Pergamon

Cement and Concrete Research, Vol. 27, No. 2, pp. 303-310, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(96)00206-2

HYDRATION KINETICS OF MODIFIED CALCIUM SULPHOALUMINATE OXIDES STUDIED BY ALUMINUM - 27 NMR SPECTROSCOPY AND PROTON MAGNETIC RELAXATION: EXPERIMENTAL DATA

A.B. Kudryavtsev and T.V. Kouznetsova
D. Mendeleev University of Chemical Technology of Russia
125190 Moscow Miusskaya sq. 9, Russia

(Refereed)
(Received January 31, 1994; in final form December 3, 1996)

ABSTRACT

Hydration kinetics of Na_2O-, MgO-, BaO- and TiO_2- doped calcium sulphoaluminate oxides, has been followed using ^{27}Al NMR and proton magnetic relaxation measurements. Aluminum - 27 NMR spectra of hydrated pastes show a narrow peak at 80 ppm corresponding to the hydroxy-aluminate ions in a liquid phase. According to the changes of intensity of this lines during the induction period considerable amounts of aluminate were dissolved, especially in the case of Na_2O-doped sulphoaluminate. With the start of crystallization of hydrated phase (marked by the appearance of a line at 0 ppm in the proton decoupled ^{27}Al spectra) the concentration of aluminate ions in the liquid phase decreases. The proton spin-lattice relaxation rates follow a usual pattern, the crystallization being indicated by a sharp increase in the relaxation rate. A significant increase of the proton relaxation rate was also observed during the induction period, when no new solid was yet formed. This relaxation enhancement might be due to the increased viscosity and gel structuring. © *1997 Elsevier Science Ltd*

Introduction

Modern methods of High Resolution in Solid State NMR (MAS, CP-MAS) have been successfully used in studies of products of cement's hydration (1-3). These methods require stabilization of reacting paste (treatment with acetone (3), e.g.) which destroys all evidence concerning liquid phase properties and composition. From ^{27}Al NMR spectra of hydrating aluminate cement it was found (4) that the *liquid phase* contains considerable quantities of tetrahedral aluminate ions, which are subsequently transformed into solid octahedral aluminum hydroxides (4).

Proton magnetic resonance has also been used for studies of cement hydration *in situ* (5, 6). By the spin grouping method based on simultaneous analysis of both the longitudinal and transverse multiexponential relaxation, several products have been identified and their content followed during hydration (6).

At the same time, description of kinetic data on cement's hydration provided by NMR methods remains on a qualitative or semi–quantitative level (7, 8). It is based on a model, which includes dissolution of original solid material accompanied by hydrolytic transformation and subsequent crystallization of the new hydrated phase. The latter process involves adsorption of the main part of free water causing a substantial increase in proton magnetic relaxation rate (decrease of relaxation time). The amount of newly formed surface has been estimated from proton relaxation data (7).

The following problems must be solved when a quantitative model, based on some reaction mechanism, will be applied to the analysis of the NMR data on hydrating cement pastes:

1. A connection must be established between measurable NMR quantities and composition of a system.
2. Methods of the MNR measurements must be found which meet the requirements of kinetic studies.
3. A mathematical model of hydration kinetics based on reaction mechanism and physico-chemical laws must be developed, which will permit estimation of its parameters by fitting experimental NMR data to the theoretical expressions.

To analyze kinetics of reaction one must have data on changes in concentrations of reagents and products or at least of some quantity which could be calculated from the system's composition. Concentrations of some products of aluminate cement's hydration may be determined from the Aluminium-27 spectra of cement's paste, the integral of the NMR line being proportional to the number of ^{27}Al nuclei in the corresponding state. For spectra recorded at sufficiently high resonance frequency a relatively small number of accumulations is required to obtain a good signal to noise ratio. Proton relaxation rate studies also yield direct information on the system's composition if multiexponential analysis of magnetization re–equilibration is performed. It requires, though, inspection of nuclear magnetization development over a wide range of delays, as well as measurements of signal amplitudes with high precision. These joint requirements demand a measurement time on the order of 5-10 minutes. Some stages of fast setting cements hydration proceed within a comparable time and could not be investigated by this time consuming method.

