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ON THE POSSIBILITIES OF *IN SITU* STUDIES OF THE HYDRATION OF ALUMINATE CEMENTS USING WIDELINE ^{27}Al NMR SPECTROSCOPY

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ABSTRACT

Wideline ^{27}Al NMR spectroscopy has been applied to the investigation of the hydration of CA, CA_2 and C_3A. A selective disappearance of the lower frequency part of the ^{27}Al NMR line of original CA was observed during hydration. The deconvolution of ^{27}Al NMR spectra of anhydrous and hydrated CA into a number (6 to 9) of gaussian components allowed for a semiquantitative analysis of the kinetics of hydration of CA. Because of a strong correlation between the components of the line of original CA reliable estimates of the intensities were obtained only concerning the total CA line and its two internal components as well as concerning the amount of aluminate ions in solution and total new hydrated solid products. The kinetics of hydration of CA_2 and C_3A have been studied using difference spectra of hydrated and anhydrous samples. These difference spectra corresponded to a gradual decrease in the amount of aluminum in the liquid phase and a prolonged induction period in the case of hydration of CA_2. The hydration of C_3A proceeds without any detectable induction period and new solid was found to crystallize in significant quantities as early as after 10 minutes of hydration. The lines of original solid CA_2 and C_3A disappear as a whole without observable selective hydration. © *1997 Elsevier Science Ltd*

Introduction

Nuclear magnetic resonance spectroscopy has been successfully used in many studies of hydration of various cements and their components. Application of advanced solid state NMR methods (MAS, PE-MAS, DOR, *etc.*[1-4]) is possible only for comparatively stable samples, i.e., those hydrated for at least one or several days, or of artificially stabilized specimens of minerals hydrated for shorter times. In the latter case the problem is that the liquid phase still present at earlier stages of hydration is destroyed and dissolved products are forced to crystallize under conditions far from normal. The *in situ* studies of cement hydration [5] provide more reliable information on the state of cement pastes during the induction period and the initial crystallization of products. In many cases these stages are of short (10 min-2 hours) duration and the measurements must be fast (about 1-15 min). Proton magnetic relaxation measurements (especially direct measurements of average relaxation rates [6]) as well as ^{27}Al NMR spectroscopy comply with these requirements. The behavior of the mean relaxation rate of water protons and the accumulation of aluminate ions in liquid phase(s) during the hydration of modified calcium sulphoaluminates have been studied [7] using these methods. A significant increase in the proton relaxation rate observed in these systems during the induction period could not be interpreted unambiguously because of the absence of data on the behavior of the aluminum in the initial solid grain. Wideline (solid state) ^{27}Al NMR spectroscopy is, in principle, able to provide such an information. The possibilities of this method for *in situ* studies of the hydration of aluminate minerals are explored in the present paper.

The ^{27}Al isotope has a 100% natural abundance and spin $I = 5/2$, i.e. it is a quadrupolar half–integer spin nucleus and its NMR powder spectra contain a central line and 4 satellites, the result of shifting of the resonance by quadrupolar interaction. The separation of the satellite signals is roughly the first order correction to the resonance frequency and the splitting of the central line is described by the second order terms. In the cases of high quadrupolar coupling constant, q.c.c., these satellites are not necessarily visible in spectra recorded over a narrow frequency range. Both the central line and satellites are broadened by dipolar and quadrupolar relaxation. The lineshape of a ^{27}Al NMR spectrum of a powdered mineral is a convolution of the gaussian lineshape (caused by relaxation) and of a complicated lineshape arising from the averaging of quadrupolar shifted resonances over all orientations. The chemical shift anisotropy, which produces effects similar to the quadrupolar interaction, must also be considered when these effects are of comparable magnitude. In many minerals (even those having a perfect crystal lattice) ^{27}Al nuclei can be found in several magnetically and electrically nonequivalent sites, i.e., having different chemical shifts, q.c.c. and electric field asymmetry factors (η). Application of high frequency NMR (which simplifies the lineshapes caused by quadrupolar interaction) and of very fast magic–angle spinning (which eliminates the dipolar and partly quadrupolar linebroadenings) makes it possible to analyze such spectra for aluminate minerals and determine the chemical shifts, q.c.c. and η of non–equivalent sites in a crystal lattice [4].

For the practical purposes of studying kinetics of hydration of aluminate minerals such an analysis of a lineshape could be useful when identifying the products of reaction and the sites in original solid undergoing a selective hydration (dissolution). In order to get quantitative results the observed lineshapes must be deconvoluted into the components representing original line as well as the products. This involves a complicated regression procedure especially when quadruplar split lineshapes are present. An alternative method which could be applied consists in the use of difference spectra obtained by subtraction (with a proper weighting factor) of the line of original solid from the line of hydrated product. Also a formal deconvolution of an observed lineshape into some number of gaussian components could be used in order to obtain a more detailed information of the transformation of original solid and formation of hydration products. The material given below illustrates the possibilities of the latter two methods for the analysis of kinetics of CA, CA_2 and C_3A.

