CALCULATION OF EFFECTIVE DIFFUSION COEFFICIENT

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Abstract: The aim of this paper is to calculate the effective diffusion coefficient for typical masonry clay on the base of experimentally recorded drying curves. Two computer programs for calculation of diffusion coefficient, which are based on mathematical calculation of Fick's and Cranck's diffusion equations, were developed. First program did not include shrinkage effect during drying into the computation algorithm while the second one has included it. Results presented in this study have show that the values of effective diffusion coefficient determined by designed computer programs have similar values as literature available values of the same coefficient for different clays. The presented models witch include shrinkage effect corresponds with experimental data well.
Key words: drying, mathematical model, effective diffusion coefficient.

1. INTRODUCTION

Drying is very complex process. It is one of the oldest and usual operations employed in industrial process. It is characterized by simultaneous mass and energy transfer process. Different nature and properties of the drying material (capillarity, pores size and its distribution, drying shrinkage effect etc.) and the fact that previously mentioned transfer process are often non stationary make the description of the drying process as a complicated one. That is the reason why a unique drying theory, which could universally described this process for different material types, is still not developed. The diffusion process regarded, as a transport of matter via random molecular motion, is inherent and characteristic to drying. Moisture transfer within the solid body, at certain temperature, is driven by the core – to – surface moisture content difference. It is necessary to say that pure diffusion is not exclusively the only mass transport process but is usually the most frequent one. The rate of mass transfer by pure diffusion is proportional to the moisture concentration gradient. Diffusion coefficient is representing a factor of proportionality.

The knowledge of the diffusion coefficient is necessary for credible simulation of mass transfer process described by Fick's equation. Cranck [(1)] presented a great number of solutions of the diffusion equation for set of different initial and boundary conditions. It is a common practice in drying applications to replace the intrinsic diffusion coefficient, which is regarded to the pure diffusion as a main mass transfer mechanism, with the effective (equivalent) diffusion which is regarded for complete internal mass transfer mechanisms such as pure diffusion, surface diffusion, Knudsen diffusion, capillary flow, thermo diffusion [(2)] etc.

Numerous drying studies conducted on different kind of materials and mathematical models resulting from them can be found in literature [(3-6)].In most drying models, available in literature, shrinkage does not configure in drying equations. It is also a common practice, to apply such models on materials that show shrinkage. Small number of papers, which describe drying process of ceramic materials and especially clay, is available in literature. Some data can be found in papers of Guerman I. Efremov [(7)] (bricks), Saber Chemkhi [(8)], F. Zagrouba [(9,10)] (clays), Darko Skansi[(11,12)] (heavy clay tiles), etc.

In this paper it was analyzed the drying behavior of typical masonry clay. A new method and computer program for determination of effective diffusion coefficient, based on mathematical calculation of Fick's and Cranck's diffusion equations, were developed.

2. GENERAL INFORMATION

2.1 Experimental conditions

The raw material, from “Banatski Karlovac”, was first dried in laboratory dryer at a temperature of 60^0C and then after cooling to room temperature, was milled down in lab perforated roll mill. It was mill down about 50 kg of raw material. From this amount, about 10 kg was identified moisturized and milled in lab differential mills first at gap of 3mm and then of 1mm. Laboratory samples, dimensions 120x50x14 mm, were formed from previously prepared raw material in laboratory extruder press “Hendle” type 4 under the vacuum of 0.8 bar units. All drying experiments presented in this study were done in a specially constructed laboratory recirculation dryer on prepared laboratory samples.

Laboratory recirculation dryer provides: regulation of drying air temperature within 0-125 C°, with accuracy 0.2 ± C°; regulation of drying air relative humidity within 20-100%, with accuracy of 0.2%; speed regulation of drying air within (0-3.5)m/s, with accuracy 1%; monitoring and recording the drying samples weight within (0-2000)g, with 0.01g accuracy; monitoring and recording the linear shrinkage within (0-23)mm with accuracy of 0.2mm; Continuous time monitoring during drying.

2.2 Characterization of raw material

In order to get the complete view of the drying process it is necessary to give some information about the drying material. In table 1 it is presented the results of chemical analysis, X- ray result is presented at fig.2, DTA and TG analysis is presented at fig. 3 while granulometric analysis is presented at fig. 4. Parameters such as coefficient, the criterion of plasticity and drying sensitivity were determined too. The amount of water needed for plastic forming of masonry products and the plasticity were measured according to Feferkorn method (table 2), while draying sensitivity was determined by recording Bigot's curves of the barelatograph device (table 3).