Another, indirect way to analyze hydration kinetics consists of the investigation of changes in some additive NMR parameter, which could be then reconstructed using calculations based on Mass Action or other kinetic laws, and additive rule equations. Statistically averaged proton magnetic relaxation rates $\langle R_{1,2} \rangle = \langle 1/T_{1,2} \rangle$ are additive with respect to the system's composition and may be calculated for reacting paste as:

$$\langle R_{1,2} \rangle = (1/C_{H2O}) \sum \nu_i [Pr_i] R_{1,2i} \tag{1}$$

where C_{H2O} is the total concentration of water in paste, $[Pr_i]$ - concentration of i-th product, containing protons (incl. water), ν_i and $R_{1,2i}$ are the corresponding stoichiometric coefficient and proton relaxation rate.

In earlier studies of proton relaxation in heterogeneous systems it was suggested that exchange processes effectively average the longitudinal relaxation rate over all species present. Kinetics of single relaxation time changes have been reported for hydration of binding materials (9, 10). In cases where multiexponential relaxation was evident some single formal parameter (delay corresponding *1/e* decrease in NMR signal amplitude (11)) was used to describe magnetic relaxation. In later works the multiexponential nature of relaxation was established (5, 6) but no attempt has been made to find practical method of direct measurement of $<R_{1,2}>$.

Recently it has been demonstrated (12), that statistically averaged relaxation rate may be rapidly measured by studying only the initial part of the re–equilibration of nuclear magnetization in multiphase systems with slow exchange, typical examples of which are hydrated cement pastes.

In the present publication, data on AlO_2^- concentrations in the liquid phase, furnished by ^{27}Al NMR spectroscopy, will be used to determine the reaction mechanism and draw up a mathematical model of hydration kinetics in doped sulphoaluminates' pastes. The results of kinetic analysis of $[AlO_2]$ plots will be then used to describe proton relaxation rate changes in the same systems.

Experimental

Recording of ^{27}Al and ^{23}Na NMR spectra as well as measurements of proton relaxation rates have been performed using multinuclear NMR Fourier spectrometer CXP-200 at 52 MHz for ^{27}Al resonance and 200 MHz for resonance of protons. Aluminium - 27 signals were accumulated (from 200 to 1000 scans) with relaxation delay 0.2 sec. Spectra, obtained by the Fourier Transform in the absolute intensity mode, were combined with the spectrum of reference sample (using artificial frequency shift) and integrated.

Concentrations of aluminate ions were determined from integrals' ratio and known amount of aluminate ions in the reference sample. Spectra of the reference sample (0.1 M solution of potassium aluminate) were recorded before and after every series of kinetic measurement in the same conditions. There may remain some discrepancies between absolute values of aluminate concentrations obtained in different series due to the variations in electric[1] properties of pastes of different minerals.

The amount of ions and molecules transferred to the liquid phase or taking part in other transformations was calculated relative to 1 kg of water originally added to the cement. For the induction period and part of the crystallization stage there is evidence (presence of intensive narrow line in proton spectrum, low proton magnetic relaxation rates, etc.) of the excess of water in the system. Under these conditions simplified mass action law equations may be applied to the description of kinetics in the investigated systems. The chosen form of concentrations is the most unambiguous and may be used in estimating rates of various stages of hydration. Errors of experimental determination of concentration within one kinetic series are + 5 - 7 %, depending on the number of accumulations done.

Measurements of proton mean relaxation rates were performed using a saturation-recovery sequence with 40 saturating $\pi/2$ pulses. Every kinetic series has been run several times for the adjustment of the pulse delays in order to get the initial part of a magnetization recovery curve adequately described by single exponent. The relaxation rate determined in this way is equal to that statistically averaged over all species present in the sample (12). Errors of estimates of $<R_1>$ vary from ±1% in semi–liquid samples at the initial stages of hydration to the ±5 % for hardened pastes.

---

[1] Highly conducting samples make the Q values of the resonance circuits of the probehead lower.

Approximation of magnetization re–equilibration curves was done using spectrometer's computer from the NMR data stored on disk. Our own software written for Aspect-2000 computer built into the spectrometer have been employed.
Calcium sulphoaluminate oxide (3CaO $3Al_2O_3$ $CaSO_4$, C_4A_3S) doped with 1.5 $\%_W$ of Na_2O, MgO, BaO and TiO_2 was synthesized as described in (13). Milled clinker had a mean diameter of particles ca. 20μ.

