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Original scientific paper

Calculation of the effective diffusion coefficient during the drying of clay samples

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Abstract: The aim of this study was to calculate the effective diffusion coefficient based on experimentally recorded drying curves for two masonry clays obtained from different localities. The calculation method and two computer programs based on the mathematical calculation of the Second Fick Law and the Cranck Diffusion Equation were developed. Masonry product shrinkage during drying was taken into consideration for the first time and the appropriate correction was entered into the calculation. The results presented in this paper show that the values of the effective diffusion coefficient determined by the designed computer programs (with and without the correction for shrinkage) have similar values to those available in the literature for the same coefficient for different clays. Based on the mathematically determined prognostic value of the effective diffusion coefficient, it was concluded that, whatever the initial mineralogical composition of the clay, there is 90 % agreement of the calculated prognostic drying curves with the experimentally recorded ones. When a shrinkage correction of the masonry products is introduced into the calculation step, this agreement is even better.

Keywords: diffusion; drying; mathematical modeling; computer program.

INTRODUCTION

The studying of a drying process, due to its complexity, still attracts the attention of researchers around the world even today. The explanation of the drying process is reduced to the establishment of a series of theoretical and empirical drying models that show agreement, to a greater or lesser extent, with the experimental data. Complex processes of simultaneous mass and energy transfer, which are often non-stationary and the distinct nature of the properties of the material (hygroscope, capillarity, pores size distribution, shrinkage effect, *etc.*) complicate even more the description of the drying process. For these reasons, a unique theo-

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retical setting of drying, which would universally describe this process for different types of clay materials has not yet been developed.

The diffusion process viewed as the transport of matter due to the random motion of molecules is characteristic for a drying process. The transfer of moisture within the solid body at a certain temperature is realized due to the different moisture content in the interior and on the surface of a solid body. The mass transfer rate by diffusion is therefore proportional to the concentration gradient of the moisture content, with the diffusion coefficient being the proportionality factor. Knowing the diffusion coefficient is essential for a credible description of the mass transfer process, described by the Fick's Equation. The analytical solution of the general Fick's Law was described by Cranck in 1975.[1] Several different ways of solving the Fick's Equation were presented by Cranck:

i) For the case when the diffusion coefficient is constant and the solid body isotropic;

ii) For the case when the diffusion coefficient is not constant, together with special cases of non-Fickian diffusion and

iii) For the case of diffusion in which a chemical reaction exists as well as the simultaneous diffusion of heat and moisture.

The drying process, in addition to pure diffusion, is characterized by the existence of other, secondary types of internal mass transfer, such as surface diffusion, Knudsen diffusion, capillary flow, evaporation and condensation, thermo–diffusion, *etc.*, which in small amounts influence the overall process of mass transfer.[2] Normally, a correction for secondary types of mass transfer is introduced into the calculation by replacing the pure diffusion coefficient with an effective diffusion coefficient.

In numerous papers, the results of drying kinetics obtained from different models for different materials, which include or neglect shrinkage of the material, are compared with the experimentally determined parameters of the drying kinetics.[3–6] During the drying of certain materials such as: various agricultural products, various constructional products from wood, cement, hydraulic binders or clay, the shrinkage effect that occurs cannot be neglected, neither in practice nor in the mathematical models that are used to describe the drying process.

In most models that describe the drying process, shrinkage does not exist in the equations because the mathematical models that would include the shrinkage effect during drying are extremely complicated; hence, in the mathematical modeling process, it is the practice to assume that shrinkage does not exist or is negligible. Such models are usually applied on materials that exhibit a shrinkage effect and shrinkage deviations are usually corrected for by the introduction of correction factors.

A small number of papers that describe the drying process of ceramic materials and especially clay are available in the literature. Some data can be found in the papers of Efremov[7] (bricks), Chemkhi[8], Zagrouba[9,10] (clays), Skansi[11,12], Lalić[13] (heavy clay tiles) and others.

