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Solid state NMR investigations on the role of organic admixtures on the hydration of cement pastes

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Abstract

The influence of different inorganic additives and organic admixtures on the hydration and hardening of Portland cement (CEM I 42.5R) were studied on a nanometer scale by advanced solid state NMR methods. Added quartz was found to be partially attacked by the alkaline media of the cement paste. Even small amounts of organic admixtures strongly influence the hydration and crystallization process of the cement paste. Methyl cellulose, poly(vinyl acetate *co* vinyl alcohol), poly(ethylene oxide), poly(acrylic acid) and poly(acrylamide) modify the hydration of the calcium aluminum oxides. Major changes in the inorganic structure were detected for low amounts of citric acid and tartaric acid which suppress silicate condensation and strongly alter calcium aluminum oxide hydration. Within this study several solid state NMR methods like 1D magic angle spinning (MAS), 2D exchange and 2D double quantum NMR were applied for the detection of ^{1}H, ^{27}Al and ^{29}Si nuclei. Thus, cement pastes, inorganic additives and organic admixtures could be monitored individually. The findings on a molecular level as provided by NMR are related to changes in the mechanical properties of the cement pastes.

Keywords: Cement (D); Admixtures (D); Solid state NMR; Hydration; Hardening

1. Introduction

Various admixtures are used in cement and construction industry to modify the properties of fresh and of hardened and hydrated cement pastes. Even admixtures which are not expected to modify the properties of the concrete significantly can clearly alter the distribution of the hydration products. The influence of various admixtures on the final hydration products of Portland cement is studied in this work.

Portland cements commonly consist of the inorganic clinker phases calcium silicate (C_3S, C_2S), calcium aluminate (C_3A), and calcium aluminate ferrite ($C_2(A,F)$) [1–4]. Several components are added to the Portland cement, e.g. calcium sulfate, or to the raw material, e.g. Fe_2O_3 before clinkerization in order to optimize the processing window, to accelerate or retard setting, or to obtain improved mechanical stability. Accordingly, one focus in cement research is related to the mechanism of cement hydration and hardening [1–9]. When water is added to the cement powder, ettringite (“trisulfate”) is formed. The high water content of ettringite ($3CaO*Al_2O_3*3CaSO_4*32H_2O$) results in an enormous volume increase at the surface of the cement grains. When the cement paste runs poor in sulfate concentration, monosulfate ($3CaO*Al_2O_3*CaSO_4*12H_2O$) is formed by partially consuming the trisulfate. In addition to this process there is a slow reaction of the silicates within the C_3S and C_2S phases as well as the ferrites. In this way, an inorganic network of calcium silicate hydrates (CSH), calcium aluminum oxide hydrates (CAH), and calcium aluminate ferrite hydrates C(A,F)H is formed. Commonly admixtures in concrete can be classified with respect to their influence on the

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setting of cement [5–8]. Admixtures which *retard* setting or hardening include sucrose, glycosides, phosphates, lignosulfonates and fruit acids (typically citric acid, tartaric acid). Admixtures which *accelerate* setting or hardening include amorphous aluminum hydroxides, soluble silicates, aluminates, aluminum sulfates, formiates, carbonates, soluble chlorides and organic components like triethanol amine. In some cases the admixture's effectiveness in accelerating/retarding setting depends on the concentration of the admixture itself and on the counterions. Concrete *plasticizers* and *super plasticizers* include lignosulfonates, melamine sulfonates, naphthalene sulfonates, polycarboxylates (usually as sodium or alkali salts) and surfactants. Commonly used *stabilizers* include cellulose ethers and polysaccharides. Low amounts of cellulose ethers are added to bind water and to adjust viscosity, thereby stabilizing the freshly prepared cement paste. *Air entraining agents* include poly(ethylene oxide) (PEO) containing surfactants, sodium dodecyl sulfate, gum resins and root resins, while finally *waterproofing agents* consist of fatty acids and latex dispersions. The polymer latex, applied in tile mortars, acts additionally as an organic binder and promotes better adhesion to the substrate. The hydrated cement paste gains increased flexibility and hydrophobicity from the latex which fills the pores and seals the material. It is important to note that these admixtures might display secondary characteristics which this classification does not take into account. For instance, some of the plasticizing organic sulfonates and sulfates also act to retard setting. Our study addresses both the primary and secondary characteristics of various admixtures with respect to their influence on the hydration and hardening of cement pastes.

Depending on the interaction forces between organic components and cement minerals, both low molecular weight compounds and high molecular weight polymers can modify crystal structure and growth, even in small amounts [10–13]. This effect is caused by either adsorbing onto the growing inorganic surfaces or by binding aqueous ions into a complex. Adsorbed organic components alter ionic diffusion and crystal growth near the inorganic substrate or can act as nucleation agents.

Within this study solid state NMR [14–17] is applied for the analysis of the individual components, the fresh and the hardened cement pastes [18–24]. Several contributions to the hydration and hardening of cement pastes as determined by using ^{27}Al and ^{29}Si NMR methods are available in the literature [19–22,25–28]. Here, we extend these to organically modified systems to monitor the influence of the organic components on the cement paste at the molecular level. A major aim is to investigate if the organic admixtures influence the calcium aluminate and silicate network of the hydrated cement paste. In a companion study, tile mortar systems based on Portland cement, quartz, methyl cellulose and different latex admixtures were investigated by solid state NMR and low voltage scanning electron microscopy to probe the influence of the latex on the hydration, hardening and the final tile mortar properties [29].

2. Solid state NMR

Nuclear magnetic resonance (NMR) spectroscopy [14–17] is a selective method for characterizing the chemical structure, dynamics and orientation of moieties in both liquids and solids. In amorphous solids solid state NMR spectra are characteristically broadened. The line width of ^{1}H, ^{13}C, ^{27}Al and ^{29}Si spectra in solid state NMR can be reduced by spinning the sample at the magic angle (magic angle spinning, MAS) [17] where typical rotational frequencies are currently in the range of 2–35 kHz. If the spinning frequency is slower than the static inhomogeneous line width, additional resonances from spinning side bands [17, p. 132] can be found beside the isotropic center line in multiple distances of the spinning frequency. In the presence of paramagnetic components like iron oxides in cement relaxation is accelerated resulting in an additional line broadening of the resonance frequencies.

