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Conference Discussion

Kinetics of Precipitation and Crystal Growth of Dicalcium Phosphate Dihydrate*

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The kinetics of the precipitation and crystal growth of dicalcium phosphate dihydrate (DCPD) was followed in 0.15 M sodium chloride solutions at constant pH (pH = 5.0) and temperature (25° C). Precipitations were performed from equimolar solutions of calcium chloride and sodium phosphate prepared by direct mixing of the reactants. The amount of precipitate formed (X moles per l) was calculated from the quantity of sodium hydroxide added by a pH-stat device. The system is of physiological interest, because precipitation of DCPD may play an important role during dental caries formation¹.

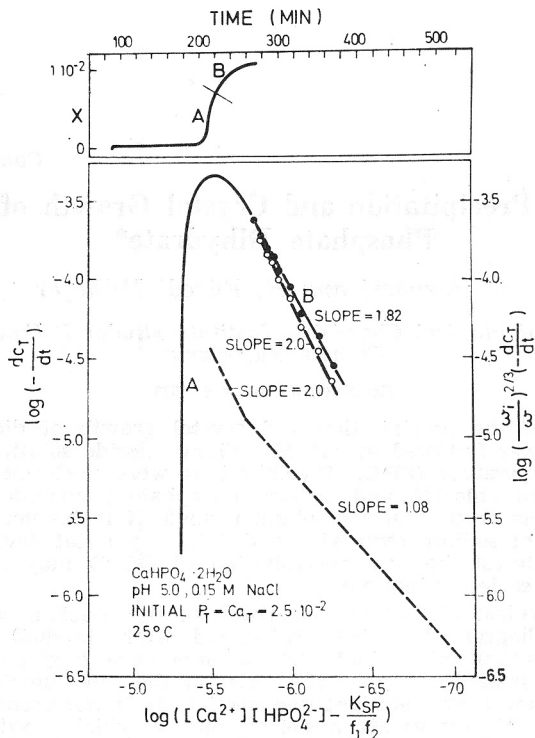
In Fig. 1, a typical plot of the logarithm of the reaction rate vs. log supersaturation (lower diagram, full lines) calculated after Marshall and Nancollas² is compared to the corresponding kinetic (X vs. time) curve (upper diagram). Provided agglomeration was insignificant, the steep rise of the rate function to a maximum (section A) was followed by a straight line (section B). It was assumed that the latter part of the curve (B) represents a period during which crystal growth of the previously formed particles was the prevailing process and no significant change of the number of particles occurred. The correction factor² $(w_1/w)^{2/3}$ was then introduced to correct the rate of growth at time t to that corresponding to the surface area of the crystals formed in the initial stage (section A). For w_1 the amount of precipitate formed at the start of the linear section, and for w the amount formed at any given time after that was substituted. The corrected straight line (empty dots) has a slope of 2.03 ± 0.04 , indicating that the rate of crystal growth is proportional with the square of the supersaturation as given by equation (1)².

$$-(w_1/w)^{2/3} (dc_T/dt) = k \cdot s \cdot ([Ca^{2+}] \cdot [HPO_4^{2-}] - K_{sp}/f_1 f_2)^2 \quad (1)$$

where $(-dc_T/dt)$ is the rate of the process expressed as a change either in total calcium (Ca_T) or total phosphate (P_T) concentration with time, K_{sp} is the solubility product of DCPD, f_1 and f_2 are activity coefficients of Ca^{2+} and HPO_4^{2-} ions respectively, k is the rate constant and s is a factor depending on the number of crystallization sites. An analysis of the experimental data according to the Christiansen-Nielsen³ theory also shows that crystal growth of DCPD under the given conditions is most probably controlled by a fourth order process of surface nucleation through a polynuclear layer mechanism.

Our result is in general agreement with that obtained for the first 15% of the reaction in seeded crystal growth experiments² (broken line in the lower part of Fig. 1). However, at comparable supersaturations the reaction rate was about 10 times greater in our experiment indicating that the number of available crystallization sites was as much higher. Further investigations will show whether the crystal growth mechanism changes at lower relative supersaturations (supersaturation per unit surface area) as shown by Marshall and Nancollas² for seeded crystal growth.

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Lower part: The reaction rate $(-dc_T/dt)$ as a function of the supersaturation (log scale) plotted according to equation (1). Full lines show the rate function obtained in the present work (full dots uncorrected slope, 1.82 ± 0.05 ; empty dots slope corrected by factor $(w_1/w)^{2/3}$, 2.03 ± 0.04). Broken line shows the rate function as obtained in seeded crystal growth experiments². Sections A and B correspond in time to the same sections on the X vs. time curve, shown in the upper part of the figure. Initial molar reactant concentrations $P_T = Ca_T = 2.5 \times 10^{-2}$ M.

REFERENCES

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IZVOD

Kinetika taloženja i kristalnog rasta dikalcium fosfat dihidrata

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Kvantitativno je praćena kinetika taloženja i kristalnog rasta dikalcium fosfat dihidrata dobivenog direktnim miješanjem ekvimolarnih otopina kalcium klorida i natrium fosfata, uz konstantan pH (pH = 5.0), koncentraciju natrium klorida 0,15 M i temperaturu (25° C).

Eksperimentalni su rezultati analizirani u skladu sa jednadžbom kristalnog rasta². Nakon početnog perioda nekontroliranog ubrzanja taložnog procesa slijedio je pediod u kojem se je brzina linearno smanjivala sa prezasićenjem. Dobiveni nagib pravca ($2,03 \pm 0,04$) ukazuje na proces kristalnog rasta četvrtog reda.

Diskutiran je mehanizam kristalnog rasta dikalcium fosfat dihidrata i nađeno je generalno slaganje sa rezultatima drugih autora.

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