

Kinetic Studies for the Transformation Process of β -Whitlockite in Hydroxyapatite

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In the paper are presented the results of the kinetic study for the transformation of β -whitlockite in hydroxyapatite (HAP). It has been showed the influence of pH and temperature over the rate of the process. The values for the rate constants and activation energy at pH = 8.5 – 12 were determined. The obtained values for the activation energies show that the process of transformation of β -whitlockite in HAP could be described using a combined macrokinetic mechanism: transfer – mass transformation.

Keywords: hydroxyapatite, macrokinetic mechanism, crystallization

Due to their properties like bioactivity, compatibility with living cells and osteoconductivity, hydroxyapatites are used since 1920, in medical applications [1-3]. The modifications that hydroxyapatite suffer at the orthopedic implants surface, the most used domain, are strongly determined by properties like: particle size, surface area, porosity, the presence of foreign ions (F^- , Me^{2+}) in the lattice, crystallinity, structure defects etc. [4-7]. On the other hand, these properties depend mainly on the preparation methods and the applied thermal or hydrothermal treatments. Due to their multiple advantages the precipitation methods are used very often in practice. This is the reason why they continue to present interest for the researchers. There are fewer studies concerning the structural transformations that hydroxyapatite undergoes during the thermal and hydrothermal treatments. A study was made about, how the pH, temperature and Ca/P ratio influence the composition and the structure of the calcium phosphates during the precipitation process [8]. The researchers concluded that even the Ca/P ratio is 1.67 during the preparation process (specific to stoichiometric hydroxyapatite), in the first stage amorphous was formed. The transformation β -whitlockite \rightarrow hydroxyapatite will take place forward, in the second stage (reaction time between 6 and 20 h). The authors relieve that, increasing of the pH and temperature has a positive effect over the hydroxyapatite formation. In the literature there are no quantitative data about the influence of these parameters over the transformation of β -whitlockite in HAP. The analysis of the preparation process of hydroxyapatite, followed by thermal treatment (at 1000 °C), shows that this process could be framed in the process category: molecular mixing – chemical reaction – forming and growing of elementary particles [9]. This category includes:

- the chemical reaction between the calcium Ca^{2+} and phosphate PO_4^{3-} ions, with the formation of an amorphous precipitate (β -whitlockite);
- forming and growing of elementary particles of hydroxyapatite;
- internal and external diffusion of calcium Ca^{2+} and phosphate PO_4^{3-} ions.

To establish the mathematical model, which describes the hydroxyapatite formation, it is necessary to know the macrokinetic mechanism. In this paper the kinetic study

for the transformation process of β -whitlockite in hydroxyapatite is presented.

Experimental part

For the preparation of hydroxyapatite the following reagents with analytical purity were used: calcium nitrate tetra – hydrated $Ca(NO_3)_2 \cdot 4H_2O$, bi-ammonium phosphate $(NH_4)_2HPO_4$ and ammonia solution NH_3 28%. The concentration of the calcium nitrate solution was 0.5 M and the pH value was turned to 8.5 by adding ammonia solution. The phosphate solution has a concentration of 0.3 M; afterwards it was added the necessary amount of ammonia to reach the pH values presented in table 1. In all the experiments the phosphate solution was added by graduation, for 30 minutes, over the calcium nitrate solution. The ammonia losses were avoided by fixing a closed ascending refrigerator and a hydraulic closing to the reaction vessel. The temperature was measured and maintained constant with a thermostat.

From time to time, during the reaction, samples were taken, filtered, washed with distilled water and dried at 105°C until constant weight. The dried samples were crushed into fine powders with $d_p \leq 50\mu m$ and were heated for 2 h at 1000 °C.

Determination of the phase composition using XRD

The quantitative analysis of the phases was made using DRON-3 by measuring the integrated intensity of the peaks. Knowing the absorption mass coefficients in a bi-phase system, the amount of HAP was determined using the equation:

$$\frac{I_1}{I_1^0} = \frac{w_1 \cdot \mu_1}{w_1(\mu_1 - \mu_2) + \mu_2} \quad (1)$$

The evolution in time of the process was followed using the transformation yield of the β -whitlockite in hydroxyapatite.

Results and discussion

The analysis of figure 1 (a-b) shows the strong influence of temperature and pH over the rate of the process. It can be seen that at pH = 8.5, even after 20 h, the conversion of β -whitlockite in hydroxyapatite is not over than 20%

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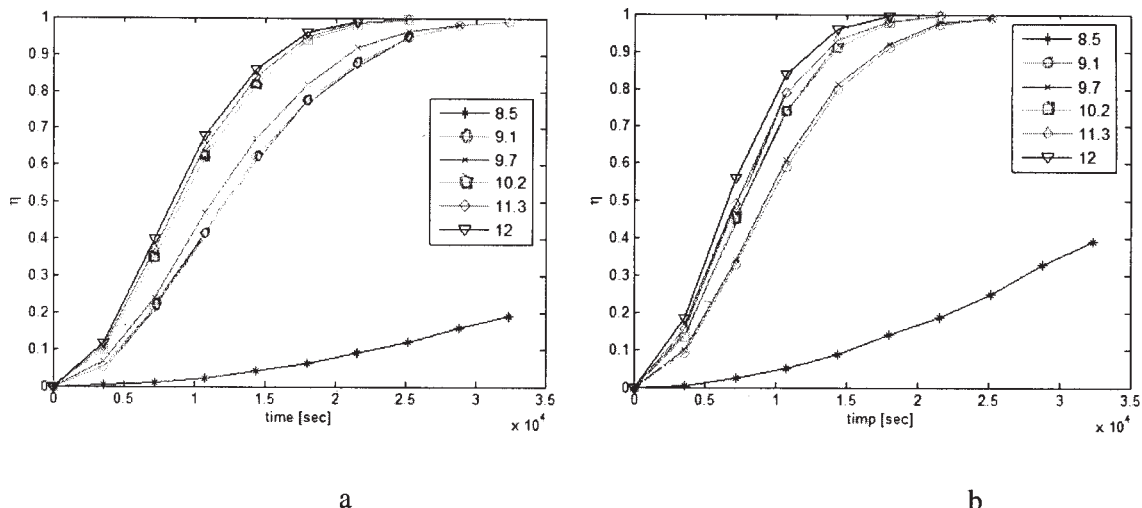


