

INTERACTION OF MATERIALS FROM SYSTEM $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{P}_2\text{O}_5$ WITH SIMULATED BODY FLUID (SBF) AND DISTILLED WATER

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Three different crystallographic modifications of mineral brianite were prepared from the melt. The temperatures of modification changes determined by DTA were 760 and 900 °C, respectively. The interaction of all modifications with simulated body fluid (SBF) and with distilled water was studied. Hydroxyapatite was identified on the sample surfaces after the interaction of brianite with SBF using X-ray diffraction and X-ray microanalysis suggesting possible bioactivity. The time dependence of amount of brianite components i in the solution can be described using equation $NL_i = B/K_i [1 - \exp(-K_i t)] + W_i t$. Considering general composition of precipitated layer $\text{Ca}_x\text{Mg}_{(10-x)}(\text{PO}_4)_6(\text{OH})_2$, the rate of dissolution and the rate of precipitation were estimated from W_i parameters using iteration method. Stechiometric parameter x changes in interval 5.2-9.7. The dissolution and precipitation rates depend on crystallographic modification both in SBF and in distilled water. Higher values of both precipitation and dissolution rates were found for the interaction of γ modification in all solutions studied compared to α and β modifications.

INTRODUCTION

In recent years, many bioactive materials based on glass and glassceramics have been developed and tested. Clinical and in vivo tests have to be preceded by in vitro tests. During these tests, the behaviour of materials in simulated body fluid (SBF) is studied in order to determine their biocompatibility and bioactivity [1]. The kinetics of interaction between the material and SBF is not influenced purely by its chemical composition. The phase composition can influence this interaction as well [2].

The aim of present study was:

- to characterise the different phases of a material from system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{P}_2\text{O}_5$ prepared from melt and
- to discuss the behaviour of three different crystallographic modifications during their interaction with distilled water and with two simulated body fluids.

Changes in structure of modifications were described by X-ray diffraction. These changes can be seen in figures 1, 2 and 3. Arrows indicate changes between XRD patterns of different phases.

Samples were grains (α , β and γ phase) or blocks (α phase) with proportions $15 \times 13 \times 10$ mm. Surface of grains fraction with diameter between 0,3-0,5 mm was determined by image analysis LUCIA. Assuming the elliptical shape of grains, the grain surface can be computed using equation (1):

$$S = \pi v \left[\frac{3}{2} (a + b) - \sqrt{ab} \right] + 2 \pi a b \quad (1)$$

where: a – major axis, b – minor axis, v – height of particles. The values $64.2 \text{ cm}^2 \text{ g}^{-1}$, $58.4 \text{ cm}^2 \text{ g}^{-1}$ and $58.3 \text{ cm}^2 \text{ g}^{-1}$ were obtained for α , β and γ , respectively.

