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Studies using ^{27}Al MAS NMR of AF_m and AF_t phases and the formation of Friedel's salt

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Abstract

This paper describes the application of the magic angle spinning (MAS) NMR spectroscopy to study the chemical environment of ^{27}Al-bearing phases in Portland cement-based concrete. A specific methodology is described that allows reliable spectra to be determined for combinations of different types of cements and fillers (in this case, Portland cement, fly ash, slag, silica fume, metakaolin and limestone filler). As well as the study of 'molecular structure' of cement matrix, the paper reviews the mechanism of Friedel's salt formation in cement systems. Mechanisms based on ion exchange of chloride for hydroxide in hydroxy-AF_m and on chloride absorption on formation are discussed. Finally, the nature of the chloride/hydrate binding phenomena are described to provide a reasonable robust and fundamental picture of the role different cements can play in the provision of overall concrete durability to chloride ingress from a chemical perspective.

Keywords: MAS NMR spectroscopy; Portland cement; Chloride; Monosulphate; Friedel's salt formation

1. Introduction

For the engineer the premature ingress of chloride ions into reinforced concrete containing carbon steel is a major problem. It affects important, as well as expensive, infrastructure worldwide and concrete technology researchers have spent considerable efforts over the past 25 years devising more durable concrete in order to combat the problem. There is broad agreement that blending Portland cement (PC) with other materials such as fly ash (PFA), slag (GGBS), or metakaolin (MK) is one way forward. These cements improve both the microstructure of concrete and degree of binding of chlorides [1,2]. However, without a good understanding of the mechanism of chloride binding it is difficult to refine and optimise mixes. In this paper, the development of a magic angle spinning (MAS) NMR technique to determine the chemical environment for the main alumina phases, i.e. monosulphate (AF_m), ettringite (AF_t) C_3A hydrate and Friedel's salt is described. The paper also addresses the mechanism of Friedel's salt formation, based on pore fluid analysis data.

2. MAS NMR method developed for ^{27}Al spectroscopy in Portland cement hydrates

2.1. The MAS NMR method

Solid-state NMR uses the magnetic properties of nuclei to characterise the isotopic species under investigation according to its physicochemical environment. In cementitious materials, the quadrupolar nucleus ^{27}Al can be used to probe chemical changes taking place both during curing and after soaking in brine.

The ^{27}Al nucleus has 100% natural abundance, is highly sensitive and, in the NMR experiment, relaxes quickly, allowing spectra to be accumulated in relatively short times.

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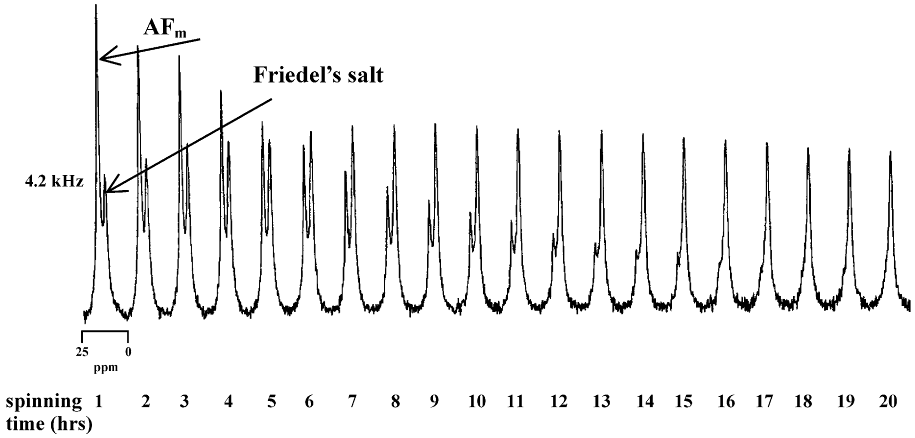

Fig. 1. Effect of spinning at 4.2 kHz for 20 h a sample of PC paste soaked in 5 M NaCl (note: AF$_m$ resonance intensity reduces, while for Friedel's salt it remains essentially constant).

