

Formation and Morphology of Struvite and Newberyite in Aqueous Solutions at 25 and 37 °C

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ABSTRACT

The influence of the initial reactant concentrations ($c_i(\text{Mg})_{\text{tot}} = 5.0 \times 10^{-6}$ to 5.0×10^{-1} mol dm⁻³, $c_i(\text{P})_{\text{tot}} = c_i(\text{NH}_4)_{\text{tot}} = 1.0 \times 10^{-3}$ to 5.0×10^{-1} mol dm⁻³) and temperature (25 and 37 °C) on the composition and morphology of the precipitates formed in the system $\text{MgCl}_2\text{-NH}_4\text{H}_2\text{PO}_4\text{-NaOH-H}_2\text{O}$ at initial $\text{pH}_i = 7.40$ has been investigated. Precipitation diagrams are presented showing the concentration regions within which different morphologies of solid phase have been formed. The solid phases aged for 24 hours were characterized by means of optical microscopy, FT-IR spectrophotometry, X-ray diffractometry and thermogravimetry. It was found that struvite was a predominant phase formed within the concentration region examined and newberyite was obtained only in the region where $\text{pH}_{24\text{h}} < 6.5$. The influence of the initial pH on the formation and transformation of these two compounds were studied in the region $5.0 \leq \text{pH}_i \leq 9.0$ and the results are discussed.

Key words: struvite, newberyite, precipitation, morphology

Introduction

A considerably high percentage of human population (4 to 15 %) suffer from urinary stone formation¹. Majority of these calculi are calcium salts (75 %), oxalates and phosphates being the most common among them. Among phosphates, magnesium phosphates (magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and magnesium hydrogen phosphate trihydrate, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) have also been reported to occur as constituents in vesical and renal calculi^{2,3}, not only in adults but also in children.^{4,5} These calculi are mostly related to urinary tract infections with ureolithic microorganisms in humans and animals^{2,6,7} and 10–20 % of them are predominantly composed of magnesium ammonium phosphate hexahydrate, commonly known as struvite. Urine of a healthy person is undersaturated with regard to struvite, but because of the conditions provoked by urease-producing microorganisms and the urine complex composition, the precipitation of struvite can occur. Under such conditions struvite often precipitates together with apatites and the sediment can easily be attached to the particles of organic matter formed as a consequence of the infection. This mechanism favours the crystal deposition and aggregation, so that struvite stones grow rather quickly. On the other hand, the formation of newberyite in urinary stones has still been a matter of discussion^{8–10}.

Due to its importance in many fields of interest (wastewater treatment systems, geological deposits, etc.), struvite has been studied from different points of view and many of its physical and chemical properties have been described^{11–14}.

For a better understanding of stone formation and its possible prevention, not only the medical studies but also a physical-chemical approach to the problem is needed. In order to contribute to the knowledge on these two compounds, in this paper a part of a systematic investigation is presented. Spontaneous precipitation of struvite and newberyite was studied in aqueous solutions at 25 and 37 °C, and the initial $\text{pH}_i = 5.0\text{--}9.0$.

Experimental

All solutions used, MgCl_2 , $\text{NH}_4\text{H}_2\text{PO}_4$, HCl and NaOH, were analytically pure and the water was of high quality (conductivity < 0.1 $\mu\text{S cm}^{-1}$). Stock solutions were standardized by classical analytical methods¹⁵, i.e. phosphate was determined spectrophotometrically as the molybdovanadato complex, magnesium by complexometric titration and sodium hydroxide by titration with the standard HCl solution.