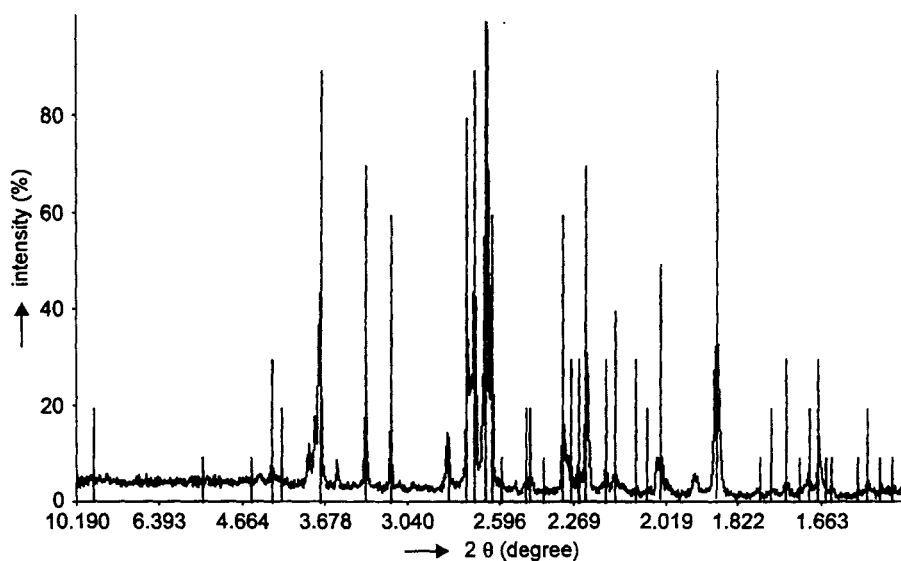
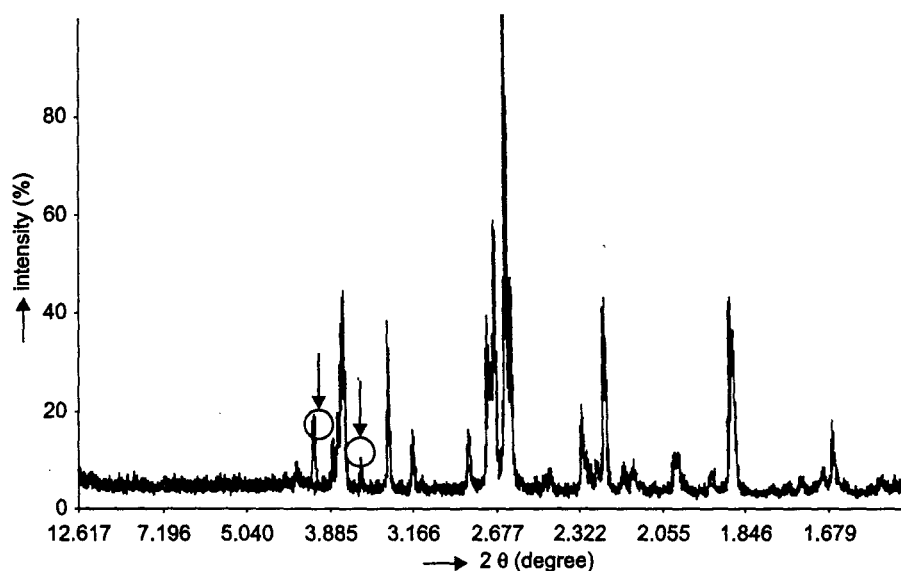
Two simulated body fluids (SBF1 and SBF2) and distilled water were used for corrosion test. Their chemical composition and pH values are given in table 1.

EXPERIMENTAL PART

Description of samples

The material with chemical composition identical with the mineral brianite (20.6 Na_2O ; 18.6 CaO ; 13.4 MgO 47.3 P_2O_5 in wt.%) was prepared in laboratory furnace. Temperatures of modification changes were determined by DTA as 760°C for $\alpha \leftrightarrow \beta$ transformation and 900 °C for $\beta \leftrightarrow \gamma$ transformation.

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Figure 1. X-ray diffraction patterns of α -phase and mineral Brianite (vertical lines).Figure 2. X-ray diffraction patterns of β -phase (changes are highlighted by arrows and circles) and α -phase.Table 1. Chemical composition of corrosion solutions (g l^{-1}).

component solution	KCl	NaCl	MgO	CaCO ₃	NaHCO ₃	KH ₂ PO ₄	TRIS	HCl (ml l ⁻¹)	pH 20 °C
SBF1	0.41	8.053	0.061	0.250	0.353	0.136	6.03	3.8	7.6
SBF2	0.41	8.05	0.06	0.250	0.353	0.136	7.79	3.8	7.6
distil. water	-	-	-	-	-	-	-	-	5.8

Interaction with corrosion solutions

Block samples were exposed to SBF2 solution under static conditions in the biological thermostat at

temperature 36.5 - 37°C and ratio $S/V = 0.05 \text{ cm}^{-1}$ [(Surface of sample) / (Volume of solution)] for 7, 14, 21 and 28 days.

