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Methods of Determination for Effective Diffusion Coefficient During Convective Drying of Clay Products

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1. Introduction

Drying research is an outstanding example of a very complex field where it is necessary to look comprehensively on simultaneous energy and mass transfer process that takes place within and on the surface of the material. In order to get the full view of drying process, beside previously mentioned, researchers have to incorporate and deal with highly non linear physical phenomena inside drying clay products, non-homogenous distribution of temperature and humidity inside dryers, equipment selection, design, control and final product quality [1]. That is the reason why a unique theoretical setting of drying has to be determined through the balance of the heat flow, temperature changes and moisture flow. Simultaneous heat and mass process are related, regarding to the fact that all phases have to remain in thermodynamic balance established on a local temperature value [2]. In the economy that is becoming increasingly global, laboratory drying process analyses should ensure enough data which are necessary for optimal drying regime establishment. In order to find optimal drying regime it is necessary to understand transport mechanisms which takes place within and on the surface of the clay product. The drying process is characterized by the existence of several internal transport mechanisms such as pure diffusion, surface diffusion, Knudsen diffusion, capillary flow, evaporation and condensation, thermo-diffusion, *etc.* Moisture diffusivity, viewed as a transport of matter due to the random motion of molecules, is the most important mass transport mechanisms, essential for the calculation and modelling of various clay processing operations. Moisture transfer within the solid clay 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 pure diffusion is therefore proportional to the concentration gradient of the moisture content, with the diffusion coefficient being the proportionality factor. Determination of the

diffusion coefficient is essential for a credible description of the mass transfer process, described by the Fick's equation [3]. It is a common practice to describe complete mass transfer with same equations as pure diffusion and to take the correction, for all secondary types of mass transfer into account simply by replacing the pure diffusion coefficient with an effective diffusion coefficient.

Relatively small number of research papers that describe the drying process of ceramic and especially clay materials are available. Some data can be found in the papers of Efremov [4] (bricks), Vasić [5] (heavy clay tiles) Chemkhi [6], Zagrouba [7, 8] (clays), Skansi [9, 10] (brick, hollow brick, heavy clay tiles, tiles) and others. In his paper Efrem [4] gave an analytical solution of diffusion differential equation with boundary conditions in the form of flux. Relying on these studies M. Vasić and colleagues [11] have developed a drying model based on the modification of Efremov's equation and the computer program for determining the effective diffusion coefficient.

Chemki and Zagrouba [6] have estimated the coefficient of moisture diffusivity from drying curve. F. Zagrouba and colleagues [7, 8] have developed a mathematical model of transfer phenomena which has involved at the same time heat, mass and momentum transfer during the convective drying of clay tiles. In their study a method for determination of the heat transfer coefficient and effective diffusion coefficient is presented. Zanden and Kerkhof [12] have performed extensive research on isothermal mass transport mechanisms during the convective drying of clay products. They presented a model which describes moisture transport inside a porous clay material during drying.

M. Vasić and colleagues [5] have developed two computer programs for determination of effective diffusion coefficient, based on mathematical calculation of the second Fick's law and Cranck diffusion equation. Skansi and colleagues [9, 10] were investigating the kinetics of conventional drying of flat tiles in experimental and industrial tunnel dryer. They presented several thin layer models such as exponential one which correlates the kinetics of the whole tile-drying process well and has physical significance. They also presented a method for determining heat transfer coefficient, effective diffusion coefficient and drying constant.

2. Materials and methods

2.1. Theoretical development

In drying studies performed on clay 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 Fick's equation is 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 is given by Cranck [3] which is represented by the expression:

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

In equation (1) X_0, X and X_{eq}, represent respectively, the initial, current and equilibrium moisture content, kg moisture/kg of dry material, D_{eff} is the effective diffusion coefficient, m²/s, l is the half plate thickness, m and t is time, s. MR represents moisture ratio and has no unit. There is a large body of literature comparing predicted results of drying models that considered as well as neglect shrinkage [16]. Most published drying models do not take shrinkage into account in the balance equations. The drying model equations are typically borrowed from corresponding non-shrinking models, frequently without appropriate physical and mathematical consideration, and are applied to a shrinkage medium. A few studies, describing the sample dimensional correction, can be found in literature. Some data can be found in the papers [17-20]. Silva [21] presented, a way of solving the diffusion equation for the case of spherical samples. Since clay products show dimensional change during drying it was necessary to develop a model that would take this phenomenon into account. By introducing into equation (1) the expression $l_{(t)}$, which represents the experimental dependence of the thickness of the tiles in time, equation (1) is corrected. It should be kept 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 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.

2.2. Description of Model A

2.2.1. Model A1 - The case when shrinkage is not included

In order to solve the equations (1) it is necessary to dispose with the experimental results and to have the experimentally determined dependence MR_{eks} - t. MR_{eks} represents the experimentally determined value of MR obtained by calculation from the experimentally measured data X_0, X and X_{eq}. Equation (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 then N in equation (2), the value of N can be determined and equation (2) is transformed form an infinite sum into a finite sum of N terms given by equation (3):