Experimental

The wideline (static) ^{27}Al NMR spectra of CA, CA_2 and C_3A minerals were recorded using CXP spectrometers (BRUKER) at 78 and 52 MHz at ambient temperature (300 ± 3 K). The minerals were synthesized from high purity grade materials then crushed and milled in ball mills and fractionated according to the grain size. The fraction 28-40 μm was used. The hydration was performed in special NMR sample tubes made of Teflon. Water was added directly to minerals in a sample tube in quantities corresponding to a water–to–solid ratio of 0.4. An acquisition of a spectrum usually took about 10 min. Phase and baseline corrections were made using standard routines.

Spectra were analyzed by subtracting a spectrum of original (anhydrous) mineral from the spectra of hydrated samples using a standard (dual display) procedure. When the original spectrum is of easily recognizable shape and its complete subtraction is possible the coefficient introduced at such a subtraction reflects the decreasing quantity of original solid in a sample, while the lines in the difference spectra reveal the nature and quantities of the products of hydration. The spectra of hydrated CA_2 and C_3A are the examples of such spectra.

On the other hand, if the original line could not be easily identified in the spectrum of hydrated mineral (because of a overlapping of lines of similar shape, for example) then the subtraction can be carried out with a weighting coefficient corresponding to the equality of the integrals of the spectra (whole) of original and hydrated samples or zero integral of a difference spectrum (i.e., considering the total amount of aluminum to be constant). The lines in such difference spectra appearing above a baseline are the lines of hydration products whilst the lines oriented downwards belong to the original species transformed into products. Spectra of hydrated CA belong to this type.

Spectra of hydrated CA were also analyzed by deconvoluting them into a number of gausian components. For this purpose a set of 40 points was chosen obviously representing all details of lineshapes. These data were extracted from the spectra and transferred to a personal computer for nonlinear regression analysis.

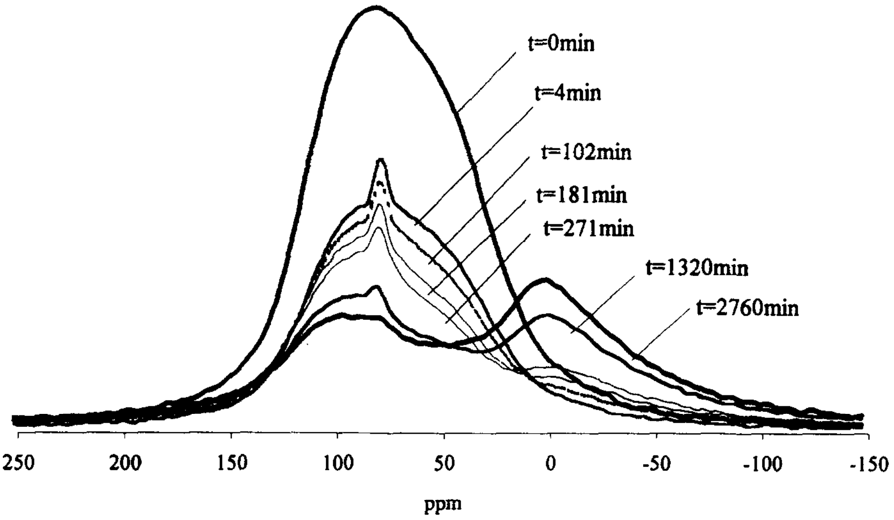

FIG. 1.

Transformation of the ^{27}Al NMR spectrum of CA (78 MHz) during hydration at 300K.

Results and Discussion

Hydration of CA. ^{27}Al NMR spectra of CA obtained at various stages of hydration are shown in Fig. 1. No characteristic points were observed in the spectrum of anhydrous mineral which was a superposition of broadened and quadrupolar split lines from 6 non–equivalent AlO_4 tetrahedra in the crystal structure of CA. In a very fast MAS spectrum six lines, showing typical second order quadrupolar splittings, were observed [4]. After the addition of water a new narrow line appeared at 80 ppm which was assigned to a liquid phase tetracoordinated Al species (tetrahydroxyaluminate anions [8]). The intensity of this line remained approximately constant during about 100 min of hydration and then started to decrease (remaining, however, non–zero after 48 hours hydration). After 100 min of hydration a new line (with a maximum at about zero ppm) appeared in the spectrum (Fig. 1, curve t = 102min) consistent with the well known formation of octahedrally coordinated hydrated aluminate species [1]. At approximately the same time the low–frequency part of the signal from the original solid began to disappear (Fig. 1).

