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Conference Paper

The Kinetics of Crystallization of Calcium Fluoride. A New Constant Composition Method.*

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A new method is described for studying reproducibly, the kinetics of crystallization of calcium fluoride under conditions of constant solution composition. The method can be used even at very low supersaturation. The rate is proportional to the square of the supersaturation, over the range of relative supersaturation, $S = 0.20 - 1.66$. The results point to a surface controlled crystallization. The rate is markedly influenced by the presence of phosphate.

INTRODUCTION

There is considerable interest in the mechanism of crystallization of sparingly soluble calcium salts ranging from the phosphates and oxalates of biological mineralization processes[1-3] to the sulfates and carbonates of importance as scaling minerals in industrial processes and as precipitants in the marine environment[4,5]. Although numerous spontaneous precipitation studies have been made, they suffer from the disadvantage that the size and size distribution of the solid particles change during the course of the reaction. Also, the usual assumption of homogeneous nucleation[10] is open to question since it is difficult to remove all foreign nucleating sites from the crystallizing systems.

The problems associated with the irreproducibility of the results of such studies were overcome with the development of seeded growth techniques[11,12] which enabled the effects of factors such as temperature, supersaturation, and ionic strength to be quantitatively studied. A number of studies were made of the rates of crystallization from supersaturated solutions by monitoring the decrease in concentration of crystal lattice ions following the addition of seed crystals to metastable supersaturated solutions of the salt[6,7]. In cases where a number of phases of different solubilities could be formed, it was impossible to determine unequivocally, using this technique, the nature of the precipitating phase at each stage of the reaction[7]. Indeed, the empirical rule of Ostwald-Lucas predicts that the least stable phase would be kinetically favoured and precipitate first with eventual transformation to the thermodynamically most

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stable form. Thus for calcium phosphate crystallization, the results indicated that at physiological pH, the thermodynamically less stable dicalcium and octacalcium phosphates formed rapidly in the initial stages of the precipitation before hydrolyzing to the thermodynamically stable hydroxyapatite[8,9].

The crystallization of calcium fluoride is of importance in view of its use as a primary source of fluorine and as single crystals in optical devices. Previous studies have been concerned with the spontaneous precipitation of calcium fluoride from the standpoint of particle size and solubility. Tovborg[13] investigated the effect of lattice ions, sodium chloride concentration, pH and temperature on the length of the induction period preceeding the spontaneous precipitation of calcium fluoride from aqueous solutions. Conductivity and turbidity measurements indicated that a rapid phase separation occurred only at high supersaturation, followed by a slow growth process until equilibrium was reached. This suggests a reaction which is not limited by the diffusion of ions through layers of solution at the crystal surface and the proposed surface reaction mechanism was consistent with the approach of Christiansen and Nielsen[14]. In terms of this model, the variation of induction period with supersaturation was interpreted in terms of a critical nucleus consisting of only a few calcium and fluoride ions[15–17].

Calcium fluoride is also of importance biologically in the topical application of fluoride solutions to tooth enamel. Such treatment results in the partial transformation of hydroxyapatite to fluorapatite on the enamel surface resulting in a much more caries resistent phase. At higher concentrations of fluoride ion, calcium fluoride forms at the tooth surface in addition to fluorapatite. The inhibition of dental caries that results from the topical application of fluoride salts has been related to a surface coating of calcium fluoride on enamel which protects the mineral phase, hydroxyapatite, from dissolution[18]. A more recent model suggests that the calcium fluoride layer serves as a medium for transporting the reacting ion to the fluorapatite/hydroxyapatite interface[19].