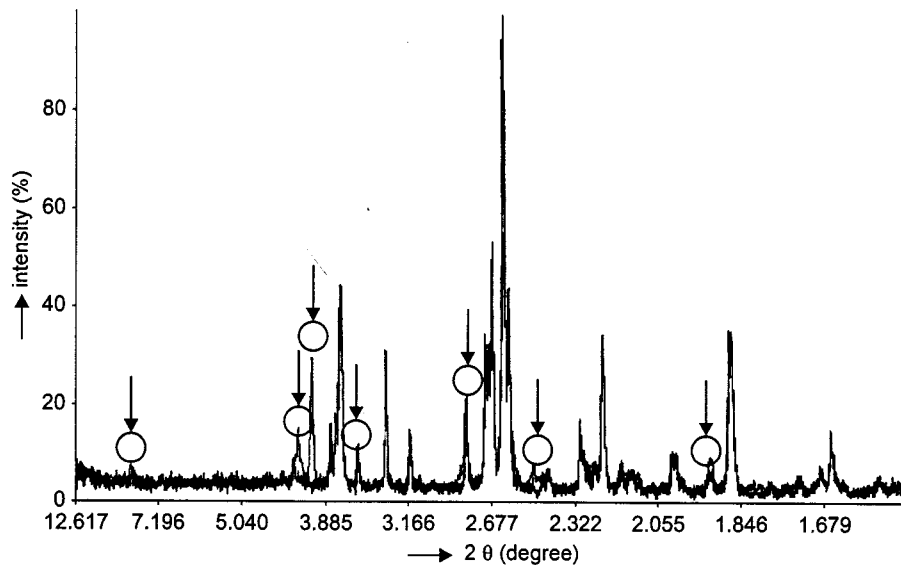


Figure 3. X-ray diffraction patterns of γ -phase (changes are highlighted by arrows and circles) and α -phase.

The grain samples were exposed to SBF1, SBF2 and distilled water during the flow-through test. In this test, the solution flowed at the rate of 1 ml min^{-1} through the 1 g of grains in polyethylene cell at the temperature of 37°C . The flow rate was maintained using peristaltic pump.

RESULTS AND DISCUSSION

Block samples

After interaction with SBF2, precipitated layers were found on the surface of samples (figure 4). The higher content of Ca and P in these layers was determined using EMPA. Using XRD (figure 5), hydroxyapatite (HA) was identified on the surface.



Figure 4. Hydroxyapatite created on the surface of materials after 7 days in SBF 2, 37°C .

Grain samples

Results of flow-through test are shown in figures 6 - 8 as time dependencies of pH and of normalised leach loss of Ca^{2+} , Mg^{2+} and PO_4^{3-} .

After the initial increase of pH values during the first hour of interaction, approximately constant value was reached. The release of sodium ions into the solution probably caused this increase.

The normalised leach loss is defined as

$$NL_i^t = \frac{\Delta c_i}{f_i} \frac{F \Delta t}{S} + NL_i^{t-\Delta t} \quad (2)$$

where Δc_i is the change of solution concentration of component i in respect to the fresh corrosion solution, f_i the mass fraction of i in briarite, S the briarite surface, F the solution flow rate and t and Δt are the time of interaction and the sampling time interval, respectively.

The experimental data were fitted by equation (3) using the least square method.

$$NL_i = \frac{B_i}{K_i} [1 - \exp(-K_i t)] + W_i t \quad (3)$$

This equation is based on the first order kinetics and was originally derived for glass dissolution in aqueous solutions [3]. In equation (3), K_i represents the rate constant, $B_i + W_i$ and W_i are the initial and steady state rate of transfer of component i into the solution, respectively.

It is obvious that the steady state was achieved in all cases after approximately three hours.

The initial and steady state rates obtained from experimental data are summarised in figure 9. The ini-

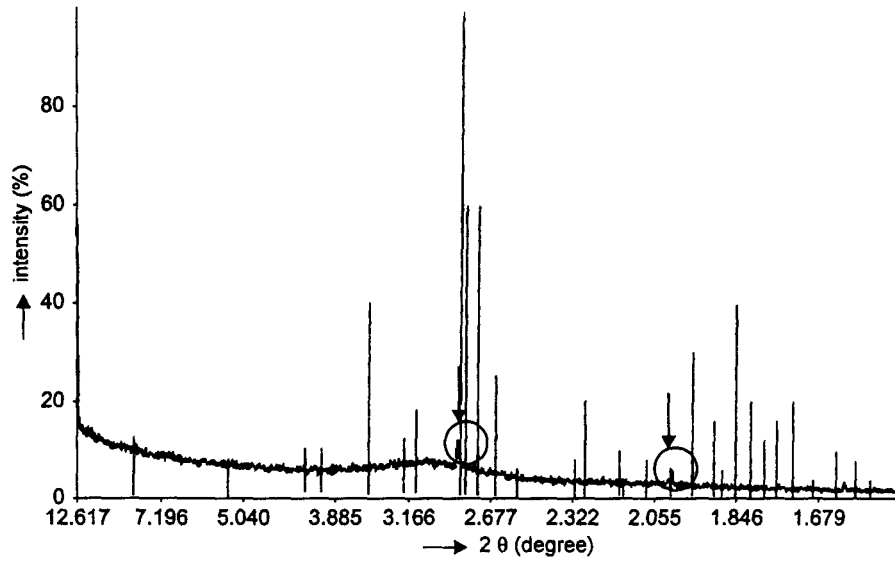


Figure 5. X-ray diffraction patterns of surface layer of block sample after interaction with SBF2, 21 days, 37 °C. Lines indicate HA positions, changes are highlighted by arrows and circles