Table 1 - Results of chemical analysis

Composition	%
Loss ignition on 1000^0C	11.71
SiO_2	53.23
Al_2O_3	13.64
Fe_2O_3	5.34
CaO	7.50
MgO	3.59
SO_3	0.00
S^{2-}	0.00
Na_2O	1.24
K_2O	3.42
MnO	0.091
TiO_2	0.60
Summary:	100.36
Insoluble rest:	71.13
Loss of moisture	2.04

Table 2 - Feferkorn method results

Forming process		Values
The amount of water for forming in (%)		20.64
Plasticity according to Feferkorn	Coefficient of plasticity	27.2
	Plasticity criteria	Good plasticity

Table 3 - Drying sensitivity results

Drying process		Values
Bigot's curve	Shrinkage at critical point (%)	5.12
	Water loss at critical point (%)	9.62
	Drying sensitivity	Sensitive

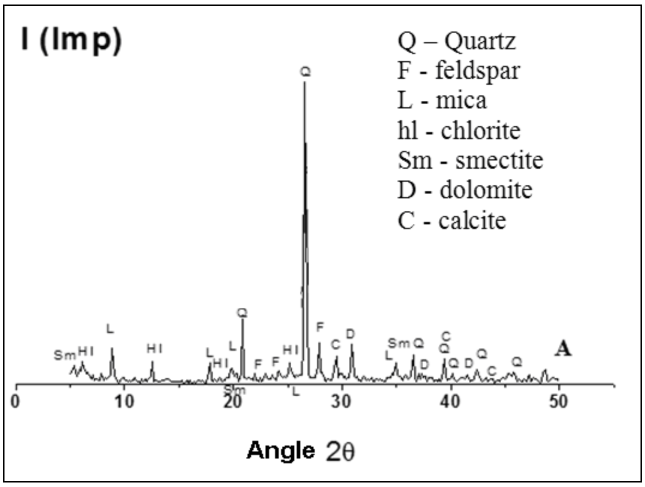

Fig. 2. X- ray of raw material

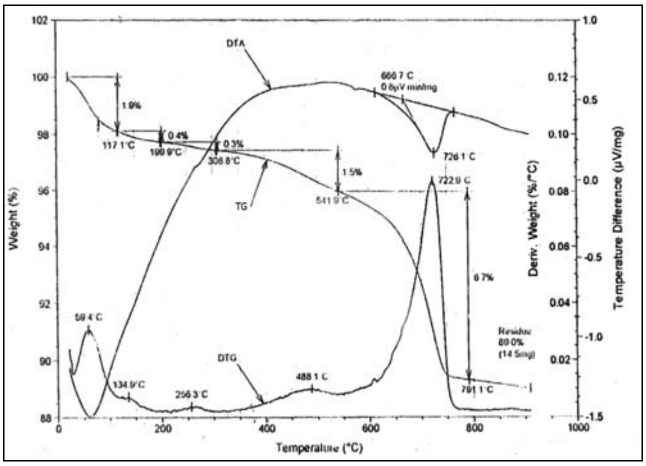

Fig. 3 - DTA and TGA of raw material

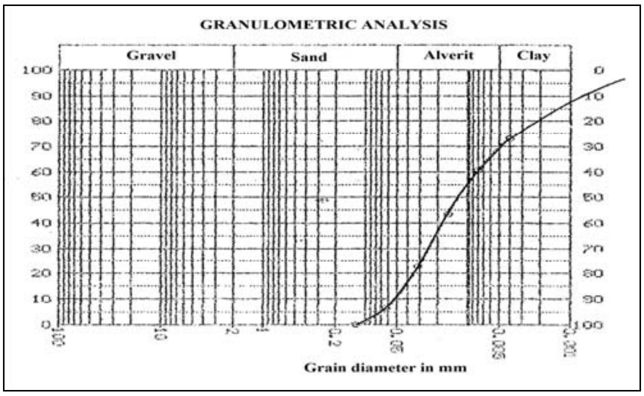

Fig. 4 - Granulometric histogram

2.3 Theoretical principes

In literature, effective diffusion coefficient can be determined using the slope method[15,16], or a comparison methods. Comparison method is based on comparison between experimental drying curves and prognostic curves. Prognostic drying curves are constructed using data obtained by solving Fick's and Crank's equation analytically [2, 3, 17] or numerically [6, 18]. Characteristic drying curve of masonry clay is consisted from: the first drying phase, the constant drying rate phase and decreasing drying rate phase. In drying studies, carried out on different materials, diffusion is generally accepted as the main mechanism of moisture transport from the interior of the material to its surface. The restriction to one-dimensional diffusion gives a good approximation in many practical systems. Analytical solution of the Fick's equation is given for various geometrical shapes. These solutions assumed that the moisture mass transport is carried out by diffusion, that shrinkage of the material during drying is neglected and that diffusion coefficient was constant. For the case of geometry "thin plate" solution was given by Crank [1] and it is represented by the expression (1).

$$\mathrm{MR} = \frac{X - X_{eq}}{X_0 - X_{eq}} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2}{4}\pi^2\frac{D_{eff}\cdot t}{l^2}\right) \quad (1)$$

X_0, X, X_{eq}, D_{eff} and l in equation (1) represents respectively initial, current and equilibrium moisture content (kg moisture / kg dry material), effective diffusion coefficient (m^2/s) and sample half thickness (m). Regarding the fact that clay products shows changes in size during the drying it was necessary to develop a model that would take this phenomenon into account. In order to enter shrinkage effect into account, the equation (1) was corrected, by introducing in it the expression $l_{(t)}$. This expression represents the experimentally determined time dependence of the sample thickness. It should