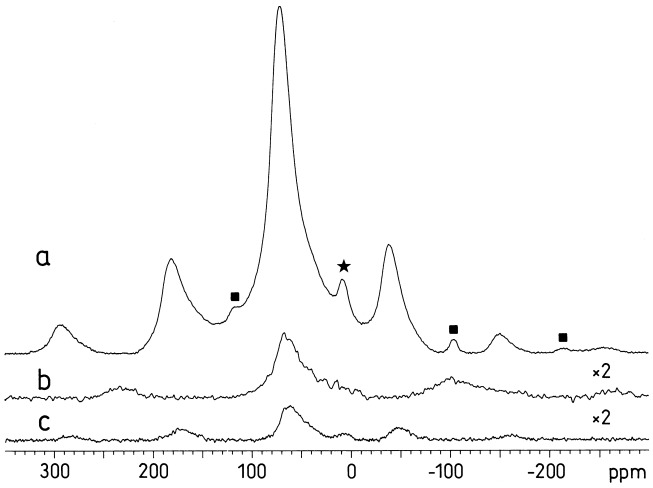

FIGURE 1. ^{27}Al MAS NMR spectra (9.4 T) of the central transition for the synthetic ferrites $Ca_2Al_{1.33}Fe_{0.67}O_5$ (a), Ca_2AlFeO_5 (b), and $Ca_2Al_{0.93}Fe_{1.07}O_5$ (c), recorded using between 18,000 and 76,000 scans and spinning speeds of 11.6, 17.5, and 11.5 kHz, respectively. The spectra in (b) and (c) are shown on identical intensity scales, which correspond to a vertical expansion by a factor of two relative to the spectrum in (a). The asterisk and squares in (a) indicate the centerband and ssb's for the Al(6) site.

studied should be in an antiferromagnetic state and the $Ca_2Al_{1.33}Fe_{0.67}O_5$ sample in a paramagnetic state.

High speed (ν_r = 11.6 to 17.5 kHz) ^{27}Al MAS NMR spectra (9.4 T) of the central transition for synthetic samples of the ferrites $Ca_2Al_{1.33}Fe_{0.67}O_5$, Ca_2AlFeO_5, and $Ca_2Al_{0.93}Fe_{1.07}O_5$ are shown in Figures 1a–1c, respectively. The ^{27}Al central transitions for these ferrites originate predominantly from tetrahedrally coordinated Al (Al(4)) and exhibit considerably broadened and rather featureless centerbands and ssbs. The centers of gravity for the Al(4) resonances are listed in Table 1. The relatively narrow centerband at 8 ppm, observed in the ^{27}Al MAS spectrum of the ferrite with the lowest Fe_2O_3 content (Figure 1a), demonstrates the presence of a small quantity of octahedrally coordinated Al (Al(6)).

TABLE 1. Resonance positions for the center of gravity for the Al(4) central transitions and relative molar ^{27}Al NMR intensities (total for Al(4) and Al(6)) from ^{27}Al MAS NMR of synthetic ferrites

	wt.% Fe_2O_3	$\delta^{c.g.}_{1/2;-1/2}$(Al(4))[a]	I^m/I^m_{Ref}[b]
$Ca_2Al_{1.33}Fe_{0.67}O_5$	23	71	0.16
Ca_2AlFeO_5	33	64	0.02
$Ca_2Al_{0.93}Fe_{1.07}O_5$	35	61	0.01

[a]The positions for the center of gravity for the Al(4) central transition are in ppm (± 1 ppm) relative to an external 1.0 mole dm^{-3} $AlCl_3$ aqueous solution.
[b]Total Al(4) and Al(6) intensities for the ^{27}Al central transition (I^m), relative to the corresponding Al(4) intensity observed for $Ca_3Al_2O_3$ (I^m_{Ref}), and after normalization to one mole Al_2O_3 for each of the samples.

Indications of the presence of Al(6) for the two other ferrites are also obtained from the ^{27}Al MAS spectra by the observation of broadened, low intensity peaks in the range of 0 to 20 ppm. The observation of Al(4) and Al(6) resonances by ^{27}Al MAS NMR is in accord with the reported crystal structure for Ca_2AlFeO_5 (brownmillerite) from single-crystal X-ray diffraction [14]. In that study it was shown that Ca_2AlFeO_5 contains (Fe, Al)O_6 octahedra and (Fe, Al)O_4 tetrahedra with a predominance of Al^{3+} ions in the tetrahedral positions (estimated site occupancies are approximately $Fe_{0.76}Al_{0.24}O_6$ and $Fe_{0.24}Al_{0.76}O_4$) [14]. Although the distribution of Al^{3+} and Fe^{3+} over the tetrahedral and octahedral positions may depend on the thermal history of the samples, the apparent relative intensities for the Al(4) and Al(6) centerbands in Figure 1 are in qualitative agreement with the X-ray diffraction results. However, the ^{27}Al MAS NMR spectra are severely affected by line broadening resulting from large anisotropic bulk magnetic susceptibilities and from the efficient relaxation mechanism produced by the strong ^{27}Al–electron dipolar couplings [15], which to a great extent impedes observation of the ^{27}Al NMR resonances. These broadening mechanisms are observed to influence the three ferrites studied; thus, even approximate values for the Al(4)/Al(6) ratios are difficult to obtain from the ^{27}Al MAS spectra shown in Figure 1.

