Experimental report

01/11/2015

Proposal: **7-04-137** **Council:** 10/2014

Title: Investigation of setting reaction of magnesium-potassium phosphate ceramics by qualsi-elastic neutron scattering

Research area: Materials

This proposal is a new proposal

Main proposer: **Alberto VIANI**

Experimental team: Alberto VIANI

Local contacts: Mohamed ZBIRI

Samples: MgO
KH2PO4

Instrument	Requested days	Allocated days	From	To
IN6	5	5	06/05/2015	11/05/2015
IN5	4	0		

Abstract:

Mg-K phosphate ceramics are chemically-bonded ceramics. They are attractive binders for many applications. They harden at room temperature through an acid-base aqueous reaction between magnesium oxide and a potassium phosphate. Several mechanisms for this reaction have been proposed, but kinetic studies are scarce and none of them provided quantitative data. The rate of MgO dissolution (which depends mainly on the calcination temperature of magnesium carbonate from which it is obtained) is considered the main factor controlling the reaction process. Recently, we showed that an amorphous fraction develops as a precursor of the crystalline product. Synchrotron diffraction allowed us to derive kinetic data and formulate hypothesis on the reaction mechanism. This interpretation needs to be confirmed and issues such as the nature of the intermediate (amorphous ?) precursor still deserves explanation. To this aim, complementing already planned calorimetric and SAXS experiments, we would like to investigate for the first time the reaction using quasielastic neutron scattering in order to derive kinetic parameters and study the chemical state of water in this system.

Introduction

Magnesium-potassium phosphate ceramics (MPCs) are chemically-bonded ceramics showing peculiar properties making them attractive for several applications [1]. The studied MPCs, harden at room temperature (*T*) owing to the acid-base aqueous reaction between magnesium oxide (MgO) and potassium phosphate (KDP, KH_2PO_4): $MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O$. We have recently proposed a mechanism for this reaction based on an *in-situ* synchrotron diffraction kinetic experiment [2].

According to the proposed model, the first reaction step is the dissolution of MgO in aqueous solution via chemical control contributing to the formation of an intermediate amorphous product. The progressive accumulation at the grain surface of a thickening layer hindered diffusion of water for the further decomposition of MgO, shifting the mechanism towards a diffusion control. On the other hand, the late formation of MKP is again a first order (F1) chemical reaction as water is available at the interface of the intermediate layer and nutrients can readily migrate through the MKP layer thanks to its open structure. Reaction rate was found to depend upon the calcination *T* of magnesite ($MgCO_3$), the source of magnesium oxide. Increasing *T* in the range 1300-1600 °C yields less reactive, well crystallized MgO crystals of higher mean grain size [3]. Results from our SANS experiment indicate that less reactive MgO leads to a more compact microstructure, the same happens during the progress of the reaction [4]. The reaction product forms from an amorphous precursor and its development was found to scale with the microstructural parameters. The nature of the intermediate (amorphous) precursor of MKP and whether this transient phase is a gel from which MKP slowly crystallizes, or not, are still open questions. The investigation of the state of water during the setting reaction is thought to shed further light on this reactionsystem complementing the information obtained from the analytical techniques employed so far. The motions of hydrogen, that at the beginning of the reaction is expected to be largely present in the freely diffusing water, changes as it is trapped, adsorbed on surfaces, and transferred into the products. Quasielastic neutron scattering (QENS) provides a direct measure of these changes that can be followed through time resolved experiments.

Experimental

Two MgO samples were obtained from magnesium carbonate by calcination for 40 min in laboratory furnace at 1550 and 1600 °C. MPC with KDP:MgO molar ratio of 1.75 was employed, the powder was then added distilled water to attain the water/solid ratio of 0.436, and mixed by hand for 30 s. This formulation is stoichiometric with respect to water and KDP, and in excess of MgO.

The MPC paste was spread into a thin 0.5-mm layer on a flat aluminium cell in order to reduce multiple scattering, which was then sealed with an indium gasket. The cell was lined with 10 μm thick Teflon foil to protect the sample holder. QENS measurements were made using the time-focussing time-of-flight spectrometer IN6 with an incident neutron wavelength (λ) of 5,12 Å. QENS spectra for kinetic experiment were obtained by merging data in the interval 0.3-1.9 $Å^{-1}$. Data were collected continuously for up to 22 h and the results time-averaged over 2 min intervals for the first 2 h and 30 min intervals for the remainder. Sample 1600 was collected at three temperatures: 293, 303 and 313 K. Sample 1550 at 293 K. QUENS spectra were rescaled to unit area.

Results and discussion

Fig. 1 depicts the first 30 QENS spectra of sample 1600 at 293 K. The lorentzian component of the quasielastic broadening, corresponding to the dynamics of water, is observed to decrease with time as water becomes bound in the MKP structure.

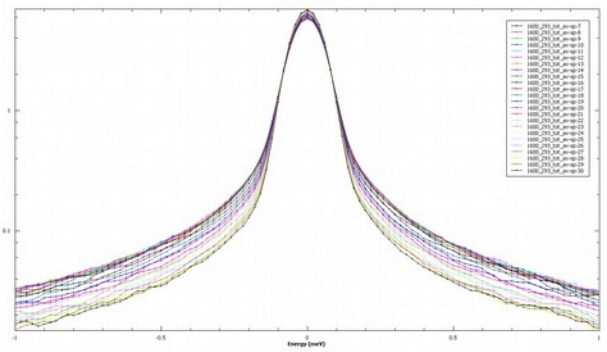

Fig. 1. QENS spectra of MPC in semi-logaritmic scale. The Lorentzian component is decreasing with time.