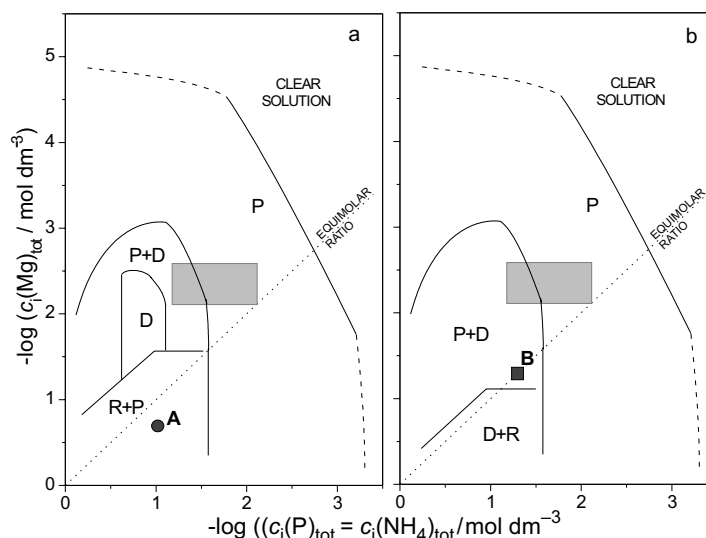


Fig. 1. Precipitation diagrams with the assigned precipitation and region boundaries of the system $\text{MgCl}_2\text{-NH}_4\text{H}_2\text{PO}_4\text{-NaOH-H}_2\text{O}$, $\text{pH}_i=7.4$, aging time 24 h, 25 °C (a) and 37 °C (b).

Dashed lines mark the uncertain parts of precipitation boundaries. Grey area in both diagrams indicates the region of magnesium and phosphate concentrations found in normal urine. Full dot (A) in diagram (a) and full quadrangle (B) in diagram (b) denote systems selected for kinetic experiments. Designations: P – platelet (elongated), D – dendrite, R – rhombohedral crystal.

Precipitation systems for the construction of precipitation diagrams were prepared as stated elsewhere¹⁶, by mixing equal volumes (5.0 cm³) of previously thermostated magnesium chloride and ammonium dihydrogenphosphate solutions, preadjusted to $\text{pH} = 7.4$ (physiological value) by adding a required amounts of NaOH. After the initial mixing of the reactants no further stirring was employed, but systems were aged for 24 h in a 25 °C or 37 °C water bath. The range of initial reactant concentrations is given in the precipitation diagrams. Twenty four hours after mixing, the samples were examined under a light microscope (equipment from E. Leitz, Wetzlar) and the pH was measured by means of a combined glass-calomel electrode (GK 2401 C) connected to a pH meter and standardized by a series of buffers 4.005 < $\text{pH} < 10.01$ (all Radiometer).

For the kinetic experiments the precipitation systems were prepared by mixing equal volumes (60.0 cm³) of magnesium chloride and ammonium dihydrogenphosphate solutions of known concentrations, both preadjusted to the initial pH of the experiment. A glass reactor tightly closed by a Teflon stopper was used for the reaction vessel. The precipitation system was thermostated and magnetically stirred at a constant rate. These experiments were performed in a range of the initial pH, $5.0 \leq \text{pH}_i \leq 9.0$. During the experiments the changes both in the solid and in the liquid phases were monitored. The progress of the reaction was followed by a measurement of pH as a function of time, using a glass-calomel electrode (GK 2401 C), dipped into the solution through a hole in the stopper. Before the experiment started the pH meter (ION 85, Radiometer) was adjusted by standard buffer solutions. During the experiments, aliquots of suspension were taken from the

system in time intervals, filtered through 0.45 μm membrane filters, washed with water and dried at 50 °C.

As the precipitates aged for 24 h, so the precipitates from the kinetic experiments were characterized by X-ray diffractometry, XRD, (Philips counter diffractometer with graphite monochromatized Cu-K α radiation), Fourier transform infrared spectroscopy, FT-IR, (Mattson FT-IR spectrophotometer, Genesis Ser.) and thermogravimetry, TG, (Metler TG 50 thermobalance with TC 11 TA processor). In the present work, the content of struvite and newberyite in the precipitate is represented by FT-IR spectra only, since this analysis gives satisfactory results.