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

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

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

MR_{an} represents the analytically determined value calculated from equation (3). It is necessary to introduce the concept of a numerical counter i, which can have only an integer value. The numerical counter i is defined for each value of the experimental pairs (MR_{eks}, t). It starts form the value zero and increases by one until it reaches a final value which is related to the last experimental pairs (MR_{eks}, t). This concept enables the number of experimental pairs (MR_{eks}, t) from its first to its last value to be countered. 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 $1 \cdot 10^{-20}$ /m²/s. Then, for each numerical counter value i, the program calculates the value χ^2 from equation (5);

$$\chi^2 = \sum_{1}^{i} \left(MR_{eksi} - MR_{an_i} \right)^2 \tag{5}$$

In the first cycle, $MR_{an\ i}$ is calculated according to equation (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 $MR_{an\ i}$ which is now used to calculate a new χ^2 according to equation (5). The program then compares 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, the program will continue 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. Then, the recorded D_{eff} interval is divided into 100 parts. A hundredth part of this interval is defined as a step s. The program commences a cycle again using the initial value for D_{eff} as $D_{eff\ third\ from\ end}$ + s. The cycle is repeated until the statement $\chi^2_{first} < \chi^2_{second} < 1 \cdot 10^{-10}$ is satisfied. In other words, the cycle is interrupted when the difference $\chi^2_{second} - \chi^2_{first}$ reaches $1 \cdot 10^{-10}$. The final D_{eff} value is then recorded. This value represents the finally calculated effective diffusion coefficient in m²/s.

2.2.2. Model A2 - The case when there shrinkage is included

For materials which shows shrinkage during drying equation (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 optimizing concept for the determination of the effective diffusion coefficient is applied.

2.3. Description of model B

2.3.1. Model B1 - The case when shrinkage is not included

If parameters of drying medium are kept constant during convective drying of solid bodies, moisture transfer could be treated on macro level as quasi diffusion with appropriate effective diffusion coefficient D_{eff}. The general expression for mass conductivity (Fick's second law) can be presented as a partial differential equation of diffusivity.

$$\frac{\partial X}{\partial t} = div(D_{eff} \cdot grad X) ; \quad \rightarrow \quad \frac{\partial X}{\partial t} = D_{eff} \frac{\partial^2 X}{\partial x^2} \qquad (6)$$

The exact solution for drying kinetics can be obtained by applying Laplace transform method in time t for equation of isotropic diffusion with boundary conditions in a form of mass flux J. This flux is proportional to the difference between an equilibrium concentration in the pores of the material X_{eq} and the current concentration X on the material surface.

$$J = -D_{eff} \cdot \frac{\partial X}{\partial x}\Big|_{x=0} = k \cdot \left(X_{eq} - X \right) \qquad (7)$$

Kinetic desorption coefficient k (m/s) in equation (7) can be calculated as a ratio l (characteristic thickness value) and time $\left(k = \dfrac{l}{t} \right)$.

By applying Laplace transform method to equation (7) Efremov in his PhD thesis [13] presented the solution given by equation (8).

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = erf\left(\frac{l}{2\sqrt{D_{eff}t}} \right) + \exp\left(\frac{k}{D_{eff}} l + \frac{k^2}{D_{eff}} \cdot t \right) \cdot erfc\left(k\sqrt{\frac{t}{D_{eff}}} + \frac{l}{2\sqrt{D_{eff}t}} \right) \qquad (8)$$

X_0, X and X_{eq}, represent respectively, the initial, current and equilibrium moisture content, kg moisture/kg of dry material, D_{eff} is the effective diffusion coefficient, m²/s, and t is time, s. The mass flux on the material surface (x=0) can be calculated through the use of the concentration ratio which is given in equation (9)

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = \exp\left(\frac{k^2}{D_{eff}} \cdot t \right) \cdot erfc\left(k\sqrt{\frac{t}{D_{eff}}} \right) \qquad (9)$$

Equation (8) was obtained for the process of molecular diffusion. If we analyze equation (9) at the beginning of the drying process (t=0; X=X_0) MR=1 and for long times (t→∞; X=X_{eq}) MR=0 will see that it has a real physical meaning. In order to get the drying equation which is valid for convective mass transport processes it is necessary to introduce the power function of the argument in equation (9), thus the drying equation becomes (10).

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = \exp\left(\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{t \cdot D_{eff}} \right)^n \right) \cdot erfc\left(\sqrt{\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{t \cdot D_{eff}} \right)^n} \right) \qquad (10)$$

Simple approximation formula for function erf (A) is defined by equation (11) and can be found in Sergei Winitzki [14, 15] papers. The relative precision of this approximation is higher than $4 \cdot 10^{-3}$, uniformly for all real A.

$$erf(A) = \left[1 - \exp\left(-A^2 \frac{1.27 + 0.14A^2}{1 + 0.14A^2} \right) \right]^{1/2} \tag{11}$$

After some mathematical manipulation, knowing that erfc (A) = 1 – erf (A), the final drying kinetic equation (12) is obtained.

$$MR = \exp\left(\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{tD_{eff}}\right)^n\right) \cdot \left(1 - \left[1 - \exp\left(-\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{tD_{eff}}\right)^n \cdot \frac{1.27 + 0.14\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{tD_{eff}}\right)^n}{1 + 0.14\frac{1}{\pi}\left(\frac{\pi \cdot l^2}{tD_{eff}}\right)^n} \right) \right]^{1/2} \right) \tag{12}$$

Efremov [4] has calculated the power function of the argument n for clay materials as 1.95. In order to calculate D_{eff} optimization concept is applied. Drying equation (3) is replaced by equation (12). When this correction is entered, the previously described optimizing concept for the determination of the effective diffusion coefficient can be applied.

2.3.2. Model B2 - The case when shrinkage is included

For materials which shows shrinkage during drying equation (12) 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 optimizing concept for the determination of the effective diffusion coefficient is applied.

2.4. Program algorithm

The algorithm presented below is the same for any software program. Program named "Drying calculator" was written in the Borland C program language on a standard Pentium IV computer (AMD 1200 MHz, 80GB HDD, 256 MB ram memory). Program has the ability to calculate effective diffusion coefficient using the calculation method A1, A2, B1 and B2.