This is best visible in difference spectra (Fig. 2) where the downward directed peak is of obviously smaller width than the line of original solid (t = 0 min) and is shifted to lower frequencies. If the lineshape of original solid is determined mainly by quadrupolar coupling [9] then these phenomena should be interpreted as a selective dissolution of one or two of the nonequivalent AlO_4 species present in the crystal structure. On the other hand, if chemical shift anisotropy plays significant role in the decay of transverse magnetization, then the observed disappearance of the low-frequency part of the line of CA would mean (according to the actual shape of this line) a selective dissolution of the crystals oriented along the direction of magnetic field, which is not very probable.

In order to follow semiquantitatively the kinetics of disappearance of the original solid and the growth of the new solid the spectrum of anhydrous CA was approximated by a sum of 6 gaussians of equal integral intensity:

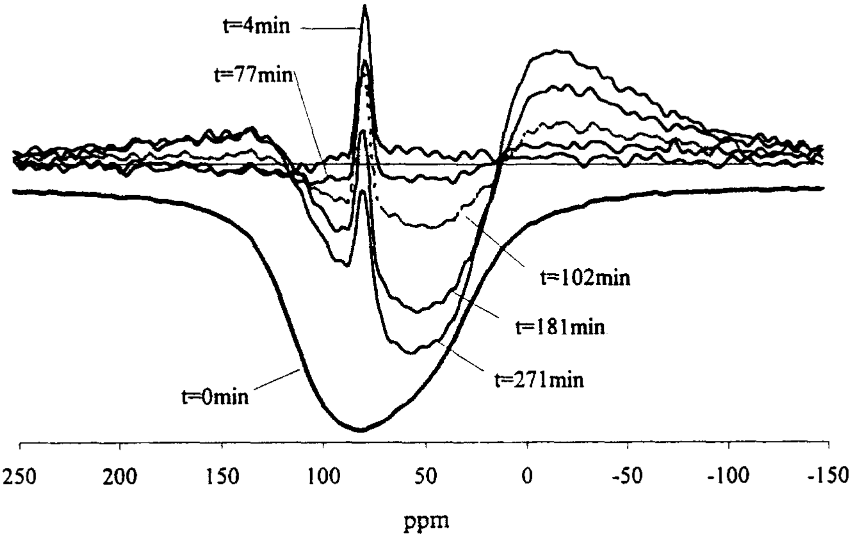

FIG. 2.
Difference ^{27}Al NMR spectra (78 MHz) of hydrated CA.

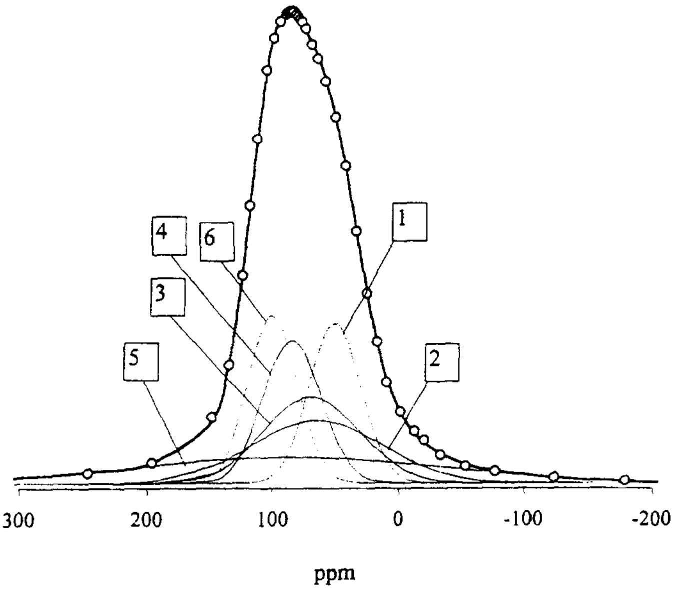

FIG. 3.

Deconvolution of the ^{27}Al NMR line of anhydrous CA by Eq.(1) and the lineshapes of the component lines.

$$A = a \sum_{1}^{6} (1/\sigma_i)\exp(-(\delta - \delta_i)^2/\sigma_i^2) \qquad (1)$$

where *a* is a normalizing factor. The number of gaussians and the *initial* approximations of their parameters were taken from the results of the analysis of the lineshape of anhydrous CA [4]. The frequencies of the six maxima (δ_i in Eq. (1)) and corresponding linewidth (σ_i) were adjusted to give best fit while retaining their equal integral intensity. It must be noted that the estimates thus obtained reflect a *formal* representation of the experimental lineshape by a sum of 6 gaussians and cannot be directly related to the six non–equivalent sites in CA structure.