Samples for hydration were prepared in Teflon sample tubes (10 mm o.d.). Approximately 500mg of cement was weighed in the tube and a calculated amount of water (water–to–cement ratio 0.4) was added by calibrated pipette. The mixture was stirred ~ 1min using a Teflon-coated rod, then it was closed and fastened in the MAS probehead. The proton decoupling channel of the probehead was used for proton relaxation rate measurements, and the X-band channel - for Al-27 acquiring spectra. The temperature in the probehead was kept constant at 303± 0.5 K.

Results and Discussion

All anhydrous calcium sulphoaluminates produce practically identical wide line ^{27}Al NMR spectra, similar to that given in Fig. 1a. These spectra may be interpreted as superimposition of at least two signals split in the second order of quadrupole interaction (14). When water was added a new narrow line appeared at 80 ppm which was attributed to the tetrahedral aluminate ion, AlO_2^-, (more properly - $[Al(OH)_4]$) ion in solution (16), Fig 1b. When recorded in the narrow frequency region, Fig. 1c, this line may be integrated and serve as the measure of amount of aluminate ions in the liquid state.

Concentration of aluminate ions, computed from the integral of the line at 80 ppm increased with hydration time, Fig. 2, reached a maximum and then dropped more or less sharply. The averaged proton relaxation rate increases slowly during the so-called induction

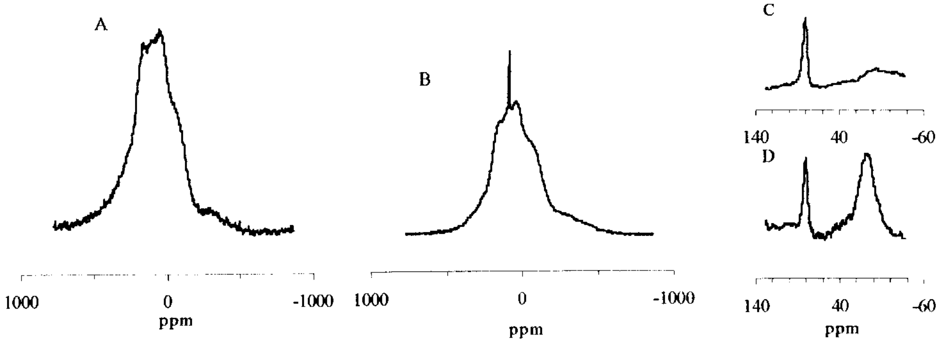


FIG. 1.
Aluminum - 27 NMR spectra of MgO doped $C_4A_3C\overline{S}$: a - wideline spectrum of the anhydrous calcium sulphoaluminate, b - wideline spectrum of reacting paste (30 min hydration), c - recorded in narrow frequency range spectra of reacting paste (1 hour hydration) with proton decoupling (top spectrum) and without it (lower spectrum).

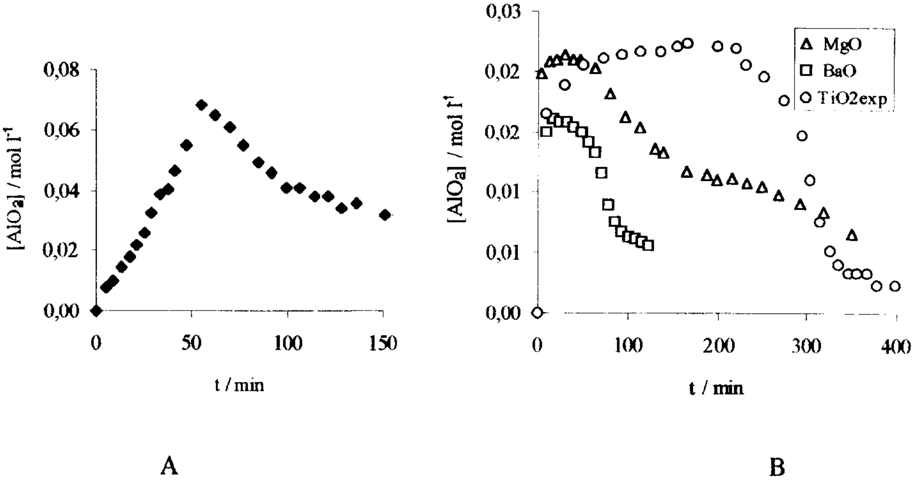


FIG.2.