In the conventional seeded crystal growth experiments outlined above, following the addition of seed crystals to metastable supersaturated solutions of the sparingly soluble electrolyte, the rate of crystallization is determined by measuring the concentration of lattice ions as a function of time. The difficulties associated with these seeded growth studies are that small errors in measured concentrations often preclude differentiation between the possible solid phases which can form. As the lattice ion concentrations in the growth media decrease, the marked changes in relative supersaturation may also modify the mechanism precipitation. Moreover, it is generally not possible to make quantitative physical or chemical measurements on the precipitated solids formed during growth at various times because so little actually precipitates. Since there is considerable interest in measuring the rate of crystallization at very low supersaturation, this is a serious disadvantage of the conventional seeded growth studies. These problems have been overcome in a new technique reported here wherein the rate of precipitation can be measured under conditions of constant solution composition for long periods of time. The method enables macro amounts of calcium fluoride to be formed by direct precipitation at low supersaturation.

EXPERIMENTAL

Reagent grade chemicals were used throughout and stock solutions were prepared using triply distilled water. Calcium concentrations were determined by atomic absorption or by exchanging the metal ion for hydrogen ion on a Dowex-50 ion exchange resin and titrating the liberated acid with standard base. Fluoride solutions were prepared in polyethylene bottles and concentrations were determined using a fluoride specific ion electrode (Orion Model 94-09) with a silver/silver chloride reference electrode (Orion Model 90-01-00) in cells of a type

$$F^- \text{ electrode}|\text{solution under study}|KCl\ (4M)|AgCl|Ag$$

Emf'f were measured with a Beckman Research pH meter or with a Dosimat Brinkmann E.512 pH meter.

Crystal growth experiments were made in a nitrogen atmosphere in a cell consisting of a double-walled Pyrex glass vessel of 500 ml capacity with a teflon lid and polyethylene liner to prevent fluoride attack on the glass surfaces. The cell was maintained at the required temperature (37.0 ± 0.1 °C) by circulating thermostated water through the outer jacket. Supersaturated solutions of calcium fluoride were prepared at the required temperature by mixing solutions of calcium chloride and sodium fluoride in the concentration range $3.2 \times 10^{-4} - 7.5 \times 10^{-4}$ mol/dm^3. These solutions were stable for periods of days without spontaneous precipitation.

Seed crystals of calcium fluoride were prepared as described previously[20] by the simultaneous addition of sodium fluoride (0.478 M) and calcium fluoride (0.252 M) to triply distilled water at 37 °C. The crystals were washed free of chloride and the solid phase was confirmed as calcium fluoride by x-ray powder diffraction (Philips Electronic Instruments, Model XRG-300). Scanning electron micrographs (ISI Model II Scanning Electron Microscope) showed them to be regular cubes (approx. 300 nm edge length) with a specific surface area of 6.3 m^2 g^{-1} (Quantasorb, Quantachrome Corp).

In the crystallization experiments, following the addition of seed crystals to metastable supersaturated solutions, the concentration of lattice ions was maintained constant to better than 1% by the simultaneous addition of calcium chloride and sodium fluoride titrant solutions from mechanically coupled burettes. The rate of addition was controlled by emf of the fluoride electrode through a Metrohm pH-stat (combitrator Model D). It is interesting to note that specific ion electrodes which typically do not respond sufficiently rapidly so as to monitor a change in ionic concentration during reaction can readily be used, together with a potentiostat, to maintain constant activity of the ions in solution.

RESULTS

Concentrations of ionic species in the supersaturated solutions, are calculated from the corresponding total concentrations by using equations for mass balance, electroneutrality, and the formation of the various associated species in the equilibria:

Reaction	K (37 °C)	Reference
$HF \rightleftarrows H^+ + F^-$	5.13×10^{-4}	21
$HF + F^- \rightleftarrows HF_2^-$	3.63	21
$Ca^{2+} + F^- \rightleftarrows CaF^+$	10.96	22
$Ca^{2+} + OH^- \rightleftarrows CaOH^+$	25.70	23
$H_2O \rightleftarrows H^+ + OH^-$	2.40×10^{-14}	24

The calculations were made by successive approximations for I, the ionic strength, calculating activity coefficients of z-valent species, y_z, from the extended form of the Debye-Hückel equation proposed by Davies[26]. The solubility of calcium fluoride obtained by allowing growth experiments to proceed to equilibrium gave a thermodynamic solubility product $K_{so} = 3.47 \times$ $\times 10^{-11}$ mol^3 dm^{-9} at 37°C. This agrees well with the value, 3.46×10^{-11}, interpolated from the data of Kohlrausch[25].