The positions at 'which the nuclei, in different chemical environments, resonate are sufficiently different to give a considerable insight into aluminium chemistry taking place. One major difficulty to be overcome in ^{27}Al NMR is the effect of the nonspherical charge distribution round the ^{27}Al nucleus ($I = 5/2$), quadrupolar effects, caused by the interactions of the magnetic fields generated by the nuclei with those of nearby electrons can make spectral interpretation difficult. In the present study only the central ^{27}Al transition ($m_I = +1/2 - m_I = -1/2$) was observed.

In the solid state, ^{27}Al NMR spectra exhibit very broad resonances. By spinning the sample, encased in a rotor, at very high speeds, at the angle of 54.7° (the 'magic' angle) [3–5] to the direction of the spectrometer magnetic field (magic angle spinning, MAS), the resonances sharpen considerably, although second-order quadrupolar effects remain. Further line narrowing can be achieved by either irradiating the sample at the frequency that protons (hydrogen nuclei) resonate, while acquiring the aluminium data. This effectively removes dipolar interactions from the hydrogen and is referred to as high-powered proton decoupling. A second technique involves cross-polarising (CP) the protons to the aluminium atoms and again decoupling during data acquisition. This has the joint effect of sharpening lines and showing only protonated aluminium species. With nuclei such as ^{27}Al different levels of cross-polarisation are possible, here true Hartmann–Hahn matching conditions were used.

Samples of Portland cement paste were prepared by mixing commercial Portland cement (PC) with water, to give a water/solids ratio of 0.4, in a high-shear blender, cast into refrigerator ice-cube trays and cured, under water for 6 months. The Portland cement/ metakaolin (MK) paste was prepared in the same way using an 85:15 PC/MK ratio. After 6 months of curing, cubes were immersed in 5 M NaCl for a further 6 months. Before NMR analysis, the cubes were powdered for NMR spectroscopy. The sample of Friedel's salt was prepared using the method of Chudek et al. [6] and Roberts [7].

CP MAS ^{27}Al NMR spectra were acquired on a Varian-Chemagnetics CMX-300 lite NMR spectrometer (^{1}H, 300.07 MHz; ^{27}Al, 78.17 MHz). Samples were spun at circa 4 kHz in 7.5 mm o.d. zirconia pencil rotors. A reference compound, tris-(2,4-pentandiaonato)aluminium(III), Al(acac)$_3$, was used both as reference for resonance positions and to confirm acquisition parameters did not vary (the shape of Al(acac)$_3$ is very sensitive to acquisition

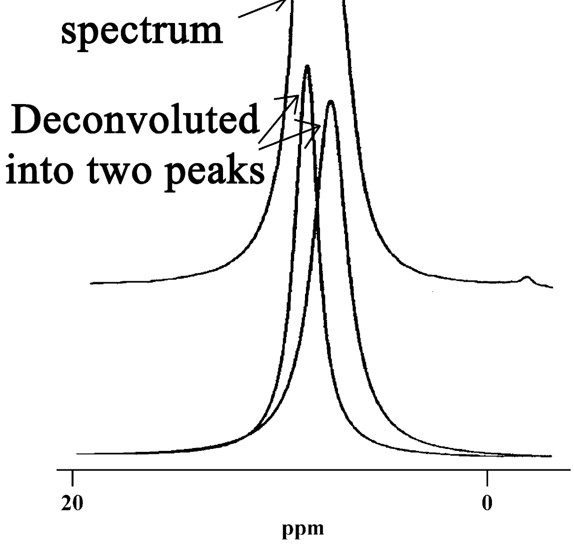

Fig. 2. ^{27}Al MAS NMR spectrum of Friedel's salt shows an asymmetric resonance this can be deconvoluted into two peaks.

conditions) [5,6,8]. An unwanted result of the high-speed sample rotation was the centrifuging of the liquid pore contents from the samples leading to a change in the spectrum (Fig. 1). Changes were dependent on spin rate and at 4 kHz took several hours. As a consequence, all acquisitions were kept to a maximum of 1 h.

