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APPLICATION OF NUMERICAL METHODS IN THE TECHNOLOGY OF HYDROXYAPATITE

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ABSTRACT. Hydroxyapatite precipitation process involves the formation in the first phase of a solid-phase with amorphous structure (amorphous calcium phosphate), which in time turns into hydroxyapatite. Polynomial spline interpolation is a numerical method useful in mathematical modeling of this phase transformation process. By this method, experimental data are interpolated to obtain cubic spline polynomial function which can approximate reasonably well the experimental values of the degree of conversion at any pH between 8.5 ÷ 12. A very good agreement between the experimental and numerical results confirms the validity of the numerical procedure.

Keywords: *hydroxyapatite, phase transformation, numerical methods, cubic spline function*

INTRODUCTION

Numerical methods are used to determine approximate solutions of complex problems and use only simple arithmetic operations [1]. One of the simplest methods of approximation is interpolation and involves choosing a function data, which has a predetermined finite number of points (Δ): $x_0, x_1, x_2, ..., x_n$ chosen from its domain of definition. There is more than one class of interpolation functions, such as rational functions for rational interpolation, spline functions (polynomial or exponential) for spline interpolation, interpolation trigonometric functions for periodic functions [2]. The most suitable class of interpolation function is that where one can find an element closer to the function that interpolates [3]. This category includes cubic spline functions. Cubic spline function for function f and the above division (which are known values $f(x_i) = f_i$, $i = 1,...,n$) satisfies the following three properties:

- It is a "segmental polynomial", meaning that each interval (x_{i-1}, x_i) is a polynomial $S_i(x)$ of degree 3

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- two neighboring polynomials $S_i(x)$ and $S_{i+1}(x)$ have the following properties:

  $S_i(x_{i-1}) = f(x_{i-1})$; for any $i = 1,...,n$ (1)

  $S'_i(x_i) = S'_{i+1}(x_i)$, for any $i = 1,...,n-1$ (2)

General expresions for two adjacent cubic fuctions $S_i(x)$ and $S_{i+1}(x)$ are:

$$S_i(x) = \alpha \cdot a_i(x) + \beta \cdot b_i(x) + \gamma \cdot c_i(x) + \delta \cdot d_i(x) \quad (3)$$

$$S_{i+1}(x) = \beta \cdot a_{i+1}(x) + \gamma \cdot b_{i+1}(x) + \delta \cdot c_{i+1}(x) + \tau \cdot d_{i+1}(x) \quad (4)$$

where:

$$a_i(x) = \frac{(x_i - x)^2 (x - x_{i-1})}{(x_i - x_{i-1})^2} \quad (5)$$

$$b_i(x) = -\frac{(x - x_{i-1})^2 (x_i - x)}{(x_i - x_{i-1})^2} \quad (6)$$

$$c_i(x) = \frac{(x_i - x)^2 [2(x - x_{i-1}) + (x_i - x_{i-1})]}{(x_i - x_{i-1})^3} \quad (7)$$

$$d_i(x) = \frac{(x - x_{i-1})^2 [2(x_i - x) + (x_i - x_{i-1})]}{(x_i - x_{i-1})^3} \quad . \quad (8)$$

Properties (1) and (2) become:

$$S_i(x_{i-1}) = \gamma = f(x_{i-1}); \quad S_i(x_i) = \delta = S_{i+1}(x_i) = f(x_i) \quad (9)$$

$$S_i^{'}(x_i) = S_{i+1}^{'}(x_i) = \beta \quad (10)$$

$$S_i^{'}(x_{i-1}) = \alpha \quad (11)$$

To solve mathematical problems (scientific calculations), advanced software systems such as Matlab, Mathematica, or Mathcad are used [2,4,5].

It is generally acknowledged that in the crystallization of calcium phosphate first occurs the formation of a precursor phase (amorphous calcium phosphate) which is subsequently dissolved or restructured as the precipitation reaction occurs and turns into hydroxyapatite [6.7]. Transformation kinetics of amorphous calcium phosphate into hydroxyapatite, which can be described by a first order reaction law, is only a function of the solution pH at constant temperature [8.9]. Solution transformation depends on the conditions that regulate both amorphous calcium phosphate dissolution and formation of the first nuclei of hydroxyapatite [10]. In a recent study [11,12], the experimental results concerning the influence of pH and temperature on the transformation of amorphous calcium phosphate into hydroxyapatite have been presented.

From the kinetic data, the values of the rate constant and activation energy at pH 8.5, 9.1, 9.7, 10.2, 11.3, 12 were calculated. Based on the values obtained for activation energy, it has been established that the transformation of amorphous calcium phosphate into hydroxyapatite can be described by a combined macrokinetic mechanism: transfer-mass conversion. The mathematical model of the process was established and the constant values from the mathematical model equation were determined [11.12]. Simulations were made based on the proposed model and the results show a good agreement with the experimental data values, which confirms the validity of the model. Starting from these results, in the present work a method that can be used to determine quickly and easily the values for degree of conversion (η) in different experimental conditions is presented. A comparison between the numerical results and analytical results indicates that predictions obtained with the new technique are closer to the analytical solutions.