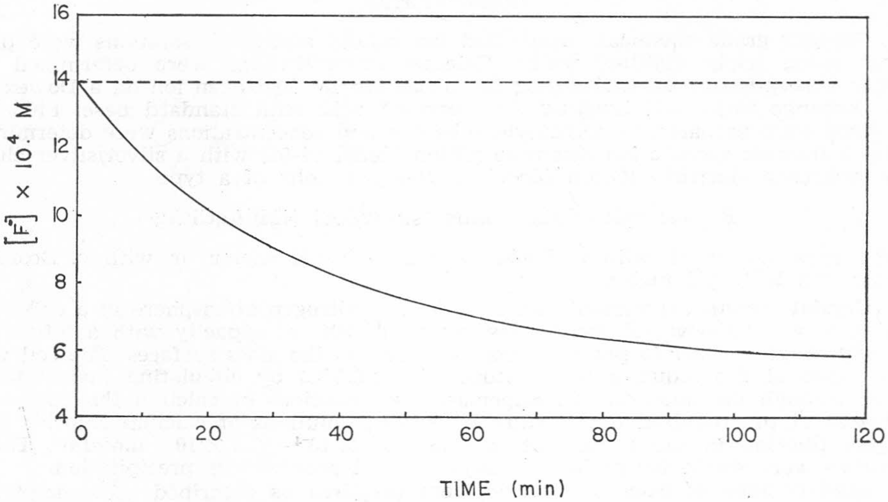

Figure 1. Plots of fluoride concentration against time for crystallization of calcium fluoride at 37 °C. Full line: conventional seeded growth method. Dotted line: constant composition method.

Figure 1 shows the results of a conventional seeded growth experiment in which the fluoride concentration is plotted as a function of time. In contrast, the constant composition method maintains the supersaturation at the initial value (Figure 1) and the rate of crystallization is given by the rate of addition of calcium chloride and sodium fluoride solutions in order to maintain constant concentration. Crystal growth experimental conditions are summarized in Table I and the results of a typical experiment are shown in Table II from which it can be seen that the lattice ion concentrations monitored at various times during the reaction, are constant to within 0.5%.

Typical plots of moles of calcium fluoride formed as a function of time are shown in Figure 2. It can be seen that the rate of crystallization after correction for the changes in total surface area is constant. Furthermore, the rate of the crystal growth is proportional to the weight of inoculating seed as can be seen from Figure 2 and the normalized rate data in Table I. This confirms

TABLE I

Crystallization of Calcium Fluoride at 37 °C

Expt. No.	T_{Ca}/ 10^3 mol dm^{-3}	T_F/ 10^3 mol dm^{-3}	I/ 10^3 mol dm^{-3}	seed / mg	Rate $\times 10^6$ / mol min^{-1} m^{-2}	$k \times 10^{-2}$ / dm^6 mol^{-1} m^{-2} min^{-1}
32	0.450	0.900	18.75	43.0	33.59	4.24
33	0.750	1.500	26.04	32.0	225.05	4.15
34	0.552	1.104	16.94	44.5	87.68	4.39
35	0.552	1.104	16.94	22.5	93.62	4.69
36	0.500	1.000	16.78	44.8	65.94	4.94
37	0.365	0.730	16.38	45.8	10.55	4.47
38	0.448	0.896	16.62	22.5	37.53	4.66
39	0.350	0.700	16.33	54.3	6.85	4.04
40	0.552	1.104	16.92	31.0	91.60	4.59