The loss of ^{27}Al NMR signal intensity because of ^{27}Al–electron dipolar couplings is best evaluated from a quantitative analysis of the ^{27}Al MAS spectra using a well-defined, weighed external reference sample. $Ca_3Al_2O_6$ is a suitable sample for this purpose since it contains two highly quadrupolar broadened Al(4) sites for which the intensities of the central transitions may be determined from high speed ^{27}Al MAS NMR [16]. The results of the quantitative ^{27}Al MAS analysis for the ferrites are shown in Table 1 by the total intensities for the central transition relative to the intensity for $Ca_3Al_2O_6$ following normalization to one mole Al_2O_3 for each sample. These relative intensities demonstrate that only a small proportion of the expected intensity is observed by high speed ^{27}Al MAS NMR and that the intensities decrease with increasing Fe_2O_3 content for the ferrites. In particular, a considerable decrease is observed on going from 23 to 33 wt.% Fe_2O_3. With the assumption that $Ca_2Al_{0.93}Fe_{1.07}O_5$ and Ca_2AlFeO_5 exhibit antiferromagnetic ordering of the Fe^{3+} spins and that $Ca_2Al_{1.33}Fe_{0.67}O_5$ is in a paramagnetic state [13], this observation indicates that ^{27}Al–electron dipolar couplings give severe line broadening in ^{27}Al MAS NMR spectra of paramagnetic as well as antiferromagnetic ferrites. From calculations of the ^{27}Al–electron dipolar couplings, Morris et al. [10] estimated that ^{27}Al atoms within a distance of ca. 6 Å of a Fe^{3+} site should be unobservable by standard MAS NMR. The Al–Fe

distances for Ca_2AlFeO_5 from the crystal structure are in the range of 3.33 to 3.86 Å [13], indicating at first sight that part of the Al atoms within a 6-Å distance from Fe^{3+} ions are observed by high speed ^{27}Al MAS NMR. However, it cannot be excluded that the observed ^{27}Al NMR intensities result from small clusters of Al(4) and Al(6) sites within the ferrite crystals. For example, using transmission electron microscopic microanalysis Richardson et al. [17] have shown that wide variations in Al/Fe ratio occurred in the ferrite phase of one cement clinker examined.

Taylor [4] has recently proposed the compositions for a normal and a low-aluminum ferrite in Portland cements with molar ratios of Al/Fe = 1.6 and 0.8, respectively, for the two ferrite phases. The normal ferrite composition should be representative of ferrites in ordinary Portland cements used in the construction industry. In Portland cements with low bulk Al_2O_3/Fe_2O_3 ratios (typically < 1.0), the ferrite phase has a mean composition that can be represented as a solid solution of the normal ferrite and the low-aluminum ferrite. In an X-ray microprobe study of the calcium aluminate and ferrite phases in production Portland cements, Bergstrom et al. [3] observed that the Al/Fe ratios for the individual ferrites do indeed scatter within the range for the molar Al/Fe ratios for the two ferrites proposed by Taylor. The composition range for these ferrites corresponds to $Ca_2Al_xFe_{2-x}O_5$ with $0.9 \lesssim x \lesssim 1.2$. Thus, the synthetic ferrites studied in this work cover about the same aluminum and iron ranges as found for the ferrites in Portland cements.

We conclude that the observed severe loss of ^{27}Al NMR intensity in the synthetic ferrites strongly suggests that Al present in the ferrite phase of Portland cements, either in the antiferromagnetic or the paramagnetic form, will contribute little or nothing to the observed ^{27}Al MAS NMR spectrum using high speed spinning ($\nu_r \approx 18$ kHz) and a magnetic field of 9.4 T. This confirms that the ^{27}Al MAS NMR spectrum of a Portland cement obtained under these conditions can be considered to be the sum of subspectra coming only from the tricalcium aluminate phase and from Al guest-ions in the alite and belite phases, all of which contain only low concentrations of Fe ions. Our results give added confidence to the practical use of ^{27}Al MAS NMR for quantitative analysis of the tricalcium aluminate phase in Portland cements.

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