Program algorithm for models A1 and B1, which neglects shrinkage, contains the following steps:

1. Read the values from database: the time (s), MR_{eks}.
2. Enter number ε (Usually ε =0.05). *(Exists only in case of A1)*
3. Enter the initial value of D_{eff} (D_{eff} =1·10^{-20})

4. Enter the characteristic dimension l (samples half thickness, m)
5. Enter the value n form equation (12) (n=1.95) *(Exists only in case of B1)*
6. For each value from the database using equation *(3) in case of A1* or *(12) in case of B1* MR_{an} will be determined.
7. For each value from database χ^2 will be determined using equation (5)
8. In next cycle step starting value D_{eff} is doubled and a new value MR_{an} will be determined and initially used for determination of new χ^2.
9. If the statement $\chi^2_{first} < \chi^2_{second}$ is satisfied, the program will continue previously described cycle, otherwise the program will temporarily stop.
10. The last three values for D_{eff} and χ^2 are then recorded. Then, the recorded D_{eff} interval is divided into 100 parts. A hundredth part of this interval is defined as a step s. The program commences a cycle again using the initial value for D_{eff} as D_{eff} third from end + s. The cycle is repeated until the statement $\chi^2_{first} < \chi^2_{second} < 1 \cdot 10^{-10}$ is satisfied. In other words, the cycle is interrupted when the difference $\chi^2_{second} - \chi^2_{first}$ reaches $1 \cdot 10^{-10}$
11. The final D_{eff} value is then recorded.
12. Result will be saved as database: time (s), MR_{eks}, MR_{an}, and value of average D_{eff}.
13. On the base of this database a graphical view can be displayed

Program algorithm for models A2 and B2, which includes shrinkage, is obtained from previously presented algorithm after a few modifications: in steps 1, and 6 are made.

1. Read the values from database: the time (s), MR_{eks}, and characteristic l (m).
6. In equation *(3) for the case A2* or *(12) for the case B2* l is a function of time; l is provided from database where values of l were determined by experimental measuring of thin plate sample shrinkage vs. time.

2.5. Description of the slope model

For long drying times, equation (1) is transformed into equation (13).

$$MR = \frac{8}{\pi^2}\exp(-\pi^2\frac{D_{eff}t}{l^2}) \quad \text{or} \quad \ln(\frac{\pi^2 MR}{8}) = -\pi^2\frac{D_{eff}t}{l^2} \tag{13}$$

From the equation (13) slope D_{eff} coefficient can be calculated.

3. Results and discussion

3.1. Clay characterization and sample preparation

Three raw masonry clays from the locality Banatski Karlovac (I), Ćirilkovac (II) and Orlovat (III) were analyzed. Characterization of raw masonry clays has included chemical, mineralogical, granulometrical, XRD, DTA and TGA examination. Results of chemical analysis are presented in table 1, while granulometric analyze is presented at fig. 1 and 2.

Composition	Clay (I) %	Clay (II) %	Clay (III) %
Loss ignition on 1000^0C	11.71	7.15	6.71
SiO_2	53.23	53.08	54.49
Al_2O_3	13.64	16.73	13.91
Fe_2O_3	5.34	7.10	5.09
CaO	7.50	6.69	8.05
MgO	3.59	1.41	3.70
SO_3	0.00	0.08	0.07
S^{2-}	0.00	0.00	0.01
Na_2O	1.24	0.48	1.14
K_2O	3.42	1.70	1.70
MnO	0.091	0.15	0.08
TiO_2	0.60	0.71	0.46
Summary:	100.36	100.40	100.19