2.2. Deconvolution of MAS NMR spectra

NMR spectra consist of series of resonances either separate or, often, superimposed. Fig. 2 shows the resonance of the synthesised Friedel's salt (upper trace); it consists of an asymmetric peak. In the case of relatively simple peaks like this, a lot can be learned from the spectrum. However, it is often necessary to extract the individual resonances making up the peaks. As the shape of the individual resonances can be calculated it is possible to fit these to the spectrum. This is called *deconvolution*. In Fig. 2, the bottom trace is that of the deconvoluted spectrum, it consists of two resonances. Deconvolution was used throughout to help assign resonances to individual species.

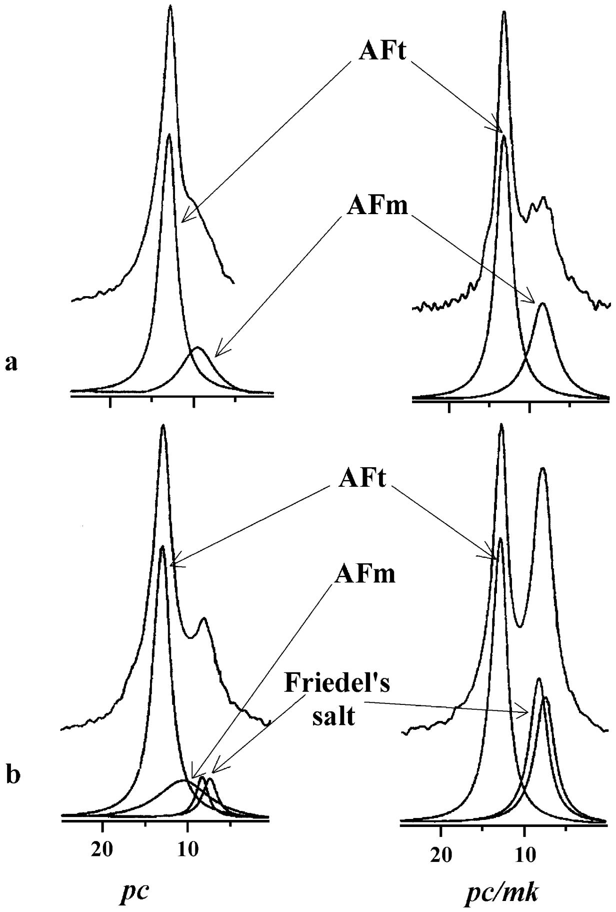

Fig. 3. ^{27}Al CP MAS NMR spectra (upper trace) and the deconvoluted peaks (lower trace) of (a) PC and PC/MK pastes cured under water for 6 months and (b) the same, left for a further 6 months under 5 M NaCl.

Fig. 3(a, top trace) shows the ^{27}Al spectra of the PC and the PC/MK pastes. The deconvoluted spectra show that both contain monosulphate (AF_m) and AF_t. The ratios of each differ, the PC/MK containing a higher proportion of monosulphate. The spectra of the pastes after soaking in 5 M NaCl are different. Fig. 3(b) shows that both pastes now contain significant quantities of Friedel's salt.

After soaking in 5 M NaCl, the PC paste contains AF_t, monosulphate and Friedel's salt while the PC/MK past only contains AF_t and Friedel's salt, the latter being in a larger proportion in the PC/MK paste. From the spectra, it would appear that the monosulphate resonance is reducing in intensity as the Friedel's salt resonance grows. In the PC/MK paste, no monosulphate is left, while in the PC-only paste, there is still an appreciable quantity of monosulphate and only a small amount of Friedel's salt formed.