Due to the presence of various NMR active nuclei within the cement paste like ^{1}H, ^{27}Al or ^{29}Si the different interacting cement minerals, water, and organic admixtures can be analyzed separately. ^{1}H NMR can be used to monitor the hydration and hardening scheme above, which includes the fast hydration/hardening process, the water uptake and the effect of organic admixtures. Several one- and two-dimensional ^{1}H NMR methods are well established in the literature [15,17]. ^{27}Al NMR monitors the fast crystallization process due to the relatively high hydration reaction velocity of the calcium aluminate clinker phases. During hydration ^{27}Al NMR resonances appear or disappear at different hydration times. In accordance with the literature on cement hydration kinetics [1–9] and in combination with previous studies of synthetic calcium aluminate clinker minerals [19,20] correlation between the ^{27}Al NMR signals and defined crystal structures within the inorganic phase is given. Because of the inherent broad lines of the ^{27}Al quadrupole moment, resulting in an additional spectral broadening, one-dimensional NMR methods are predominant in the literature [15,19–23,25].

^{29}Si NMR of hardened cement pastes and quartz samples is limited by the long relaxation times ($T_1 > 20$ s) of the silicon atoms within the quartz and the hardened cement, requiring long measuring times. ^{29}Si NMR is sensitive to the slow silicate crystallization process during hydration and hardening.

Using two-dimensional NMR spectroscopy, local connectivities up to 0.5 nm can be analyzed by double quantum NMR methods as described elsewhere [30–33]. Using ^{1}H and ^{27}Al 2D exchange experiments [17,34,35], information about spatial proximities in a range of 2–200 nm can be obtained. The (off diagonal) exchange signals in the cement paste are generated by transfer of magnetization (spin diffusion) between the different components during a mixing time. The intensity of the exchange peaks as a function of this mixing time reflects the proximity of the different components (e.g. phase separation versus complete mixture).

3. Experimental part

3.1. Sample preparation

Several hydrated and hardened cement samples were prepared from Portland cement CEM I 42.5R. Its chemical composition is summarized in Table 1. The main Portland cement ingredients are calcium silicates, aluminum oxides and gypsum. For the NMR investigations several components were added to modify the paste, such as fine milled quartz, methyl cellulose, poly(vinyl alcohol *co* vinyl acetate), poly(acrylic acid), poly(ethylene oxide), poly(acrylamide), citric acid and tartaric acid. Methyl cellulose Walocel® MKX 40000 PF 01 from Wolff Walsrode was used. Samples of poly(vinyl alcohol) at a degree of 88 mol.% hydrolysis and $M_n = 25{,}000$ g/mol, of poly (acrylic acid) at $M_n = 4 \times 10^6$ g/mol and of poly(acrylamide) at $M_n = 5 \times 10^6$ g/mol were obtained from Polyscience, while two poly(ethylene oxides) at 600 and 35,000 g/mol were purchased from Fluka. Citric acid and L(+) tartaric acid were obtained from Aldrich. All chemicals were used as received.

Cement samples were carefully mixed for 10 min to achieve a sufficient homogeneity and stored in closed PE flasks. Hydrated and hardened cement pastes were obtained from these powder samples by adding distilled water to the admixtures, using a constant water cement ratio ($w/c = 0.838$), while stirring them carefully for several minutes. Applying this relatively high w/c ratio, the ettringite monosulfate resonances are even more obvious, while the effect of altering e.g. the ettringite monosulfate ratio upon addition of additives is unchanged as presented in a recent publication (see Ref. [29] below). The composition of the cement powder Cem1 and the hardened cement samples HCem1 to HCem10 are summarized in Table 2. Preparation and curing (hydration and hardening) were again performed in closed PE flasks to prevent water evaporation from the samples, carbonization by CO_2 from the air, or alkali contamination from glass. For hydration experiments, samples were stored at room temperature for a variable time. After specific hydration times (0–3 d, 28 d, ⩾1 month), the hardened cement pastes were milled at room temperature and investigated by different solid state NMR methods. Only in special cases like ^{27}Al NMR measurements of the short time kinetics, the wet samples were initially dried at room temperature in a dry air stream for 5 min before milling to prevent proceeding hydration and to avoid further changes in the spectra during the measurements. Generally, samples were milled to particle sizes of 1 mm to 100 μm.

Table 1
Chemical composition with respect to the elements (given as oxides) of the applied cement CEM I 42.5R

Component	Amount (wt.%)
CaO	64.03
SiO_2	20.13
Al_2O_3	6.00
MgO	3.24
Fe_2O_3	3.16
K_2O	0.68
SO_3[a]	3.5
CO_2[a]	1.31

[a] Sulfate, carbonate given as SO_3, CO_2.

3.2. NMR measurements

The ^{1}H, ^{27}Al and ^{29}Si NMR spectra were acquired using Bruker DSX 300, DSX 500 and DRX 700 spectrometers, operating at magnetic fields of 7.05, 11.74 and 16.44 T, respectively. All ^{1}H solid state NMR MAS spectra were measured using 2.5 mm rotors with a commercial double-resonance probe and spinning frequencies of up to 30 kHz at a temperature of 295 K. ^{27}Al NMR measurements were performed with 2.5 and 4 mm probes, ^{29}Si NMR with a 7 mm probe. The 2D (NOESY type) exchange experiments [34,35] ($90°_x - t_1 - 90°_{-x} - t_m - 90°_x$ acquisition—recycle delay) were performed in States TPPI mode (time proportional phase incrementation). Mixing times t_m of 10–200 ms were used to probe spatial proximity

Table 2
Composition of the cement powder and hydrated cement CEM I 42.5R samples

Sample	Cement (wt.%)	Quartz (wt.%)	Organic admixture	Amount of org. admixture (wt.%)	Water (wt.%)
Cem1	100				0
HCem1	100				83.85
HCem2	43.75	56.25			36.66
HCem3	43.73	56.23	Methyl cellulose	0.4	36.65
HCem4	43.73	56.23	Poly(vinyl alcohol *co* vinyl acetate)	0.4	36.65
HCem5	43.73	56.23	Tartaric acid	0.4	36.65
HCem6	43.73	56.23	Citric acid	0.4	36.65
HCem7	43.73	56.23	Poly(acrylic acid)	0.4	36.65
HCem8	43.73	56.23	Poly(acrylamide)	0.4	36.65
HCem9	43.73	56.23	PEO 6000	0.5	36.65
HCem10	43.73	56.23	PEO 35000	0.5	36.65