Dependencies of aluminate concentration in liquid phase on hydration time. Note the difference in coordinates' scale for Na_2O (A) and other (B) samples.

or dormant period and, at the moment nearly (but not strictly) coincident with the drop in AlO_2^- concentration, there was a sharp rise in the proton relaxation rate, Fig. 3.

For Na_2O- and TiO_2-doped calcium sulphoaluminates a significant increase in proton relaxation rate was observed, Fig. 4, before the concentration of AlO_2^- reached a maximum. For other samples, significant increases in $<R_1>$ occurred only after the concentration of aluminate ions begin to drop. Should any direct evidence be found of formation of a new hydrated solid phase before the concentration of AlO_2^- ions reaches maximum, these changes in proton relaxation rate should be interpreted as crystallization proceeding on a small scale during induction period. Contrary to it, a new signal at ~ 0 ppm (octahedral Al (3)) was observed, Fig. 1c, upper spectrum, in proton decoupled ^{27}Al spectra of all samples *only after the first significant decrease in* AlO_2^- *concentration.* According to these facts crystallization starts abruptly upon reaching some critical concentration of products of AlO_2^- transformations in the liquid phase. The initial increase in the proton relaxation rate might be caused by an increase of viscosity due to aluminate dissolution and nucleation.

The line at 80 ppm in aluminium-27 NMR spectra does not change upon proton decoupling, the Overhauser effect being canceled by fast quadrupole relaxation of ^{27}Al nuclei while line broadening caused by ^{27}Al - ^{1}H interactions averaged to zero by fast molecular motion in liquid phase. In newly hydrated solid phase, dipole-dipole ^{27}Al - ^{1}H interactions cause an effective broadening of the ^{27}Al line. In a normal ^{27}Al spectrum without decoupling this line is not visible because of this linebroadening, Fig. 1c, lower spectrum. High power decoupling effectively suppresses aluminum - proton interactions and cancels dipole-dipole contribution to the ^{27}Al linewidth. Our experiments with decoupling power $P < 20$ W[2] produced only partial narrowing. The integral of such a partially narrowed line was dependent on decoupling power and could not be used to calculate the quantity of new solid phase.

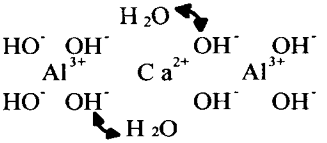
---

[2] In order not to get sample heated by the decoupling pulses.

By X-ray analysis and High Resolution in Solid State NMR (4,15) it was found that the primary crystallized products of C_4A_3S hydration were various forms of aluminum hydroxide (including e.g. boehmite). Some amount of hydroxides have to be present in solution at the moment when crystallization begins. As no new signal of Al species in solution appeared it may be concluded that aluminum preserves its tetrahedral coordination in the hydrolyzed form. Measured concentration is, therefore, a sum of concentration of aluminate ions and hydroxide:

$$[AlO_2^-] = [Al(OH)_4^-] + [Al(OH)_3]_{soln} \qquad (2)$$

The fact that in many cases the concentration of aluminate ions in solution reaches saturation, Fig. 2b, suggests, that formation of hydroxide in solution is reversible. Should the conversion of aluminate in solution into the hydroxides be irreversible this reaction should cause a constant redistribution of Al nuclei between the $Al(OH)_4^-$ and $Al(OH)_3$ species. The saturation of solution with respect to the aluminate ions would then be canceled and tetrahedral aluminum would be accumulated in the liquid phase at a permanently increasing rate[3] Reversible hydrolysis of calcium aluminate in solution may occur *via* proton transfer in structure:



(I)

There is also a possibility of such proton transfer occurring in the solid phase, the initial crystallization being of hydrated calcium aluminate (I). In this case experimental points were to be fitted to a simpler model using the solubility of the hydrated solid as an adjusting parameter to account for the residual concentrations of aluminates' in solution. The slow changes in proton relaxation rate occurring after the first (crystallization) step would be interpreted as reflecting transformations in the solid phase. But the mathematical model in this case will be much more over–parameterized (having too many adjustable parameters) than if reversible hydrolysis will be supposed to proceed in liquid state and assuming solubility of the solid product to be very small.