TABLE II

Crystallization of CaF_2 at 37 °C. Constant composition Exp # 34

Time/min	T_{Ca}/mmol dm^{-3}	T_F/mmol dm^{-3}	% growth
22	0.554	1.104	79
31	0.550	1.104	106
39	0.553	1.104	132
48	0.552	1.104	159

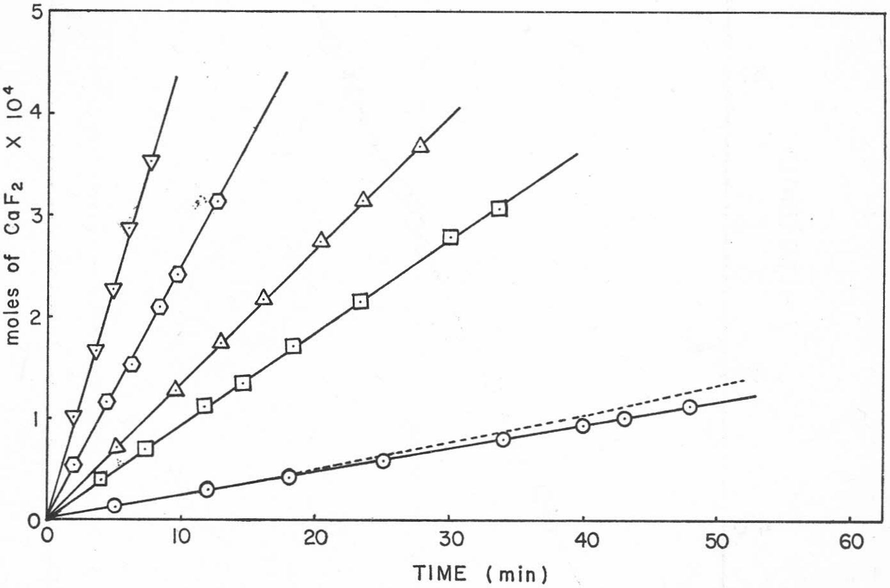

Figure 2. Plots of moles of calcium fluoride grown as a function of time. Experiment 39, ○; 32, □; 35, △; 34, hexagon; 33, triangle on vertex. Dotted curve, uncorrected data of experiment 39.

that crystallization takes place on the added seed and that no secondary or heterogeneous nucleation takes place during the experiments.

A recent conventional seeded precipitation kinetic study of calcium fluoride[20] has indicated a surface-controlled growth mechanism with a rate of crystallization following the equation.

$$\text{Rate of growth} = \frac{\mathrm{d}m}{\mathrm{d}t} = ks\left\{([\mathrm{Ca}^{2+}]\,[\mathrm{F}^{-}]^2)^{1/3} - \frac{K_{\mathrm{so}}^{1/3}}{y_\pm}\right\}^n = ks\,\Delta^n \qquad (1)$$

where $\mathrm{d}m/\mathrm{d}t$ is the moles of CaF_2 grown per unit time, k is the rate constant, s is a function of surface area, $y_\pm$ is the mean activity coefficient, and square brackets enclose molar concentrations. The effective order of reaction, n in equation (1) was shown to be 2 at relative supersaturations, $S = 0.75$ to 2.0 ($S = [\mathrm{Ca}^{2+}] - [\mathrm{Ca}^{2+}]_o/[\mathrm{Ca}^{2+}]_o$, where $[\mathrm{Ca}^{2+}]_o$ is the equilibrium concentration of calcium), but at lower supersaturation ($S < 0.75$), n was found to be 3.

