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A solid state NMR and *in-situ* infrared spectroscopy study on the setting reaction of magnesium sodium phosphate cement

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A B S T R A C T

In the present work, the setting reaction of magnesium sodium phosphate cement was followed in time with *in-situ* attenuated total reflectance Fourier-transform infrared spectroscopy and solid state nuclear magnetic resonance spectroscopy, in order to gain insights into the products and phase transformations. The results indicated that, during the progress of the reaction, amorphous phases containing the $H_2PO_4^-$ structural group converted into phases containing HPO_4^{2-} and finally PO_4^{3-}. The increase in pH triggered by the MgO dissolution was considered as the driving force for the transformations. This is supposed to promote the establishment of a high degree of supersaturation close to the surface of MgO grains, resulting in kinetically driven transformations and favouring the amorphous nature of the products. It is suggested that in the later stages of the reaction, two orthophosphate amorphous phases, hosting bound water molecules, coexisted, with the one showing a relatively more ordered ^{31}P local environment, converting into a second with a more disordered phosphorous environment. The densification of the ceramic can be considered as a structural reorganization encompassing bonding of water molecules into a pervasive amorphous phase, containing magnesium-phosphate structural units and involving limited structural rearrangements of the local environment of P and, especially, of Na.

1. Introduction

Magnesium phosphate cements (MPCs) are a class of chemically-bonded ceramics forming through an acid-base reaction between magnesium oxide and phosphoric acid, or an acid phosphate, which proceeds at ambient temperature and results in rapid setting of the final product [1]. The properties of the cement depend on the reactivity of MgO powder, which decreases with increasing the calcination temperature of magnesium carbonate from which is produced [2], and the solubility of the phosphate-bearing compound [1]. Ammonium or potassium dihydrogen phosphate salts are among the most commonly employed acid components in the formulation of MPCs; the final product contains crystalline struvite ($NH_4MgPO_4{\cdot}6H_2O$) or the potassium analogue, struvite-K ($MgKPO_4{\cdot}6H_2O$), respectively, and a variable amount of an amorphous or disordered phase [3]. When sodium dihydrogen phosphate (NaH_2PO_4) is used instead, the resulting cement is completely amorphous [4, 5].

Magnesium sodium phosphate (MNP) cements have been found attractive for biomedical applications, a recent and active field of research. Examples include MNP dental cements showing good injectability, mechanical and antibacterial properties [4, 6, 7], and a novel cement for bone regeneration and repair applications [8]. Partial substitution of potassium dihydrogen phosphate with disodium hydrogen phosphate has been also reported to bring benefits in a cement for civil engineering applications [9].

All these studies were focused on the properties of the final material and on the possibilities of tuning them by changing its composition. However, cement formulation remains mostly empirical, because basic knowledge of the nature of the reaction products and of the processes driving the transformations during setting, is lacking. As for other acid-base cements, the first step of the MNP setting reaction is the dissolution of the acid phosphate in water. This lowers the pH of the solution to a value around 4.3 [3], and under these conditions MgO starts to dissolve. The released Mg^{2+} ions form aqueous metal complexes, which eventually condense into a gel by reaction with the phosphate anions [2]. During this process the pH gradually rises. After the first minutes, with the onset of a diffusion limited mechanism [10], MgO grains dissolve very slowly [1]. Therefore, it is advisable to work in excess MgO in order to ensure complete reaction of the phosphate salt [4, 11].

It has been proposed that, in MPCs, the nature of the reaction

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products is influenced by the equilibria between the four protonated forms of phosphoric acid stable at different pH values [1, 12, 13]: H_3PO_4 (pH 0–4), $H_2PO_4{}^-$ (pH 0–9), $HPO_4{}^{2-}$ (pH 4–14), and $PO_4{}^{3-}$ (pH 9–14) [14, 15]. However, experimental evidences in this direction are scarce, also because investigations have been hampered by the fast reaction rates and the amorphous nature of the products. In fact, owing to the high degree of supersaturation attained in proximity of the MgO grains and the fast decrease in ion mobility during the densification of the ceramic, the transformations largely occur far from equilibrium. It follows that they are dominated by kinetic parameters [16], a condition which favours the formation of amorphous products [17].

Solid state nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the study of disordered materials, where classical diffraction techniques are silent, because of its ability to provide information about the local structure at an atomic level. Solids can be characterized on the basis of changes in chemical shift and distinct resonances in NMR spectra, which arise as a consequence of significant variations in the local environment around individual nuclei. In the present study, ^1H, ^{23}Na and ^{31}P solid state magic-angle spinning (MAS) NMR techniques have been employed to investigate a MNP cement at different times during the setting reaction. Since in a disordered material the spectrum is the sum of the signals from every single environment, a broadening of the spectral features is often obtained, complicating the analysis, and sometimes preventing from applying more sophisticated NMR techniques [18]. In this respect, complementary study with Fourier-transform infrared spectroscopy (FTIR) may help in the interpretation of the results obtained with NMR.

FTIR is capable of identifying the functional groups in amorphous materials, although also limited by broadening and band overlap. Its combination with the attenuated total reflectance (ATR) technique allows for the investigation of solid and liquid samples without any prior sample preparation, making it ideally suitable for time-resolved experiments of cement setting reactions [19, 20]. The sample is placed on the ATR crystal recording the spectra in short time intervals (from ms to s) regardless of the changes in the state of the sample during the hardening process. To gain insights into the reaction mechanisms, especially during the first minutes, the reaction was therefore studied *in-situ* with ATR-FTIR spectroscopy, further supported by two dimensional (2-D) correlation spectroscopy [21]. The evolution of the state of water in the sample has been also investigated by simultaneous thermogravimetric analysis (TGA).