Table 1. Results of chemical analysis
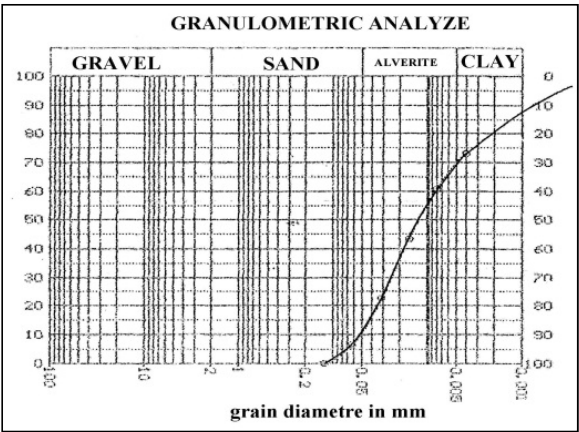
Figure 1. Granulometric test results for clay (I)
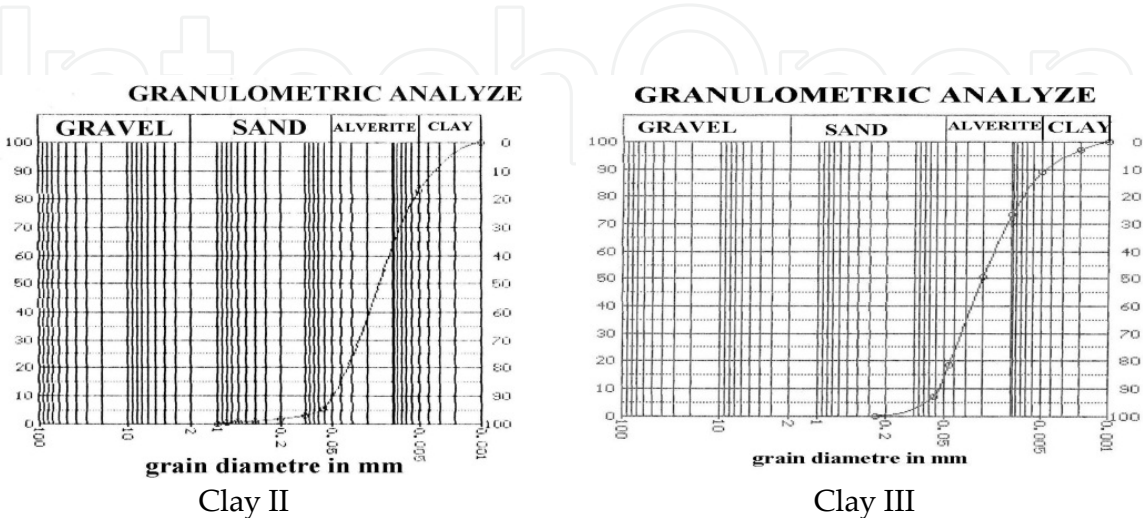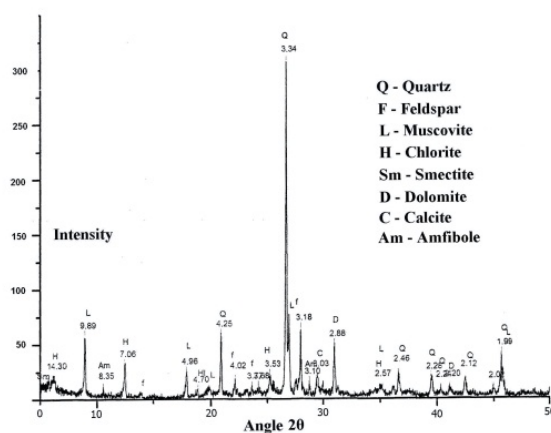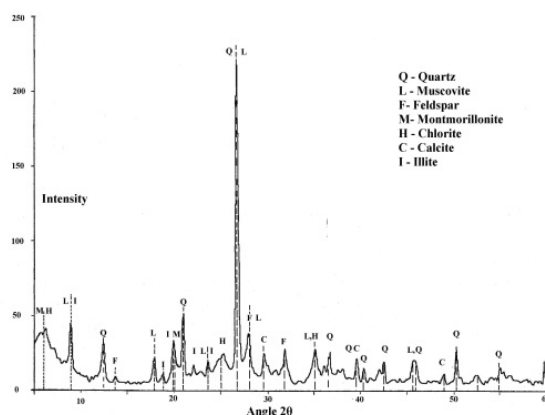

Clay II

Clay III

**Figure 2.** Granulometric test results for Clay (II) and (III)

XRD examinations far all three clays were recorded on the Belgrade faculty of mining and geology, using the device PHILIPS PW 1710. DTA and TGA examinations for clay (I) was recorded in Belgrade ITNMS institute, using the device SDT Q600 (TA Instruments), while for clay (II) and clay (III) these examinations were done on the Belgrade chemistry faculty, using the device DERIVATOGRAPH-C (MOM Budapest) and DUPON.