3. Mechanisms of Friedel's salt formation

The conversion of the AF_m phase, monosulphate to Friedel's salt as observed by NMR techniques can be discussed in terms of the structural similarities between the phases. Friedel's salt and monosulphate are both members of the AF_m family of structurally related phases, which have layered structures, the basic building unit of which has the constitution $[Ca_4Al_2(OH)_{12}]^{2+}$. The net positive charge of this layer is balanced by anions: either monovalent, e.g., OH^-, Cl^-, or divalent, e.g., CO_3^{2-}, SO_4^{2-}, etc. To maintain charge balance, the number of interlayer anions may be variable; for example, $2Cl^- \sim SO_4^{2-}$. The different numbers of anions required for charge balance, as well as their different sizes and polarisabilities, control the variable interlayer water contents and control the exact layer stacking sequence. Hence, Friedel's salt (in which the balancing ion is mainly Cl^-) is readily distinguished from monosulphate, the main AF_m type phase occurring in Cl^--free cement pastes. The distinction between Friedel's salt and hydroxy-substituted AF_m, e.g., C_4AH_{13}, is not easy and supplementary microprobe analyses may be required [9].

The mechanism of Friedel's salt formation in cement pastes has not been unambiguously identified. Essentially, two mechanisms have been proposed [10] as follows:

> **Mechanism 1. The conversion of hydroxy-AF_m to Friedel's salt by ion exchange.** This mechanism can be tested by following the conversion process as a function of added NaCl. However, NaCl behaves not as a single component but as two components, Na^+ and Cl^-. In this instance, the concentration of Na ($[Na^+]$) becomes greater than $[Cl^-]$ in the aqueous phase of cements because the Cl^- becomes structurally incorporated into the precipitating Friedel's salt. In order to compensate for the charge imbalance in solution, OH^- is released so that $[Cl^-]_{bound}=[OH^-]_{released}$.

Table 1
Average ionic concentrations in the pore solutions obtained from the SRPC/30% of metakaolin paste system

Cl level	Time (days)	Free Cl^- (mM)	Bound Cl^- (mM)	OH^- (mM)	Na^+ (mM)	K^+ (mM)	Ca^{2+} (mM)	SO_4^{2-} (mM)
No Cl^- addition	1	1.1	–	53	9	13	17	0.79
	7	1.1	–	53	17	23	8	0.74
	14	0.97	–	53	15	32	4	0.69
	30	0.89	–	57	16	35	4	0.63
	50	–	–	90	20	54	8	0.27
705 mM	1	704	1	68	731	51	19	24
	7	548	157	93	598	65	12	23
	14	499	206	102	582	49	7	22
	30	401	304	121	523	31	7	23
	50	258	447	154	421	23	5	21

> **Mechanism 2. The absorption of Cl^- as Friedel's salt forms by precipitation.** Friedel's salt consists of two principal $[Ca_2Al(OH)_6\ 2H_2O]^+$ layers that require balancing negative charge for stability. The availability of Cl^- (from dissolved NaCl) would satisfy charge neutrality in the solid but this would disturb the ionic charge balance in the pore solution. To compensate for this however, an equivalent amount of Na^+ ions would be required to leave the pore solution, i.e. be absorbed into solid phases.

The most likely candidate for absorption is C-S-H gel. Having a high surface area, typically 3000 m^2/g, surface reactions are likely to be significant but surface absorption as a means of explaining a major sink for Na^+ ions, as proposed by Suryavanshi et al. [10], presents some difficulties with respect to charge balance. We also propose that Na^+ is absorbed into C-S-H also but suggest that it undergoes ion exchange with protons from surface silanol groups. Released protons balance deficiency of positive charge in solution but are quickly absorbed themselves by free hydroxyl ions to produce water. This means that more OH^- ions are likely to have been released by ion exchange in AF_m than the previous model would have predicted [10].