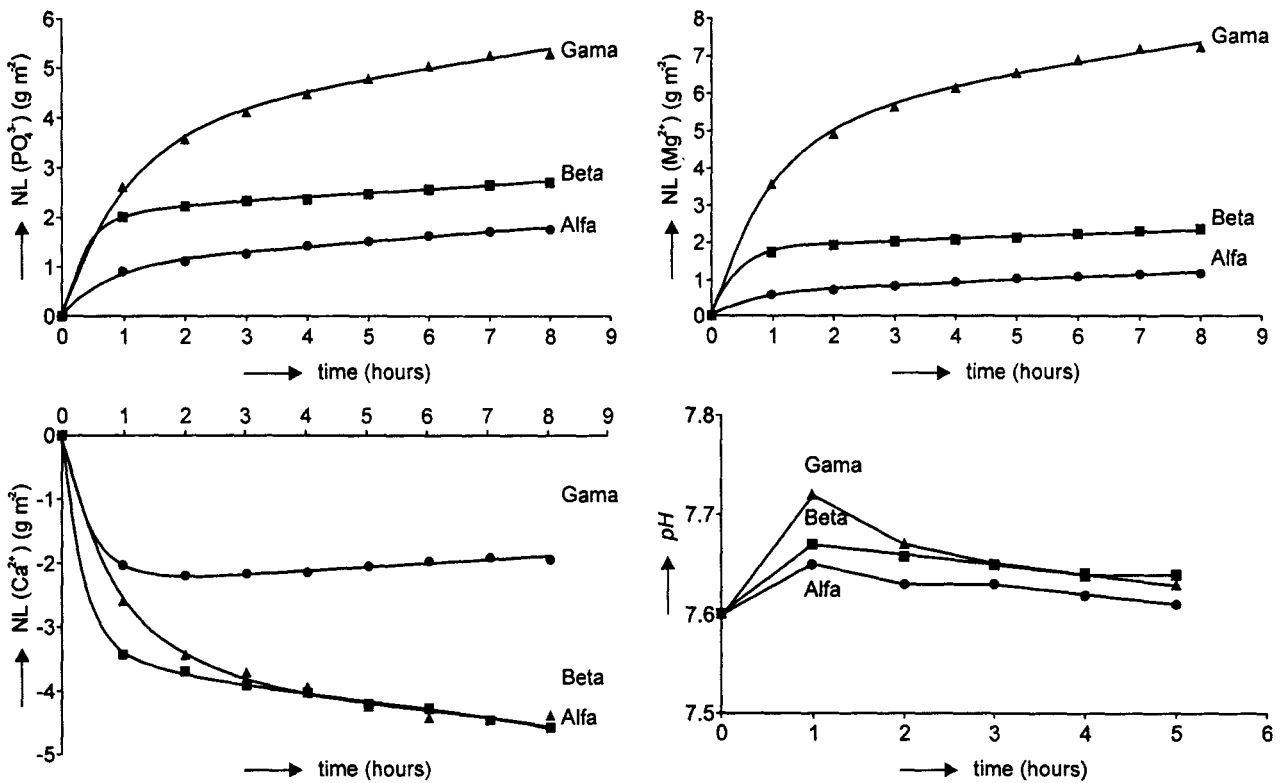


Figure 6. Flow-through test for α , β and γ phase on 37 °C, flow rate 1 ml min⁻¹, grain size 0.3-0.5 mm, corrosion medium: SBF1; normalised leach loss NL of PO_4^{3-} , Mg^{2+} , Ca^{2+} defined by equation (2) and pH changes. Lines represent the best fit of experimental data by equation (3).

tial rates are by about one order of magnitude higher in comparison with the steady state ones. Due to the fast flow rate of corrosion solution, this effect cannot be explained by the solution saturation. The more probable

explanation could be the protection role of secondary precipitated layer when products of surface reaction have to diffuse through this layer into the bulk solution [4]. Both the initial and the steady state rates differ for