Hardened cement samples were adjusted to a constant cement water and admixture water ratio.

via spin diffusion or mass diffusion. ^{1}H 2D double quantum NMR spectra were measured, applying the technique of back to back 90 degree pulse cycles [30,31,33] to span one rotor period at 30 kHz MAS. The 90° pulse length of all ^{1}H measurements was 2.5 μs and the recycle delay 3–5 s. For ^{27}Al NMR measurements the 90° pulse length was 4 μs at a recycle delay time of 5 s, while all the ^{27}Al 1D single pulse NMR experiments were performed at a magnetic field of 11.74 T and 15 kHz MAS. A 90° pulse length of 5 μs at a delay of 60 s was applied for ^{29}Si NMR, which is sufficient for recording ^{29}Si NMR spectra but not for full quantitative measurements.

4. Results and discussion

4.1. Portland cement and quartz as additive

In order to compare the effect of quartz and different organic admixtures on the hydration and hardening of Portland cement, CEM I 42.5 R, Cem1, (Table 1) was analyzed initially as a control. Similar studies have already been reported [14,16,25–28] but had to be repeated here as they form the basis for detecting changes in hydration products due to the additives. In this way, ^{1}H NMR was performed to monitor the hydration of the cement and the immobilization of the water at low and high speed MAS to characterize proton mobility and distribution of H_2O or OH groups [14,16,18]. After 1 month of hydration and hardening of the cement paste only broad ^{1}H resonances indicating immobilization of the water are present at slow MAS.

The aluminum in the ^{27}Al NMR spectra of the cement powder is detected in both tetrahedral and octahedral co-ordination at a chemical shift of 80–90 ppm and at 0–20 ppm, respectively. The hydration of the calcium aluminum oxide clinker phases within Portland cement in the early age of hydration can be best understood from ^{27}Al NMR spectra as shown in Fig. 1. Within the Portland cement aluminum oxides and aluminate clinker phases are converted from tetrahedral to octahedral co-ordination [25]. After 1 h of hydration an intense, narrow signal at 13.2 ppm, corresponding to ettringite [19,20], arises in the ^{27}Al NMR spectra consuming both the initial narrow and the broad signal at 10 ppm. In addition to the increasing ettringite signal, additional contributions at 5 ppm of aluminate hydrates [20,40] can be detected. Calcium alumino silicates [20,23] contribute to both, the weak ^{27}Al NMR signal at 60–80 ppm and at -5 to 10 ppm. With respect to the spectral intensity, most of the aluminum is bound to the calcium aluminum oxide and calcium aluminate sulfate hydrate phases, not to the silicates. After 24 h of hydration the initial narrow signal at 10 ppm and most of the broad signal below, corresponding to the octahedral coordinated aluminum oxides, have vanished. The corresponding components are consumed and are converted to ettringite and aluminate hydrates. After 76 h of hydration, ^{27}Al NMR spectra are modified by a new resonance appearing at 9.8 ppm corresponding to monosulfate [20]/AFm. Additionally the remaining signals of the tetrahedral aluminum are shifted from 80–90 ppm to 70 ppm. Finally, after 2 months of hydration three signals of octahedral aluminum can be found within the ^{27}Al NMR spectra: ettringite, monosulfate and other aluminate hydrates. This is in accordance with the literature [1–3], as ettringite is initially formed during hydration of pure Portland cement followed by all the other phases.

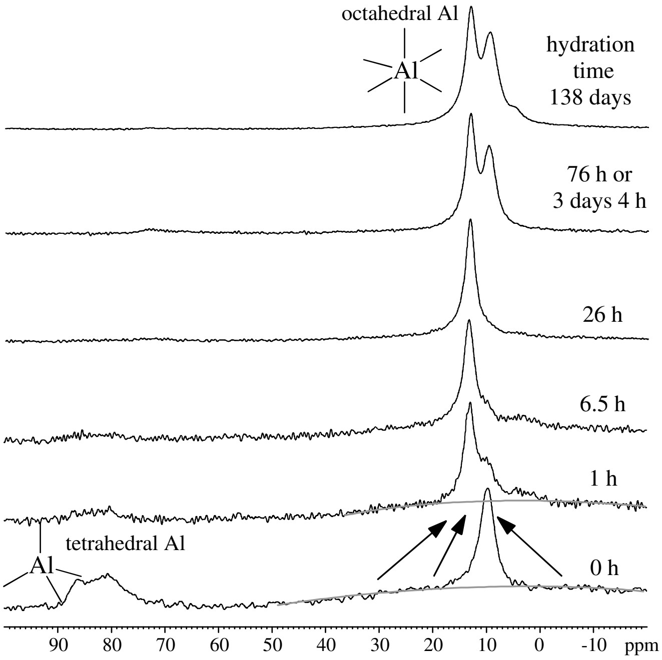

Fig. 1. ^{27}Al solid state NMR spectra of Cem1 and HCem1 before and after different hydration times measured at a resonance frequency of 130.31 MHz and at 15 kHz MAS.

The condensation of the silicate components [21,22] can be monitored by ^{29}Si NMR. Original Portland cement contains Q^0 groups in the initial CS phases (calcium silicate) without a network of Si–O–Si bonds within the silicates. During hydration and hardening to CSH phases (calcium silicate hydrates) additional Q^1 and Q^2 groups are formed. While Q^1 groups represent end groups within the silicate network, Q^2 groups indicate middle groups in silicate chains [15]. During the hydration and hardening of the Portland cement silicates undergo condensation.