A consequence of this is that the importance of ion exchange as a mechanism for Friedel's salt formation would be underestimated using the approach of Suryavanshi et al. [10]. If it is assumed that both ion exchange and absorption mechanisms are simultaneously active, it would therefore be incorrect to assume that:

$$[OH^-]_{\text{free}} = [OH)^-]_{\text{measured}} - [OH^-]_{\text{measured when NaCl is absent}}$$

since $[OH^-]_{\text{measured}} < [OH^-]_{\text{released}}$ as a consequence of Na^+–H^+ ion exchange at silanol sites (Mechanism 2). The following arguments can instead be proposed:

Mechanism 1. As Cl^- is bound by ion exchange (IX) in monosulphate,

$$[Na^+]_{\text{IX(init)}} = [Na^+]_{\text{IX(final)}}$$

$$[Cl^-]_{\text{IX(bound)}} = [OH^-]_{\text{IX(released)}}.$$

Note that $[Cl^-]_{\text{IX(bound)}}$ is the concentration of Cl^- absorbed by ion exchange and is equivalent to the difference between the initial $[Cl^-]$ and the equilibrium $[Cl^-]$.

Mechanism 2. As Cl is absorbed in precipitation (PT) of Friedel's salt:

$$[Cl^-]_{\text{PT(bound)}} = [Na^+]_{\text{PT(bound in C-S-H)}} = [H^+]_{\text{PT(released)}}.$$

Note that $[Na^+]$ is not constant during this process and $[H^+]_{\text{PT(released)}}$ combines with an equivalent amount of OH^-. This means that as a consequence of Cl^- absorption, OH^- ions, possibly already released from hydroxy-AF_m (Mechanism 1) are effectively removed from solution by neutralisation.

Thus, chloride bound by both mechanisms,

$$\begin{aligned}[Cl^-]_{\text{bound}} &= [Cl^-]_{\text{IX(bound)}} + [Cl^-]_{\text{PT(bound)}}\\ &= [OH^-]_{\text{IX(released)}} + [Na^+]_{\text{PT(bound in C-S-H)}}.\end{aligned}$$

$[Cl^-]_{\text{(bound)}}$ and $[Na^+]_{\text{PT(bound)}}$ can, as before [10], be derived from analyses of systems aged in the presence and absence of chlorides. $[OH^-]_{\text{IX(released)}}$ can be calculated by difference allowing the relative importance of the two mechanisms to be assessed, i.e. $[OH^-]_{\text{IX(released)}}$ reflecting the ion exchange mechanism and $[Na^+]_{\text{PT(bound in C-S-H)}}$ being a measure of the precipitation route.

4. Investigation of Friedel's salt formation

Two test pastes were studies, (i) a sulphate-resistant Portland cement (SRPC) with a low C_3A content and (ii) an SRPC/30% metakaolin, both with a water/cement ratio (w/c) of 0.7. In each case, one test mix was mixed with deionised water and another 0.705 M NaCl was added into the mix.

Cylindrical mortar specimens were made and pore fluid was extracted using a hydraulic press after 1, 7, 14, 30 and 50 days ageing at 20 °C and approximately 100% relative humidity. Pore solutions were maintained in a CO_2-free

Table 2
Chloride ions concentration binding by exchange mechanism at different ages

Age (days)	Average Cl^- binding concentration (mM)	$[OH^-]_{IX(released)}=[OH^-]_{measured}+[Na^+]_{PT(bound)}$. $[OH^-]_{measured}=[OH]_{with\ NaCl}-[OH]_{without\ NaCl}$	$[Na^+]_{PT(bound)}/[OH^-]_{IX(released)}$
7	157	164	0.75
14	206	187	0.73
30	304	262	0.76
50	447	348	0.83

Influence of ions other than OH^- and Na^+ are ignored.

environment and analysed for Cl^-, OH^-, SO_4^{2-}, Na^+, K^+ and Ca^{2+}. Chloride and sulphate concentrations were measured by ion chromatography (Dionex DX-120), the Na^+, K^+ and Ca^{2+} ions concentration were measured in a VARIAN (Spectr.AA-10) atomic absorption spectrometer (1% v/v $LaCl_3$ was added as ionisation suppressant and releasing agent) and OH^- concentration were calculated by a ionic charge balance. Table 1 gives the analytical data arising from pore solution analysis; cements were mixed either with 0.705 M NaCl or with deionised water.