The behaviors during the drying process of two different clays with different mineralogical compositions were considered in the present study. An appropriate shrinkage correction, caused by thickness shrinkage during drying, was introduced into the mathematical models for the calculation of the effective diffusion coefficient.

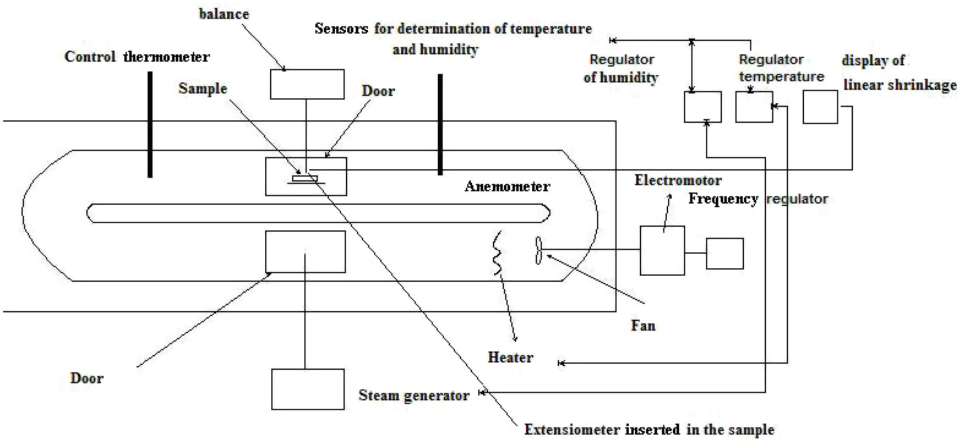
EXPERIMENTAL

Sample preparation

Two raw masonry clays from the localities Banatski Karlovac and Ćirilkovac were analyzed. After an initial characterization of these materials, which included chemical, mineralogical, X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA) and granulometric examination, the raw materials were subjected to further classical preparation. The raw material samples were first dried at 60 °C and then milled down in a laboratory perforated rolls mill. After that, the clays were moisturized and milled in a laboratory differential mill, first at a gap of 3 mm and then of 1 mm. Laboratory samples of size 120 mm×50 mm×14 mm were formed in a laboratory extruder "Hendle" type 4, under a vacuum of 0.8 bar. These samples were used in the further experimental work.

Drying experimental conditions

The behavior of the clay samples during drying was investigated by monitoring and recording the changes in weight and linear shrinkage of the test samples during drying in a laboratory dryer, especially created for this purpose, the schematic view of which is shown in Scheme 1.



Scheme 1. Laboratory recirculation dryer.

The laboratory recirculation dryer provides: regulation of the drying air temperature within 0–125 °C, with accuracy ±0.2 °C; regulation of the relative humidity of the drying air within 20–100 %, with an accuracy of 0.2 %; velocity regulation of the drying air within 0–3.5 m s^{-1}, with an accuracy of 1 %; monitoring and recording of the weight of the drying samples within 0–2000 g, with an accuracy of 0.01 g; monitoring and recording the linear shrinkage within 0–23 mm with an accuracy of 0.2 mm and continuous time monitoring during drying.

Data acquisition, continuous time monitoring and recording of the temperature and relative humidity of the drying medium and the linear shrinkage of the drying samples were realized automatically using PLC controllers and a standard Pentium IV computer.

Drying kinetic curves were recorded for the drying of the prepared heavy clay tiles (samples) in a laboratory recirculation dryer under the experimental conditions presented in Table I.