TABLE 1

The Parameters of the Deconvoluted Components of the Wideline ^{27}Al NMR Spectrum of CA

σ/ppm[b]	δ /ppm[c]	#[d]
27.81	103.5	6
29.11	54.1	1
32.64	88.0	4
53.61	72.8	3
74.55	68.5	2
176.03	91.6	5

[b] estimate of linewidth

[c] estimate of the position of maximum

[d] lines numbered according to the frequency of their maximum

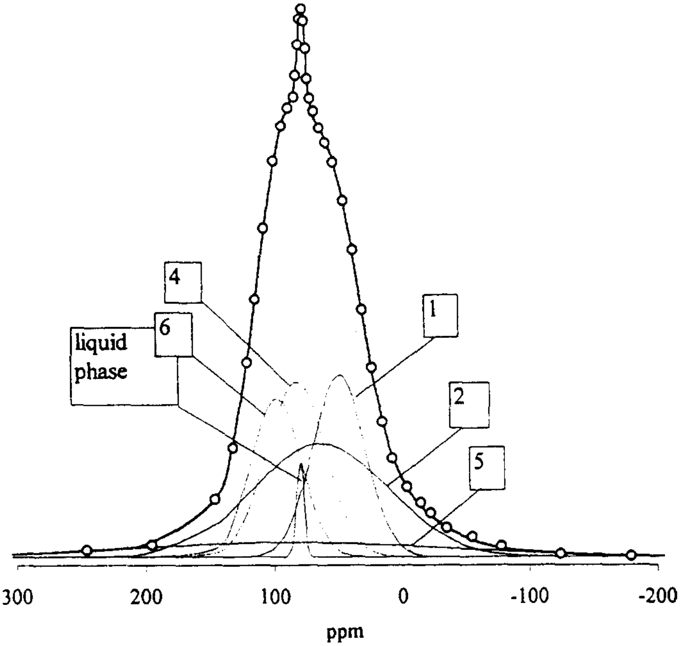

FIG. 4.
Deconvolution of the ^{27}Al NMR spectrum of CA obtained after 4 minutes hydration.

The results of this optimization are shown in Fig. 3 and the best fit parameters are given in Table 1. The description of lineshape was adequate.

When a spectrum of *hydrated* CA is to be analyzed the regression procedure must include new lines: a narrow line of dissolved aluminate ions at 80 ppm (see Fig. 4) and, at later stages of hydration, broad overlapping lines of hydrated solid products (CAH_{10} and C_2AH_8 according to [10]) ranging from -6 to -140 ppm. The intensities of the components of the *original* line can not be now considered as equal because the difference spectra clearly show a selective disappearance of a lower frequency part of the original line. In fact, it proved to be impossible to obtain an adequate description of a lineshape of a hydrated sample after 100 min of hydration assuming the original line to disappear as a whole. Therefore the individual intensities of all 6 components were adjusted while keeping their positions of maxima and linewidths fixed. This variation of individual intensities brings about several artifacts connected with a strong overlapping of these lines. For example, in the earliest observed spectrum of the hydrating sample (after 4 min of hydration) one of the lines (#3: δ_{exp} = 72.8ppm, σ = 53.6ppm) of the original solid 'vanished' completely while the intensity of the line #2 (δ_{exp} = 68.5ppm, σ = 74.6ppm) apparently increased substantially. At this stage of hydration a new solid was unlikely to have formed and the difference spectra (Fig. 2) do not indicate to it. Therefore the apparent disappearance of line #3 must be correlated with its very close overlap with line #2.

Fortunately the lines of hydrated products were significantly shifted and their intensities were not so strongly correlated with the intensities of the original lines. In particular, the signal attributed to aluminate in a liquid phase was distinguished by its small width. Therefore it is only the correlation between the lines of the original solid which caused the

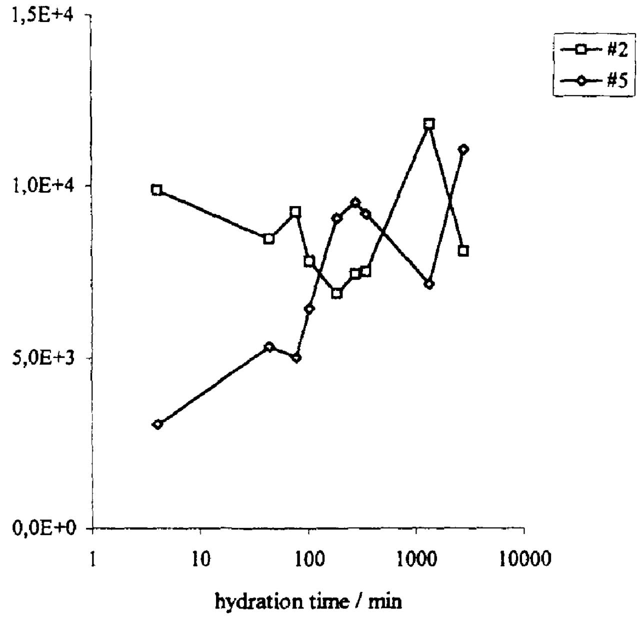

FIG. 5.
Correlated changes in the intensities of the lines #2 and #5 during the hydration of CA.