Clay I

Clay II
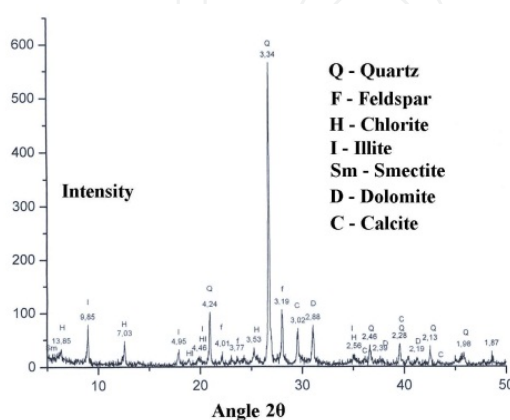
Clay III

Figure 3. XRD diagrams

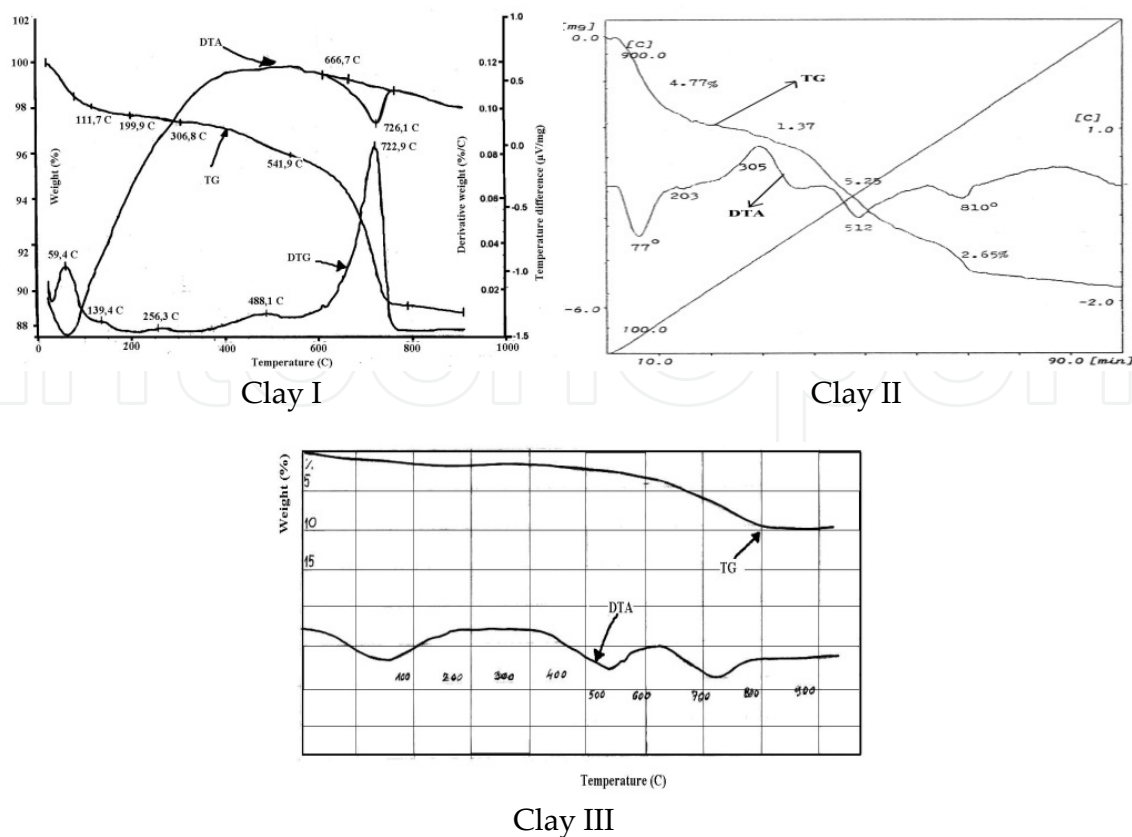Clay I   Clay II

Clay III

Figure 4. DTA/TG diagrams

Based on chemical test results it can be concluded that all three clays are representing usual masonry raw materials, with a relatively low content of aluminium oxide, a relatively small content of clay minerals and feldspars and increased carbonate content. Clay (III) has the highest SiO_2 and carbonate content. From fig. 1 and fig. 2 it can be seen that Clay (I) has the largest clay content of 30.18%, while in the case of Clay (II) and Clay (III) clay content were respectively 16.75% and 11.11%. From fig. 3 and fig. 4 it can be seen that the most common mineral in all three clays is quartz. Carbonate minerals: calcite and dolomite were present in all three clays too. Beside previously mentioned minerals clay (I) is consisted of mica, chlorite and a small amount of smectites, clay (II) is consisted of muscovite, montmorillonite, chlorite, and illite in traces, while clay (III) is consisted of illite, chlorite, and a small amount of smectites.

After initial clay characterization, the raw materials were subjected to further classical preparation. The raw material samples were first dried at 60⁰C 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 120x50x14 mm were formed in a laboratory extruder "Hendle" type 4, under a vacuum of 0.8 bar. These samples were used in further experimental work.

3.2. Drying experiments

Moropoulou [22] was investigating the influence of drying air, temperature (20 - 40⁰C), humidity (30-80%) and velocity (1 - 8 m/s) in order to develop a drying model which will

include in its structure the drying air parameters. Mancuhan [3] was studying industrial drying of bricks in a tunnel dryer in order to find optimal drying air parameters which were necessary for rationalization an optimization of the drying process. On the base of previously mentioned studies and along with the years of industrial production experience range of drying air parameters: temperature (40-70^{0}C), humidity (40-80%) and velocity (1-3 m/s) has been set up in this study as the boundaries of the planned drying experiment.

Drying kinetic curves were recorded, under the experimental conditions presented in Table 2, on the prepared heavy clay tiles (samples), by monitoring and recording the changes in weight and linear shrinkage of the clay tiles in a laboratory dryer, especially created for this purpose. Schematic view of the laboratory recirculation dryer is presented in Scheme 1.
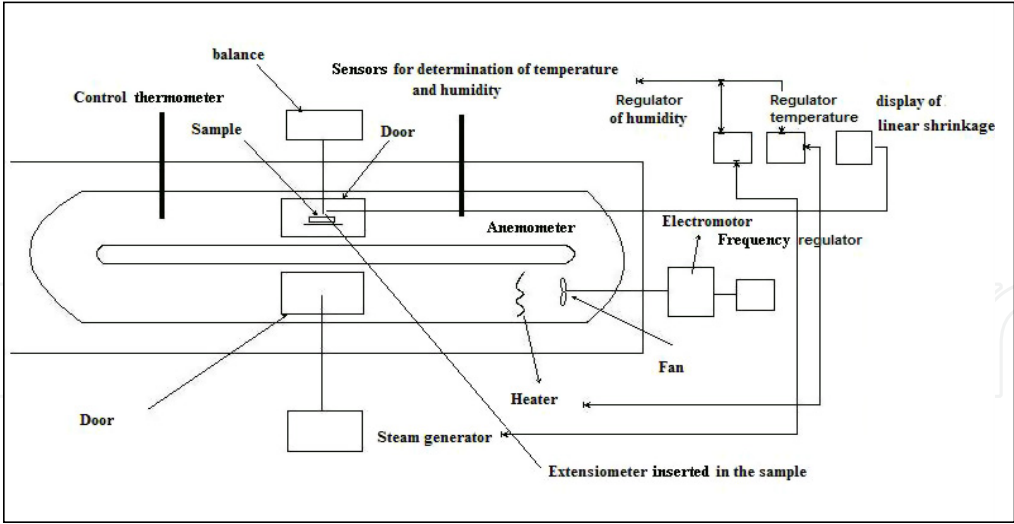
3.2.1. Laboratory recirculation dryer

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, 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.

Experiment	Air velocity, W / m/s	Air temperature, T / ^{0}C	Air humidity, V / %
1	1	40	40
2	3	40	40
3	1	40	80
4	3	40	80
5	1	70	40
6	3	70	40
7	1	70	80
8	3	70	80

Table 2. Experimental conditions

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.