To study the role of quartz, ^{29}Si NMR spectra of quartz, Portland cement and the hydrated and hardened cement pastes HCem1 and HCem2 with and without quartz are compared in Fig. 2. Only Q^0 groups at -71 ppm can be found within the Portland cement powder, and Q^4 groups at -108 ppm within the milled quartz. The most prominent, yet trivial observation is that in the ^{29}Si NMR spectra of HCem2 the signals of the quartz Si–O–Si network consisting of Q^4 groups are still detected. Moreover, a tiny amount of Q^3 groups at -90 ppm and less Q^0 groups at -71 ppm can be traced within the ^{29}Si NMR spectra of

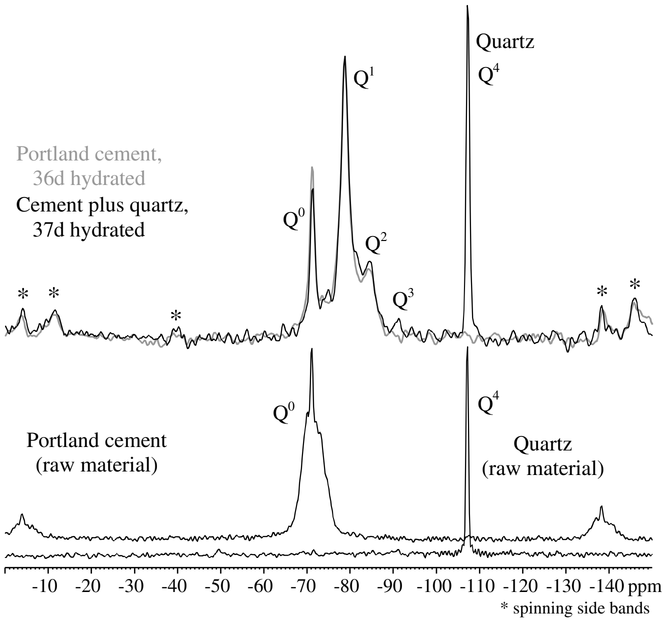

Fig. 2. ^{29}Si solid state NMR spectra of HCem1 and HCem2 with and without quartz after 36 days of hydration and hardening, measured at 4 kHz MAS.

HCem2. The Q^3 groups result from quartz, reacting with OH^- of the pore solution. These findings are in good accordance to previous results [36] on added silica fume [37] and metakaoline (amorphous $Al_2Si_2O_7$) [38].

4.2. Stabilizing admixtures in the cement paste

In general the cement paste is modified by organic admixtures to alter the performance of the paste, hydration and hardening. In this study the Portland cement quartz mixture was first modified with methyl cellulose and poly (vinyl alcohol *co* vinyl acetate). Both are commonly used as stabilizers to bind water to the freshly prepared cement paste. A ^{1}H NMR spectrum of HCem3 modified by 0.4 wt.% methyl cellulose measured at 30 kHz MAS after 1 month of hydration and hardening is given in Fig. 3. For comparison purposes the ^{1}H NMR spectrum of pure methyl cellulose and of unmodified cement HCem2 are depicted below. For low spinning speeds broad ^{1}H signals are observed in the spectra, as water is immobilized and bound to the cement matrix. Spectra at 30 kHz MAS speed with improved resolution as presented here show two main ^{1}H signals. The ^{1}H NMR signal at 1 ppm of HCem2 corresponds to OH groups like in $Ca(OH)_2$ [16,18], while the one at 4.7 ppm in HCem3 corresponds to strongly H bound H_2O within the oxide matrix (e.g. bound water of amorphous hydrates or crystals). No narrow signals of bulk methyl cellulose are found in the spectra of the hardened cement paste HCem3, indicating that methyl cellulose is immobilized by the inorganic matrix. By adding increased amounts (>2 wt.%) of the admixture to the cement paste, signals of the organic bulk material can be detected beside the immobilized methyl cellulose [39].

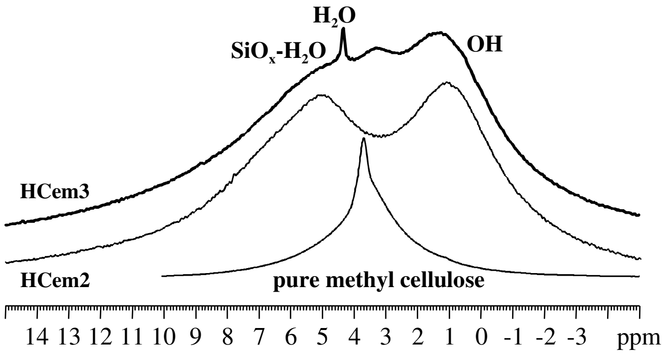

Fig. 3. ^{1}H solid state NMR spectra of cement mixtures after 1 month of hydration HCem3 including methyl cellulose, HCem2 without it and of pure methyl cellulose measured at 30 kHz MAS.

The close proximity of the organic admixture to the inorganic components can be demonstrated by 2D exchange NMR or by 2D double quantum NMR. In both cases proximities show up as off-diagonal signals in 2D spectra [17,30], yet the double quantum technique is better suited to detect short hydrogen–hydrogen distances of about 0.2–0.5 nm. The 2D double quantum spectrum of HCem3 is shown in Fig. 4. In addition to the dominant signals of ^{1}H incorporated in the inorganic components at 1 ppm, weak double quantum signals of the methyl cellulose with the inorganic components can be detected (see marked connectivity lines). Since the applied 2D double quantum NMR technique is more sensitive to rigid components, this indicates that the methyl cellulose is immobilized by adsorption onto the hardened cement or by incorporation into the inorganic matrix after hydration.

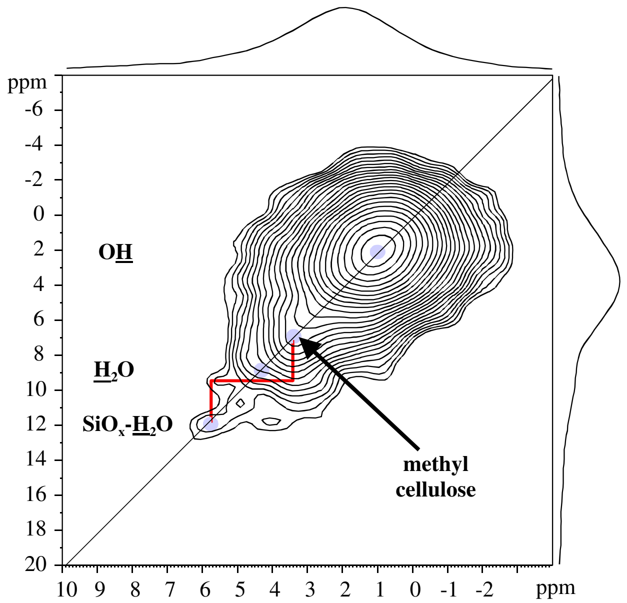

Fig. 4. ^{1}H 2D double quantum NMR spectrum of HCem3 after 1 month of hardening at 30 kHz MAS. The weak double quantum signals between the methyl cellulose and the H_2O incorporated in the silicate matrix are marked by connectivity lines [30,33].