keep in mind that this type of correction is not mathematically one hundred percent accurate because the resulting equation (1) was obtained using the assumption of the unchangeable sample thickness. Formally speaking, mathematically accurate correction can be obtained by entering the expression $l_{(t)}$ in the equation from which, in the case of constant sample thickness, after integration step equation (1) has been formed. Small number of papers, which describe the sample dimensional correction, can be found in literature. Some data can be found in papers of L. Hassini [21], and A.O. Disse[22]. Wilton Pereira da Silva [19, 20] has presented in his studies a way of solving the diffusion equation for the case of spherical samples.

2.4 Program description

In order to solve the equation (1) it is necessary to create the dependence MR_{eks} – t. MR_{eks} represent the experimentally determined value of MR calculated from experimentally measured data X_0, X, X_{eq}.

If we define value ε, as a relative error of neglecting terms higher then N in equation (1), the N value can be determined and equation (1) will be transformed form infinite sum into finite sum of N terms given by equation (2).

$$\mathrm{MR} = \frac{8}{\pi^2}\sum_{n=1}^{N}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2}{4}\pi^2\frac{D_{eff}t}{l^2}\right) \quad (2)$$

MR_{an} represent the analytically determined value calculated from equation (2). It is necessary to introduce the concept of the numerical counter i, which can have only a value of the integer. Numerical counter i is defined for each value of the experimental pairs (MR_{eks}, t). It starts form the value zero and is increasing by one until it reach a final value which is related to the last experimental pairs (MR_{eks}, t). This concept has allowed us to actually count the number of experimental pairs (MR_{eks}, t) from their first to their last values.

In order to work properly program is asking to enter the initial value of the effective diffusion coefficient D_{eff}, and the ε value. Let's say the initial value of the effective diffusion coefficient D_{eff} is given as a value of $1\cdot10^{-20}$ (m^2/s). Then for each numerical counter value i program has calculated the value χ^2 from the equation (3).

$$\chi^2 = \sum_{1}^{i}(MR_{eks\ i} - MR_{an\ i})^2 \quad (3)$$

In the first cycle $MR_{an\ 1}$ is calculated according to equation (2) using the previously determined value N and starting D_{eff}. In the next cycle D_{eff} value is doubled giving a new value for $MR_{an\ i}$ which is now used to calculate new χ^2 according to equation (3). Program is then comparing the value χ^2 obtained in the first cycle and the newly obtained χ^2 value. If the statement $\chi^2_{first} < \chi^2_{second}$ is satisfied program will continue previously described cycle else program will temporarily stop.