RESULTS AND DISCUSSION

The interpolation of experimental data in order to obtain spline interpolation function was performed with Mathcad 15. The experimental data presented in a previous communication [11.12] were used in the present study. Thus, for two temperatures $T_1^0 = 20\ ^0C$ and $T_2^0 = 50\ ^0C$, the spline $S(t)$ was determined, which is a function of one variable and approximates function η experimentally determined. Figures 1 and 2 show the spline function at various pH values:

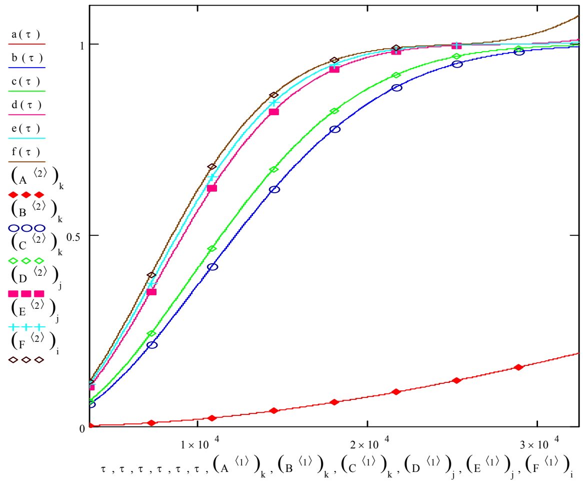

Figure 1. Graphic representation of the degree of transformation of amorphous phase in hydroxyapatite using spline function at 20 ^{0}C and 6 pH values.

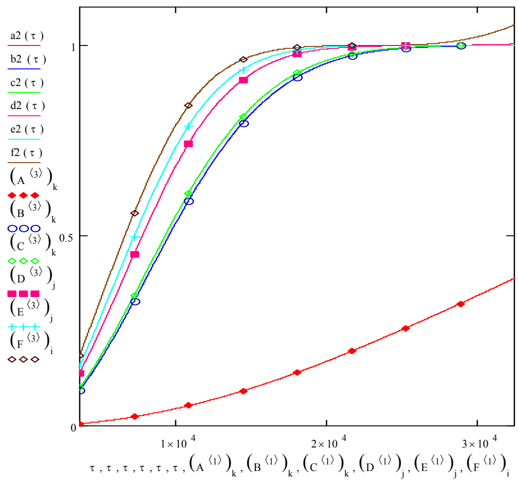

Figure 2. Graphic representation of the degree of transformation of amorphous phase in hydroxyapatite using spline function at 50 ^{0}C and 6 pH values

The analysis of the graphs obtained show that the interpolation spline nodes (t, T_1) have no large variations between nodes, so they model correctly the process of phase transformation.

Because function η varies with respect to time and pH, the interpolation of the function of two variables $\eta(t, pH)$ on domain containing (t, pH) experimentally determined at a fixed temperature T = 20 ^{0}C was made. The result is shown in Figure 3:

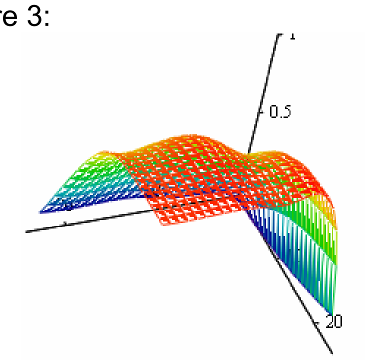

Figure 3. Function F (interpolation spline)

To determine the values of function η at fixed time and pH, the surface is divided with a plan that corresponds to ordinate pH point selected. The section curve of the plan with the spline surface $F(t, pH)$ is the same with the one obtained for one variable function η (in plan) at that temperature and pH.

So, the 3D cubic spline interpolation of function $\eta(t, pH)$ enables the determination of approximate values for function η for any other value from time and pH interpolation range at fixed temperature T.

CONCLUSIONS

In this paper we showed the possibility of using numerical methods in the technology of hydroxyapatite preparation. Compared with the mathematical model obtained in previously published works, this method is much simpler and allows the rapid determination of the degree of conversion values η, which in mathematical modeling of the process have a great importance. The advantage of mathematical formulation of the process is the reduction of the number of experiments, providing the ability to determine the values of function η at any time and in the pH range of interpolation.

Elaboration of experimental data obtained through spline functions is a new issue to the modeling domain when using the "black box" method. Polynomial spline interpolation method allows a rapid determination of conversion at any time and pH in the range of interpolation. It is necessary to continue the research in this field in order to determine the coefficients in polynomial equation of the spline functions. Therefore, using these functions in solving engineering problems, automation, management and optimization of processes would be more effective.

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