During cement curing the cellulose ether is well known to stabilize water in cement pastes [6]. In addition to the stabilizing effect there is a weak effect of the organic admixture to modify the inorganic structure. This can be elucidated from the ^{27}Al NMR spectra. In Fig. 5, ^{27}Al NMR spectra of hardened cement pastes with (HCem3) and without (HCem2) methyl cellulose are shown after two month of hydration at a constant water cement ratio ($w/c = 0.838$). The cellulose ether modifies the Al distribution within the octahedral species of ettringite, monosulfate and other aluminate hydrates. As to be seen in ettringite, monosulfate, and other aluminate hydrates. As seen in Table 3, relatively more ettringite is formed if low amounts of the cellulose ethers are used. Without the admixture more intense resonances at 5 ppm, related to the third aluminate hydrate phase consisting of amorphous or disordered aluminate hydrates which contain e.g. $Al(OH)_6$ units [40], and at 9.8 ppm related to monosulfate/AFm are found in the spectra. Therefore, the formation of ettringite as one hydration product is preferred by applying a small amount of 0.4 wt.% of methyl cellulose as found in the ^{27}Al NMR spectra. All integral ratios of the three components summarized in Table 3 are determined by spectral deconvolution. Generally ^{27}Al NMR spectra show broad spectral patterns even under MAS due to second order quadrupolar interactions that cannot be averaged by the MAS technique. Here all components show a relative small line width in the ^{27}Al NMR MAS spectra. This allows integration by spectral deconvolution including an error of about 10%.

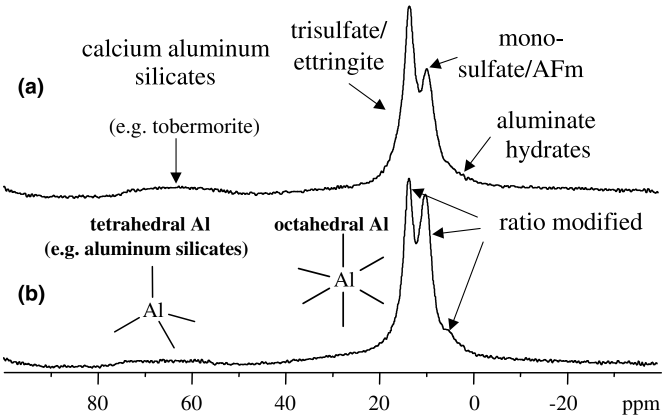

Fig. 5. ^{27}Al solid state NMR spectra of hardened cement pastes from (a) Portland cement, quartz, methyl cellulose and water (HCem3) and (b) without methyl cellulose (HCem2) after 2 month of hydration measured at 12 kHz MAS. The different aluminate hydrate phases corresponds to separate signals within the ^{27}Al spectra.

Complementary results are obtained from the ^{29}Si NMR spectra of HCem2 and HCem3 using the same water to cement ratio (spectra not presented). Comparing both spectra, a slight increase in Q^2 and Q^3 groups can be detected for HCem2. Therefore, the silicates of the cured sample without the cellulose ether show a higher degree of condensation.

Poly(vinyl alcohol *co* vinyl acetate) is commonly used as surfactant to protect colloid in emulsion polymerization of latex dispersions e.g. of vinyl acetate copolymers [41] and as additive in tile mortars. Poly(vinyl alcohol) at 88% hydrolysis acts as a surfactant and a viscosity modifier. Here the influence of the protecting colloid itself on the hydration and hardening of cement pastes was investigated. The close proximity of the organic admixture to the inorganic components can be probed by 2D exchange NMR spectra. In this spectrum by applying a mixing time of 100 ms, spatial proximities of molecules within a distance of about 10 nm are detected. In Fig. 6a, the ^{1}H 2D exchange spectrum of HCem4 including poly(vinyl alcohol *co* vinyl acetate) is shown. For comparison, the ^{1}H 2D exchange NMR spectrum of HCem2 is given in Fig. 6b. In addition to the dominant signals of the inorganic components demonstrating that H_2O and OH groups are close to each other, weak signals of the poly(vinyl alcohol *co* vinyl acetate) at 1.1 and 4 ppm and (off diagonal) exchange signals with the inorganic components can be detected. Therefore, the poly(vinyl alcohol *co* vinyl acetate) is adsorbed onto or incorporated into the hydrated and hardened cement paste.

While the influence of poly(vinyl alcohol *co* vinyl acetate) on the slow hydration of the calcium silicate phases is weak as detected by ^{29}Si NMR spectra (data not shown),

Table 3
Integrals of the octahedral coordinated aluminum components as determined by spectral deconvolution of the ^{27}Al NMR spectra of the hardened cement samples HCem2 to HCem10

Sample	Organic admixtures	Hydration time	13.2 ppm	9.8 ppm	5 ppm	Figure
HCem2	–	2 month	1.00	0.89	0.07	5
HCem2	–	64 days	1.00	0.87	0.09	–
HCem3	Methyl cellulose	2 month	1.00	0.68	0.06	5
HCem4	P(VA *co* VAc)	67 days	1.00	0.68	0.18	–
HCem5	Tartaric acid	64 days	1.00	0.28	0.11	–
HCem6	Citric acid	64 days	1.00	$\leqslant$0.05	0.20	–
HCem7	Poly(acrylic acid)	64 days	1.00	0.83	0.07	–
HCem8	Poly(acrylamide)	66 days	1.00	0.80	0.02	–
HCem9	PEO 6000	61 days	1.00	0.77	0.10	–
HCem10	PEO 35000	61 days	1.00	0.78	0.05	–

The integrals of monosulfate at 9.8 ppm and of the other aluminate hydrate phases at 5 ppm were referenced to the ettringite signal at 13.2 ppm (at error bars of about 10%).