Results and Discussion

The precipitation system $\text{MgCl}_2\text{-NH}_4\text{H}_2\text{PO}_4\text{-NaOH-H}_2\text{O}$ can be represented by a precipitation diagram, in which the concentrations of the components are varying in a range shown in Figure 1. Two such diagrams of the same system aged for 24 h at 25 °C (Figure 1a) and 37 °C (Figure 1b), are shown. The aging time of 24 h has been found to be long enough to establish an apparent equilibrium between the liquid and the solid phases in the system. The precipitation boundary separates the systems in which no detectable formation of the solid phase was observed (clear solution) from the systems with the first detectable precipitate (precipitation body). Dashed lines in continuation of the precipitation boundaries denote their uncertain parts. The concentration region examined was much larger than the region of magnesium and phosphate concentrations found in urine of healthy persons (grey areas)¹⁷. Inside the precipitation body the region boundaries, that separate regions

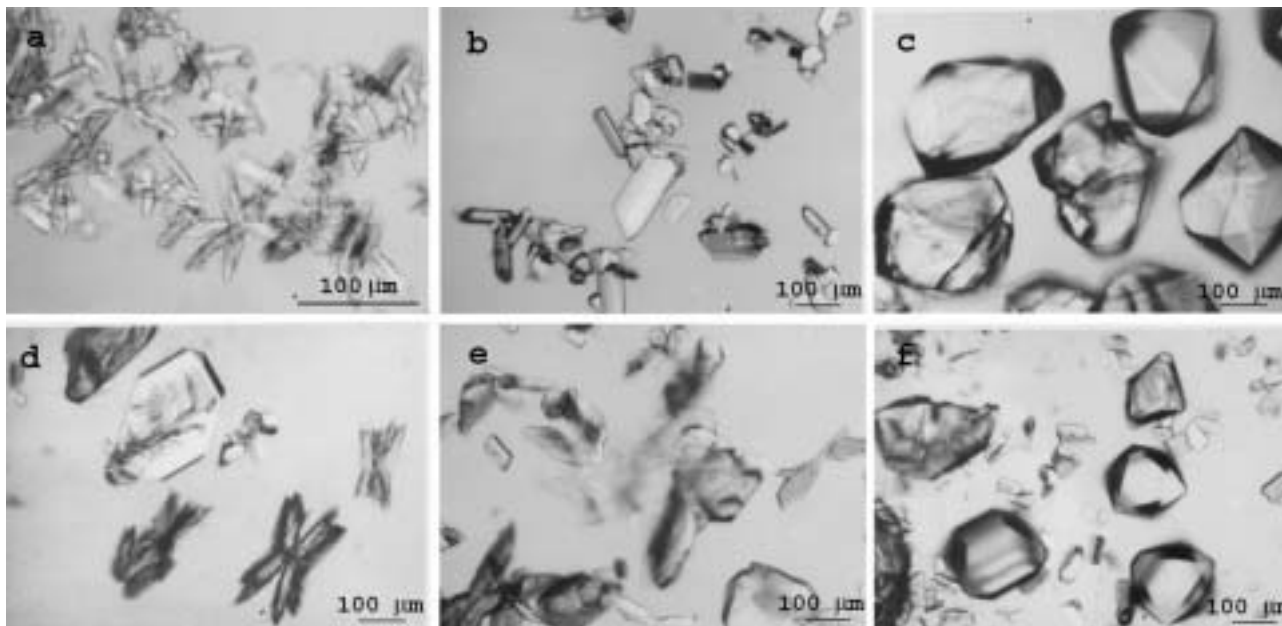


Fig. 2. Optical micrographs showing typical morphologies of precipitates obtained under conditions given in Fig. 1: (a) dendrites, (b) elongated platelets, (c) rhombohedral crystals, (d) mixture of platelets and dendrites, (e) mixture of dendrites and rhombohedral crystals, and (f) mixture of rhombohedral crystals and platelets.

