

THERMOMETRIC STUDY OF BRUSHITE CEMENTS

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INTRODUCTION: This study is part of a broader work on Brushite cements [1]. The effects of various experimental factors on the working characteristics of Brushite cements are being investigated, with the aim of understanding the physico-chemical aspects of the setting and consolidation processes, and the mechanisms of the chemical reactions leading to consolidation.

In the present study, thermometric measurements are being used in order to monitor the early stages of the setting and hardening processes of Brushite cements. The thermometric approach gives access to useful working characteristics such as working and setting times, in very good agreement with standard experimental techniques such as the Vicat needle method.

METHODS:

Principle of the method : Advantage is taken of the fact that the setting reactions leading to brushite formation are slightly exothermic.

A freshly prepared cement paste (about 2 mL) is inserted into a polyurethane foam block placed within a Dewar flask, and covered with an insulating lid ; thus, the sample is thermally insulated in a way similar as it would be upon implantation into cancellous bone. A thermocouple is stuck in the middle of the cement sample. Temperature is sampled every few seconds and recorded by a computer (Fig. 1). The thermometric curve results from two competing processes : heat is generated by the chemical reactions responsible for the consolidation of the cement and slowly dissipated by thermal conduction through the walls of the container and through the thermocouple. Compensation for thermal dissipation can be calculated from a control thermometric curve (Fig. 2), obtained by placing in the measuring cell a sample of hardened cement preheated to about 45°C, and recording its cooling curve.

The kinetics of enthalpy production due to the consolidation reactions is obtained by summing the apparent enthalpic curve and the

thermal dissipation curve deduced from the experimental and control thermometric curves (Fig. 3).

The progress of the cementation reaction is calculated by taking the ratio of the measured enthalpy over the theoretical reaction enthalpy (which can be calculated on the basis of known thermochemical data). The kinetic curve (Fig. 4) shows a sigmoidal shape, from which several characteristics of the consolidation process can be deduced : induction (or working) time, setting time, maximum β -TCP conversion.

Full details on the experimental setup and on the treatment of the experimental data are presented in reference [2].

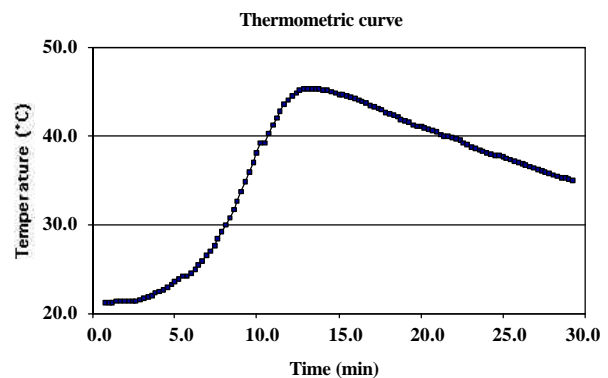


Figure 1. Experimental thermometric curve.

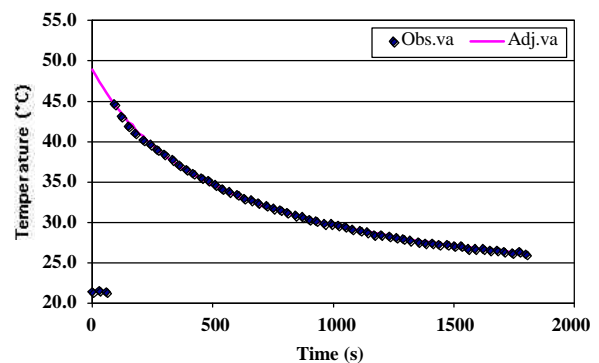


Figure 2. Control thermometric curve.

EXPERIMENTAL DESIGN :

Table I. Definition of factors and levels in the experimental design

Factor	Definition	Low Level	High
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			Level
A	Polymer*	HA	HPMC
B	Sulfate	Plaster	Sulf. Ac.
C	Magnesium ^o	0 % wt	8 % wt
D	Porosity	35% vol	45% vol

* HA : Hyaluronic acid ; HPMC : Hydroxypropylmethyl cellulose. ^o In the form of Mg.HPO₄.2H₂O (Newberryite).