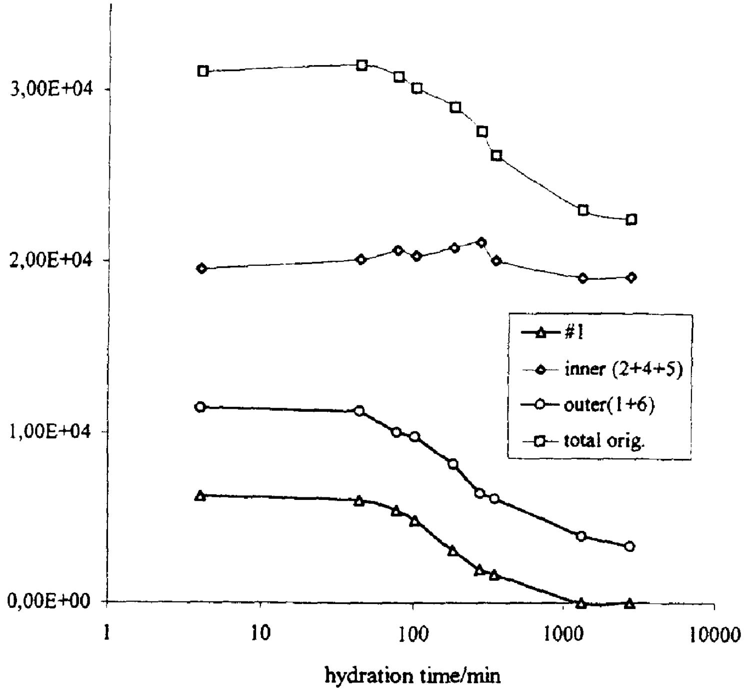

FIG. 6.
Variation with hydration time of the total integral intensity of the deconvoluted outer and inner lines in the spectrum of CA.

TABLE 2

Integral Intensities (arb. u.) of the Lines of the Products of Hydration of CA

t/min	new3	new2	new1	liq.	new solid	total new
4	0	0	0	4.62E+02	0	4.62E+02
44	0	0	0	4.21E+02	0	4.21E+02
77	0	0	0	3.86E+02	0	3.86E+02
102	3.46E+02	2.75E+02	1.54E+02	4.24E+02	773.9	1.20E+03
181	6.11E+02	6.29E+02	4.05E+02	4.24E+02	1645.5	2.07E+03
271	7.21E+02	9.01E+02	9.14E+02	3.74E+02	2536.3	2.91E+03
341	1.18E+03	1.45E+03	1.08E+03	3.47E+02	3716	4.06E+03
1320	1.91E+03	3.11E+03	3.12E+03	2.28E+02	8132	8.36E+03
2760	2.52E+03	7.20E+03	2.64E+03	9.89E+01	12358	1.25E+04

complicated changes in their relative intensities (Fig. 5). Such changes of intensity should not be interpreted independently; only a set of lines whose total intensity does not increase and/or smoothly runs downwards may be considered as representing the real changes in the solid. For example, the total sum of the intensities of *all* the original lines after being constant for 100 minutes of hydration decreased smoothly during the remaining period of observation (Fig. 6).[1]

The widest lines of the original solid were the inner lines (#2, #4, #6) and their behavior was the most correlated. However, the sum of their integrals was approximately constant during the observation (Fig. 6). The outer lines (#1, #6) were comparatively narrow and #1 (having the lowest resonance frequency) showed an approximately exponential decay down to practically zero intensity after 2 days of hydration. Line #6 only slightly decreased in intensity.

