



	<b>Experiment title:</b> Hydration reaction kinetics of magnesium potassium phosphate cements (chemically bonded magnesium phosphate ceramics)	<b>Experiment number:</b> MA-2021
<b>Beamline:</b> BM01b	<b>Date of experiment:</b> from: 26/09/2013 to: 30/09/2013	<b>Date of report:</b> August, 10 <sup>th</sup> , 2014
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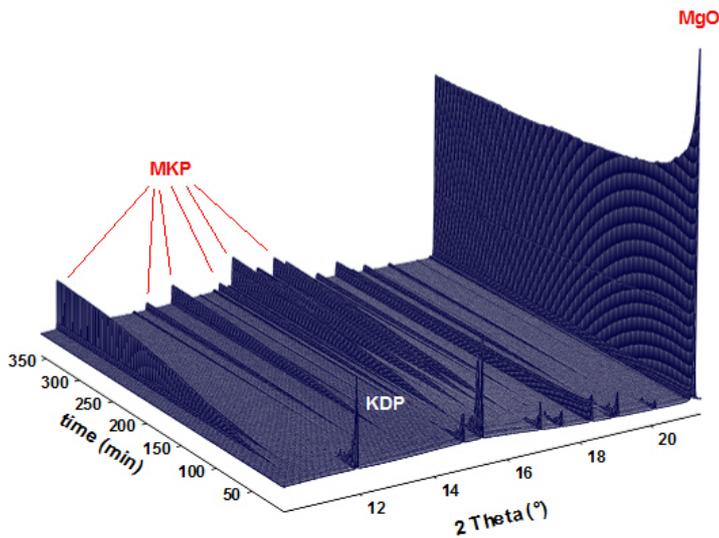
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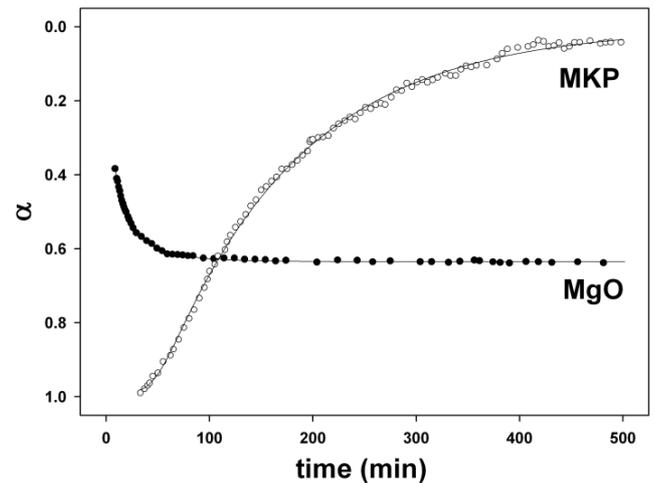
**Report:**

Magnesium-potassium phosphate ceramics are chemically-bonded ceramics [1]. Their properties make them attractive for applications like waste encapsulation, bone repair, natural fibre composites. When MgO reacts with potassium di-hydrogen phosphate (KDP) in solution, formation of K-struvite (MKP) occurs:  $\text{MgO} + \text{KH}_2\text{PO}_4 + 5\text{H}_2\text{O} = \text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  (MKP). Several mechanisms for this reaction have been proposed, but kinetic studies are scarce and none of them provided quantitative data [2-7]. Experiments were devoted to the realization of a kinetic study of the formation of magnesium-potassium phosphate ceramic (MPC) using *in-situ* synchrotron powder diffraction. The reaction was followed *in situ* in the attempt of contributing to explain the overall reaction mechanism and assess the influence of grain size and periclase (MgO) calcination temperature (1400-1600 °C) on the reaction kinetics. Numerical kinetic parameters for the setting reaction of MPCs have been provided for the first time. Kinetic analysis was accomplished with the available models describing solid state reactions and the best fit was obtained using a weighted nonlinear model fitting method with two kinetic equations, representing two consecutive, partially overlapping processes. MgO decomposition could be described by a first order (F1) model followed by a Jander diffusion (D3) controlled model. MKP crystallization reaction was modeled using an Avrami model (An) followed by a first order (F1) chemical reaction. The reaction was described as initially driven by the dissolution of MgO in aqueous solution (chemical control) to form an intermediate amorphous brucite-like product. This thickening layer hindered further diffusion of water shifting the mechanism towards a diffusion control one. The late formation of MKP is again a first order chemical reaction, as water is available at