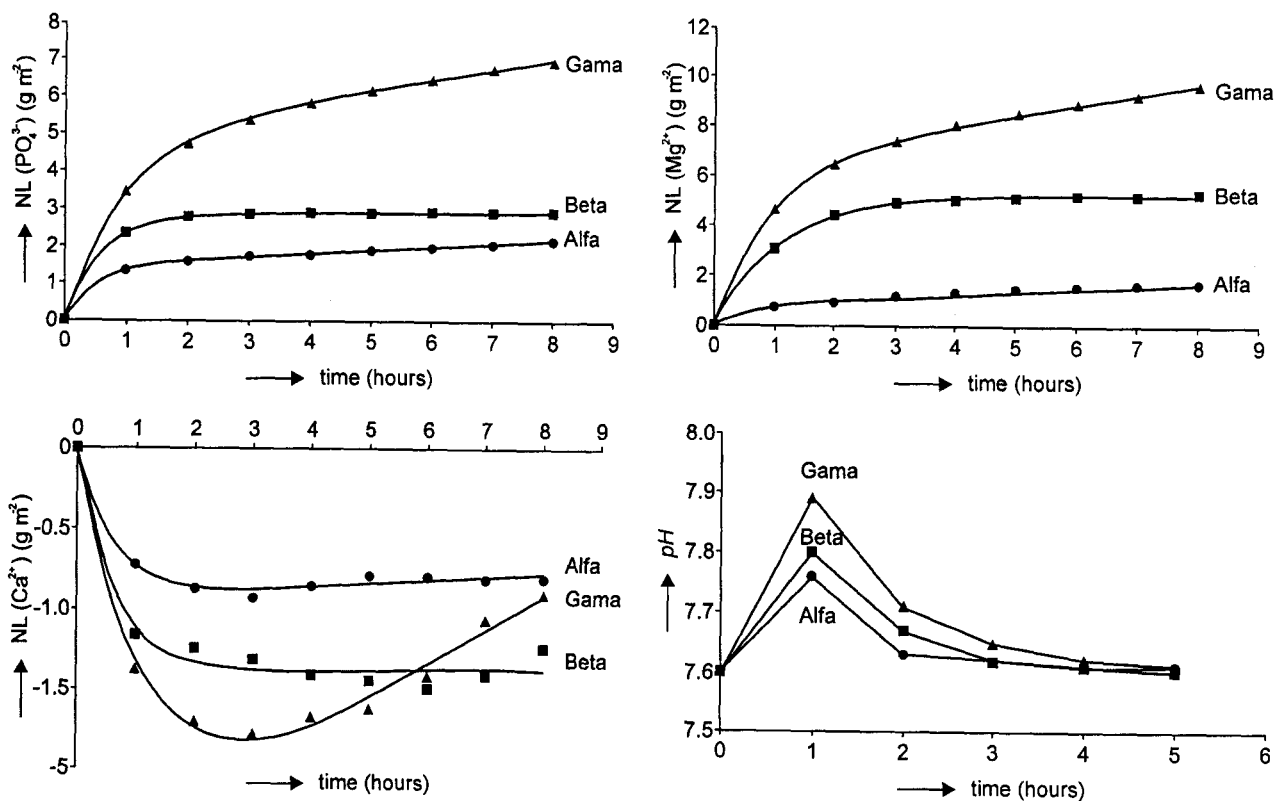


Figure 7. Flow-through test for α , β and γ phase on 37 °C, flow rate 1 ml min^{-1} , grain size 0.3-0.5 mm, corrosion medium: SBF2; normalised leach loss NL of PO_4^{3-} , Mg^{2+} , Ca^{2+} defined by equation (2) and pH changes. Lines represent the best fit of experimental data by equation (3).