Fig. 1. The influence of pH and temperature over the transformation rate of β - whitlockite in hydroxyapatite (a-20 °C and b-50 °C)

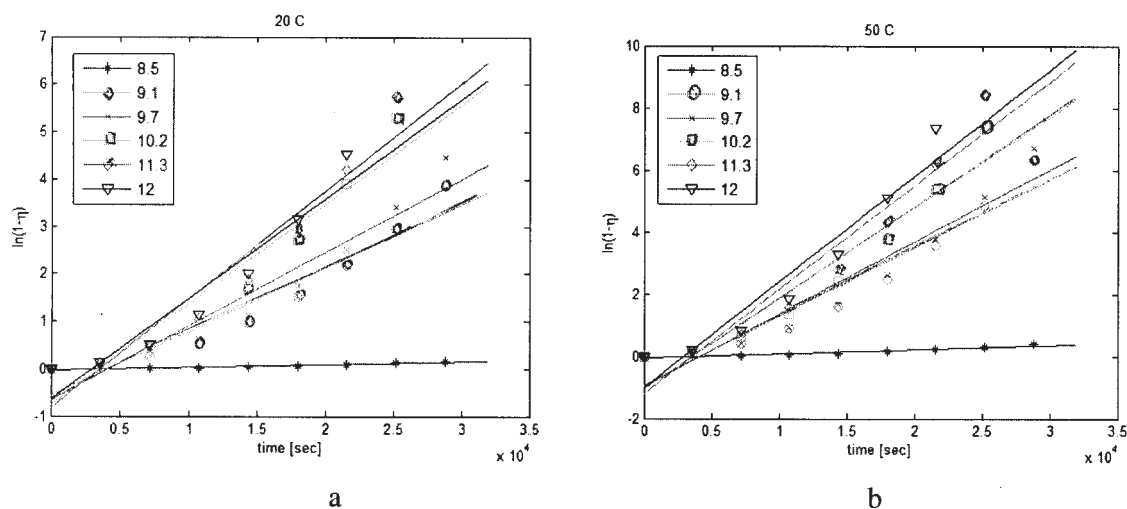


Fig. 2. $-\ln(1-\eta)$ -time

(at 20 °C) and 45% (at 50 °C). At pH = 9.1 the necessary time for a total conversion of β -whitlockite in hydroxyapatite is significantly decreased. In the pH interval between 9.1 and 10.2, the pH continue to influence the rate of the process, but not significantly. Also, at pH > 10.2 its influence is not relevant. The obtained experimental data were used to determine the rate constants, K. Considering that the process is developing after a first order kinetic:

$$\eta = 1 - e^{-K_1 \cdot \tau} \quad (2)$$

we plotted $-\ln(1-\eta)$ against time (fig. 2 a - b).

From the slope there were calculated the values for the rate constants. The results obtained for two temperatures (20 and 50°C) and pH values between 8.5 and 12 are presented in table 1.

Table 1
THE VALUE FOR THE RATE CONSTANTS
AND ACTIVATION ENERGY

pH	T [K]	K		Ea J/mol
		293 °C	323 °C	
8.5		0.01	0.02	11359.92
9.1		0.15	0.25	15897.02
9.7		0.17	0.26	17339.57
10.2		0.24	0.33	18839.13
11.3		0.26	0.38	17724.13
12		0.25	0.40	16072.13

Knowing that the variation of rate constant with temperature is given by an Arrhenius type equation [16]:

$$E = R \times \ln \frac{k_1}{k_2} \times \left(\frac{T_1 \times T_2}{T_1 - T_2} \right) \quad (3)$$

were calculated the values for activation energy using equation (2). The results are presented in table 1.

It can be seen that the values for the rate constants at pH < 9.5 are smaller with one order of magnitude at any temperature. The activation energy offers information about the macrokinetic mechanism of the process. Its values are in the range $15.87 \cdot 10^3$ - $18.84 \cdot 10^3$ J/mol for pH = 9.5 - 12 and this leads to the conclusion that the overall process is controlled by a combined model: mass transformation (surface integration of the elementary particles) – mass transfer. The activation energy $E_a = 11.35 \cdot 10^3$ J/mol is specific for the diffusion controlled processes. The small value could be explained by the fact that at small pH values the vibration energy and the mobility of the lattice ions decreases.

Conclusions

It was relieved the influence of temperature and pH over the rate of transformation of β -whitlockite in hydroxyapatite. It is concluded that at pH < 9.5 its value decreases at both temperatures.

From the experimental data the rate constants K were calculated, at 20°C and 50 °C and the range of $pH=8.5 - 12$ also the activation energy of the process in these working conditions.

The values for the activation energy of the process between the ranges 11359.92 - 18839.13 J/mol indicate the fact that the transformation of β -whitlockite in hydroxyapatite is developing after a combined macrokinetic model: transformation – mass transfer.

Nomenclature

- η - conversion
- t - time
- R - ideal gas constant
- A - preexponential factor
- k - rate constant
- μ - mass absorption coefficient
- E - activation energy
- w_i - mass fraction of phase
- I_0^i - integrated intensity of pure phase
- I_1^i - integrated intensity of pure phase in mixture
- T - temperature

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