TABLE I. Experimental conditions

Experiment	Air velocity, W / m s^{-1}	Air temperature, T / °C	Air humidity, V / %
Clay Banatski Karlovac (experiments from this work)			
1	1	40	60
2	3		
3	1	80	
4	3		
5	1	40	80
6	3		
7	1	80	
8	3		
Clay Ćirilkovac (experiments taken from previous research phases[21])			
9	3	40	60
10		55	
11		70	
12			40

Theoretical principles

In order to determine the moisture diffusion in porous systems, it is necessary to use data analysis obtained from: drying, sorption kinetics and permeability measurements. An estimation of the diffusion coefficient can be obtained from drying curve by the slope method,[14,15] or by comparing experimentally determined drying curves with curves obtained from the Fick Equations predicted analytically[2,3,16] or numerically.[6,17]

The drying curve of typical masonry clay consists of a first phase of drying, the constant velocity phase, and a phase of decreasing drying rate. In drying studies performed on different materials, diffusion is generally accepted as the main mechanism of moisture transport from the material interior to its surface. The restriction to one-dimensional diffusion gives a good approximation in many practical systems. Analytical solution of the Fick Equation are given for various geometrical shapes, assuming that the transport of moisture occurs by diffusion, that sample shrinkage is neglected and that diffusion coefficient and temperature have constant values. For the case of "thin plate" geometry, a solution was given by Cranck,[1] that is represented by the expression:

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

where X_0, X and X_{eq} represent, respectively, the initial, current and equilibrium moisture content, kg moisture kg^{-1} dry material, D_{eff} is the effective diffusion coefficient, m^2 s^{-1}, l is the half plate thickness and t is time, s. MR represents the moisture ratio and has no unit. Since clay products show dimensional change during drying, it was necessary to develop a model that would consider this phenomenon. By introducing into Eq. (1) the expression $l_{(t)}$, which represents the experimental dependence of the thickness of the tiles in time, Eq. (1) is corrected. It should be born in mind that this type of correction is not mathematically one hundred percent accurate because the resulting Eq. (1) was obtained using the assumption of unchangeable sample thickness. Formally speaking, a mathematically accurate correction can be obtained by entering the expression $l_{(t)}$ into the equation for the case of constant sample thickness, after an integration step. A small number of papers describing the sample dimensional correction can be found in literature. Some data can be found in the papers of Hassini,[20] and Disse.[21] Da Silva[18,19] presented in his studies a way of solving the diffusion equation for the case of spherical samples.

Program description

In order to solve Eq. (1), it is necessary to dispose with the experimental results and to have the experimentally determined dependence MR_{exp}–t. MR_{exp} represents the experimentally determined value of MR calculated from the experimentally measured data X_0, X and X_{eq}. Eq. (1) can be converted into the form:

$$MR = \frac{8}{\pi^2}\sum_{n=N+1}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2}{4}\pi^2\frac{D_{eff}t}{x^2}\right)+ \\ +\frac{8}{\pi^2}\sum_{n=0}^{N}\frac{1}{(2n+1)^2}\left(-\frac{(2n+1)^2}{4}\pi^2\frac{D_{eff}t}{x^2}\right) \tag{2}$$

If the value of ε is defined as the relative error of neglecting terms higher than N in Eq. (2), the value of N can be determined and Eq. (2) is transformed from an infinite sum into a finite sum of N terms given by Eq. (3):

$$MR = \frac{8}{\pi^2}\sum_{n=0}^{N}\frac{1}{\left(2n+1\right)^2}\left(-\frac{\left(2n+1\right)^2}{4}\pi^2\frac{D_{eff}t}{l^2}\right) \tag{3}$$