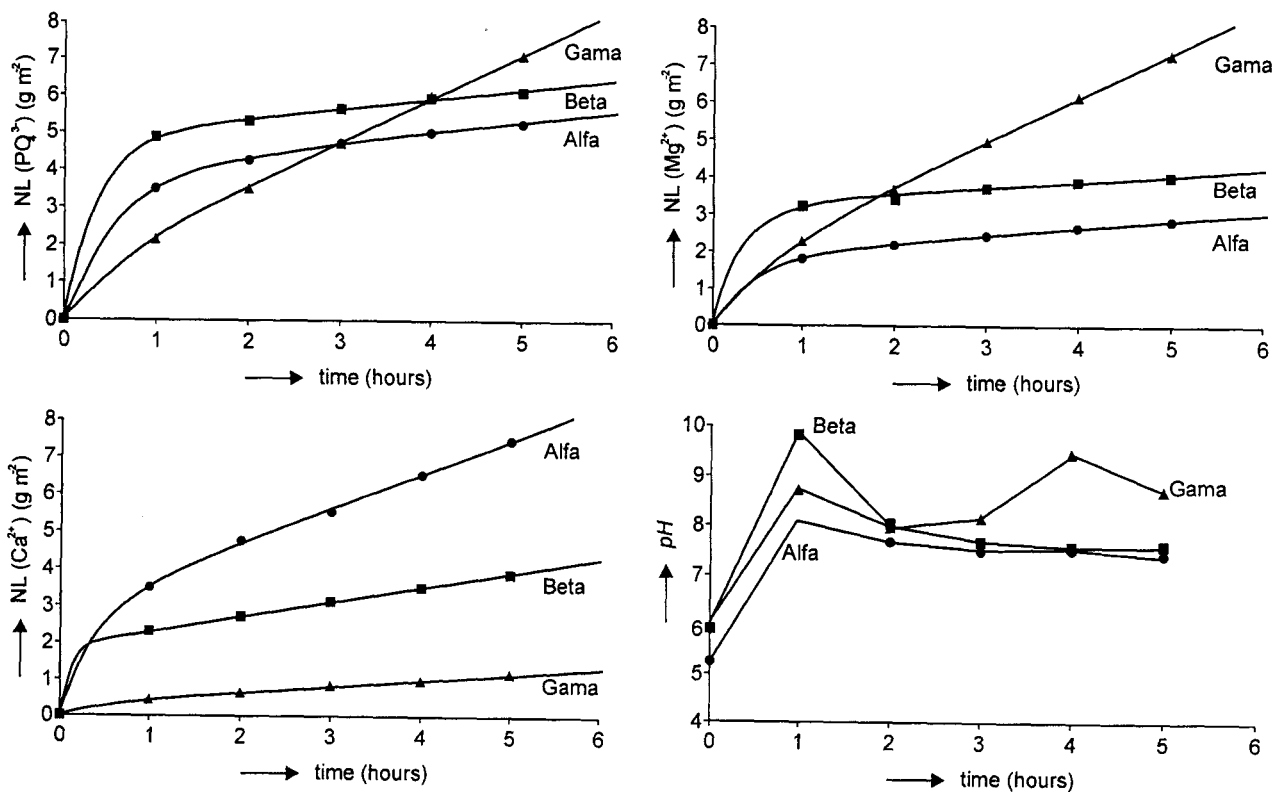


Figure 8. Flow-through test for α , β and γ phase at 37 °C, flow rate 1 ml min^{-1} , grain size 0.3 - 0.5 mm, corrosion medium: distilled water; normalised leach loss NL of PO_4^{3-} , Mg^{2+} , Ca^{2+} defined by equation (2) and pH changes. Lines represent the best fit of experimental data by equation (3).