In the present study, the rate of crystallization could be measured with a greater precision than in the previous work[20] and plots of $-\log R$ against

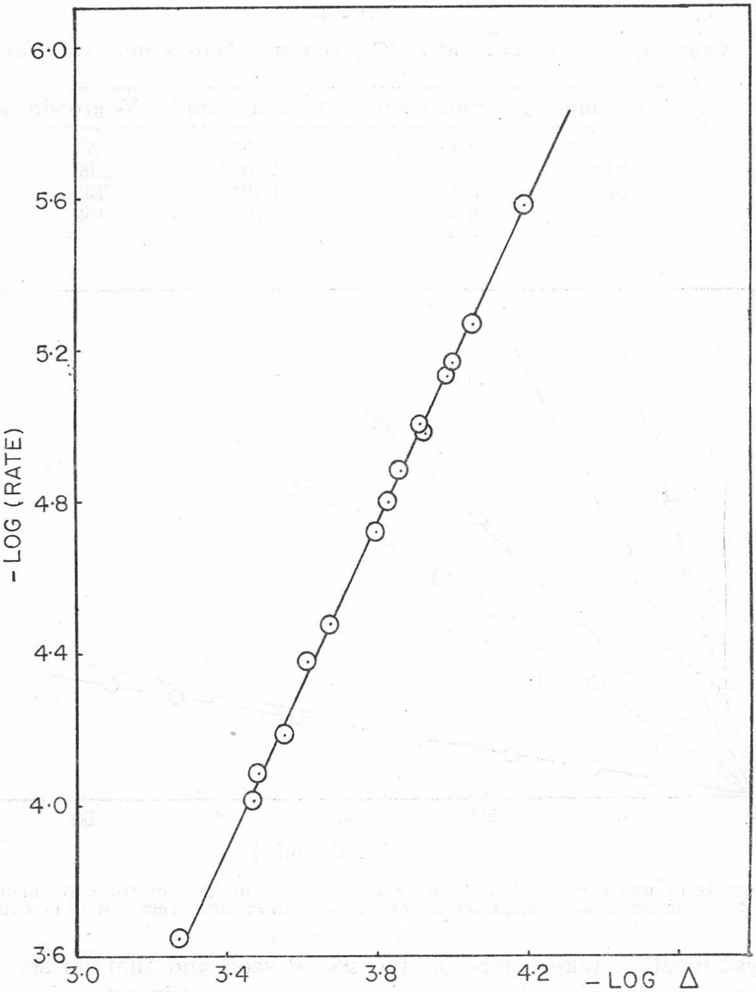

Figure 3. Plots of -log (rate) against -log Δ.

$-\log \Delta$ are shown in Figure 3. The slope of the line, 2.0 ± 0.1 indicates a value of $n = 2$ in equation (1) and plots of the rate of crystallization against Δ^2 in Figure 4. confirm the applicability of this kinetic rate equation. The apparent order of the crystallization $n = 2$ again suggests a surface controlled crystallization. The change in reaction order to $n = 3$ at low supersaturation suggested by the results of the conventional seeded crystallization experiments[20] could not be confirmed using this more sensitive constant composition method. Experiments at different rates of stirring indicated that fluid dynamics had no effect upon the rate of crystallization again pointing to a surface-controlled process. Scanning electron micrographs of the growing crystals showed that they maintained their cubic structure.

The influence of inhibitors of crystal growth may be studied under highly reproducible conditions by the constant composition method. The remarkable