The value of $\varepsilon = 0.05$ was accepted for the further calculations in this paper. When $t = 0$, $MR = 1$ and Eq. (2) is transformed into Eq, (4). The value of N used in Eq. (3) can be determined from Eq. (4):

$$1 = \frac{8}{\pi^2}\sum_{n=0}^{N}\frac{1}{\left(2n+1\right)^2}+0.05 \tag{4}$$

MR_{an} represents the analytically determined value calculated from Eq. (3). It is necessary to introduce the concept of a numerical counter i, which can have only integer values. The numerical counter i is defined for each value of the experimental pairs (MR_{exp}, t). It starts from the value zero and increases by one until it reaches a final value, which is related to the last experimental pairs (MR_{exp}, t). This concept enables the number of experimental pairs (MR_{exp}, t) from its first to its last value to be counted. In order to work properly, the program requires the initial value of the effective diffusion coefficient D_{eff}, and the ε value to be entered. Let the initial value of the effective diffusion coefficient D_{eff} be given the value of 1.0×10^{-20} m^2 s^{-1}. Then, for each numerical counter value i, the program calculates the value χ^2 from Eq. (5):

$$\chi^2 = \sum_1^i \left(MR_{\text{exp,i}} - MR_{\text{an,i}} \right)^2 \tag{5}$$

In the first cycle, $MR_{an,1}$ is calculated according to Eq. (3) using the previously determined value of N and the initial value of D_{eff}. In the next cycle, the value of D_{eff} is doubled giving a new value for $MR_{an,i}$ that is now used to calculate a new χ^2 according to Eq. (5). The program then compares the value of 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, the program will continue the previously described cycle, otherwise the program will temporarily stop. Note: χ^2_{first} and χ^2_{second} refer to the last and the penultimate value of the cycle in which χ^2 is determined.

The last three values for D_{eff} and χ^2 are then recorded. The recorded D_{eff} interval is then divided into 100 parts. A hundredth part of this interval is defined as a step, s. The program commences the cycle again using the initial value for D_{eff} as $D_{eff,third\ from\ end} + s$. The cycle is repeated until the statement $\chi^2_{first} < \chi^2_{second} < 1.0\times10^{-10}$ is satisfied. In other words, the cycle is interrupted when the difference $\chi^2_{second} - \chi^2_{first}$ reaches 1.0×10^{-10}. The final D_{eff} value is then recorded. This value represents the finally calculated effective diffusion coefficient in $m^2\ s^{-1}$.

For long drying times, Eq. (1) can be transferred into Eq. (6):

$$MR = \frac{8}{\pi^2} \exp\left(\pi^2 \frac{D_{eff} t}{l^2} \right) \tag{6}$$

In a previous study,[21] the effective diffusion coefficient was determined by the slope method from Eq. (7):

$$\ln\left(\frac{\pi^2 MR}{8} \right) = \ln(A) = -\pi^2 \frac{D_{eff}}{l^2} t \tag{7}$$

The case when there is shrinkage

For materials that show shrinkage during drying, Eq. (3) needs to be changed by the introduction of the expression $l_{(t)}$ into it. This expression represents the experimentally determined time dependence of the sample thickness. When this correction is entered, the previously described method for the determination of the effective diffusion coefficient can be used.

Two programs were designed to compute the effective diffusion coefficient. The first program did not include the shrinkage effect during drying into the computation algorithm while the second one did. Both programs were written in the Borland C program language on a standard Pentium IV computer (AMD 1200 MHz, 80GB HDD, 256 MB RAM memory) based of the previously described algorithm.

RESULTS AND DISCUSSION

Two models for predicting the drying behavior (MR_{an}–t dependence) were obtained from these two programs. The first model did not include shrinkage (Model 1), while the second one (Model 2) did. Graphical views of the experimental and predicted drying behavior are presented in Figs. 1–3. The D_{eff} values obtained using the described programs and from the slope of Eq. (7) are presented in Table II.

From Table II, it can be clearly seen that in all experiments, the value of effective diffusion coefficient, D_{eff}, determined by Model 2 was lower than the value of the same coefficient determined by Model 1. On analyzing the experiments

1–8 (clay "Banatski Karlovac"), it can be seen that by increasing the velocity of the drying air from 1 to 3 m s^{-1}, the value of the effective diffusion coefficient also increased by up to 38 %.