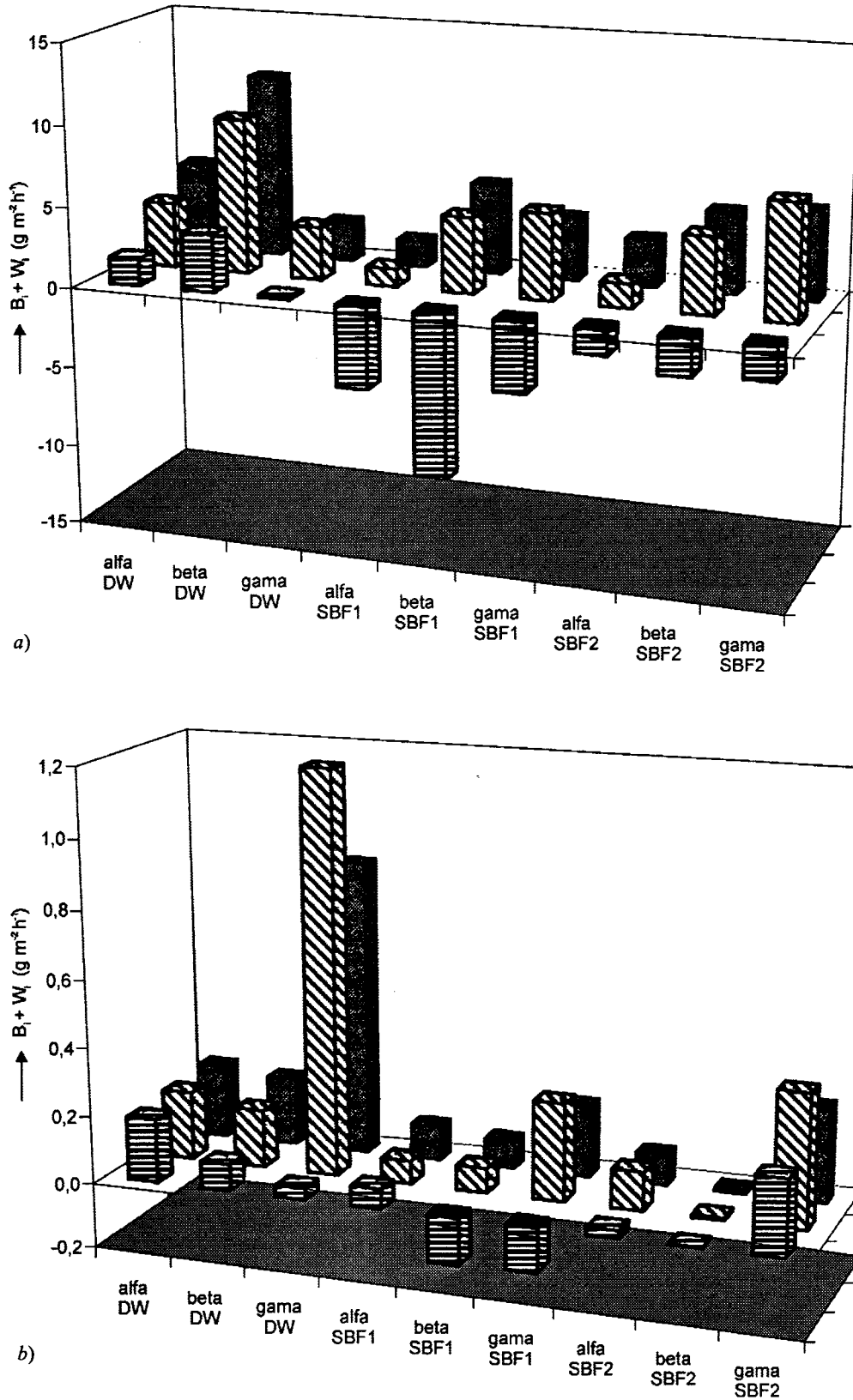


Figure 9. The initial *a*) and steady state *b*) rates of transfer of brianite components into the solution obtained by fitting the experimental data by equation (3). Flow-through test for α , β and γ phase at 37 °C, flow rate 1 ml min⁻¹, grain size 0.3 - 0.5 mm.

Table 2. The rates of brianite dissolution and of $\text{Ca}_x\text{Mg}_{(10-x)}(\text{PO}_4)_6(\text{OH})_2$ precipitation during the interaction with distilled water (DW), SBF1 and SBF2 obtained from equation (4).

	α +DW	α +SBF1	α +SBF2	β +DW	β +SBF1	β +SBF2	γ +DW	γ +SBF1	γ +SBF2
X	5.5	5.2	8.8	6.2	6.8	5.8	9.3	8.0	9.7
R_D ($\text{g m}^{-2} \text{h}^{-1}$)	0.253	0.160	0.128	0.313	0.256	0.023	1.265	0.416	0.401
R_P ($\text{g m}^{-2} \text{h}^{-1}$)	0.038	0.061	0.040	0.119	0.184	0.012	0.437	0.221	0.137

different phases and components excepting the α -phase in distilled water. During this interaction, the apparently congruent dissolution was observed at the steady state. However, the time dependence of NL_i is given by two different processes: brianite dissolution and the precipitation of secondary phase on the brianite surface. The positive NL_i values indicate higher rate of dissolution of component i , the negative values indicate the prevailing precipitation. The dissolution prevails over the precipitation both at the beginning of the interaction and at steady state for PO_4^{3-} and Mg^{2+} in all solutions and for Ca^{2+} in distilled water (figure 9). On the contrary, calcium precipitation is higher than calcium dissolution in SBF1 and SBF2 at the beginning of the interaction. Prevailing Ca precipitation was observed for β and γ phase in SBF1 at steady state. The W_{Ca} values near to zero were found for α and β phase in SBF2.