The hydration of the sample with Na_2O additive, Fig. 2a, proceeded differently from all other samples investigated: no saturation regarding AlO_2^- ions was reached and the maximum concentration achieved exceeded that of other samples by a factor 3 - 4. The form of the maximum is sharp with a singular point at the top Fig. 2a. These facts are easily explained by the much greater solubility of sodium aluminate in relation to calcium or other aluminates. The preferential dissolution of sodium aluminate was proved by ^{23}Na NMR spectra. At the earliest moment of hydration (t_h = 5 min) a strong signal was observed in ^{23}Na NMR spectra at 0 ppm (hydrated sodium ion) integral of which corresponded to ~0.1

---

[3] This was actually one of the first stumbling blocks in the fitting of the experimental data to a mathematical model: the theoretical curves showed increasing rate of accumulation of tetrahedral Al in liquid state.

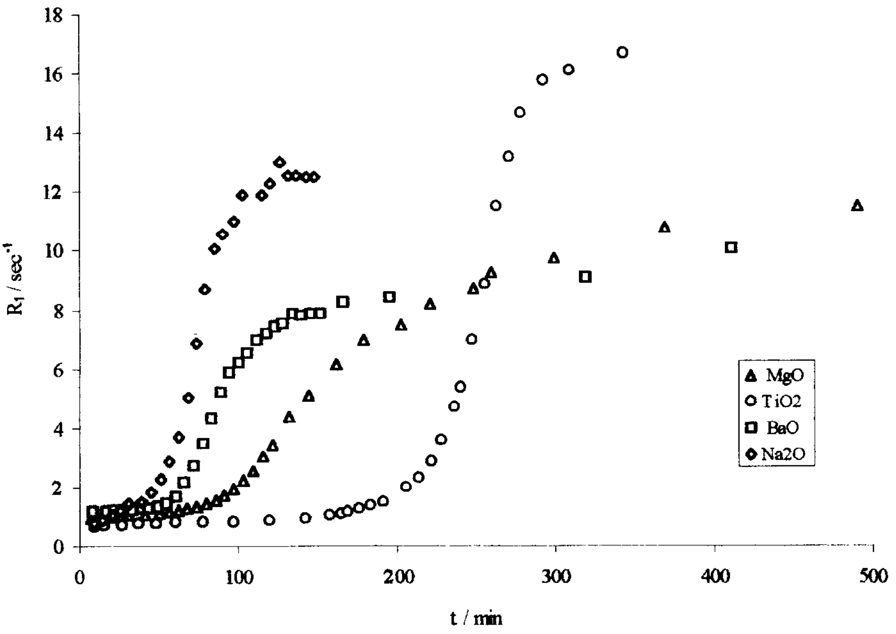
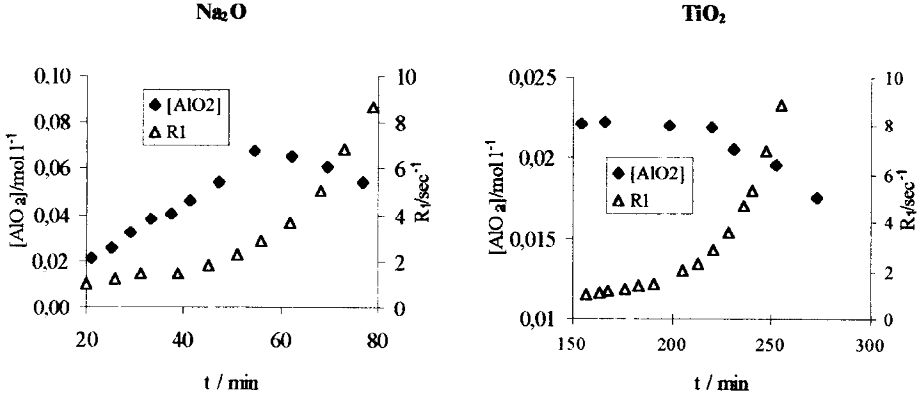


FIG. 3.
Dependecies of the mean proton magnetic longitudinal relaxation rate on hydration time.

mole/kg concentration, and which remained unaltered during further stages. This means that ~ 12% of all sodium added to the original solid phase was dissolved during first minutes of hydration. Since the solubility of sodium aluminate is very high the kinetics of aluminate ions accumulation was controlled in this sample by the surface reactions of formation of aluminates.