Scheme 1. Laboratory recirculation dryer

3.2.2. Interpretation

Four models for predicting the drying behavior (MR_{an}–t dependence) were obtained from previously described programs. Models A1 and B1 did not include shrinkage, while Models A2 and B2 did. Drying models results are presented in a form of table 3. Deviation of the predicted drying models form experimentally recorded data, presented in table 3, were given as a root mean square error (RMSE) calculated from equation (14). Typical graphical views of the experimental and predicted drying behaviour are presented in Fig. 5.

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} (MR_{exp,i} - MR_{pred,i})^2 \right]^{1/2} \qquad (14)$$

Lower value of RSME is representing better agreement between model predicted and experimental drying behaviour.

Exp.	RSME											
	Clay (I)				Clay (II)				Clay (III)			
	Model				Model				Model			
	B2	A2	B1	A1	B2	A2	B1	A1	B2	A2	B1	A1
1	0.0281	0.0351	0.0517	0.0624	0.0241	0.0286	0.0586	0.0714	0.0166	0.0836	0.1079	0.1191
2	0.0111	0.0219	0.0694	0.0926	0.0194	0.0225	0.0523	0.0689	0.0186	0.0756	0.0995	0.1125
3	0.0143	0.0415	0.0731	0.0838	0.0174	0.0458	0.1104	0.1445	0.0524	0.0675	0.1159	0.1296
4	0.0128	0.0142	0.0461	0.0570	0.0219	0.0460	0.1002	0.1165	0.0378	0.0603	0.0944	0.1130
5	0.0121	0.0295	0.0611	0.0506	0.0212	0.0282	0.0856	0.1029	0.0474	0.0705	0.0935	0.1090
6	0.0073	0.0344	0.0689	0.0636	0.0232	0.0176	0.0532	0.0672	0.0173	0.0235	0.0841	0.1009
7	0.0125	0.0355	0.0467	0.0433	0.0188	0.0562	0.0996	0.1126	0.0171	0.0216	0.0709	0.0835
8	0.0201	0.0263	0.0730	0.0866	0.0247	0.0472	0.0942	0.1160	0.0242	0.0356	0.0820	0.0986

Table 3. Calculated RSME parameters

In all experiments value of RMSE had the lowest value for model B2, which means that model B2 had less deviation from experimental results than all other drying models.
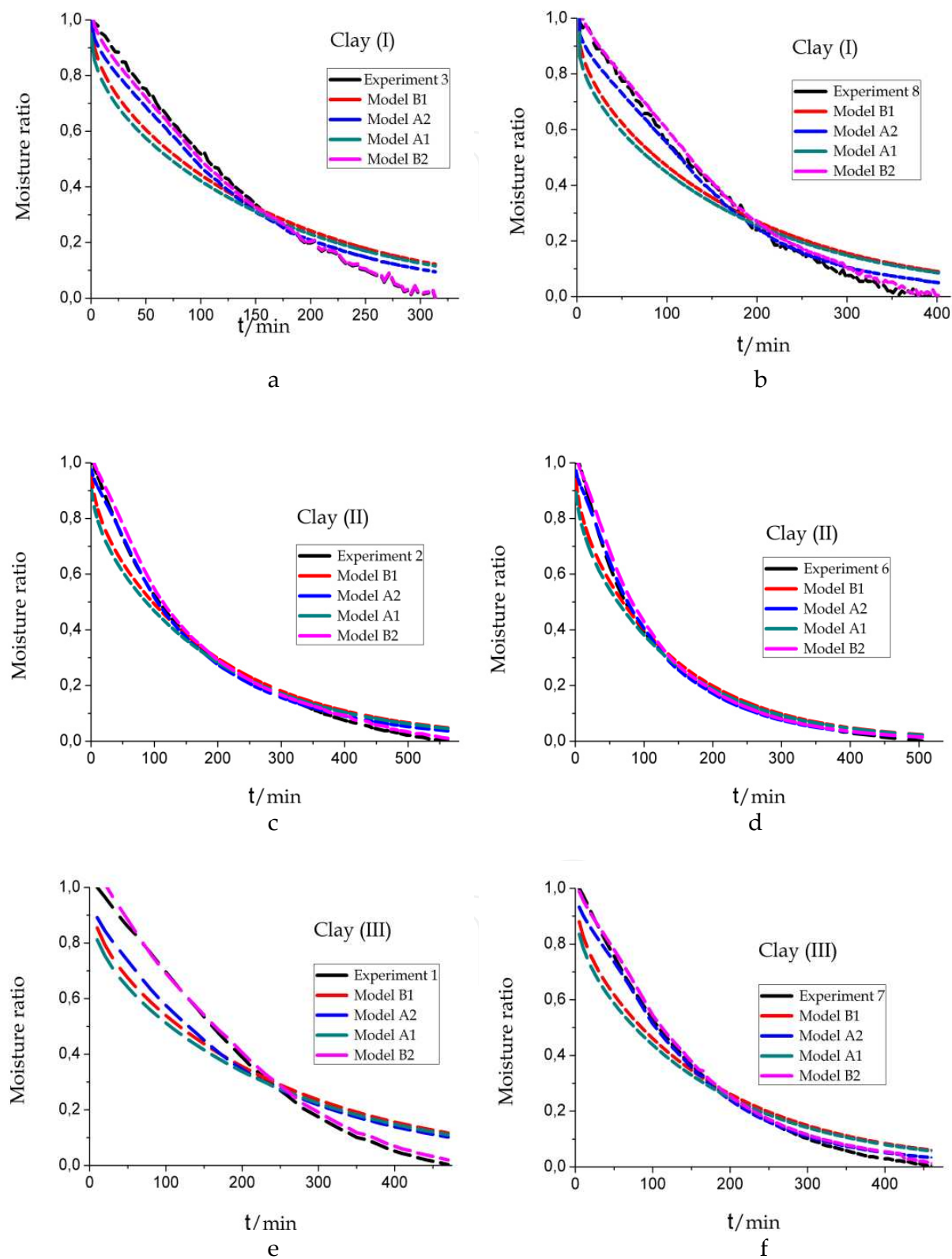

Figure 5. Experimental and calculated moisture ratio vs. drying time

The D_{eff} values obtained through the use of the described programs and from slope of equation (13) are presented in Table 4.

