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In situ synchrotron powder diffraction study of the setting reaction kinetics of magnesium-potassium phosphate cements

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ABSTRACT

This work reports a kinetic study of the formation of magnesium-potassium phosphate cements accomplished using *in-situ* synchrotron powder diffraction. The reaction: $MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$ was followed *in situ* in the attempt of contributing to explain the overall mechanism and assess the influence of periclase (MgO) grain size and calcination temperature (1400-1600 °C) on the reaction kinetics. Numerical kinetic parameters for the setting reaction have been provided for the first time. The best fit to the kinetic data 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. Crystallization of the product of reaction was modelled using an Avrami model (A_n) followed by a first order (F1) chemical reaction. A reaction mechanism accounting for such results has been proposed.

1. Introduction

Magnesium-potassium phosphate cements (MPCs) are chemically-bonded ceramics (CBCs) [1,2]. Because of their peculiar properties, like high early age and long term strengths, good water resistance, high adhesive properties and affinity for cellulose materials [3,4], they have been considered attractive for many applications [5–14]. Like other CBCs, they harden at room temperature as a consequence of the acid-base aqueous reaction between magnesium oxide and acid potassium phosphate. When MgO (periclase) reacts with potassium di-hydrogen phosphate (KDP): KH_2PO_4, formation of the isomorphous potassium equivalent of mineral struvite (MKP) occurs, according to the reaction: $MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$. The reaction is rapid and exothermic, and its mechanism has been investigated by several authors [4,15–17]. When MgO powder is gently stirred in phosphate solution, a three-step mechanism for MKP formation was devised [16]. This involves: (i) formation of aquosols composed by water molecules complexing dissolved cations; (ii) formation of a gel by reaction of the sol with phosphates in water; (iii) crystallization of a thickened gel into a ceramic around the unreacted core of MgO grains. This gel converts into a saturated phosphate solution with undissolved oxide particles representing nuclei for crystallization. The rate of MgO dissolution is considered the main factor controlling the degree of crystallinity of the final ceramic. The pH of the solution is critical in favouring or inhibiting precipitation. Following another view [18], MKP sets through the onset of an insoluble barrier coating, consisting of polyphosphate units cross-linked with Mg^{2+} ions. This gel then slowly crystallizes into an interlocking microstructure of MKP. A solution mediated process, in which dissolved phosphate and a part of MgO are involved, has been also inferred [4,19]. Crystallization starts at nucleation points by gathering ions in solution. This hypothesis was later excluded on the basis of considerations about the mechanism of MgO dissociation in water, supposed to occur via the formation of $Mg(H_2O)_6^{2+}$ complexes [15]. Some of them replace water molecules at the magnesia surface, hindering further wetting of MgO grains. Together with PO_4^{3-} ions in solution, they supply the structural units required for crystallization of MKP. The reaction is thus controlled by the reactivity of MgO powder, the amount of $Mg(H_2O)_6^{2+}$ complexes formed at the grain surface (preventing water molecules from further wetting magnesia), and the relative amount of each reactant. The reaction stops when the magnesia grains are entirely covered by hydrates and can no longer dissolve.

When MgO grains (1-2 mm in size) are immersed in mono-potassium phosphate solution MKP was observed to form preferentially as elongated crystals lying parallel to the grain surface [20]. They accumulate quickly, bonding grains together. Kinetic studies are scarce and none of them provided quantitative data for this reaction. Isothermal calorimetric experiments [21], conducted with water to solid weight ratios (*w/s*) ranging between 2.5 and 10, showed a first endothermic peak followed by two exothermic ones. Dissolution of KDP in water was believed to produce the first peak, while the following exothermic events were ascribed to MgO dissociation and MKP formation, respectively. All these events largely overlap in time, and the superimposition

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of the calorimetric signals prevented for an accurate quantification of each contribution. For practical applications the range of *w/s* is usually comprised between 0.2 and 0.4. Evidence was also found of the presence of an amorphous or poorly crystalline phase with a lower degree of hydration in mortars prepared with low water content (<8 wt%) [17], and in ammonium phosphate cements [20,22]. The quantification of amorphous content in MPCs at different times after hydration, allowed us to prove that consumption of MgO occurred faster than formation of crystalline MKP [23,24]. Over long times, amorphous content decreases, whereas MKP increases [23], suggesting that the amorphous phase might be a precursor of MKP. At the current state of knowledge, the nature of this amorphous phase remains unexplained. One of the major factors affecting reaction kinetics was recognized to be the calcination temperature of magnesite ($MgCO_3$), the primary source of magnesium oxide. As confirmed by the literature on MgO dissolution in various acidic environments [25], it has proven to be critical in determining the reactivity of MgO formed [2,20,24,26,27]. At temperatures above 1300 °C, less reactive well crystallized MgO crystals of higher mean grain size and without amorphous coatings are formed [2].

In this work the MPC setting reaction was followed by means of *in-situ* synchrotron powder diffraction in the attempt of providing insights into the overall mechanism of this reaction and the influence of the reactivity of MgO on the reaction kinetics. As recently pointed out [28], these aspects are of crucial importance for a better understanding of the development of the microstructure in view of designing products for applications.

2. Experimental

2.1. Materials

The raw materials employed in this study were pharmaceutical grade $MgCO_3$ (42 wt% MgO) and reagent grade KDP (assay 99.8%) (Lach-ner s.r.o). MgO was obtained from magnesium carbonate by calcination for 40 min in laboratory furnace at 1400 °C, 1500 °C, 1525 °C, and 1600 °C. Two additional samples for each annealing temperature were obtained by milling MgO in agate shatterbox for 1 min and 5 min, respectively, for a total of 12 MgO samples.