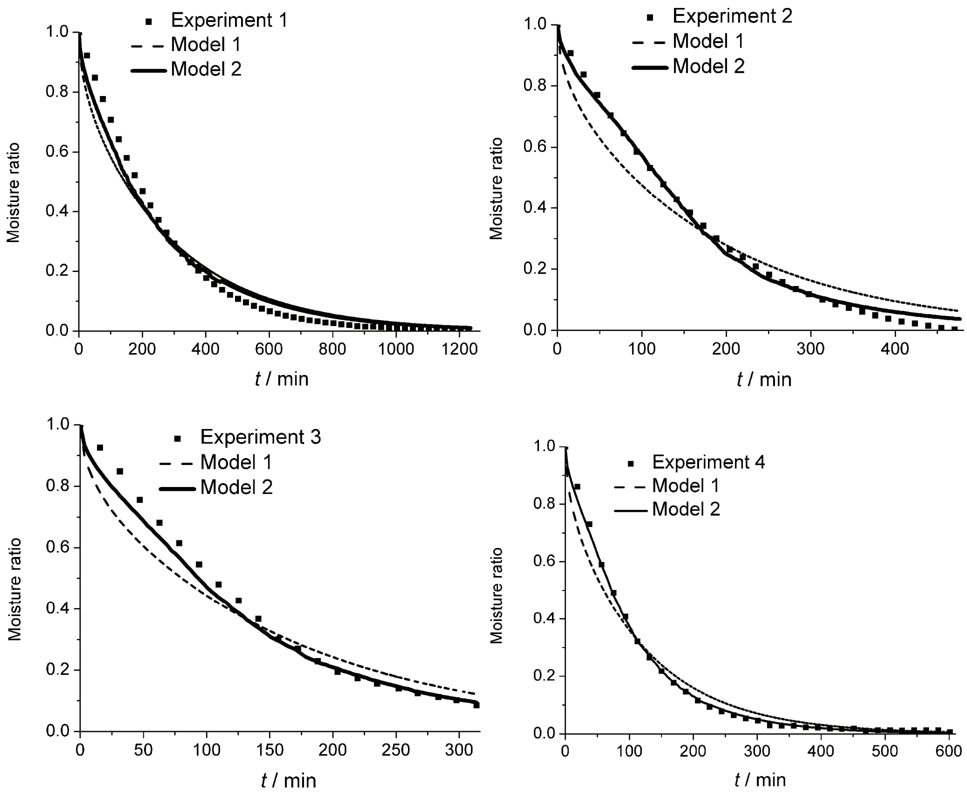


Fig. 1. Experimental and calculated moisture ratio *vs*. drying time for experiments 1–4.

The drying experiments from this and a previous study[21] can be compared, because in both studies, the experimental conditions and the clay material (clay "Ćirilkovac") were the same.

A kinetic diagram analysis showed that the kinetic curves representing the model that neglects the shrinkage effect (Model 1) do not completely follow the configuration of the experimentally determined kinetic curves. Deviations of this model from the experimental drying curves are higher at the beginning of the drying process and after some time the deviations disappear. The moment of the disappearance matches the moment at which the sample continues to dry but without shrinkage. Drying kinetic curves of the model that includes shrinkage (Model 2) follow the configuration of the experimentally determined curves and their matching can be more than 95 %, as could be seen in experiments 2, 4 and 9–11. If minor deviations do exist, they are at the beginning of the drying process and are most probably caused by the time interval which has to pass before stationary experimental conditions are fulfilled and the products are heated up to the required temperature in the dryer. The intersection point of the experimental drying curves and modeled drying curves is characterized as the critical point. The critical point is a characteristic kinetic parameter, which is important because it determines the moment after which the products no longer shrink.