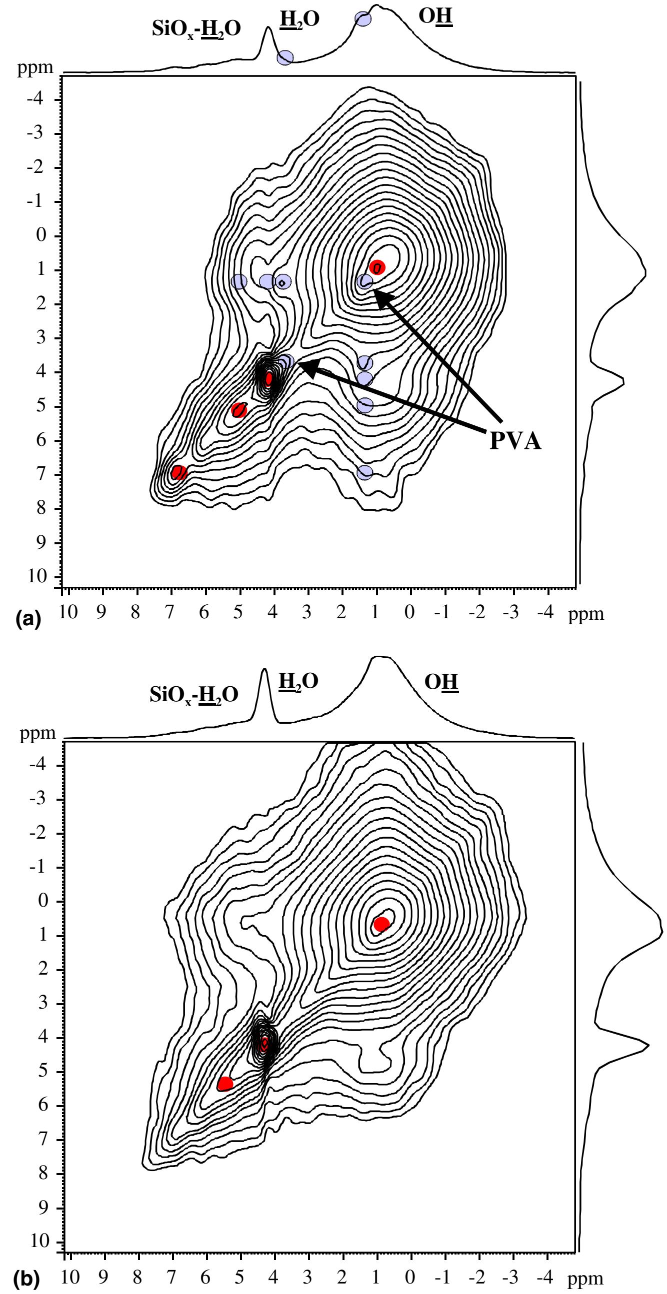

Fig. 6. ^{1}H 2D exchange NMR spectra of hardened cement pastes (a) with 0.4 wt.% poly(vinyl alcohol *co* vinyl acetate) (HCem4) and (b) of HCem2 after 1 month of hydration at 30 kHz MAS frequency, applying a mixing time of 100 ms.

its' influence on the calcium aluminum oxide hydrate phases is still quite strong and can be detected via ^{27}Al NMR spectra. ^{27}Al NMR spectra of hardened cement pastes with (HCem4) and without (HCem2) poly(vinyl alcohol *co* vinyl acetate) were taken after 2 months of hydration. In a similar way as for methyl cellulose the signal intensity of the various components is changed within the ^{27}Al NMR spectra. The integral ratios of the octahedral aluminate components are summarized in Table 3. Poly(vinyl alcohol *co* vinyl acetate) has an effect on the Al distribution within the octahedral aluminum species of the calcium aluminate sulfate hydrate phases in a similar way as methyl cellulose resulting in a higher relative amount of ettringite within the hydration products.

4.3. Fruit acids as retarders

While the above investigated admixtures act as stabilizers, citric acid and tartaric acid are well known to retard setting of cement pastes [6, p. 23]. In order to probe the influence of these retarding admixtures on the curing of the inorganic structure, cement samples HCem5 and HCem6 were prepared as described above by adding 0.4 wt.% of these organic acids. Macroscopically, it could be observed that hardening was retarded and pastes remained viscous for several days. Even after 38/49 days of hydration samples contained excessive bulk water beside the hardened cement. Therefore, the water uptake was reduced. In the ^{29}Si NMR spectra (Fig. 7), no condensation of the silicates to Q^1 and Q^2 groups within the CSH phases can be detected if citric or tartaric acid are added to the cement paste. But cement hydration and hardening is not completely suppressed, as seen in the ^{27}Al NMR spectra, which are sensitive to the calcium aluminum oxide hydrate (CAH) phases. Within the ^{27}Al NMR spectra the signal ratios of the different CAH phases have changed (Table 3). Thus, in presence of the natural organic acids the formation of ettringite is dominant while that of monosulfate is suppressed, especially in the presence of citric acid to a ratio of 20:1. Due to the strong interaction of these additives with the calcium ions of the cement no NMR signals of the fruit acids were detected at 0.4 wt.% dosage in ^{1}H fast MAS NMR signals. Therefore, both acids are immobilized by the hardened cement matrix after hydration by adsorption to the surface of the cement grains or by the incorporation into the hydrated cement matrix. The cement hydration is strongly influenced even by small amounts of admixtures.

Before additional ^{1}H NMR measurements were performed the bulk water was removed from the samples by mild drying as described above. Differences can also be detected in the ^{1}H NMR spectra of HCem5 and HCem6 (Fig. 8). Spectra are compared with the spectrum of HCem2 without these low molecular weight acids. Here, ^{1}H slow MAS NMR spectra are presented, which show less sensitivity to the chemical composition but monitor the mobility of the protons. The reduced ^{1}H NMR signal intensity of HCem5 and HCem6 are due to the fact that less water is bound to the inorganic matrix. Additionally, the hydration products are more homogeneous with respect to proton mobility. In all cases, broad resonances are detected, due to water/protons being strongly adsorbed to the hardened cement paste. In addition to this the ^{1}H NMR spectrum of hydrated and hardened cement without admixtures (Fig. 8) contains components with intensive spinning side bands, indicating increased mobility [17, p. 132]. As a consequence these hydration products dominate in the presence of 0.4 wt.% fruit acids, where water is strongly bound to the hydrated cement matrix.