MPCs with KDP/MgO molar ratio of 1 were obtained by mixing 675.3 mg of KDP with 200 mg of MgO by hand in agate mortar. The powder was then added 262.6 mg distilled water to attain the *w/s* of 0.3, and mixed by hand for 1 min. MPC samples were then loaded in a syringe from the back side to be injected into capillaries 0.7 mm in diameter, open on both sides. Capillaries were then immediately sealed and mounted on a goniometric head for synchrotron data collection.

2.2. Analytical Methods

Data were collected with the MYTHEN solid-state silicon microstrip detector implemented at the beamline MS X04SA, Paul Scherrer Institut, Swiss Light Source (SLS), Villigen (Swiss), employing a wavelength of 0.775 Å, and at the beamline BM01b, European Synchrotron Radiation Facility (ESRF), Grenoble (France), employing a wavelength of 0.505 Å with the Dexela CMOS-2D detector (PerkinElmer). Isothermal runs at room temperature (20 °C) were conducted on spinning capillaries following the reaction for variable times (from few up to 13 hours). Samples will be labelled with their activation temperature followed by milling time (in min). Setting was followed *in situ* employing the following 7 samples: 1400_0, 1400_1, 1500_0, 1500_1, 1500_5, 1525_5, 1600_5.

Scanning electron microscope (SEM) observations have been conducted on samples of MgO and hardened MPC. Instrument (Model Quanta 450 FEG, FEI) was equipped with an energy dispersive X-rays fluorescence spectrometer (EDS) (Model Apollo X, EDAX). A tiny amount of sample was loaded on an aluminum stub and coated with a gold 10 nm thick film. Observations were performed using secondary electrons.

BET specific surface area measurements have been accomplished on MgO (Model ASAP 2020, Micromeritics). Grain size distribution of MgO was determined on samples dispersed in isopropyl alcohol with a laser granulometer (Model LD 1090, CILAS).

2.3. Kinetic Analysis

Kinetic analysis was conducted using a combination of different approaches suitable for isothermal data. After inspection of the *in situ* synchrotron XRPD patterns, the decomposition of the reactant MgO and crystallization of MKP were independently analysed, using the integrated area of the (002) diffraction peak (corresponding to a d-spacing of 2.10 Å) for MgO, and the (021) diffraction peak (corresponding to a d-spacing of 4.10 Å) for MKP, as a direct evidence of these processes. Their values are proportional to the weight fractions of the corresponding phases. Integrated areas of Bragg reflection peaks were normalized to phase fraction (α) and plotted as α vs. time curves. Integration was accomplished with the software PeakFit employing 2 pseudoVoigt functions and a flat background for each diffraction peak. For many datasets, both processes showed in the second part an asymptotic behaviour. It must be noted however, that, as explained later in Section 5, only a fraction of the amount of MgO expected to react (according to the stoichiometry of the reactants) was consumed during the experiments, indicating that this final stage is extremely sluggish and likely extends in time beyond the end of the experiment. In this description, the choice was made to adopt for both processes the same approach in the definition of the point corresponding to complete conversion, that is, $\alpha = 1$ was assumed as the asymptotic value obtained from the fit of the curve with an exponential function rising to a maximum for MKP crystallization, and from the fit of the curve with an exponential decay function ($y = y_0 + A_1{*}\exp(-x/t_1) + A_2{*}\exp(-x/t_2)$) for MgO decomposition. In the latter case, as the reaction was not followed from time $t = 0$, the integrated area of XRPD peaks corresponding to $\alpha = 0$ was extrapolated from the fit of the curve to time $t = 0$ using the same function, whereas in the case of MKP crystallization, the value of $\alpha = 0$ is automatically set, as no MKP peaks in the XRPD pattern are initially observed.

The study of each α-time plots was preliminarily attempted using the classical linear-model fitting method for heterogeneous solid-state reactions described by the general expression of the Avrami or Johnson-Mehl-Avrami–Erofe'ev-Kolmogorov - JMAEK equation [29].

$$\alpha = 1 - \exp\left[(-kt)^n\right] \qquad (1)$$

The logarithmic transform of this equation is used to build a graph of $ln[-ln(1-\alpha)]$ vs. $ln(t)$ in which isothermal experimental data are made linear in the so-called *ln–ln plot*, where the reaction order (n) is calculated from the slope of the regression line and the rate coefficient k is calculated from the intercept.

To get an idea about the reaction model and assess if the reaction is single-step or multi-step, plots of $d\alpha/dt$ vs. α were drawn and compared to master plots [30].

Because the dependency upon temperature was not investigated, isoconversional methods such as the Friedman model [31,32] were not applied. Initially we tried to fit the data with a single nucleation and growth model (diffusion models and reaction-order models which belong to the class of deceleratory reactions) without success. Fitting was attempted with the major kinetic equation relative to deceleratory reactions [29] D1, D3, F0/R1, F1, F2, and F3 (see below) but resulted unsuccessful. Plots testifying the poor quality of the fits are available as supplementary material Fig. S1. According to the indications of multi-step reactions, we decided to fit the data with a more complex combined model. Each α-time plot was fitted using the nonlinear regression approach in the so-called nonlinear model fitting method [32]. In principle, if the reaction is single step, data should be fitted with one of the kinetic models developed for solid state reactions. The most important kinetic models used in solid state reactions in integral form