

ALUMINOSILICATE NETWORK FORMATION DURING GEOPOLYMERIZATION FOLLOWED BY IN-SITU ²⁷Al NUTATION NMR

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In classical cement systems, hydration reactions can typically be stopped by a solvent exchange (such as isopropanol) or by drying¹. Subsequently, the chemical reactions are studied by separating and characterizing independently the solid and the liquid phases at different times, to follow their respective compositions and to establish a reaction process by finding chemical intermediates and products. As for geopolymers, they are formed by a dissolution-condensation mechanism resulting from the mixing a solid aluminosilicate source (for example metakaolin) with a highly concentrated alkali-silicate solution. The properties of the suspension do not allow to employ phase separation. This is the reason why the reaction mechanism leading to geopolymers is still said to be unclear, because it has only been studied by indirect methods so far, such as calorimetry, time-resolved rheology or small-angle scattering² for instance.

In-situ static ²⁷Al NMR has already been used as a direct method to probe and quantify the aluminate species in the liquid phase during geopolymerization, using the quadrupolar nature of ²⁷Al nuclei. Aluminum is not present in the liquid state at the very beginning of the process but goes to the initial aluminosilicate powder to the final solid product, naturally making it the nucleus of interest for an NMR study. While dissolved species are mobile enough for the quadrupolar interaction to be averaged, the quadrupolar coupling persists in less mobile species or in solids, leading to different nutation behaviors.

In the present study, it will be demonstrated that a nutation experiment, which simply consists in varying the pulse length and measuring the resulting signal, allows filtering out the reactant aluminosilicate source from the ²⁷Al NMR signal to detect reaction intermediates, and apparently also products. The evolution of the ²⁷Al NMR signal was followed over longer periods of time up to several days during the geopolymerization process of metakaolin-based systems. It was shown that more than two steps can be identified in the geopolymerization process, depending on the frequency of the radiofrequency field applied during the experiment. Simulation of nutation curves at different times of the reactions allowed to follow the evolution of the quadrupolar coupling constant, and gave insight on the aluminate intermediates. Finally, the NMR results were confronted to time-resolved rheology and isothermal calorimetry in order to understand processes occurring on different time scales.

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