Exp.	$Deff \cdot 10^{10}$ / m²/s														
	Clay (I)					Clay (II)					Clay (III)				
	Model					Model					Model				
	A1	A2	B1	B2	SL	A1	A2	B1	B2	SL	A1	A2	B1	B2	SL
1	4.50	2.30	4.00	1.80	19.00	2.90	0.50	1.70	0.35	10.5	0.34	0.17	0.27	0.13	15.80
2	7.20	2.20	6.10	1.20	23.50	4.20	0.90	2.30	0.83	19.3	0.58	0.34	0.45	0.28	25.30
3	8.10	3.20	7.30	2.30	24.70	0.98	0.19	0.75	0.12	4.7	0.09	0.05	0.003	0.001	3.90
4	10.10	3.40	8.80	2.50	30.50	1.61	0.31	1.17	0.24	6.7	0.19	0.09	0.13	0.005	6.30
5	2.40	0.70	1.00	0.10	9.50	3.81	0.94	3.13	0.79	17.2	0.53	0.29	0.49	0.15	24.80
6	3.30	0.90	2.60	0.30	11.70	5.83	1.25	5.14	1.05	27.6	0.86	0.49	0.75	0.41	44.60
7	4.80	1.80	4.20	1.70	19.50	1.20	0.15	1.05	0.08	4.2	0.22	0.11	0.13	0.008	9,30
8	7.40	3.20	6.30	2.30	24.10	2.19	0,52	1.95	0.37	9.6	0.65	0.42	0.59	0.37	35.30

Table 4. Calculated values of effective diffusion coefficient

In all experiments, the value of effective diffusion coefficient D_{eff} determined by models, which has included the shrinkage correction in the calculation step (A2 and B2), was lower then the value of the same coefficient determined by other models. On analyzing experiments it can be seen that by increasing the drying air velocity from 1 to 3 m/s, the value of the effective diffusion coefficient also increases up to 38% for clay (II), 45% and 60% for clay (III). Diagrams have showed that the kinetic curves representing the models which neglect the shrinkage effect (A1 and B1) do not completely follow the configuration of the experimentally determined drying curves. Drying model B1 had less deviation from experimental results than drying model A1, in all experiments and for all three clays. It can be concluded that whatever the initial mineralogical composition of the clay model B1 is better than model A1. Deviations of these models from the experimental drying curves are higher at the beginning of the drying process and after some time in most case the deviations disappear. The moment of disappearance matches the moment from when the sample continues to dry further without shrinkage.

Drying kinetic curves of the model which includes shrinkage (A2 and B2) follow the configuration of the experimentally determined curves and their matching can be more than 98% as can be seen in experiments 3, 8 in case of clay (I) or in experiments 2, 6 in case of clay (II) or in experiments 1, 7 in case of clay (III). Drying model B2 had less deviation from experimental results than drying model A2, and all other drying models, in all experiments and for all three clays. It can be concluded that whatever the initial mineralogical composition of the clay model B2 is the best drying model. In the case of model B2, if minor deviations 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 temperature in

the dryer. The intersection point of the experimental drying curves and modelled 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 no longer shrink.

From Table 4 it can be concluded that value of effective diffusion coefficient D_{eff} determined using the models which included the sample shrinkage correction is lower than the corresponding value determined using the models which neglected sample shrinkage or the slope model. The determined values of data of the D_{eff} from the slope model were higher than the data determined by other models. This result is in agreement with the D_{eff} determination and is representing additional proof that the models which included the shrinkage effect during drying have given more precise D_{eff} values. Effective diffusion coefficients for masonry clay products are in range of 10^{-7} up to 10^{-12} m²/s according to references [6,10]. 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 Tables 4 are lying below the previously mentioned range.

4. Conclusions

Calculation methods and computer programs specially designed for calculation of effective diffusion coefficient were developed. First calculation method was based on the mathematical calculation of the second Fick's law and Cranck diffusion equation. Second calculation method was based on the analytical solution of the Efremov differential diffusion equation with a boundary condition in the form of the flux. In both calculation methods, two program variations were designed to compute the effective diffusion coefficient. First program variation did not include shrinkage effect during drying into the computation algorithm while the second one has included it. Four models (A1, A2, B1 and B2) for predicting the drying behaviour were obtained as the result of cited program. This was the first time in the mathematical modelling of the drying of masonry clay that a shrinkage correction was entered into the calculation step. Drying diagram analysis have showed that irrespective of the nature the initial mineralogical composition of the clay, the drying curves representing the models which neglects the shrinkage effect (A1 and B1) did not fully follow the configuration of the experimentally determined kinetic curves, while in the case of the models which include shrinkage (A2 and B2), the resulting curves follows the experimental ones. From Figs. 1 - 6 it can be seen that the introduction of the shrinkage correction into equations (3) and (12) was entirely justified. Drying model B2 had less deviation from experimental results than drying model A2, and all other drying models, in all experiments and for all three clays. It can be concluded that whatever the initial mineralogical composition of the clay model B2 is the best drying model. 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 models which includes shrinkage were less than the values determined using the models which neglects shrinkage or the values obtained using the slope method. The intersection point of the experimental drying curves and the modelled drying curves is characterized as the critical point.