The positions and the widths of the lines of hydrated products (denoted as 'new' in the Tables 2 and 3) could not be assumed to be fixed parameters because of the changes of the composition of hydrated products. According to Kosmach and Lahajnar [10] the primary

TABLE 3

Positions of Maxima (δ) and Linewidths (σ) of the Lines
of the Products of Hydration of CA

t/min	δ_{new1} /ppm	δ_{new2} / ppm	δ_{new3}/ ppm	δ_{liq} / ppm	σ_{new1} /ppm	σ_{new2} /ppm	σ_{new3} /ppm	σ_{liq} / ppm
4				80.30				4.21
44				80.30				4.45
77				80.20				4.41
102	-6.00	-25.0	-72.0	80.40	11.2	17.8	43.8	4.30
181	-4.50	-27.0	-82.0	80.90	13.4	22.2	48.6	4.44
271	-5.00	-33.0	-82.0	80.80	16.8	23.7	40.8	4.86
341	-6.00	-39.0	-137	80.60	17.7	32.4	85.5	5.01
1320	-1.00	-40.0	-142	82.00	23.6	39.6	98.3	4.78
2760	3.00	-17.0	-142	79.80	21.1	52.6	109	4.90

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[1] The integral of the whole spectrum only slightly deviated from a constant value (±3%) during the first 6 hours of hydration. The integral of all lines in the spectra of samples after hydration for two days was about 20% *higher* than on the first day of hydration, most probably because of different tuning of the probehead.

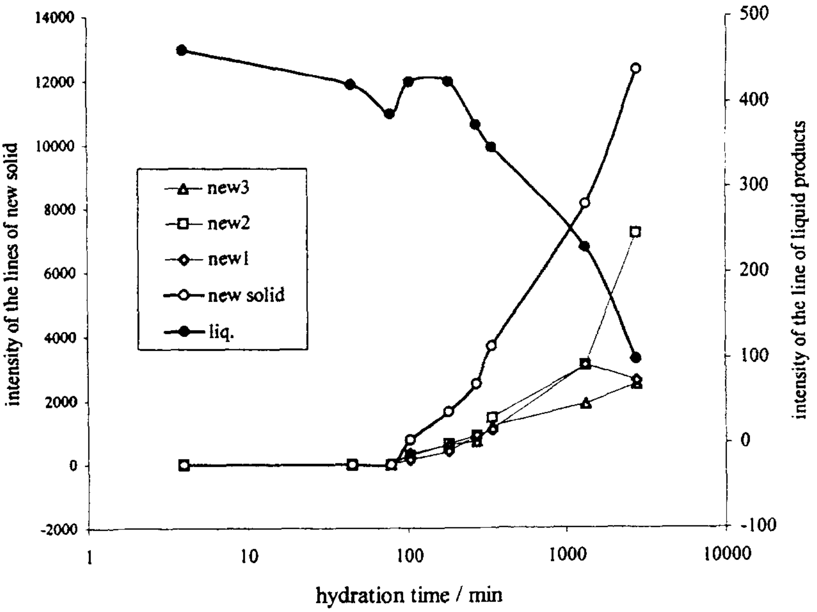

FIG. 7.
Changes in the component line intensities of the products of hydration of CA.

product of the hydration of CA (CAH_{10}) is partially dehydrated after approximately 10 hours of hydration at room temperature and transformed into C_2AH_8. The overlapping of lines of different products might be interpreted as a shift of the maximum or an increase in a linewidth for a single line. Therefore all parameters (position, linewidth and intensity) of the lines of new solid were optimized (Tables 2 and 3).

A further one to three lines assigned to solid hydrated products were necessary for the adequate description of the experimental lineshapes at different stages of hydration. As with the original solid, the intensities of new lines varied in a correlated manner (Fig. 7). The total signal intensity of the new solid components increased smoothly and was always much higher than the amount of aluminum in the liquid phase (note the different scales for these intensities in Fig. 7). The growth of a new hydrated solid phase was thus only seemingly at the expense of the concentration of aluminum in the liquid phase, indicating that the latter should be considered not as a mother liquor but as an intermediate layer between the original solid and hydrated products.

During the induction period both the amount of dissolved aluminate and the total amount of *aluminum* in the original solid remained constant. Therefore significant changes in physical parameters during the induction period may be connected with either selective dissolution of CaO or with the nucleation and other processes in liquid phase.

Hydration of CA_2 proceeded much more slowly than that of CA. After 10 hours of hydration the peak of hydrated products was barely visible as a shoulder to the central line in the ^{27}Al NMR spectrum, Fig. 8A (upper spectrum). The difference spectrum, Fig. 8B, of a hydrated sample and the original solid showed a gradual decrease in the intensity of the narrow signal at 80 ppm and a growth in a line at ca. 0 ppm (hydrated solid products). The time of the first appearance of new solid was easily determined from these spectra (between 277 and 313 min). The absolute amounts of the dissolved aluminum (as $[Al(OH)_4]^-$ ions) and of

