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APPLICATION OF D_{EFF}-MR CURVE ANALYSIS TO EXTERNAL DRYING DATA FOR IDENTIFYING THE MOISTURE TRANSPORT MECHANISMS

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Abstract: The D_{eff}–MR (effective diffusivity vs. moisture ratio) curve approach, developed by the authors, has been successfully used over the past 15 years to optimize drying regimes for clay-based materials. While its practical value in industrial and laboratory settings is well-established, its theoretical contribution to identifying internal moisture transport mechanisms remains underutilized in broader drying applications. To assess its universal relevance, this study applies Deff–MR curve analysis to digitized drying and shrinkage data from multiple external sources. The data were extracted from literature graphs and reanalysed using the proposed Deff–MR framework. Despite differences in experimental procedures and diffusivity calculation methods, the analysis revealed consistent transition points corresponding to known moisture transport mechanisms, including capillaryflow, vapor diffusion, and Knudsen diffusion. These findings support the broader applicability of the Deff–MR method as a diagnostic tool for identifying dominant internal moisture movement mechanisms across different drying scenarios and materials.
Keywords: drying porous material, effective diffusivity, clay tile, shrinkage

1. INTRODUCTION

The growing impact of climate change has catalyzed numerous shifts in European legislation over the past decade, particularly in environmental, energy, mining, and construction sectors. These changes reflect a commitment to the green agenda, safety concerns, and resource and energy limitations. This evolution has also extended to the traditional building materials industry. In response, the international scientific and engineering community has proposed diverse solutions from refining existing processes to developing entirely new systems. Efforts have centered around increasing efficiency in energy and resource use, reclaiming waste heat, and improving drying and firing process protocols [1].

As a result, fundamental research into the drying processes of porous materials and the development of computer-aided design have become essential drivers of technological innovation. According to Mujumdar, various mass and heat transfer phenomena occur during the drying process. Mass and heat transport can be either diffusive or convective in nature, or both processes may occur simultaneously [2].

Drying remains one of the most energy-intensive unit operations in industrial production, particularly in sectors such as ceramics, food processing, and construction materials. In the case of porous materials, including clay-based products like roofing tiles, the drying process is not only critical for achieving the required physical properties but also highly complex due to the simultaneous occurrence of heat and mass transfer, capillary phenomena, phase transitions, and structural shrinkage.

Over the years, numerous models have been developed to simulate and optimize drying behavior. Three have gained widespread scientific acceptance: diffusion theory, capillary flow theory, and the "evaporation and condensation" theory. The literature highlights several models that describe these processes, including diffusion models (Crank [3], Silva [4], Efremov [5], etc.), receding-front drying models (Luikov [6], Tsotsas [7], etc.), and macroscopic continuum models for combined multiphase heat and mass transport in porous materials. Macroscopic continuum models can be further categorized into four subgroups: phenomenological models (Philip and De Vries [8], Luikov [9], Krischer [10]), models based on volume averaging at the microscopic level (Whitaker [11], etc.), models derived from mixing theory (Bowen [12], Kowalski [13], etc.), and pore network models (Prat [14], Yiotis [15], etc.).

Besides in each of reported theories simultaneous heat and mass transfer equations can be solved under different boundary conditions using three coupling levels (non, semi and conjugated) depending on how heat and moisture transport coefficients are determined. For information about how to properly select the coupling level we refer readers to the reference [16]. That is the reason why modeling of real drying process for example in brick & clay industry is undoubtedly complex.

Despite these advancements, a persisting limitation in most models is their inability to unambiguously identify the dominant internal moisture transport mechanisms and the transitions between them during drying especially during the falling-rate period, where transport dynamics become highly nonlinear and heterogeneous.

The authors previously proposed a physically-informed approach to this problem through the introduction of D_{eff}–MR curves, where D_{eff} denotes the effective moisture diffusivity and MR the dimensionless moisture ratio. This curve, derived using a modified slope method that accounts for sample shrinkage, provides a dynamic profile of diffusivity as a function of drying progress. Importantly, inflection points on the D_{eff}–MR curve were shown to correspond with distinct internal mechanisms of moisture migration, such as capillary flow, viscous flow, Stefan flux, Knudsen diffusion, and evaporation–condensation sequences. This approach was initially validated through controlled laboratory drying experiments on clay tiles, where comprehensive measurements of mass loss, temperature gradients, and shrinkage were used to construct mechanistically meaningful D_{eff}–MR profiles.