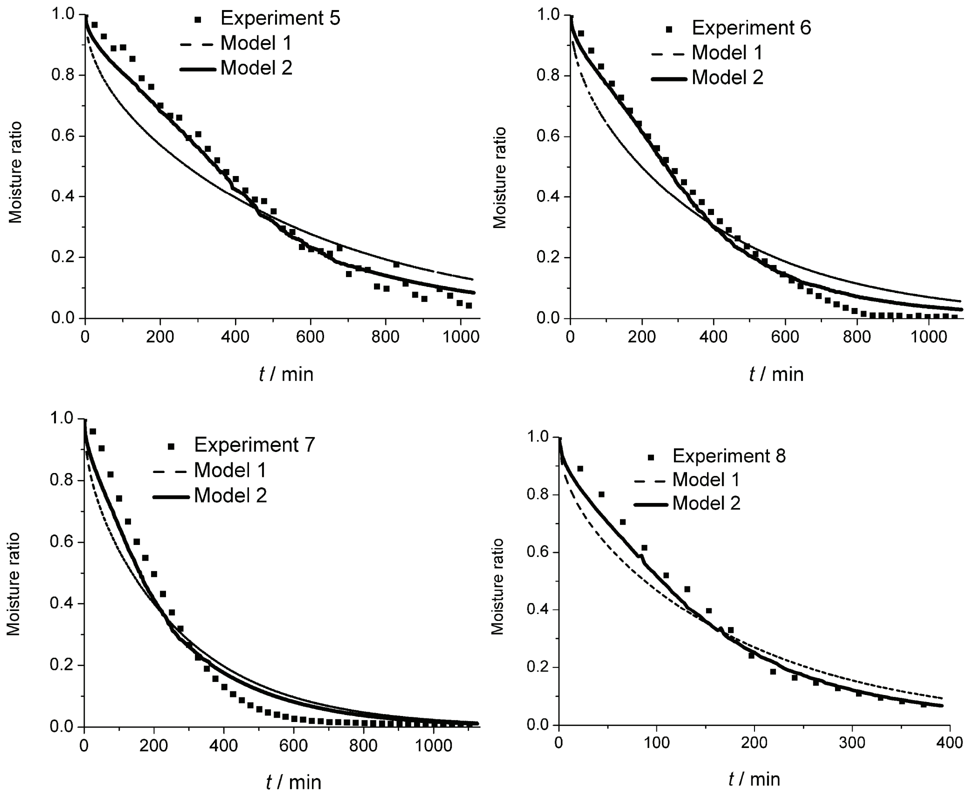


Fig. 2. Experimental and calculated moisture ratio *vs*. drying time for experiments 5–8.

From Table II, it could be concluded that value of the effective diffusion coefficient, D_{eff} determined using the model that included the sample shrinkage correction was lower than the corresponding value determined using the model that neglected sample shrinkage or the slope model. The data for D_{eff} determined by the slope model were higher than the data determined by the other two models. This is an expected result that is in agreement with the D_{eff} determination. This is additional proof that the model that included the shrinkage effect during drying gives more precise D_{eff} values. Only a few scientific papers[8,11] in which the effective diffusion coefficients for masonry clay products were determined are available in the literature. In these papers, the D_{eff} values are in range of 10^{-7}

up to 10^{-12} m^2 s^{-1}. This relatively large range for the D_{eff} values is connected with the different nature of the heavy clay and the different methods employed for their determination. The D_{eff} values presented in Table II lie below the previously mentioned range.