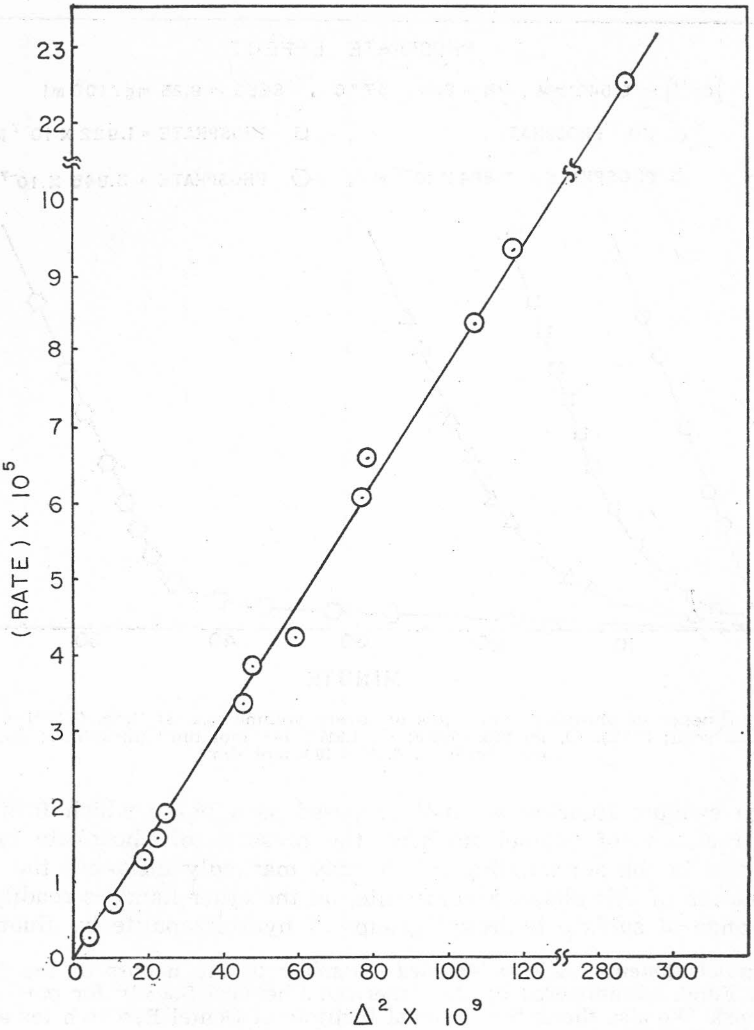

Figure 4. Plots of rate against Δ^2.

effect of phosphate ion of concentration T_p, upon the rate of calcium fluoride crystallization is illustrated in Figure 5. At a phosphate concentration of 1.92×10^{-6} mol/dm^3, growth is entirely inhibited for at least 24 h. At lower concentrations of 3.85×10^{-7}, 2.88×10^{-7} and 1.92×10^{-7} mol/dm^3, induction periods of 44, 18, and 10 min, respectively, precede crystallization which then takes place with a rate characteristic of that in the absence of phosphate ion. The adsorption of phosphate ion at the solid/liquid interface thus markedly modifies the crystal growth process. At higher phosphate concentrations, the formation of calcium phosphate phases is seen in scanning electron micrographs of the growing solids. The marked influence of phosphate upon calcium fluoride crystallization may have significant implications in our understanding of the reactions at bone and tooth surfaces in the presence of fluoride ion.