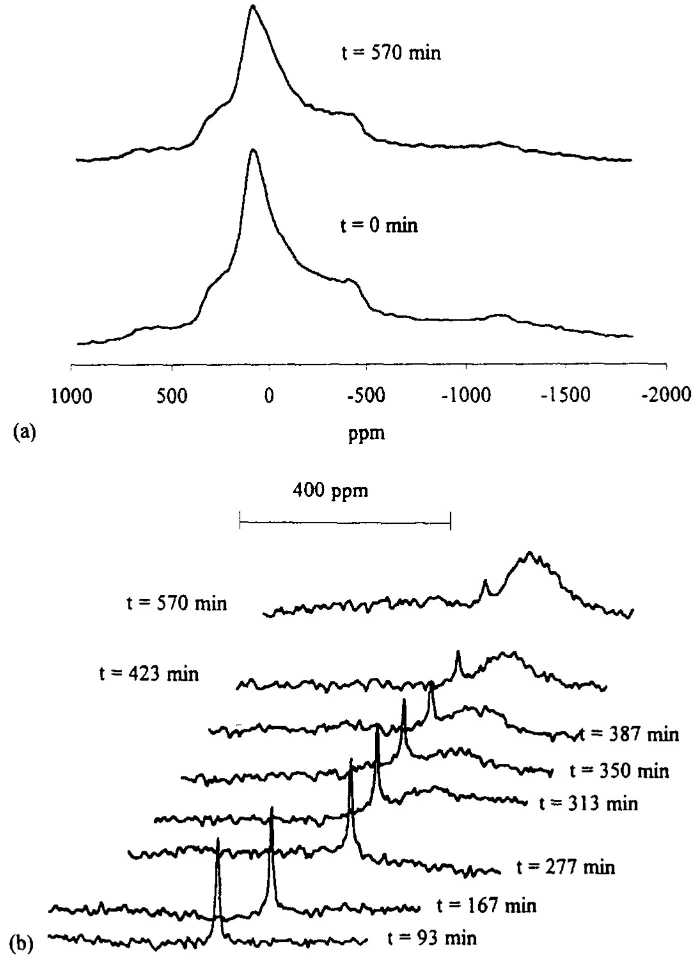

FIG. 8.

Wideline ^{27}Al NMR (52 MHz) spectra (A) and the difference spectra of hydrated and anhydrous CA_2.

crystallized hydration products were much smaller than in the case of hydrated CA. Therefore the time necessary to obtain a comparable signal–to–noise ratio was longer for this mineral than for CA.

Hydration of C_3A proceeded very rapidly and without a detectable induction period. An intense new solid line was visible at the shortest possible hydration times which can be investigated by ^{27}Al NMR (Fig. 9A). Because of its well resolved singularities, the original solid signal was easily subtracted from the spectra of hydrated samples (Fig. 9A, upper spectrum). The difference spectra contained one comparatively narrow central line of hydrated products, accompanied by broad satellites (Fig. 9B). A good signal–to–noise ratio in such spectra was only achieved with a minimum of about 200 scans (measurement time about 4 min).

The hydration of C_3A was so fast that only three experimental points could be obtained before the intensity of the line due to hydration product reached a constant level (Fig. 10).

