

# 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 <sup>1</sup>H, <sup>27</sup>Al and <sup>29</sup>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. © 2005 Elsevier Ltd. All rights reserved.

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## 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<sub>3</sub>S, C<sub>2</sub>S), calcium aluminate (C<sub>3</sub>A), and calcium aluminate ferrite (C<sub>2</sub>(A,F)) [1–4].

Several components are added to the Portland cement, e.g. calcium sulfate, or to the raw material, e.g. Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub>\*3CaSO<sub>4</sub>\*32H<sub>2</sub>O) 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<sub>2</sub>O<sub>3</sub>\*CaSO<sub>4</sub>\*12H<sub>2</sub>O) is formed by partially consuming the trisulfate. In addition to this process there is a slow reaction of the silicates within the C<sub>3</sub>S and C<sub>2</sub>S 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, ligno-sulfonates 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 rosin 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  $^{27}\text{Al}$  and  $^{29}\text{Si}$  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  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  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  $^1\text{H}$ ,  $^{27}\text{Al}$  or  $^{29}\text{Si}$  the different interacting cement minerals, water, and organic admixtures can be analyzed separately.  $^1\text{H}$  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  $^1\text{H}$  NMR methods are well established in the literature [15,17].  $^{27}\text{Al}$  NMR monitors the fast crystallization process due to the relatively high hydration reaction velocity of the calcium aluminate clinker phases. During hydration  $^{27}\text{Al}$  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  $^{27}\text{Al}$  NMR signals and defined crystal structures within the inorganic phase is given. Because of the inherent broad lines of the  $^{27}\text{Al}$  quadrupole moment, resulting in an additional spectral broadening, one-dimensional NMR methods are predominant in the literature [15,19–23,25].

$^{29}\text{Si}$  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.  $^{29}\text{Si}$  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  $^1\text{H}$  and  $^{27}\text{Al}$  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).

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