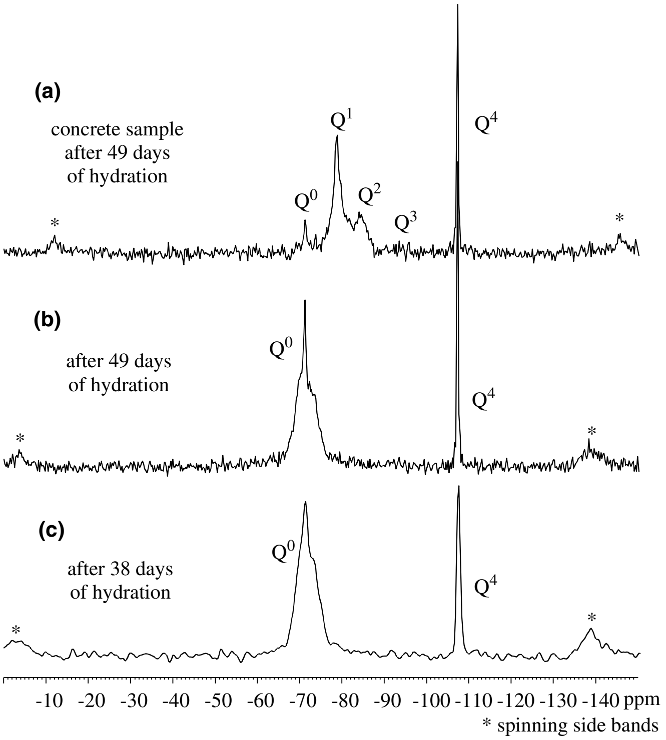

Fig. 7. ^{29}Si MAS NMR spectra of hydrated cement pastes (a) without organic admixtures (HCem2), (b) with 0.4 wt.% tartaric acid (HCem5) and (c) with 0.4 wt.% citric acid (HCem6) at a constant water cement ratio after hardening measured at 4 kHz spinning frequency.

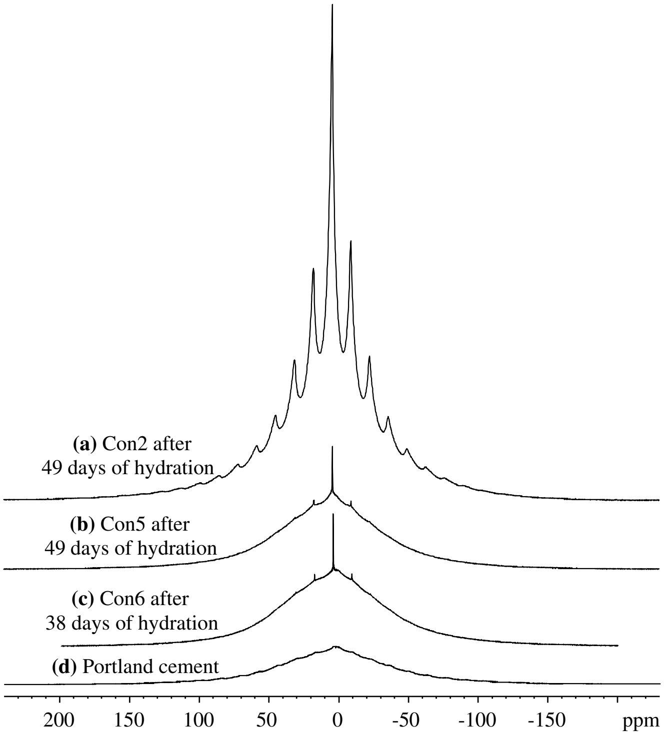

Fig. 8. ^{1}H solid state NMR spectra of hardened cement pastes from Portland cement, quartz and water (a) without admixtures (HCem2), (b) with 0.4 wt.% tartaric acid (HCem5), (c) with 0.4 wt.% citric acid (HCem6) after and (d) of Cem1 before hydration measured at 4 kHz MAS. Excessive bulk water was removed from HCem5 and HCem6 by drying before NMR spectra were taken.

4.4. Other polymers as cement admixtures

For comparison poly(acrylic acid) and poly(acrylamide) were used as admixtures with similar interacting groups as the fruit acids but of higher molecular weight. While poly (acrylic acid) was used as a gel to the cement powder, poly(acrylamide) was used as a solution, both containing the complete amount of water (Table 2). Macroscopically, both admixtures have a strong influence on the mechanical properties of the freshly prepared cement paste (thickening/stabilizing). In contrast to the mechanical properties there is only a weak influence on the ^{1}H and ^{29}Si spectra of the final hardened cement paste. In the ^{27}Al NMR spectra, small differences in the signal ratio can be found, indicating a 10% reduction of monosulfate and aluminate hydrates formation if the polymers were used. Integral ratios are summarized in Table 3. The strong interactions especially between the poly(acrylic acid) gel and the cement are expected to be similar to those of the citric and tartaric acid. But the influence on the final spectra of the cured cement pastes and therefore to the inorganic structure is much reduced. Due to the high molecular weight of the polymers the stabilizing effect dominates versus adsorption and modification of crystal growth.

In cement industry poly(ethylene oxide) PEO is commonly used within PEO containing surfactants as an air-entraining agent and in polycarboxylates having PEO side chains as super plasticizer. Air-entraining agents increase the resistance of the hardened cement towards freeze/thawing cycles and road salt. Like superplasticizers, the flexible PEO side chains provide flexibility to the hardening cement. Here, two different PEO samples were used as admixtures, a liquid-like PEO at a molecular weight of 6000 g/mol and a waxy one of 35,000 g/mol. In the ^{29}Si NMR spectra (data not presented here), a slightly reduced condensation of the silicates can be observed for the organically modified systems after 2 months of hydration. The ^{27}Al NMR spectra show weak changes of the Al distribution (signal ratio) of the different calcium aluminate sulfate hydrate phases. As seen from the integral ratios of the different components given in Table 3, 10% less monosulfate/AFm is formed during hydration if PEO is added to the cement powder. Again only minor differences can be found in fast (30 kHz) MAS ^{1}H NMR spectra, probing structure, but spectra clearly change if slow (4 kHz) MAS is applied, which probes mobility. In the ^{1}H NMR spectra (Fig. 9), the ^{1}H intensity distribution between the different dynamic regimes of the hydrated and hardened cement samples is changed by PEO addition. Spectra with intensive spinning side bands indicate increased mobility: The addition of PEO results in an increased amount of less rigid bound water in the cured cement matrix. Two main signals can be detected (see expanded region), a narrow one at 3.5 ppm originating from the PEO and a dominating broad one at 4.8 ppm caused by immobilized water of higher mobility. The influence of the pure PEO on the hydration and hardening of the cement pastes is similar to that of