2. Materials and methods

2.1. MNP cement preparation

Pharmaceutical grade $MgCO_3$ (42% wt% MgO) and reagent grade $NaH_2PO_4{\cdot}H_2O$ (NDP) (Sigma-Aldrich Co.) were used as raw materials. Magnesium carbonate was calcined for 40 min in a laboratory furnace at 1500 °C to produce MgO. The obtained powder was milled for 2 min in a Mini-Mill Pulverisette 23 (Fritch) at 30 oscillations/min, resulting in a powder with BET surface area of 4.5 m^2/g and mean particle size (d_{50}) of 3.9 μm. Full characterization of MgO powder is reported elsewhere [22].

MNP cement was prepared by hand-mixing 100 mg of MgO with 195.65 mg of $NaH_2PO_4{\cdot}H_2O$ in an agate mortar, corresponding to MgO:NDP molar ratio of 7:4. Then, 127.71 mg of distilled water were added to the powder to attain a water-to-solid weight ratio of 0.432, and mixed by hand for 30 s. A drop from the freshly prepared MNP slurry was used for the *in-situ* ATR-FTIR experiment. Three batches were prepared to be employed in *ex-situ* ATR-FTIR, solid state NMR and TGA experiments, respectively. In this case the slurries were casted in the form of discs about 5 mm thick and 12 mm in diameter (three samples) and kept sealed in plastic bags at room temperature to be ground in agate mortar prior to measurements.

2.2. Experimental techniques

In-situ ATR-FTIR spectroscopy measurements were performed at room temperature using an external module iZ10 of Nicolet iN10 spectrometer equipped with a DTGS detector, KBr beamsplitter and smart ATR accessory with diamond crystal. The spectra were collected at 4 cm^{-1} resolution in the range 4000–650 cm^{-1}.

Three different experiments were performed. An *in-situ* experiment was implemented by putting a drop of the freshly prepared MNP cement slurry in direct contact with the diamond crystal, while starting the data collection by a macro program. One scan for each spectrum was collected (collection time 1.18 s) and typical loop lasted about 2.5 s. The experiment started 40 s after mixing and ended after 1000 s. In addition, the ground MNP cement samples were measured *ex-situ* with ATR, recording 64 scans, at times 30, 60, 150, 300 and 1440 min after mixing, as well as after 3, 7 and 28 days. In a further experiment, aimed at obtaining the reference spectra of the three forms of phosphoric acid under similar experimental conditions employed for MNP, the pH of a 3 M solution of NDP was adjusted by adding a 10 M NaOH solution. The spectra were collected from a drop of solution deposited on top of the ATR diamond crystal, recording 64 scans. The FTIR spectra of the phosphate ions were collected at pH values 4.0, 9.0 and 12.4 for $H_2PO_4{}^-$, $HPO_4{}^{2-}$ and $PO_4{}^{3-}$, respectively [14, 15]. All FTIR spectra were baseline corrected using airPLS algorithm [23], adopting the same parameters for all. 2-D correlation plots were calculated using the software 2D Shige (Shigeaki Morita, Kwansei-Gakuin University, Nishinomiya, Japan).

NMR experiments were conducted with a Bruker Avance III 400 WB NMR spectrometer (magnetic field of 9.4 T), using a 4-mm CP/MAS probe at the Larmor frequencies for ^1H, ^{31}P and ^{23}Na nuclei, of 400.23 MHz, 162.02 MHz and 105.87 MHz, respectively. Ground MNP samples were loaded into a zirconium oxide rotor of 4 mm in diameter spinning at 12.5 kHz. Liquid tetramethylsilane, 85% H_3PO_4 in H_2O and 0.1 M NaCl in H_2O were used as external references for ^1H, ^{31}P and ^{23}Na, respectively. One-pulse ^1H, ^{31}P and ^{23}Na MAS NMR spectra were acquired at 20 °C recording 4, 64 and 128 scans with 1.5 μs, 1.6 μs and 1 μs pulse length and 10 s, 2 s and 1 s relaxation delay, respectively. Short delay times between the excitation cycles were used, in order to obtain in a short time sufficiently good signals with high signal-to-noise ratio, given that the rate of structural changes in the cement is quite high and the relaxation time T1 is quite long, especially in the case of ^{31}P nuclei (Supplementary material Fig. S1). The experiments were performed at 30, 60, 150, 300 and 1440 min after mixing, as well as 9 and 14 months after cement preparation. In addition, NMR spectra were collected for NDP to be used as reference spectrum.

Component deconvolution of ATR-FTIR and solid state NMR spectra was accomplished with PeakFit software version 4.12 (SeaSolve Software Inc.).

TGA was performed with a BÄHR Thermoanalyse STA 504 instrument, in the temperature range 30–750 °C, at heating rate of 20 °C/min and N_2 gas flow. The measurements were performed on finely ground MNP samples placed in alumina crucible at 60, 150, 300 and 1440 min after mixing.

3. Results

3.1. ATR-FTIR experiments

Fig. 1 illustrates the time-evolution of the collected ATR-FTIR spectra of the MNP sample. Only 3 times (40 s, 1000 s and 24 h) are displayed for sake of clarity. The ATR-FTIR technique, is, in principle, well-suited for the description of the hydrogen bonding state of structural water molecules, in order to understand the role of water in complex systems [24], being less affected by IR oversensitivity to hydrogen bond formation. To this aim, the analysis of the O − H stretching region (3700–2600 cm^{-1}), ν(OH), and H_2O bending