Thermal reactions of brushite cements

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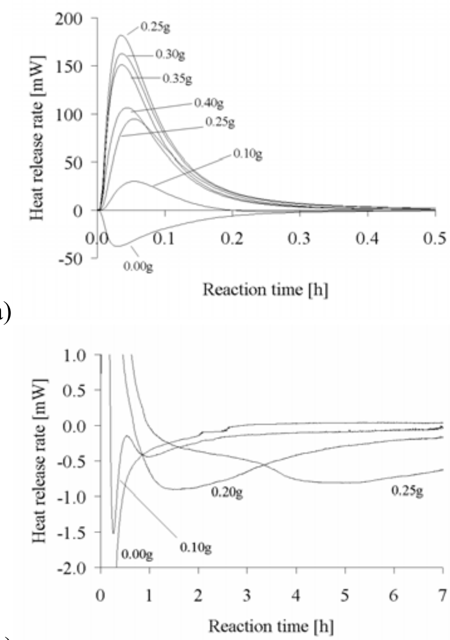
Statement of Purpose: There are two kinds of calcium phosphate cements (CPC): apatite and brushite (= $CaHPO_4 \cdot 2H_2O$) CPC. Apatite CPC are relatively well known, contrary to brushite CPC. To gain some understanding about the setting reaction of the latter CPC type, the heat exchanges occurring during brushite CPC reaction were followed.

Methods: Brushite CPC was made of a mixture of β-tricalcium phosphate (β-$Ca_3(PO_4)_2$; β-TCP), monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2 \cdot H_2O$; MCPM, Albright Wilson; Lot MCP W 20B1; England) and water. β-TCP powder was produced by sintering an equimolar mixture of $CaCO_3$ and monetite (= $CaHPO_4$). The sintered powder was milled in a planetary mill for 15, 30, 45, 60 and 120min. The various milling durations resulted in particle sizes and specific surface area in the range of 3-6μm and 3-4m^2/g, respectively. The additives used to modify the setting reaction were di-sodium di-hydrogen pyrophosphate ($Na_2H_2P_2O_7$), tri-sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), and sodium sulfate ($Na_2SO_4$). An isothermal calorimeter (TAM Air Cement, Thermometric AB, Sweden) was used to study the heat exchanged during and after mixing the powder (β-TCP + MCPM = 0.50g) and the solution (0.20 to 1.00 mL) at 37ºC. The measurements were started and terminated after a constant thermal signal had been reached. At least three repeats of each composition were made. Citrate, pyrophosphate and sulfate ions were added in solution.

Results/Discussion: Cements containing an excess of β-TCP (>0.276g) produced one main exothermic peak at early reaction time (<10min) but reaction easily lasted several days until full completion (Fig 1a). Cements containing an excess of MCPM had similar thermograms apart from the presence of an endothermic peak at late reaction time due to the transformation of brushite into monetite (Fig 1b). The total released heat varied from negative values to positive values close to the isomolar content of β-TCP and MCPM (Fig 2). The main exothermic peak was attributed to a concomitant dissolution of MCPM (endothermic) and β-TCP (exothermic). The slow heat release observed at the end of the reaction was believed to be due mainly to β-TCP dissolution and brushite precipitation. A relatively good agreement was found between calculated and measured released heat, especially considering the occurrence of brushite→monetite conversion at low β-TCP content (Fig 2). Few changes were observed with a change of liquid-to-powder ratio or an increase of β-TCP milling time (larger first peak). Sulfate, citrate and pyrophosphate ions generally widened and lowered the main exothermic peak, and decreased as well the total heat released during the reaction (Fig 3). All these effects can be ascribed to the inhibitory effect of the additives on DCPD crystallization.



(a)

(b)

Figure 1: Effect of β-TCP amount on the heat release rate (β-TCP + MCPM = 0.5g). Fig 1b is an enlargement of Fig1a.

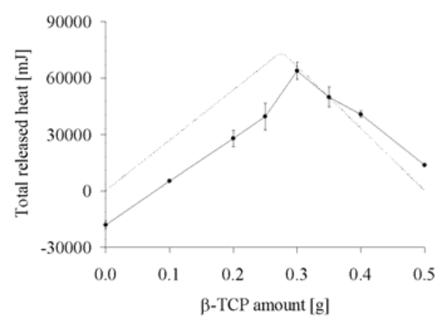


Figure 2: Calculated and measured released heat as a function of β-TCP content (15min milling). The dotted line was calculated based on thermodynamic data for the reaction: β-TCP + MCPM = DCPD + excess β-TCP/MCPM powder.

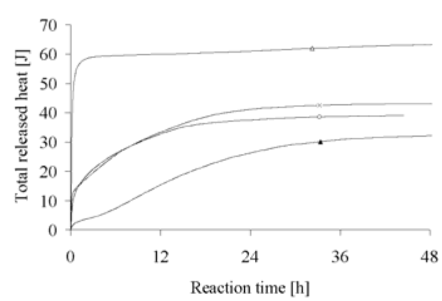


Figure 3: Effect of various additives on the total heat released from mixtures of 0.3g β-TCP (15min milling), 0.2g MCPM and 1.0mL aqueous solution: (Δ) No additives; (x) 0.8M Na_2SO_4; (o) 0.2M $Na_3C_6H_5O_7 \cdot 2H_2O$; (▲) 0.2M $Na_2H_2P_2O_7$.