Note: $\chi^2_{first}, \chi^2_{second}$ regards to last and penultimate value of the cycle in which χ^2 is determined.

Last three values for D_{eff} and χ^2 will be then recorded. Then the recorded D_{eff} interval is divided in 100 parts. Hundredth part of that interval is defined as a step s. Program will start a cycle again using the initial value for D_{eff} as $D_{eff\ third\ from\ end}$ + s. The cycle is repeated until the statement $\chi^2_{first} < \chi^2_{second} < 1\cdot10^{-10}$ is satisfied. In other words the cycle is interrupted when the difference $\chi^2_{second} - \chi^2_{first}$ reach $1\cdot10^{-10}$. Last D_{eff} value is then recorded. This value is representing the effective diffusion coefficient in (m^2/s). For materials which shows shrinkage during drying equation (2) need to be changed by introducing in it the expression $l_{(t)}$. This expression represents the experimentally determined time dependence of the sample thickness. When this correction is entered previously described method for determination of the effective diffusion coefficient can be used. Program for effective diffusion determination was created using the previously described algorithm. It was written in Borland C program language on a standard P IV computer (AMD 1200 MHz, 80GB HDD, 256 MB ram memory). Program with the using instructions can be obtained by contacting the author.

3. ANALYSIS AND DISCUSSION OF RESULTS

The chemical analysis results have showed that this is a usual masonry raw material, with a relatively low content of aluminum oxide, relatively small content of clay minerals and feldspars and increased carbonate content. Granulometric histogram is protractedly unimodal with a mild drop to the left side. Dominant fraction size is in the interval of

0,001-0,004 mm. X-ray analysis has showed the presence of quartz, some layer silicates (mica, chlorite and a little smectite), feldspar from the group of plagioclase and carbonate minerals (calcite and dolomite). Recorded DTA / TG diagrams for raw material have confirmed the presence of quartz, micas, montmorionit and a certain content of dolomite and calcite in raw material.

Experimental conditions which were used in a laboratory recirculation dryer are presented in table 4.

Table 4 – Experimental conditions

Experiment number	Air velocity	Air temperature	Air humidity
1	3	40	60
2	3	40	40
3	3	55	60
4	3	70	60
5	3	70	40
6	1	40	40
7	1	70	40
8	1	80	40

Drying data X_0, X, X_{eq}, $l_{(t)}$ experimentally recorded for each experiment mentioned in table 4 were used for creation of the MR_{eks} – t dependence. This dependence is necessary as an input for previously described computer programs. Two programs were designed to compute the effective diffusion coefficient. First program did not include shrinkage effect during drying into the computation algorithm while the second one has included it. Two models for predicting the drying behavior (MR_{an} – t dependance) were obtained from these two programs. First model did not include shrinkage (Model 1) and second one (Model 2) has included it. Graphical view of experimental and predicted drying behavior were presented at fig. 5 - fig. 12. Determined effective diffusion coefficient values obtained through the use of described programs are presented in table 5.

Table 5 – Effective diffusion coefficient values

Experiment	Deff · 10^9 (m^2/s)	
	with correction	without correction
1	0.067	0.341
2	0.100	0.415
3	0.077	0.431
4	0.150	0.472
5	0.126	0.583
6	0.050	0.289
7	0.094	0.381
8	0.019	0.098