Experimental factors summarized in Table I have been selected on the basis of previous *in vivo* and *in vitro* studie, which have shown considerable changes in biodegradability of brushite cements according to the presence of Mg, sulfate ions and on the nature of hydrosoluble polymers incorporated for rheological control. The experiments were organised into a 2⁴ multifactorial statistical design. The results were analysed using the ANOVA technique.

RESULTS AND DISCUSSION:

Thermometric observations show a systematic decrease of the maximum temperature for Mg-containing samples. Statistical analysis of the results expressed in terms of maximum β -TCP conversion (Fig. 5) demonstrates clearly a marked inhibitory effect of Mg on the consolidation reactions ; the effect is more contrasted for samples with 35% vol porosity containing hyaluronic acid. The presence of sulfate in any form does not seem to play any significant role.

Thus the presence of Mg, especially in conjunction with hyaluronic acid appears to inhibit strongly the chemical reactions leading to the formation of brushite.

CONCLUSIONS: A new experimental approach based on thermometric measurements allows to calculate the kinetics of enthalpy production, and hence the kinetics of transformation of calcium phosphate cements. These kinetic curves allow to calculate several working characteristics of the cements : working and setting times, maximum fraction of converted β -TCP, reaction rate, maximum temperature increase upon cement consolidation.

Based on thermometric analysis, the inhibiting effect of magnesium on the setting reaction of Brushite cement has been clearly evidenced.

REFERENCES:

- [1] A.A Mirtchi, J.Lemaître, N.Terao. Calcium phosphate cements : study of the β -Tricalcium phosphate-monocalcium phosphate system. *Biomaterials*, 10 [septembre] 475-480 (1989).
- [2] C. Pittet "Development and Characterisation of Injectable Calcium Phosphate Cements for Use in Vertebroplasty." Thesis n° 2509, EPFL, 2001.

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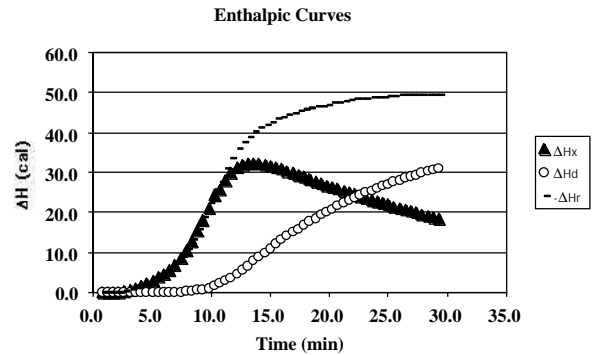


Figure 3. Enthalpic curves : $\bullet H_x$ experimental enthalpy vs time ; $\bullet H_d$ dissipated enthalpy.

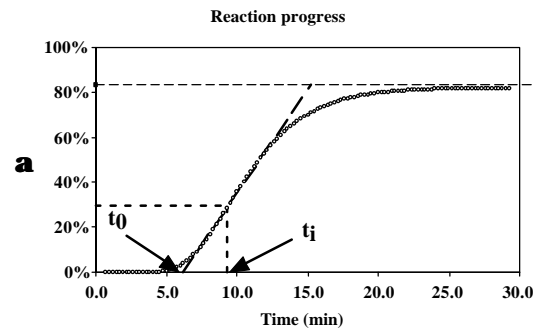


Figure 4. Reaction progress vs time. t_0 : working time ; t_i setting time.

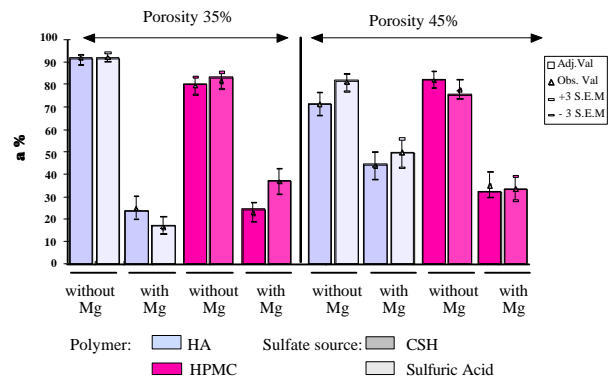


Figure 5. Evolution Effects of experimental factors on the ultimate conversion of the cement.