The OH^- ions in the interlayers of the C_4AH_{13} (and other AF_m hydrates related) are particularly prone to ion exchange [11]. However, the impact of Mechanism 2 has to be considered to quantitatively assess the importance of the ion exchange. If one assumes that the concentration of bound sodium ions, $[Na^+]_{PT(bound)}$ is balanced by that of released H^+ ions, $[H^+]_{PT(released)}$, and therefore by that of neutralised OH^-, then total released $[OH^-]$ by ion exchange is the sum of $[OH^-]_{measured}$ and $[Na^+]_{PT(bound)}$. Analyses of the data in Table 2 indicates that this total, $[OH^-]_{IX(released)}$, follows a reasonable trend with $[Cl^-]_{bound}$ as a function of time (Table 3). Note that $[OH^-]_{measured}$ and $[Na^+]_{PT(bound)}$ correspond to the respective concentrations in solution after ageing in the presence of NaCl.

Table 2 also shows the relative importance of the two mechanisms. The ratio of $[Na^+]_{PT(bound)}/[OH^-]_{IX(released)}$ indicates the increasing role that the precipitation mechanism plays with increasing time but in the early stages, the trend indicates that the ion exchange mechanism is dominant. This might be expected given the early presence of AF_m phases in a relatively open structured matrix. It should be noted also that K^+ might be expected to play a similar role to Na^+. The effect of this on the data in Table 2 can be readily calculated from the data in Table 1.

Table 3
$NaCl+C_3AH_6$ reaction: range of concentration of Cl^- and Na^+ at each age

Concentration (mM)	Cl^- (mM)	Na^+ (mM)
350		
1 day	326	354
3 days	322	352
7 days	311	352
705		
1 day	667	698
3 day	642	710
7 days	637	702
1450		
1 day	1420	1459
3 days	1415	1458
7 days	1400	1444

5. Conclusions

The MAS NMR technique has been shown to provide a useful additional technique in the analysis of cement hydrates. The method can be used to observe directly the formation of AF_m and AF_t phase, particular the more amorphous phases, which cannot be readily detected with XRD or thermal analysis.

It is clear from the study that experimentation has to be carried out with some care. The very high centrifugal forces imposed by spinning the test samples at very high rotational velocities can effect the relative concentrations of the aluminate phases as a result of pore fluid expression.

The MAS NMR study has helped clarify the chemical environment for Friedel's salt formation with monosulphate being by far the most important precursor phase. It would appear the AF_t has virtually no capacity for reacting with chlorides. It should be noted, however, that aluminoferrites cannot be detected by NMR techniques, due to the close proximity of the ferromagnetic centres but it is considered that this phase makes no contribution to chloride binding and Friedel's salt formation.

Blending PC with metakaolin or similar cements such as PFA and GGBS increases the ratio of monosulphate to AF_t and, thereby, greatly increases the potential sites for chloride binding. However, there are several caveats to the whole scale adoption of high levels of these materials, the most important being the increased rate of carbonation that occurs. In troublesome infrastructure, such as bridge, carbonation can occur seasonally and must be allowed for in determining whole-life performance.

The mechanism of Friedel's salt formation may occur by two different mechanisms, but results of this work indicate that the ion exchange of chloride with hydroxide ions in monosulphate is dominant, at least at ages of up to 50 days. The data suggest that the precipitation route becomes more important at longer ages. This means that ion exchange mechanism has more importance than the previous model would have predicted [10].

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