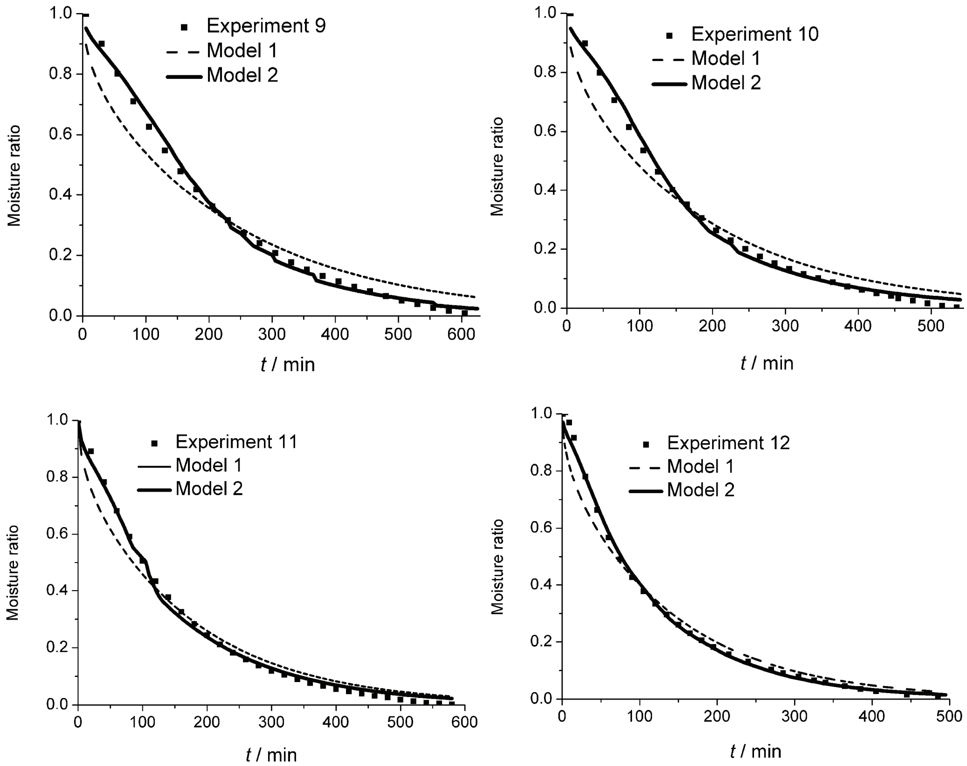


Fig. 3. Experimental and calculated moisture ratio *vs*. drying time for experiments 9–12.

TABLE II. Calculated values of the effective diffusion coefficient, $D_{eff}\times10^9$ / m^2 s^{-1}

Experiment	Model		
	1	2	Slope model
1	0.452	0.213	1.90
2	0.718	0.222	2.35
3	0.810	0.318	2.47
4	1.088	0.339	3.05
5	0.240	0.068	0.95
6	0.328	0.084	1.17
7	0.475	0.184	1.95
8	0.738	0.302	2.41
9	0.341	0.068	1.24
10	0.431	0.077	2.00
11	0.472	0.150	2.32
12	0.583	0.126	2.76

CONCLUSIONS

A new method and computer program for the determination of diffusion coefficients, which is based on the mathematical calculation of the Fick and Cranck Diffusion Equations, were developed. Two programs were designed to compute the effective diffusion coefficient. The first program (Model 1) did not include the shrinkage effect during drying in the computation algorithm, while the second one (Model 2) did. This was the first time in the mathematical modeling of the drying of masonry clay that a shrinkage correction was entered into the calculation step.

Kinetic diagram analysis showed that, irrespective of the nature the initial mineralogical composition of the clay, the kinetic curves representing the model that neglected the shrinkage effect (Model 1) did not fully follow the configuration of the experimentally determined kinetic curves, while in the case of the model that included shrinkage (Model 2), the resulting curves follows the experimental ones. From Figs. 1–3, it can be seen that the introduction of the shrinkage correction into Eq. (2) was entirely justified. The determined values of the effective diffusion coefficient were lower than the value that could be found in the literature. The values of the effective diffusion coefficient determined using the model that includes shrinkage were lower than the values determined using the model which neglected shrinkage or the values obtained using the slope method. The intersection point of the experimental drying curves and the modeled drying curves is characterized as the critical point.