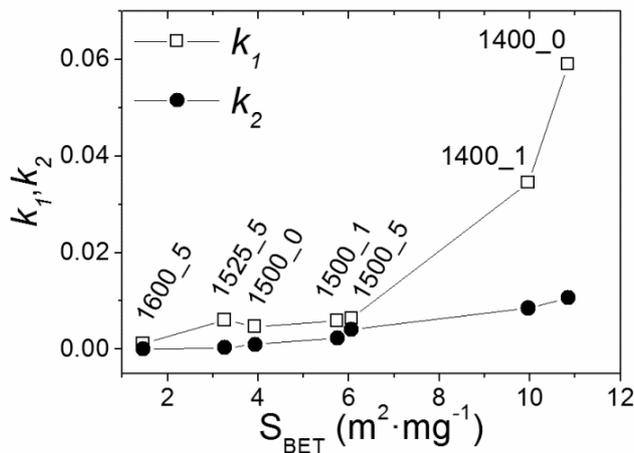
the interface of the intermediate layer, and  $K^+$  and  $PO_4^{3-}$  ions readily migrate through the open structure of elongated MKP crystals. This mechanism shows analogies with that of some Ca-P cements [8]. Reaction rates constants ( $k$ ) of the two mechanisms describing MKP formation showed to be dependent on BET surface area of MgO (See Figure 3).



**Figure 1.** 3D plot of the time evolution of diffraction spectra of the MPC reaction.



**Figure 2.** Example of plots of degree of conversion ( $\alpha$ ) vs. time for MKP crystallization and MgO decomposition during the MPC reaction.



**Figure 3.** Rate constants  $k_1$  and  $k_2$  vs. specific surface area of MgO for the 2 reaction mechanisms of MKP formation.

## References

- [1] Wagh AS. Magnesium phosphate ceramics, in: E. Hurst, editor. Chemically bonded phosphate ceramics: 21st century materials with diverse applications, Elsevier, Amsterdam, 2004.
- [2] E. Soudée, J. Péra, Mechanism of setting reaction in magnesia – phosphate cements. *Cem. Concr. Res.* 30(2) (2000) 315–21.
- [3] D. A. Hall, R. Stevens, B. El-Jazairi, Effect of water content on the structure and mechanical properties of magnesia-phosphate cement mortar, *J. Am. Ceram. Soc.* 81(6) (1988) 1550–1556.
- [4] A. S. Wagh, S. Y. Jeong, Chemically Bonded Phosphate Ceramics: I, A Dissolution Model of Formation, *J. Am. Ceram. Soc.* 86(11) (2003) 1838–1844.
- [5] Z. Ding, B. Dong, F. Xing, N. Han, Z. Li, Cementing mechanism of potassium phosphate based magnesium phosphate cement, *Ceramics Int.* 38 (2012) 6281–6288.
- [6] F. Qiao, C. K. Chau and Z. Li, Calorimetric study of magnesium potassium phosphate cement, *Materials and Structures*, 45 (2012) 447–456.
- [7] A. Viani and A. F. Gualtieri, Preparation of magnesium phosphate cement by recycling the product of thermal transformation of asbestos containing wastes, *Cem. Concr. Res.*, 58 (2014) 56-66.
- [8] C. Durucan and P. W. Brown, “Kinetic Model for  $\alpha$ -Tricalcium Phosphate Hydrolysis”, *J. Am. Ceram. Soc.* 85 [8] (2002) 2013–18.