While these early findings confirmed the capacity of D_{eff}–MR analysis to detect internal moisture transitions and improve drying regime design in ceramics [17-19], their broader applicability to other materials and experimental conditions remained unverified.

In many published studies, especially those focused on food drying or thin-layer biological materials, diffusivity is treated as a fitting parameter without direct interpretation of the underlying transport mechanisms. As a result, inflection behaviors or deviations in moisture profiles are often attributed to experimental error or noise rather than physical transitions.

To address this gap, the present study applies the D_{eff}–MR framework to external data sets sourced from a diverse range of drying literature. Using digitized MR–time and MR–shrinkage diagrams from materials such as tropical fruits, fish muscle, chitosan, and grape skins, this work reconstructs D_{eff}–MR curves and compares them against the theoretical pattern developed from ceramic drying. The objectives were: to evaluate the universality of the D_{eff}–MR methodology for identifying internal moisture transport transitions across materials and geometries, and to challenge conventional interpretations of "scatter" in D_{eff} profiles by demonstrating their underlying physical meaning.

This comparative, cross-material analysis demonstrates that despite differing experimental procedures and Deff calculation techniques, the D_{eff}–MR curves consistently exhibit similar segmentations and inflection points, which can be reliably interpreted using the proposed drying theory. Ultimately, this supports the utility of Deff–MR analysis not just as a modeling tool, but as a diagnostic method for detecting the sequence and interaction of internal transport mechanisms during drying. By emphasizing external data validation, this study reinforces the scientific robustness and practical relevance of the proposed approach.

2. MATERIALS AND METHODS

The experimental data were digitized from published diagrams using the GetData software, as stated in the Methods section. The model which verification is reported in this study represents a modification of the slope model. The calculation was refined by introducing the expression l(t). Additionally, D_0 (F_0) values were calculated according to the B2 model, as was outlined in [18]. The B2 model is based on the analytical solution of the diffusion equation with flux-type boundary conditions, originally proposed by Efremov. Unlike simpler models, B2 incorporates the effect of sample shrinkage by introducing a time-dependent thickness function $l_{(t)}$ into the calculation. This adjustment allows for a more accurate representation of the drying behavior of porous materials, particularly clay tiles, where dimensional changes are significant. The model demonstrated excellent agreement with experimental data and provided reliable estimates of the effective diffusion coefficient, making it the most accurate of the evaluated models in that study. The effective diffusion coefficient D_{eff} was determined for each MR value using Equation (1). The theoretical Deff–MR curve taken from reference [19] is shown in Figure 1. The transport mechanisms governing liquid and vapor movement during drying are summarized in Table 1, with corresponding segments mapped directly onto the theoretical Deff–MR curve presented in Figure 1. Each labeled segment (I, II and III.) represents a characteristic zone within the drying process (constant, transition and falling), defined by dominant internal moisture mechanisms such as capillary flow, hydrodynamic flow, evaporation–condensation sequences, and various forms of vapor diffusion. These transitions are detected as inflection points on the D_{eff}–MR curve and provide insight into the physical processes occurring within the porous material during drying. These segments represent a sequence of physical transitions that were both theoretically conceptualized and experimentally validated in the work of Vasić et al. (2014). For example, the early segments (A–D) are associated with capillary and hydrodynamic flow, where moisture moves through fully and partially saturated pores under the influence of capillary pressure and viscosity. As drying progresses (segments D–F), the material transitions from the funicular to the pendular state, with moisture transport increasingly governed by evaporation–condensation mechanisms and creeping flow along capillary surfaces. In the later stages (segments G–L), vapor transport mechanisms such as Stefan flow, molecular diffusion, transition diffusion, and Knudsen diffusion become predominant as the pore network dries out and the mean free path of vapor molecules increases. This segmentation provides a structured framework for interpreting the complex drying behavior of porous materials and reinforces the physical relevance of the Deff–MR curve as a diagnostic tool. The table thus serves as a mechanistic interpretation of the drying history and governing internal transport mechanism occurrence over time.

