**In-situ** time resolved XAS investigation of Mg in magnesium-potassium phosphate cements

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Magnesium-potassium phosphate cements (MPCs) are chemically-bonded ceramics which set at room temperature through an acid-base reaction in presence of water, between MgO and an acid potassium phosphate. They attracted interest for a countless number of applications, ranging from nuclear waste encapsulation [1], bone repair [2], dentistry and in civil engineering as eco-sustainable fast repair materials for damaged structures [3]. During the reaction, a crystalline magnesium-potassium phosphate hydrate (MgKPO$_4·$6H$_2$O) forms by progressive incorporation of water, according to the following reaction:

\[
\text{MgO + KH}_2\text{PO}_4 (\text{KDP}) + 5\text{H}_2\text{O} = \text{MgKPO}_4·6\text{H}_2\text{O (MKP)}
\] \hspace{1cm} (1)

In MKP, Mg is coordinated by 6 oxygen atoms from water molecules, in a slightly distorted octahedral coordination [4]. However, an amorphous precursor form first, and owing to the slow rate of the conversion into the crystalline product and to the progressive reduction in ion mobility with the progress of the reaction, it is always observed in the cement. Structural information on it is lacking, but it is of importance in order to understand the mechanism of the reaction, and, in turn, the development of the microstructure and the properties (e.g. mechanical, adhesive, dissolution) of the cement for applications.

A mechanism of the reaction has been proposed based on the nature of the products and kinetic analysis of synchrotron X-ray diffraction data [5]. Using quasielastic neutron scattering, nuclear magnetic resonance and time-resolved infrared spectroscopy, the hypothesis is that the amorphous precursor is an orthophosphate hydrate possessing structural motives of Mg similar to those in the crystalline phase [6-8].

In order to confirm this model, \textit{in-situ} time resolved XAS experiments at the Mg K-edge have been performed at the LUCIA beamline of the SOLEIL synchrotron facility in Saint-Aubin (France). The experiment can be considered as state of the art because of the complexity of the investigated system (studied for the first time through \textit{in-situ} XAS at the Mg K-edge) and of the peculiar set-up that has been used.

Various time-resolved measurements were conducted on samples with and without different types (and amount) of retardants, in order to better highlight the formation steps of the amorphous phases; in addition, spectra were collected on pellets of many Mg-bearing reference compounds (some of which have never been studied with XAS), representing potential candidates for the local chemical environment of Mg in the amorphous meta-stable phases.

Despite the time-resolved spectra suffered of low signal-to-noise ratio (all measurements were performed in fluorescence mode), we managed to successfully perform XANES linear combination fitting (LCF) analysis using the pure spectra of some of the Mg-reference compounds. LCF was performed at least 3 times on each spectrum and both on the raw and smoothed data, in order to test for the reproducibility.

The obtained results clearly highlight the effects of the retardant, allowing to identify the evolution of the amorphous through time and to better describe the oxidation state and coordination geometry of Mg in this meta-stable phase.