with different precipitate morphologies, are given. Figure 2 shows typical morphologies of precipitates found in these regions after 24 h of aging. Although the same morphologies of the precipitate were observed at 25 and 37 °C, the regions within which these morphologies appeared were different. It is evident from Figures 1a and 1b that dendrites, alone, appeared only at 25 °C while at 37 °C this form of crystals precipitated always in a mixture with elongated platelet crystals or with rhombohedral ones. However, the region of dendrite appearance, on the whole, is much larger at 37 °C than at 25 °C. Characterization of the crystals (XRD, FT-IR and TG) obtained in such a way showed that the elongated platelets and dendrites were exclusively struvite, the rhombohedral crystals were newberyite. Since within the concentration region of reactants found in urine (grey areas in Figure 1) only struvite in the form of dendrites and elongated platelets could be expected to precipitate, the systems outside this region were chosen for the kinetic investigations of struvite and newberyite formation and detailed analysis. Therefore, two systems from the precipitation diagrams represented, one from each diagram, were selected. In one of them, A, ($c_i(\text{Mg}^{2+}) = 2.3 \times 10^{-1} \text{ mol dm}^{-3}$, $c_i(\text{PO}_4^{3-}) = c_i(\text{NH}_4^+) = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, 25 °C; marked as a full dot in Figure 1a), a mixture of rhombohedral and elongated platelet crystals was obtained 24 hours after mixing the reactants. In the other one, B, ($c_i(\text{Mg}^{2+}) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, $c_i(\text{PO}_4^{3-}) = c_i(\text{NH}_4^+) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, 37 °C; marked as a full quadrangle in Figure 1b), elongated platelets and dendrites were the morphologies of crystals observed after 24 hours of aging. In order to study the mutual relationship between struvite and newberyite,

these systems were treated differently from the way they were treated for the construction of the precipitation diagrams. This time, after mixing the reactants, the systems were continuously stirred at a constant rate and were studied in a range of initial pH_i , as mentioned above. The changes in the systems were followed during the first 5 hours of the process.

Figure 3 shows changes of pH as a function of time in system A (25 °C), when the reactions were initiated at $\text{pH}_i = 6.99$, $\text{pH}_i = 7.40$ and $\text{pH}_i = 9.08$. The three pH_i were chosen to be represented here, since the experiments initiated at these pH_i values characterize the whole pH_i region examined. In all three experiments, the solid phase appeared in the system immediately after mixing the reactants, which was followed by an

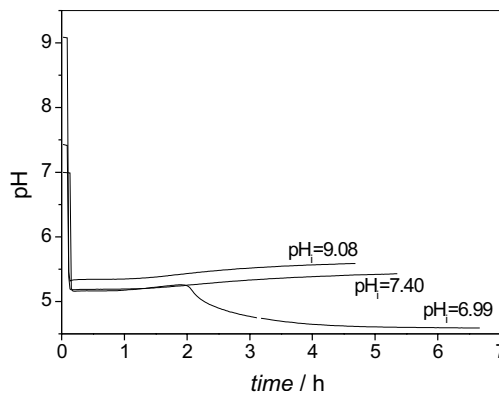


Fig. 3. Changes of pH as a function of time in the system $c_i(\text{Mg}^{2+}) = 2.3 \times 10^{-1} \text{ mol dm}^{-3}$, $c_i(\text{PO}_4^{3-}) = c_i(\text{NH}_4^+) = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$ at 25 °C and different initial pH_i .