$$D_{eff} = \frac{(\frac{dMR}{dt})_{exp}}{(\frac{dMR}{F_0})_{th}} l_{(t)}^2 \; ; \mathrm{MR} = \frac{X - X_{eq}}{X_0 - X_{eq}} \; ; \; F_0 = \frac{D_0 t}{l_{(t)}^2} \qquad (1)$$

where: D_{eff} – Effective moisture diffusion coefficient (m²/s); MR – Moisture ratio (dimensionless); t – Drying time (s); F_o – Fourier number (dimensionless); l(t) – experimentally determined variation in sample thickness during drying (mm); D_0 – Referenced constant diffusion coefficient calculated based on reference [18] (m²/s); $(\mathrm{dMR/dt})_{exp}$ – Slope of the experimentally measured moisture ratio vs. (s^{-1}); $(\mathrm{dMR/d}F_0)_{theroretical}$ – Slope of the theoretical moisture ratio vs. Fourier number curve (dimensionless)

To assess the general applicability of this Deff–MR relationship, the same modeling framework was applied to data extracted from about ten independent studies. Since the sources often displayed drying and shrinkage data in graphical format, the "Get Data - Graph Digitalize" software was employed to convert these visual plots into precise tabular datasets suitable for analysis under the proposed theory.

Table 1. Occurrence of Internal transport mechanisms according to the Vasic drying theory

Segment		Liquid Water	Water Vapor
I	A-B	Capillary flow (CF) through the largest capillaries	/
	B-C	CF through meso-capillaries, Hydrodynamic flow (HF)	/
	C-D	CF through meso-capillaries, HF	/
II	D-E	CF (through capillaries in the "funicular state"), HF, and liquid diffusion through pores	HF
	E-F	Creeping along capillaries when water is in the funicular state or successive evaporation and condensation mechanisms	HF
III	G-H	/	Stefan Flux
	H-I	Successive evaporation and condensation mechanisms	HF
	I-J	/	Molecular diffusion
	J-K	/	Transitional diffusion
	K-L	/	Knudsen diffusion

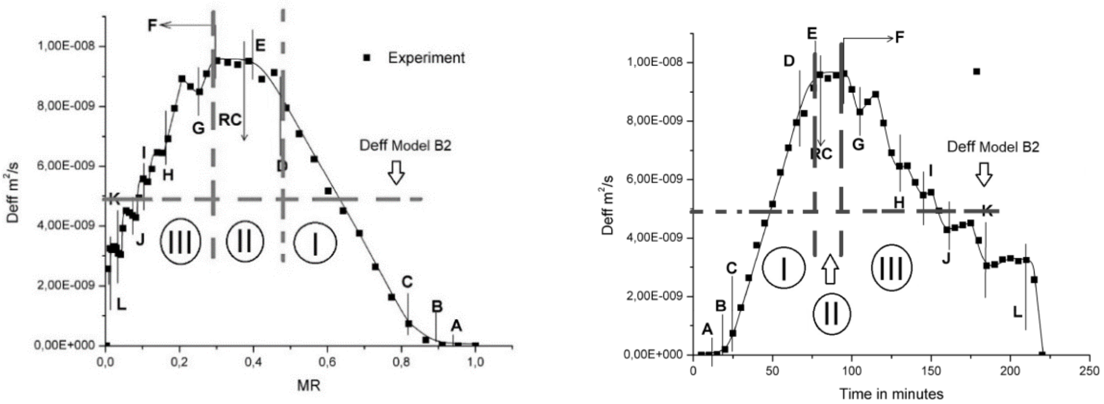


Fig. 1. Theoretical Deff – MR and Deff - t curves, [19]

3. RESULTS AND DISCUSSION

Pinto's Figures 3, 6, and 7 were firstly taken from reference [20] and were afterwards converted into tabular form. Data was analyzed in accordance with the developed drying theory. Results are presented in Figure 2. The slope model employed by Pinto is based on comparing the experimental drying curve (MR–t) with the theoretical diffusion curve (MR–F_0). To determine the theoretical slope of the curve, Pinto has utilized the diffusion curve proposed by Keey [21]. The effective diffusion coefficient (Deff) corresponding to each value of the dimensionless average moisture content MR (X/X_0) was then calculated using Equation (2).