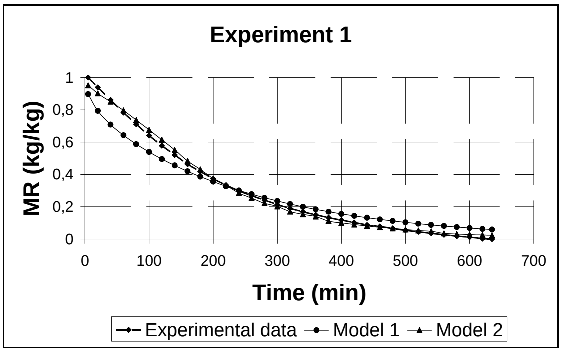

Fig. 5 – Drying results for experiment 1

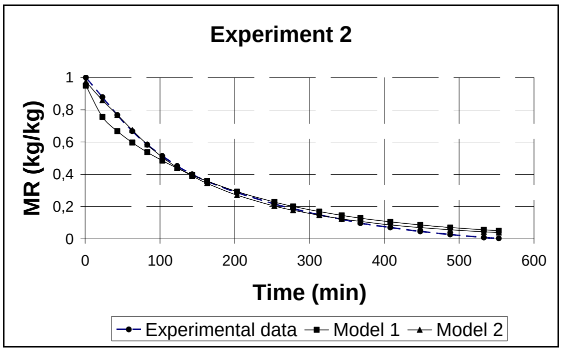

Fig. 6 – Drying results for experiment 2

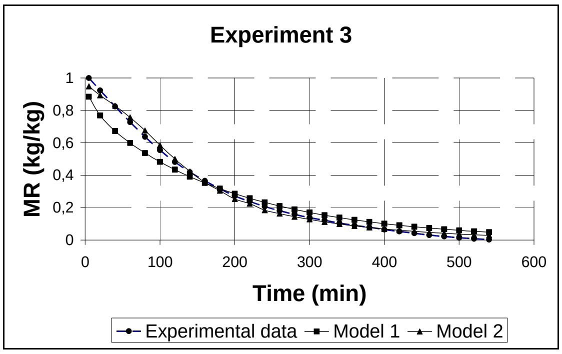

Fig. 7 – Drying results for experiment 3

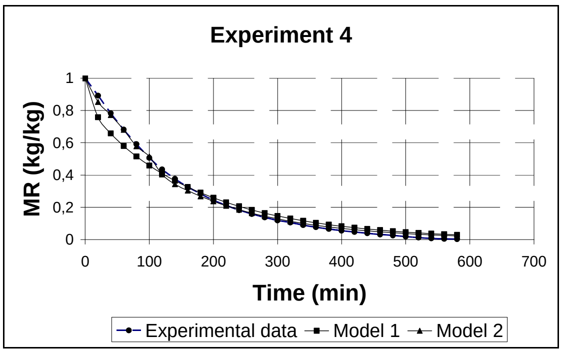

Fig. 8 – Drying results for experiment 4

For long drying time, equation (1) can be transferred into equation (5). In Lalić's master work[24] effective diffusion coefficient was determined by the slope method from equation (5). Drying experiments from this and the Lalić study can be compared, because in bout studies experimental conditions and the raw material were the same.