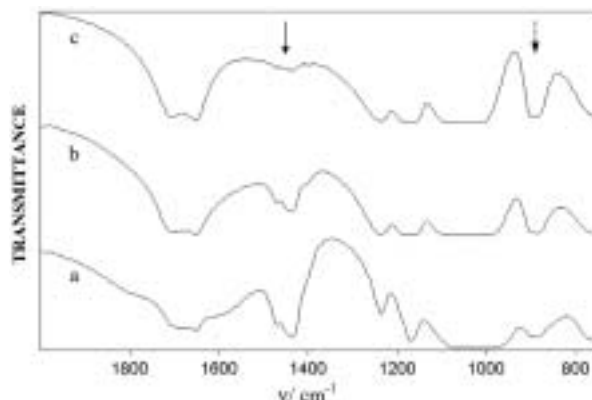


Fig. 4. Compilation of FT-IR bands for struvite (full arrow) and newberyite (dashed arrow) taken from the system $c_i(Mg^{2+}) = 2.3 \times 10^{-1} \text{ mol dm}^{-3}$, $c_i(PO_4^{3-}) = c_i(NH_4^+) = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, 25 °C and initial $pH_i = 9.08$, at: (a) 1 min, (b) 120 min and (c) 270 min.

abrupt decrease of pH to the values of about 5.2 to 5.4. The first precipitate in all these systems was a mixture of struvite and newberyite, and, morphologically, the crystals were mostly dendrites with some small rhombohedrals. During the time, in the experiment initiated

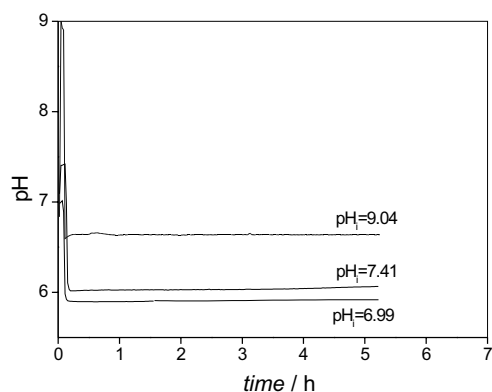


Fig. 5. Changes of pH as a function of time in the system $c_i(Mg^{2+}) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, $c_i(PO_4^{3-}) = c_i(NH_4^+) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ at 37 °C and different initial pH_i .

at $pH_i = 9.08$, the amount of rhombohedral crystals increased, dendrites gradually disappeared from the system and the analyses showed an increase of newberyite in the system. As an example, Figure 4 shows three of the FT-IR spectra taken during that experiment from which this change in the precipitate composition is evident. The whole process was accompanied with a slight increase in pH, which probably is the result of struvite to newberyite transformation and a consequence of the formation of new protolytic equilibria, restored because of a simultaneous dissolution of struvite and growth of newberyite. Similarly, in the other two experiments, initiated at $pH_i = 7.40$ and 6.99, the process of struvite to newberyite transformation also occurred, only that the process was much faster and was completed within about 2 hours in the experiment initiated at $pH_i = 6.99$. The drop of pH after that time (see Figure 3) could be ascribed to the growth of newberyite rhombohedral crystals that remained as the only solid phase in the system. All this is consonant with the previous findings^{8,16,18} according to which newberyite is a stable form at low pH and high concentrations of magnesium.

The experiments conducted at 37 °C (system B in Figure 1b) in which, according to the precipitation diagram, a mixture of elongated platelets and dendrites, i.e. only struvite was expected, behaved differently from the comparable systems at 25 °C. The changes of pH as a function of time in system B, in which the reaction was initiated at $pH_i = 9.04$, $pH_i = 7.41$ and $pH_i = 6.99$, are shown in Figure 5. Similarly to the comparable systems conducted at 25 °C, no measurable induction periods were detected for the appearance of precipitate, although in these experiments the reactant concentrations were lower. Such behaviour of the systems can be ascribed to the higher temperature of the experiment, the consequence of which was the speeding up of reaction. In the experiment initiated at $pH_i = 9.04$, the formation of precipitate caused an abrupt drop in pH from the initial value to the value of $pH = 6.63$ and did not change significantly during 5 hours of the experiment. The entire precipitate consisted of dendritic crystals and this shape of crystals was consistent throughout the experiment (Figure 6). The analyses (XRD, FT-IR, TG)