The steady state rate W_i could be also interpreted as constant difference between the total rate of brianite dissolution (R_D) and the rate of precipitation of secondary phase (R_P):

$$W_i = R_D - R_P \frac{f_i^P}{f_i^D} \quad (4)$$

where f_i^D and f_i^P denotes the mass fraction of i in the brianite and in the secondary phase, respectively.

An attempt was made to estimate the rates of both processes. If the mass fraction of two components in both dissolved and precipitated phase is known, the rates R_D and R_P can be determined using equation (4). The value of W_i can be determined by fitting the time dependence of NL_i by equation (3). Unfortunately, the results of EMPA analysis of precipitated layer were strongly dependent on the position of electron beam on the sample surface. Probably, the composition of precipitated layer is not constant. In this case, the R_D and R_P values were estimated by following iteration method:

1. The approximate composition was proposed considering the electroneutrality of the precipitated layer and XRD results from block samples. The general formula of precipitated layer $\text{Ca}_x\text{Mg}_{(10-x)}(\text{PO}_4)_6(\text{OH})_2$ was assumed.
2. The R_D and R_P values were computed from equation (4) for proposed composition of precipitated layer using the mass fractions of Ca^{2+} and PO_4^{3-} .

3. From these rates and experimental value of W_{Mg} , the mass fraction of Mg^{2+} in precipitated layer was obtained. This fraction was compared with the proposed composition of precipitated layer.
4. The proposed composition was modified by the value obtained in step 3 and the new R_D and R_P values were computed until the same values of f_{Mg}^P were estimated in two subsequent iterations.

The results are summarised in table 2. Obviously, the different composition of precipitated layer has to be assumed for different interactions. In any case, the reactivity of γ phase seems to be higher than the reactivities of α and β modifications.

CONCLUSION

The material based on mineral brianite was prepared in three crystallographic modifications a, b and g. The transformation temperatures 760 °C for $\alpha \leftrightarrow \beta$ transformation and 900 °C for $\beta \leftrightarrow \gamma$ transformation were determined. Hydroxyapatite precipitation on the brianite surface during the interaction with simulated body fluid promises the bioactive behaviour of the material studied. The rates of brianite dissolution and secondary layer precipitation differ for different crystallographic modifications. The γ modification is the most reactive one. The relative small increase of buffer concentration influences the kinetics of interaction considerably.

Acknowledgement

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INTERAKCE MATERIÁLŮ ZE SYSTÉMU Na₂O-CaO-
MgO-P₂O₅ SE SIMULOVANOU TĚLNÍ TEKUTINOU (SBF)
A DESTILOVANOU VODOU

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Účelem této studie bylo charakterizovat různé krystalografické modifikace (α , β , γ) minerálu brianitu získané z taveniny a popis chování těchto fází při interakci se simulovanou tělní tekutinou (SBF) a destilovanou vodou. Pro identifikaci a charakterizaci krystalografických fází byly použity rtg. difrakce, diferenční termická analýza a rtg. mikroanalýza. Teploty transformace jednotlivých krystalografických fází byly

760 a 900 °C. Koncentrační změny v korozních roztocích byly sledovány za statických a dynamických korozních podmínek na drťových i celistvých vzorcích. Pro chemickou analýzu roztoků byla použita kolorimetrie (PO₄³⁻), plamenová fotometrie (Na⁺, Ca²⁺) a atomová absorpce (Mg²⁺).

Metodami rtg. difrakce a rtg. mikroanalýzy byl, po interakci vzorků s SBF, na povrchu vzorků identifikován hydroxyapatit. Časovou závislost koncentračních změn v roztoku lze popsat pomocí matematického modelu vycházejícího z kinetických rovnic prvního řádu. Za předpokladu vzniku sekundární fáze složení Ca_xMg_(10-x)(PO₄)₆(OH)₂ byla pomocí modelu odhadnuta celková rychlost rozpouštění brianitu i celková rychlost srážení sekundární fáze. Stupeň rozpouštění a precipitace závisí na krystalografické modifikaci jak při interakci s SBF tak s destilovanou vodou. Vyšší hodnoty rychlosti rozpouštění a precipitace byly nalezeny ve všech studovaných případech u γ modifikace.