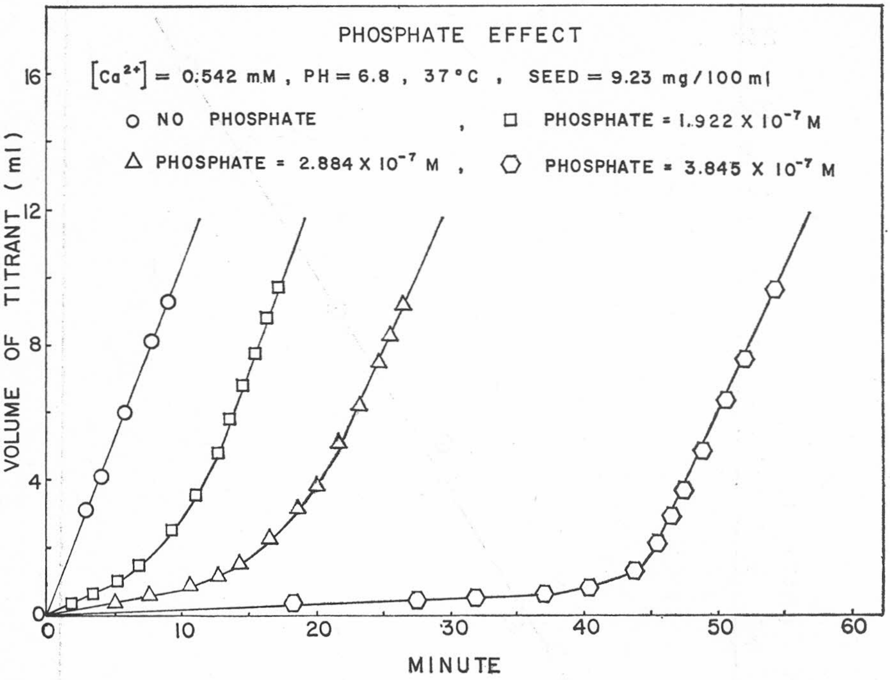

Figure 5. Influence of phosphate ion. Plots of titrant volume against time. ($[Ca^{2+}]$ = 0.542 mmol dm^{-3}; 23 mg seed; 37 °C). ○, no phosphate; □, 1.922 × 10^{-7} mol dm^{-3} phosphate; △, 2.884 × 10^{-7} mol dm^{-3}; , 3.845 × 10^{-7} mol dm^{-3}.

Although calcium fluoride is often proposed as a phase which forms in the topical treatment of enamel surfaces, the presence of phosphate ion at the surface and in the surrounding saliva, may markedly influence the tendency for formation of this phase. Fluorapatite, on the other hand, is readily formed by exchange of surface hydroxyl groups of hydroxyapatite by fluoride ions.

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REFERENCES

1. G. H. Nancollas and M. B. Tomson, *Faraday Discuss. Chem. Soc.* **61** (1976) 175.
2. G. H. Nancollas, *Biological Mineralization,* Colston Research Symposium, »The Behaviour of Ions in Macromolecular and Biological Systems«, Bristol, 1977, p. 245.
3. G. H. Nancollas, in: H. Fleisch, W. G. Robertson, L. H. Smith, and W. Vahlensieck, (Eds.), *International Symposium, Urolithiasis Research,* Plenum Press, New York 1976, p. 5.
4. G. H. Nancollas, A. E. Eralp, and J. S. Gill, *J. Petroleum Eng.* **18** (1978) 133.
5. M. N. Elliot, *Desalination* **6** (1969) 87; **8** (1970) 221.
6. G. H. Nancollas and M. S. Mohan, *Arch. Oral. Biol.* **15** (1970) 731.
7. G. H. Nancollas and B. Tomazic, *J. Phys. Chem.* **78** (1974) 2218.
8. M. B. Tomson and G. H. Nancollas, *Science* **200** (1978) 1059.

9. Z. Amjad, P. Koutsoukos, M. B. Tomson, and G. H. Nancollas, *J. Dent. Res.* **57** (1978) 909.
10. J. A. Gray, *J. Dent. Res.* **37** (1958) 638.
11. Z. Liang and W. I. Higuchi, *J. Phys. Chem.* **77** (1973) 1704.
12. J. A. Tovborg, *Z. physik. Chem.* **A180** (1937) 93.
13. B. Černicki and B. Težak, *Croat. Chem. Acta* **28** (1956) 175.
14. J. A. Christiansen and A. E. Nielsen, *Z. Electrochem.* **56** (1952) 465.
15. A. E. Nielsen, *J. Coll. Sci.* **10** (1955) 576.
16. G. L. Gardner and G. H. Nancollas, *J. Dent. Res.* **55** (1976) 342.
17. G. H. Nancollas, *Interactions in Electrolyte Solutions*, Elsevier Publ. Co., Amsterdam 1966.

SAŽETAK

Kinetika kristalizacije kalcijeva fluorida. Nova metoda konstantnog sastava

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Opisana je nova metoda za proučavanje kinetike kristalizacije kalcijeva fluorida. Metoda se zasniva na konstantnom sastavu otopine, a prikladna je za primjenu pri vrlo niskim presićenjima. Brzina kristalizacije je proporcionalna kvadratu presićenja u području relativnog presićenja, *S*, od 0,20 do 1,66. Rezultati istraživanja pokazuju da je kristalizacija kontrolirana površinski, te da je njezina brzina znatno utjecana prisutnošću fosfata.

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