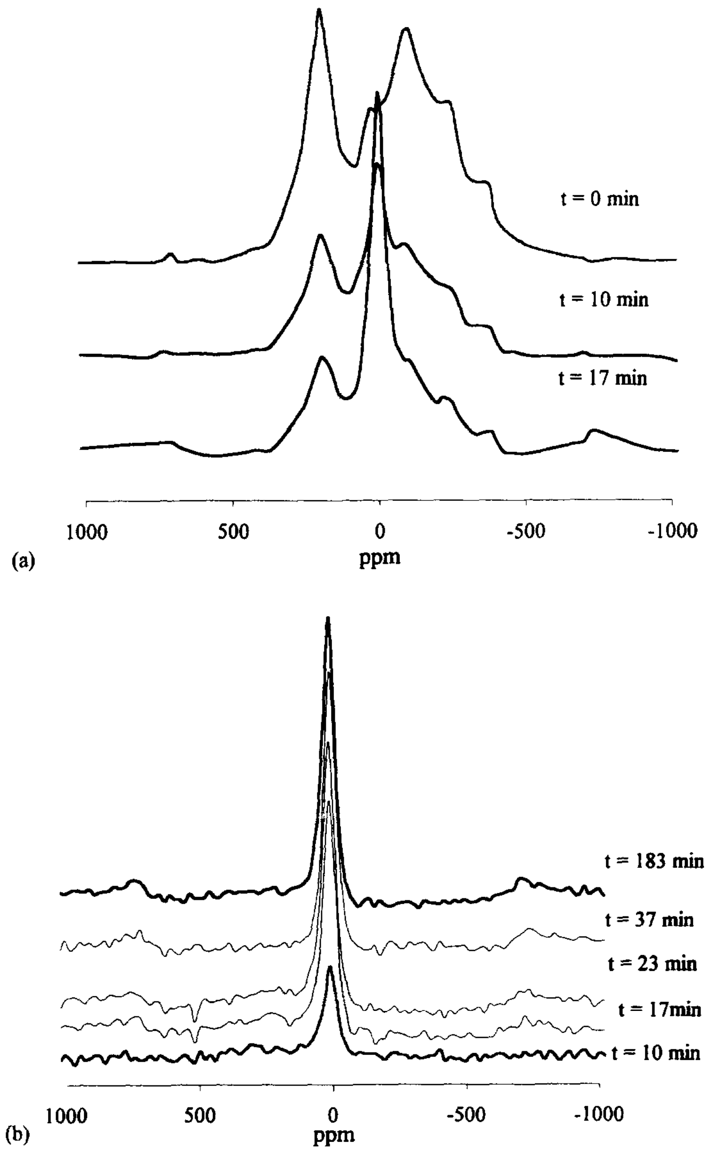

FIG. 9.

Wideline ^{27}Al NMR (78 MHz) spectra (A) and the difference spectra (B) of hydrated anhydrous C_3A (B).

We consider that the initial deep drop in the weighting factor was caused mainly by the difference between the electric conductivity of the anhydrous mineral and that of its aqueous suspension.

Conclusions

There are two possible ways of obtaining difference spectra of hydrated aluminate minerals: (i) achieving a complete compensation of original line alone and (ii) compensating overall

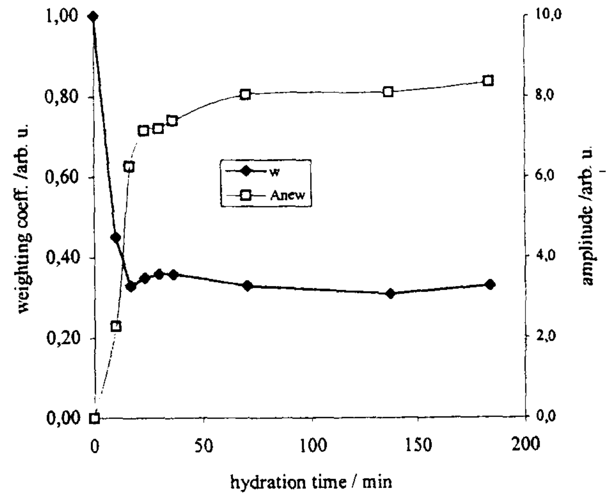

FIG. 10.

Curves showing an increasing amount of hydrated products (A_{new}) and the decreasing content of the original mineral (w) in hydrated pastes of C_3A.

integral of the whole spectrum. The first way produce spectra of the products of reaction alone which is convenient but could only be applied in the cases when the lines of original reactants could easily be distinguished in experimental spectra. The second method is generally applicable and produces the lines of the products above the baseline and the lines of transformed species-below. Such spectra could be quantitatively analyzed when lines are well separated. When lines of original reactants and products overlap such difference spectra could only be qualitatively analyzed.

The analysis of difference spectra (of the second type) of hydrated CA show that the low-frequency part of original line selectively disappears during 48 hours of hydration. This is connected most probably with a selective hydration of Al atoms in one or two non–equivalent sites in the crystal structure of CA. This is supported by the results of a formal deconvolution of the lines of anhydrous and hydrated CA into 6 gaussians. The number of gaussians was taken equal to the number of nonequivalent sites in CA structure, however, such mathematical model was overparametrized which brought about correlated changes in the intensities of components. Assuming that the intensities of lines of original solid should not increase during hydration it became possible to select a set of lines representing the hydrating part of original solid.

Hydration of CA_2 and C_3A can be advantageously studied by difference spectra because the lines of original solids could easily be distinguished by their singularities. According to the obtained spectra the lines of CA_2 and C_3A disappear as a whole. The difference spectra of hydrated CA_2 (obtained by compensation of the original line) show a gradual and slow decrease the amount of dissolved aluminate ions and subsequent increase of the line of solid hydration products. It must be noted that in common spectra of hydrated CA_2 the line of dissolved aluminate ions is barely visible and the line of solid products of hydration could not be distinguished at all.

In contrast, the signal of dissolved aluminate ions could hardly be detected even in the difference spectra of hydrating C_3A. These spectra reflect mostly the growth of a new solid phase.

The difference ^{27}Al NMR spectra are much simpler and should admit a quantitative analysis by deconvolution into gaussians or lines of a more suitable lineshape. However, the accurate determination of the relative amounts of different products depends on the signal-to-noise ratio and the elimination of the ring signal which is only possible at resonance frequencies of at least 78 MHz.

Acknowledgments

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