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ИЗВОД

ОДРЕЂИВАЊЕ ЕФЕКТИВНОГ КОЕФИЦИЈЕНТА ДИФУЗИЈЕ ПРИЛИКОМ СУШЕЊА УЗОРАКА ОД ГЛИНЕ

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Циљ овог рада је да се на примеру две опекарске глине са различитих локалитета одреди ефективни коефицијенат дифузије на основу експериментално снимљених кривих сушења. Развијен је метод и направљена су два компјутерска програма за одређивање овог коефицијента, који се заснивају на математичком решавању Фикове, односно Кранкове дифузионе једначине. По први пут узето је у разматрање и скупљање опекарских производа у току сушења а одговарајућа корекција је унета у прорачун. Резултати показују да су вредности ефективног коефицијента дифузије одређени компјутерским програмима (са корекцијом и без корекције на скупљање опекарских производа) реда величине које су наведене у литератури за друге врсте опекарских глина. На основу математичким путем прогнозираних вредности ефективног коефицијента дифузије констатовано је, да без обзира на полазни минералошки састав опекарске сировине, постоји 90 % слагања прогнозираних

кривих сушења са експериментално снимљеним кривима сушења. За случај када је уведена у прорачуне и корекција на скупљање опекарских производа ово слагање је још веће.

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REFERENCES

1. J. Cranck, *The mathematics of diffusion*, II ed., Oxford University Press, London, 1975
2. G. Efremov, T. Kudra, *Drying Technol.* **22** (2004) 2273
3. I. I. Ruiz-Lopey, M. A. Garcia-Alvarado, *J. Food Eng.* **79** (2007) 208
4. L. M. Batista, C. A. da Rosa, L. A. Pinto, *J. Food Eng.* **81** (2007) 127
5. J. A. Hernandez, G. Pavon, M. A. Garcia, *J. Food Eng.* **45** (2000) 1
6. K. J. Park, T. H. Ardito, A. P. Ito, K. J. B. Park, R. A. de Oliveira, M. Chiorato, *Drying Technol.* **25** (2007) 1313
7. G. I. Efremov, *Drying Technol.* **20** (2002) 55
8. S. Chemkhi, F. Zagrouba, *Desalination* **185** (2005) 491
9. D. Mihoubi, F. Zagrouba, M. Ben Amor, A. Bellagi, *Drying Technol.* **20** (2002) 465
10. F. Zagrouba, D. Mihoubi, A. Bellagi, *Drying Technol.* **20** (2002) 1895
11. A. Sander, D. Skansi, N. Bolf, *Ceram. Int.* **29** (2003) 641
12. S. Tomas, D. Skansi, M. Sokele, *Ceram. Int.* **20** (2004) 9
13. Ž. Lalić, M. Arsenović, Đ. Janacković, M. Vasić, Z. Radojević, *Rom. J. Mat.* **39** (2009) 175
14. N. Hamdami, J.-Y. Monteau, A. Le Bail, *J. Food Eng.* **62** (2004) 85
15. G. Efremov, M. Markowski, I. Bialobrzewski, M. Zielinska, *Int. Commun. Heat Mass Transfer* **35** (2008) 1069
16. , *Handbook of Industrial Drying*, III ed., A. S. Mujumdar, Ed., CRC Press, Boca Raton, FL, 2006
17. W. P. da Silva, J. W. Precker, C. M. D. P. S. e Silva, D. D. P. S. e Silva, *J. Food Eng.* **95** (2009) 298
18. W. P. da Silva, J. W. Pecker, C. M. D. P. S. e Silva, J. P. Gomes, *J. Food Eng.* **98** (2010) 302
19. L. Hassini, S. Azzouz, R. Peczalski, A. Belghith, *J. Food Eng.* **79** (2007) 47
20. A. O. Dissa, H. Desmorieux, J. Bathiebo, J. Koulidiati, *J. Food Eng.* **88** (2008) 429
21. Ž, Lalić, *M.Sc. Thesis*, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, 2006.