The integration of the area under the curves was accomplished through a fit with the convolution of a delta function, a lorentzian, and the experimental resolution (obtained from the measurement of Vanadium). The results from the fit allowed for building the kinetic curves reported in Fig. 2, expressing the fraction of water molecules that becomes bound with time.

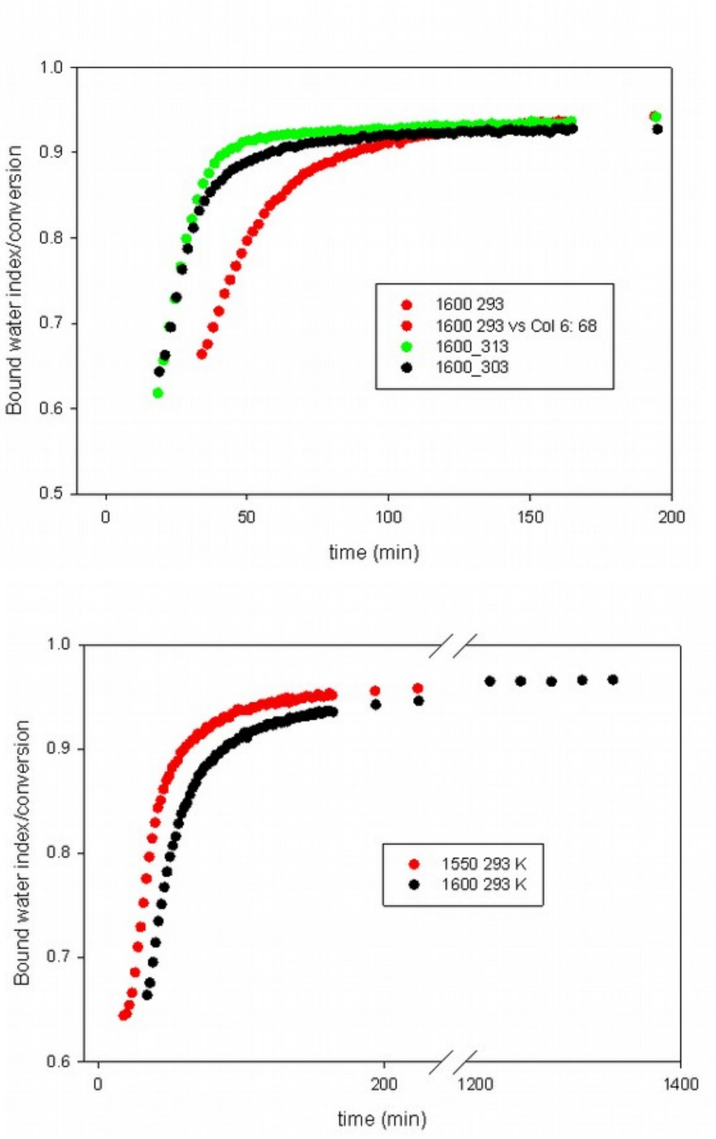

Fig. 2. Kinetic curves for MPC obtained from QENS data. Sample 1600 at 3 temperatures (top) and samples 1550 and 1600 at 293 K (bottom).

The use of only one lorentzian component to fit the evolution of QENS broadening suggests that the water molecules don't show more than one degree of confinement at the time scale accessible to the experiment. This is at variance with what was observed during setting reaction of cements, for example. We can thus infer that the amorphous precursor is likely amorphous MKP rather than possessing a gel structure as in cementitious systems.

Fig. 2. shows that after 5 min (the time after which data collection started) about 65 % of water is already bound, at the same time, the second part of the kinetic curves, is indicative of the onset of a second mechanism. Both aspects are in agreement with the results of previous experiments, indicating a fast reaction rate and a two-step reaction. Although the first stage of the reaction cannot be described, kinetic analysis is possible by applying the isoconversional method for sample 1600.

The comparison between samples 1550 and 1600 show that MgO annealed at higher *T* is less reactive. Kinetic analysis with derivation of parameters of the reaction, like activation energy and rate costants, is underway. The study of water dynamics will be accomplished by comparing samples at the same degree of conversion during the reaction. Data collected at 0.1 Å^{-1} interval in the range 0.3-1.9 Å^{-1} will be used. Fig. 3 depicts the spectra at different Q values for sample 1600 at 293 K at conversion 0.695.

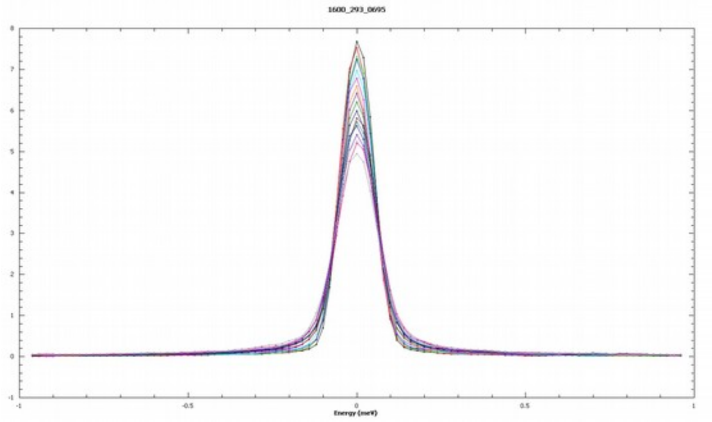

Fig. 3. Spectra at different Q values for sample 1600 at 293 K degree of conversion 0.695.

References

[1] D.M. Roy, Science. 235 (1987) 651–658.
[2] A. Viani, M. Pérez-Estébanez, S. Pollastri, A.F. Gualtieri. Cem. Concr. Res. (2015), in press.
[3] A. Viani, A. Radulescu, M. Pérez-Estébanez. Materials Letters, 161 (2015) 628-630.