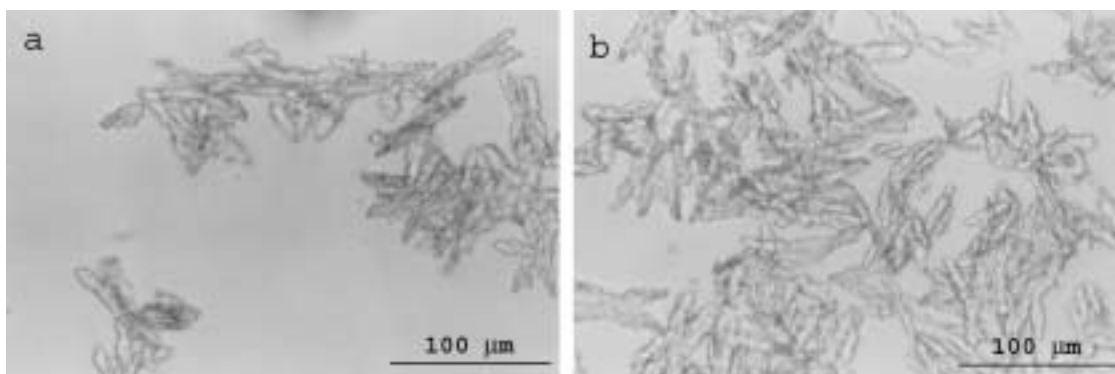


Fig. 6. Optical micrographs of dendritic crystals obtained in the system $c_i(Mg^{2+}) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, $c_i(PO_4^{3-}) = c_i(NH_4^+) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, 37 °C and initial $pH_i = 9.04$, at: (a) 10 min and (b) 180 min.

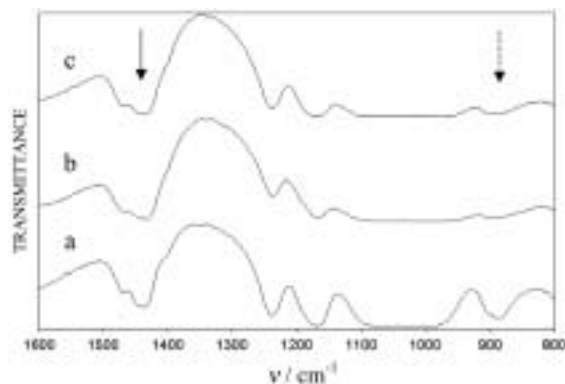


Fig. 7. Compilation of FT-IR bands for struvite (full arrow) and newberyite (dashed arrow) taken from the system ($c_i(\text{Mg}^{2+}) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, $c_i(\text{PO}_4^{3-}) = c_i(\text{NH}_4^+) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, 37°C and initial $\text{pH}_i = 9.04$, at: (a) 1 min, (b) 60 min and (c) 300 min.

showed a mixture of struvite and newberyite, which was surprising since no dendritic shape of newberyite was found previously. Opposite to all previous results of our experiments conducted at 25°C , the amount of newberyite decreased in favour to struvite during the time, as shown by a series of FT-IR spectra in Figure 7. The disappearance of newberyite occurred because newberyite is not stable at $\text{pH} > 6.5^{8,16,18}$ and it is to be assumed that all newberyite dendritic crystals disappeared from the system by the time of 24 hours, the time when the samples for the construction of precipitation diagrams were taken for analyses. The appearance of newberyite in the system was probably the result of kinetic rather than thermodynamic limitations and, because unstable under such circumstances, its disappearance was a consequence of reinstatement of equilibrium in the system. In the system started at $\text{pH}_i = 7.41$, pH dropped to the value of $\text{pH} \approx 6.02$ (Figure 5) and remained around this value throughout the experiment. As detected, the first precipitate in the system was newberyite, although this pH is favourable to the both compounds, struvite and newberyite. The results of the analyses of samples taken during the experiment showed that struvite started to appear in the system after about 15–20 min and was present in the system until the end of experiment, 5 hours later. This is evident from FT-IR spectra shown in Figure 8. Since no other changes in the system were recorded, after the period of struvite appearance in the system, it could be concluded that the same mechanism of struvite formation occurred in both experiments (ini-