$$\text{MR}=\frac{8}{\pi^2}\exp(-\pi^2\frac{D_{eff}t}{l^2}) \quad (4)$$

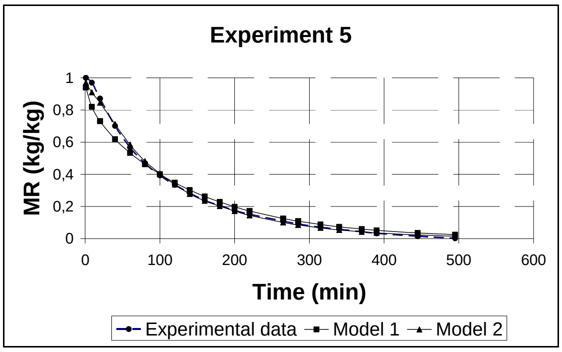

Fig. 9 – Drying results for experiment 5

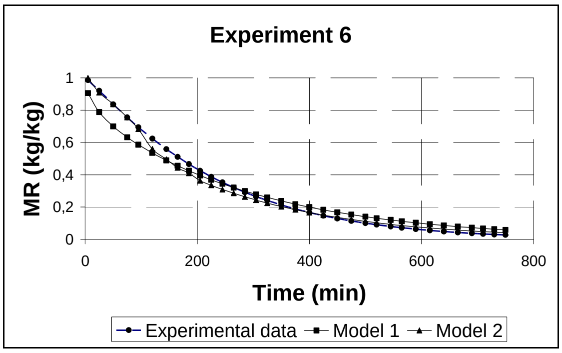

Fig. 10 – Drying results for experiment 6

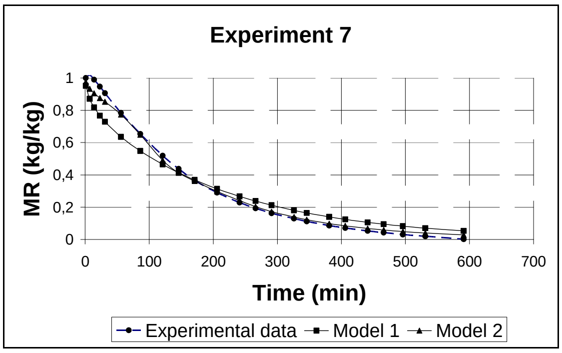

Fig. 11 – Drying results for experiment 7

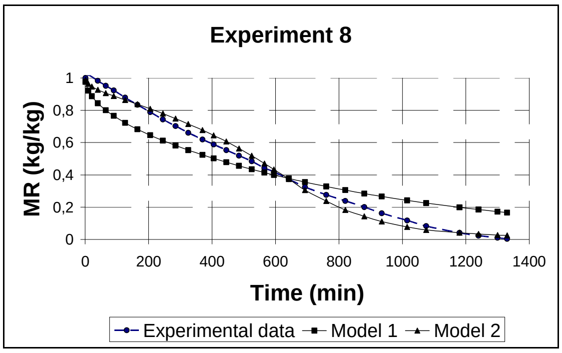

Fig. 12 – Drying results for experiment 8

Effective diffusion coefficient values[24] determined from the slope of the equation (5) are presented in table 6.

$$\ln(\frac{\pi^2 MR}{8}) = \ln(A) = -\pi^2\frac{D_{eff}}{l^2}t \quad (5)$$

Table 6 – Effective diffusion coefficient values

Experiment number	Deff · 10^9 (m^2/s)
1	1.24
2	1.93
3	2.00
4	2.32
5	2.76
6	1.05
7	1.72
8	0.47

Kinetic diagram analysis has shown that the kinetic curves representing the model which neglects shrinkage effect (Model 1) do not completely follow the configuration of experimentally determined kinetic curves. Deviations of that model from experimental drying curves are higher at the beginning of the drying process and after some time deviations disappear. Disappearing moment matches the moment from which sample dries further without shrinkage. Drying kinetic curves of the model which includes shrinkage (Model 2) follow the configuration of experimentally determined curves and their matching can be more than 95% as it is can be seen in experiments 2, 4 and 5. If minor deviations exist it is at the beginning of the drying process and are most probably caused by time interval which has to pass until stationary experimental conditions are fulfilled and products are heated up to the temperature in the dryer. The intersection point of experimental drying curves and modeled drying curves is characterized as the critical point. Critical point is a characteristic kinetic parameter which is important because it determines the moment after which the products do not shrink anymore.

From table 5 it can be concluded that value of effective diffusion coefficient D_{eff} determined using the model which included sample shrinkage correction is less than the same coefficient value determined using the model which neglected the sample shrinkage. Determined values of data for D_{eff} presented in table 6 were higher from the data presented in Table 2. This is the expected result which is in agreement with the D_{eff} determination. That is another proof that the determination model which included shrinkage effect during drying has given more precise D_{eff} values. Only a few scientific papers [8,11] in which effective diffusion coefficients for masonry clay products were determined are available in literature. In these papers D_{eff} values are in range of 10^{-7} up to 10^{-12} m^2/s. This relatively large range for D_{eff} values is connected with the different nature of heavy clay and different methods used for its determination. D_{eff} values presented in Tables 5 and 6 are beneath previously mentioned range.

4. CONCLUSIONS

A new method and computer program for determination of diffusion coefficient, which is based on mathematical calculation of Fick's and Cranck's diffusion equations, were developed. Two programs were designed to compute the effective diffusion coefficient. First program did not include shrinkage effect during drying into the computation algorithm while the second one has included it. Two models for predicting the drying behavior (MR_{an} – t dependance) were obtained from these two programs. First model did not include shrinkage (Model 1) and second one (Model 2) has included it. Kinetic diagram analysis show that the kinetic curves representing the model which neglects shrinkage effect (Model 1) do not totally follow the configuration of experimentally determined kinetic curves while in the case of the model which includes shrinkage (Model 2) representing curve follows experimental one. From the figures 5 -12 it can be seen that the introduction of shrinkage correction into equations (2) is entirely justified. Determined values of effective diffusion coefficient are beneath the value that could be found in literature. Effective diffusion coefficient values determined by using the model which includes shrinkage are less then the values determined by using the model which neglects shrinkage or the values obtained by using the slope method. The intersection point of experimental drying curves and modeled drying curves is characterized as critical point.

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