Other samples differ from each other not so much in concentration of dissolved aluminates as in duration of induction period. Addition of TiO_2 to C_4A_3S evidently retards dissolution of aluminate ions, which may be followed in detail by ^{27}Al NMR data, Fig 2b. In other


Na_2O

TiO_2

FIG. 4.
Comparison of changes in relaxation rates and AlO_2^- concentrations during initial hydration of Na_2O- and TiO_2-doped sulphoaluminates.

cases, the concentration of aluminate ions quickly reaches saturation at 0.02 - 0.015 mole/kg (Fig. 2b).

All curves [AlO_2^-] - t_h start not from zero concentration, but indicate some initial concentration of aluminate - as if present in solution at zero hydration time. It is caused by the non-stationary regime of the dissolution of solvable aluminate initially present on the surface. The dissolution rate was rapidly varying: during the first seconds it was limited by the fast diffusion of water to the surface were diffusional layer was being formed. After the diffusional layer was completed, the transfer of new portions of aluminate ions to the liquid phase was governed by the diffusion of bulky aluminate, which proceeded at a much lower rate.

The conclusions drawn during this qualitative description of the experimental data will be used to develop the physico - chemical mechanism of sulphoaluminates' hydration (17).

Acknowledgments

We thank Dr. Yu. Kriwoborodow and Dr. S. Sivkov who have synthesized samples and we acknowledge financial support from the concern "Tsementnik" under the grant # 219-H.

References

1. J.R. Barnes, A.D.H. Clague, N.J. Clayden. J. Mater. Sci. Lett., 4, 1293, (1985).
2. E. Lipmaa, M. Magi, M. Tarnak. Cem. Concr. Res. 12, 597, (1982).
3. D. Mueller, A. Rettel, W. Gessner and G. Scheler. J. Magn. Reson., 57, 152, (1984).
4. A.B. Kudryavtsev, T.V. Kouznetsova and A.V. Pyatkova. Cem. Concr. Res. 20, 407, (1990)
5. H. Peemoeller and M.M. Pintar. J. Magn. Reson., 41, 358, (1980).
6. J.C. MacTavish, L. Miljkovic, M.M. Pintar, R. Blinc and G Lahajnar. Cem. Concr. Res., 15, 367, (1985)
7. R. Blinc, M. Burgar, G. Lahajnar, M. Rozmarin, V.Rutar, I. Kocuvan, J. Ursic. J. Amer. Ceram. Soc., 61, 35 (1978).
8. R. Blinc, P. Merljak, I. Zupancic. J. Amer. Ceram. Soc., 65, 25 (1982).
9. G. Lahajnar, R. Blinc, V. Smolej, I. Zupancic, J. Ursic. Cem. Concr. Res., 7, 385, (1977)
10. V.I. Ermakow, A.B. Kudryavtsev and Ya.Sh. Shkolnik. Zh. Prikl. Khim., 50,1024 (1977).
11. B.M. Fung, W. Tim McGaughy. J. Magn. Reson., 43, 316, (1981)
12. A.B. Kudryavtsev, W. Linert and A.V. Pyatkova. Chem. Phys., 186, 53, (1994)
13. T.V. Kouznetsova, S.G. Bergunova. Trudy NII Tsement, v 45, 40, (1977).
14. H.J. Behrens, B. Schnabel. Physica, 114 B,185 (1982)
15. T.V. Kouznetsova, A.V. Pyatkowa, V.G. Akimov, A.B. Kudryavtsev. Trudy MKhTI, 137, 101(1987).
16. D. Mueller, D. Hoebbel and W. Gessner. Chem. Phys. Lett., 84, 25 (1981).
17. A.B. Kudryavtsev, T.V. Kouznetsova. Cem. Concr. Res. to be published.