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5. References

[1] Chemkhi S.; Zagrouba F. (2008). Development of a Darcy-flow model applied to simulate the drying of shrinkage media, *Braz. J. Chem. Eng*. Vol. 25, pp.503-514, ISSN 0104-6632

[2] Whitaker S. (1977). Simultaneous heat mass momentum transfer in porous media: A theory of drying, *Adv. Heat. Mass. transfer*. Vol. 13, pp. 110-203

[3] Cranck J. (1975). The mathematics of diffusion, (II edition), Oxford University press, London

[4] Efremov G. (2002). Drying kinetics derived from diffusion equation with flux-type boundary conditions, *Dry. Technol.* Vol. 20, pp. 55-66, ISSN: 0737-3937

[5] Vasić M.; Radojević Z. (2011). Establishing a method for determination of effective diffusion coefficient, *Proceedings of the 15th International Conference Modern Tecnologies, Quality and inovation, MODTECH 2011*, pp. 673-676, ISSN 2069-6739 Vadul lui Voda, Chisinau, Republic of Moldavia, May 25-27, 2011

[6] Chemkhi S.; Zagrouba F. (2005). Water diffusion coefficient in clay material from drying data, *Desalination*. Vol. 185, pp. 491-498, ISSN 0011-9164

[7] Mihoubi D.; Zagrouba F.; Amor Ben M. & Bellagi A. (2002). Drying of clay. I Material characteristics, *Dry. Technol.* Vol.20, pp. 465-487, ISSN: 0737-3937

[8] Zagrouba F.; Mihoubi D. & Bellagi A. (2002). Drying of clay. II Reheological Modelisation and simulation of physical phenomena, *Dry. Technol*. Vol.20, pp. 1895-1917, ISSN: 0737-3937

[9] Skansi D.; Tomas S. & Sokole M. (1994). Convection drying of porous material, *Ceram. Int.* Vol. 20, pp. 9-16, ISSN: 0272-8842

[10] Sander A.; Skansi D & Bolf N. (2003). Heat and mass transfer models in convection drying of clay slabs, *Ceram. Int.* Vol. 29, pp. 641-653, ISSN: 0272-8842

[11] Vasić M.; Radojević Z.; Arsenović M. & Grbavčić Ž. (2011). Determination of the effective diffusion coefficiente, *Ro. J. Of Mat.* Vol. 2, pp. 169-176, ISSN 1583-3186

[12] Zeden A.J.J. & Kerkhof P.J.A.M. (1996). Isothermal vapour and liquid transport inside clay during drying, *Dry. Technol.* Vol. 14, pp. 647-676 ISSN: 0737-3937

[13] Efremov, G. (1999). Development of the Generalized Calculation Methods for Non-stationary Heterogeneous Process in Chemical Technology and in a Furnish of Textile Materials, *PhD. Thesis*, MSTU, Moscow, Russia, (in Russian).

[14] Winitiziki S. (2008). A handy approximation for the error function and its inverse, avaliable at http://www.mendeley.com/research/a-handy-approximation-for-the-error-function-and-its-inverse-1/#page-1

[15] Winitiziki S. (2003). Uniform approximations for transcendental functions, *Computational Science and Its Applications—ICCSA, Proceedings, Part I International Conference,* Vol. 2667, DOI: 10.1007/3-540-44839-X, Montreal, Canada, May 18–21, 2003

[16] Katekawa M.E. & Silva M.A. (2006). A review of drying models including shrinkage Effects, *Dry. Technol.* Vol. 24 pp. 5-20 ISSN: 0737-3937

[17] Dissa A. O.; Desmorieux H.; Bathiebo J. & Koulidiati J. (2008). Convective drying of Amelie mango (Mangifera Indica L. Cv. Amelie) with correction for shrinkage,*J. Food Eng.* Vol. 88 pp. 429-437, ISSN: 0260-8774

[18] Ruiz-Lopez I.I.; Ruiz-Espinosa H.; Arellanes-Lozada P.; Barcenas-Pozos M.E. & Garcia-Alvarado M. (2011). Analytical model for variable moisture diffusivity estimation and drying simulation of shrinkable food products, *J. Food Eng, doi:10.1016/j.jfoodeng.2011.08.025*

[19] Silva W.P.; Pecker J.W.; Cleide M.D.P.S. & Gomes J.P. (2010). Determination of effective diffusivity and convective mass transfer coefficient for cylindrical solids via analytical solution and inverse method: Application to drying of rough rice",*J. Food Eng.* Vol. 98, pp 302-308, ISSN: 0260-8774

[20] Park K.J.; Ardito T.H.; Ito A.P.; Park K. J.B. & Oliveira R.A. (2007). Effective Diffusivity determination considering shrinkage by means of explicit Finite difference method, *Dry. Techn.* Vol. 25, pp. 1313-1319, ISSN: 0737-3937

[21] Silva W.P.; Pecker J.W.; Cleide M.D.P.S. & Diogo D.P.S. (2009). Determination of the effective diffusivity via minimization of the objective function by scanning: Application to drying of cowpea, *J. Food Eng.,* Vol. 95, pp 298-304, ISSN: 0260-8774

[22] Moropoulou A.; Karoglou M.; Giakoumaki A.; Krorida M.K.; Maroulis B.Z. & Saravacos D.G. (2005). Drying kinetic of some building materials, *Braz J Chem Eng.* Vol. 22, pp 203-208, ISSN 0104-6632

[23] Mancuhan E. (2009). Analzsis and Optimization of Drying of Green Brick in a Tunnel Dryer, *Dry Technol.* Vol. 27, pp. 707-713, ISSN: 0737-3937