It is important to note that different methods for estimating the effective moisture diffusivity D_{eff} can lead to significant scale differences in the resulting values. Approaches that assume constant sample geometry throughout the drying process typically used in conventional models tend to overestimate D_{eff}, as they neglect the dimensional changes caused by material shrinkage. In contrast, models that incorporate time-dependent geometry, such as those using an experimentally determined l(t) function to account for shrinkage, provide more physically accurate diffusivity values. This correction is particularly critical in materials like clay, where shrinkage during drying is substantial and strongly influences the internal moisture transport path length. As a result, diffusivity values obtained from shrinkage-corrected models are generally lower and more consistent with the true transport conditions within the porous structure. It should be noted, however, that the influence of shrinkage during drying was not considered in Pinto's approach, which may affect the accuracy of the estimated diffusivity values in cases where dimensional changes are significant.

$$D_{eff} = \frac{(\frac{dMR}{dt})_{exp}}{(\frac{dMR}{F_0})_{th}} l_0^2 \tag{2}$$

Besides Pinto's used a linear-exponential equation to fit experimental data. This curve was labeled as B in figure 2. Curve D was not generated by fitting a regression line through experimental data points; rather, it was constructed by calculating D_{eff} values using the model developed by Vasić. This procedure was thoroughly documented in reference [18], enabled the interpretation of internal moisture transport mechanisms based on theoretical analysis, without relying on empirical curve fitting.

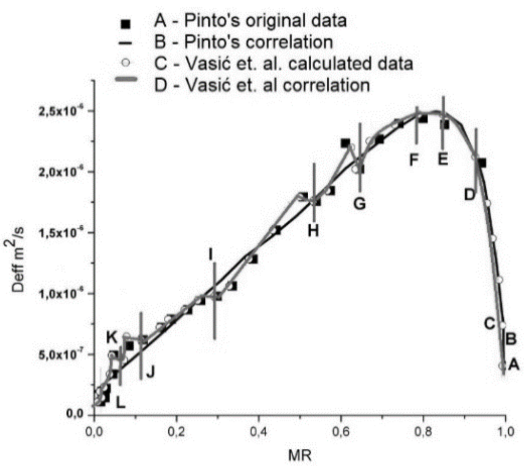
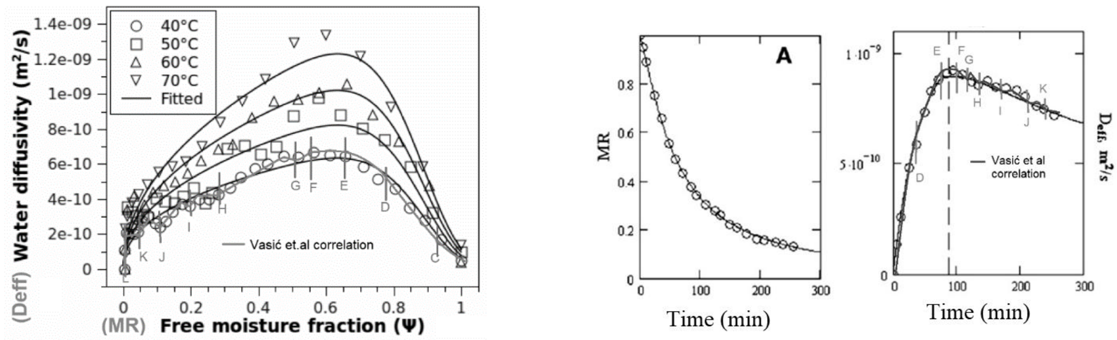


Fig. 2. First comparison example

Curve D exhibits a shape similar to Curve B, though the latter primarily reflects statistical correlation ($R^2 = 0.96$) without a deeper physical interpretation that could link the collected data with the internal mechanisms of mass and energy transfer that occurred during the drying process. That curve indicates only the transition phases between constant and falling drying rate periods. On the other hand, Curve D, based on our theory, contains inflection points that correspond directly to internal drying mechanisms described in Table 1. These points are closely associated with the mechanisms that govern the internal mass and energy transfer throughout the drying process. The physical significance of Curve D provides valuable insights, particularly when it is applied to the design of drying regimes.

The data obtained from the isothermal drying of tropical fruit slices, "chayote," at 40°C (Diagrams 1 and 2) in Lopez's study [22] were used in this study as the second validation example. Data taken were used as input parameters to evaluate the novel D_{eff}–MR relationship. Results are presented in Figure 3a.