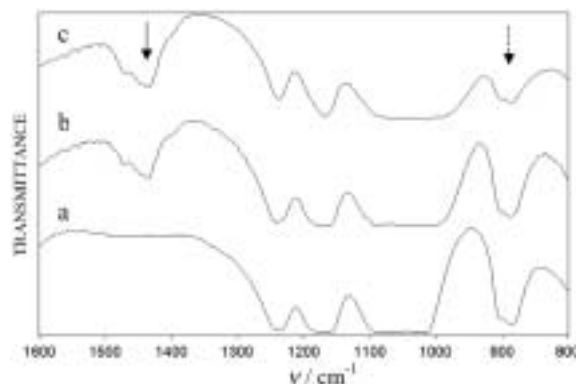


Fig. 8. FT-IR spectra (in the region $1600\text{--}800 \text{ cm}^{-1}$) of the samples taken at: (a) 5 min, (b) 60 min and (c) 300 min, from the system $c_i(\text{Mg}^{2+}) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, $c_i(\text{PO}_4^{3-}) = c_i(\text{NH}_4^+) = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$, 37°C and initial $\text{pH}_i = 7.41$, showing bands characteristic for struvite (full arrow) and newberyite (dashed arrow).

tiated at $\text{pH}_i = 9.04$ and $\text{pH}_i = 7.41$) conducted at 37°C . All this has to be proved in further, quantitative, treatment of these processes, which is planned for the near future studies. In the experiment initiated at $\text{pH}_i = 6.99$ (Figure 5) newberyite, alone, precipitated and no struvite appeared within 5 hours of the experiment. The value of pH dropped initially to $\text{pH} \approx 5.90$, which is the pH of newberyite stability.

The results presented in this work indicate that there is a possibility for both struvite and newberyite to be constituents of urinary stones, since both of them can precipitate simultaneously and can coexist under certain conditions. Nevertheless, the urine conditions are those that have to be considered before drawing any final conclusions. Up to now, newberyite has been reported to be found in old urinary stones in which, presumably, it was a product of struvite transformation that occurred in the solid state by the loss of water and ammonium^{9,19,20}. Newberyite was also detected as a constituent in the calculi formed under conditions of chronic urinary infection²¹, but such findings are rather rare.

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STVARANJE I MORFOLOGIJA STRUVITA I NJUBERITA U VODENIM OTOPINAMA PRI 25 I 37 °C

S A Ž E T A K

Istraživan je utjecaj početnih koncentracija reaktanata ($c_i(\text{Mg})_{\text{tot}} = 5.0 \times 10^{-6}$ do 5.0×10^{-1} mol dm⁻³, $c_i(\text{P})_{\text{tot}} = c_i(\text{NH}_4)_{\text{tot}} = 1.0 \times 10^{-3}$ do 5.0×10^{-1} mol dm⁻³) i temperature (25 and 37 °C) na sastav i morfologiju taloga u sustavu MgCl₂-NH₄H₂PO₄-NaOH-H₂O pri početnom pH_i = 7.40. Pokazani su taložni dijagrami u kojima su označena područja nastajanja čvrste faze različitih morfologija, a sastav tih čvrstih faza, starenih 24 sata u matičnoj otopini, je karakteriziran pomoću optičke mikroskopije, FT-IR spektrofotometrije, röntgenske difrakcije i termogravimetrije. Nađeno je da struvit prevladava u istraživanom koncentracijskom području, dok je njuberit dobiven samo u području gdje je pH_{24h} < 6.5. Utjecaj početnog pH na nastajanje i transformaciju struvita i njuberita proučavan je u području 5.0 ≤ pH_i ≤ 9.0, a dobiveni rezultati su raspravljani.