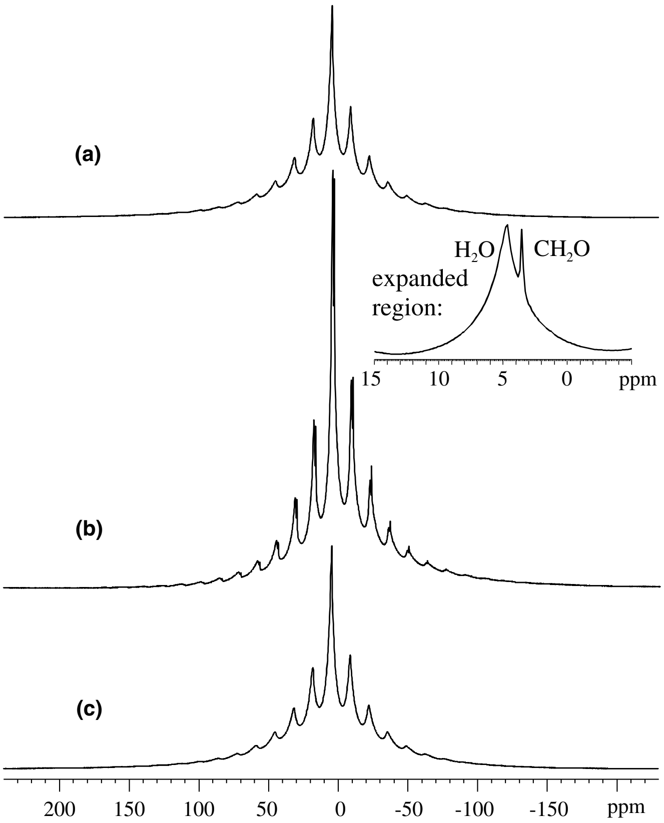

Fig. 9. ^1H solid state NMR spectra of hardened cement quartz pastes (a) without admixtures (HCem2), (b) with 0.5 wt.% PEO at 35,000 g/mol (HCem10) and (c) with 0.4 wt.% poly(acrylic acid) (HCem7) after 2 month of hydration at 4 kHz MAS.

the stabilizers methyl cellulose and poly(vinyl alcohol) but additionally the hardened inorganic matrix is partially mobilized.

5. Conclusion

Solid state NMR is an advanced tool to determine both the inorganic structure within mortar systems and the influence of inorganic and organic admixtures on its hydration process. In this work it is applied in a qualitative but fundamental way to determine the influence of different additives on the hydration and hardening process of Portland cement. Addition of quartz to the cement paste results in a reduced amount of Q^0 groups and increased amounts of Q^2 and Q^3 groups within the hardened cement. During the condensation/hydration of the cement the inorganic filler quartz made of Q^4 groups is partially sallied by the pore solution and is integrated into the concrete network.

In the final hydrated and hardened cement paste, organic admixtures at a dosage of less than 0.5 wt.% were found to be immobilized and therefore to be adsorbed to or incorporated into the inorganic components. Methyl cellulose, a well known stabilizing admixture, alters the distribution of the crystallization products as detected by ^{27}Al NMR. Even by adding small amounts of methyl cellulose, the ratio of ettringite to monosulfate and other aluminate hydrates within the cured cement samples is increased. Therefore, methyl cellulose modifies hydration. Additionally the condensation of the silicates is reduced, resulting in less Q^2 and Q^3 groups.

Poly(vinyl alcohol *co* vinyl acetate) at 88% hydrolysis is commonly applied as stabilizing admixture and protecting colloid, especially in latex modified tile mortars. The influence of the pure poly(vinyl alcohol *co* vinyl acetate) admixture on the NMR spectra of the hardened cement paste is weaker but similar to methyl cellulose. Again less monosulfate and other aluminate hydrates and more ettringite are formed, if 0.4 wt.% of the admixture is used.

Spectra are clearly changed if citric or tartaric acids are added as admixtures to the cement paste even in small amounts. Both low molecular weight carboxylic acids are well known to mechanically retard cement hydration and hardening. The mechanical retarding effect is reflected in the NMR spectra. There is less water, in the final cured cement paste but strongly bound to the inorganic matrix, as detected by ^1H NMR. Hydration proceeds selective as seen in the ^{27}Al NMR spectra. The signal of ettringite dominates, only small amounts of monosulfate and other aluminum oxide hydrates were found. The condensation of the silicates seems to be completely suppressed as detected by ^{29}Si NMR. Therefore, setting retarding by fruit acids on a macroscopic level effects a modified (reduced) hydration as manifested in a suppressed silicate condensation and a dominant ettringite formation.

The role of organic admixtures modifying hydration and hardening was found to depend strongly on the molecular weight. If poly(acrylic acid) or poly(acrylamide) of high molecular weight are added in solution or as an aqueous gel to the cement, comparable interactions between the organic admixtures and the cement especially for the poly (acrylic acid) are expected. Both polymers were found to have a strong influence on the mechanical properties of the cement paste as thickener and stabilizer, but there is only a weak influence on the ^1H and ^{29}Si NMR spectra. By analogy, to the role of the stabilizing agents above, more ettringite and less other hydration products can be found within the ^{27}Al NMR spectra of the cured cement pastes.

Poly(ethylene oxides) are commonly used in an air-entraining and plasticizing agents. The influence of the pure PEO on the ^{27}Al and ^{29}Si NMR spectra of hardened and hydrated cement is comparable to that of the stabilizing agents. In addition to the stabilizing effect a large amount of bound water is mobilized in the PEO/hardened cement interface as detected by ^1H NMR spectroscopy.

In the final hardened cement, the ^{27}Al NMR integral ratio of monosulfate to ettringite drops from 0.85–0.9 to about 0.7–0.75 for all the above listed stabilizing polymers used at 0.4–0.5 wt.%. This integral ratio decreases to 0.3 or even below if small amounts of the retarders are applied. The above presented studies allow a fast analysis of the cement paste samples. Such studies are important with respect to the enormous number of additives and organic admixtures as well as their concentration.

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