The data used for validation were also taken from references [23] (Diagram 2 and 3), [24] (Diagram 5), and [25] (Diagram 4). Equation reported in reference [24] as 9 was utilized, in combination with the least square technique and the fourth-order Runge-Kutta method with a variable step size, to determine the local moisture profile. Additionally, Simpson's method was applied to calculate the average moisture concentration profile. Equations labeled as (10) and (11) in reference [24] were respectively used to determine the effective diffusion coefficient as a function of time during the constant and falling drying rate periods. Due to the lack of space, verification results are given only for reference [23]. Although calculation methods across references [23–25] differ from ours, the resulting Deff–MR curves were remarkably similar. The critical transition points, as laid out in reference [19], were identified consistently across all reviewed datasets.



a) b)

Fig. 3. Additional comparison example: a) second validation reference 23; b) third validation reference 24

At the end, Sander [27] has highlighted the modified Page II thin-layer model as the most effective for describing the drying kinetics of nearly all materials his research group examined over the years. The parameters of this modified model, including the drying constant (K), time (tk), n, mass transfer coefficient (km), and effective diffusion coefficient (Deff) were estimated by fitting the model to experimental data. These authors have identified the physical significance of tk as the precise point at which the first or second falling drying rate period begins, marking the moment when moisture diffusion within the material becomes the dominant mechanism. Moreover, a clear correlation between the drying constant (K) and the parameter tk was established [28]. It is particularly noteworthy that the time tk, detected across all previously referenced diagrams from various studies, consistently aligns with the duration calculated using our methodology from the start of the drying process to the critical point E. This finding is another external proof that our model has a physical significance and that identified points on the theoretical Deff–MR curve accurately map the sequence and interaction of all potentially active drying mechanisms.

4. CONCLUSIONS

This study demonstrates that the D_{eff}–MR curve analysis, originally developed and validated through experimental work on clay-based materials, holds significant promise as a universally applicable tool for diagnosing internal moisture transport mechanisms in porous materials during drying. By extending the methodology to include data digitized from published studies involving biological and food-based materials, the research substantiates the generalizability of the D_{eff}–MR approach across diverse material systems and geometries. A major scientific contribution of this work lies in shifting the interpretation of effective diffusivity profiles from empirical curve fitting to mechanistically grounded analysis. Where previous studies often dismissed irregularities or inflection points in D_{eff} behavior as experimental noise or artifact, the current approach reinterprets these features as meaningful indicators of phase transitions and shifts in moisture migration mechanisms. This reframing enables researchers and engineers to establish a direct, physically-informed connection between D_{eff} profile morphology and internal moisture transport regimes such as capillary flow, Stefan flux, molecular and Knudsen diffusion, and evaporation–condensation processes. The novelty of the proposed methodology is twofold: first, in its incorporation of time-dependent sample shrinkage into the calculation of diffusivity, thereby enhancing the physical accuracy of the model; and second, in its ability to decompose the drying process into distinct mechanistic segments. This segmentation allows for the clear identification of transition points between drying stages, offering new diagnostic capability not available in classical diffusion models or simplified empirical fits such as the Page or Newton models.

The validation of the D_{eff}–MR framework using data from at least five independent studies spanning different drying methods, materials, and modeling techniques adds a layer of robustness to the theoretical assumptions. From a practical standpoint, this methodology offers a valuable tool for process engineers, particularly in the ceramics, food, and agricultural sectors, where optimization of energy-intensive drying operations is critical. By providing mechanistic insight into moisture movement at various drying stages, the D_{eff}–MR method facilitates more informed decisions in drying regime design, potentially improving product quality and energy efficiency. Future work will be focused on integrating this model into real-time monitoring systems using non-invasive measurement and expanding its application to dynamic drying environments. Furthermore, efforts to develop software tools for automatic D_{eff}–MR curve generation from drying data could help mainstream this methodology in both academic and industrial settings.

In summary, this study not only validates a novel modeling approach but also contributes to a paradigm shift in drying science, promoting the interpretation of diffusivity as a window into internal transport phenomena rather than a mere fitting parameter. The D_{eff}–MR curve emerges not just as a modeling tool, but as a scientifically rigorous diagnostic framework for understanding and optimizing the complex, multistage process of drying in porous materials.

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