Review and development of the drying theory of porous medium

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Abstract. The theories of moisture transfer inside a wet solid during a drying process, which were deduced based on the hypothesis of a continuous porous body, were reviewed. The hypotheses of their transformation mechanisms, the mathematical models, the merits and limitations, and the applications of these theories were summarized. Besides, some new and possible study trends on drying theory in the last decade and the near future, especially those obtained and to be obtained by applying the outcomes from other correlative fields, e.g. the pore network model, the multi-scale method and the fractal geometry, were anticipated for a deeper investigation into the micro mechanisms of inner transfer phenomena in solid.

1. Introduction

The drying process of wet matter, especially the thermal drying process, is essentially a coupled transfer process of heat and mass. On the one hand, the material absorbs heat from the dry medium, that is, the heat is transferred from the outside of the wet material to its interior; On the other hand, the moisture within the wet material is transferred from the inside to the outside until the moisture content of the wet material decreases to meet the requirements of the process. Therefore, the heat and mass transfer in the boundary layer of solid and surrounding fluids is one of the most important basic problems in the study of drying process.

Porous medium covers a very wide range of rocks, minerals, ceramics, building materials, thermal insulation materials, catalysts, roots and leaves of plants, as well as a variety of agricultural products, food, etc., all belong to the category of porous medium. It can be said that porous medium is the main object of industrial drying process[1].

2. Development history of drying theory of porous medium

As early as 1856, Darcy studied the underground water source in Dijon, France, and put forward Darcy's Law, which is applicable to the fluid flow in porous medium under certain conditions. This law laid a theoretical foundation for the study of the flow in wet saturated porous medium[2]. At the beginning of the 20th century, studies on the internal mass transfer process of solid materials began. Lewis proposed the liquid diffusion theory as early as the 1920s, believing that the moisture content in solid materials migrated in the form of liquid diffusion during drying and its driving force was the internal moisture content gradient.[3] In 1929, Sherwood proposed a similar Lewis theory of drying diffusion[4]. In 1934, Sherwood and Comings found that capillarity may contribute significantly to the drying process[5]. In 1938, Krischer established two partial differential equations to describe the heat and mass transfer coupling process in the drying process of porous medium, and first noticed the
importance of energy transfer in the drying process[6]. However, due to the limitations of the scientific and technological level and experimental equipment at that time, scholars were unable to learn more about the internal water-holding structure and micro-scale of porous medium, so they were unable to further discuss the wet separation migration rule of porous medium, which made the theoretical research on drying of porous medium progress slowly[7].

In the 1960s, the study of wet separation migration of porous medium entered a new climax. Philip and De Vries in 1957 were the first to establish the volumetric average equation for heat and mass transfer in porous medium using a continuous simulation method[8, 9]. In 1962, Krischer believed that the contribution of vapor to heat transmission could be regarded as evaporation-condensation theory, which was recognized by many scholars[6].

In the early 1960s, the school led by Luikov analyzed the heat and mass transfer process in porous medium by non-equilibrium thermodynamic principle, and established the differential equation of the unstable field of transport potential in the process of heat and mass transport, which described the internal relationship between the coupling of heat and mass transfer in porous medium.[10-12]. Since Luikov established the system theory of heat and mass transfer in porous medium based on the principle of irreversible thermodynamics, the mathematical simulation and analysis of heat and mass transfer in the drying process of porous medium have become the focus of research. However, due to the characteristics of Luikov theory, the coefficient in the model is assumed to be constant, which limits the universality of the results[7, 13]. Therefore, in recent years, the research on the transfer mechanism and its mathematical model of the drying process of porous medium has attracted wide attention at home and abroad, and many scholars have proposed their respective drying mechanism and model based on the materials and drying methods studied respectively[11, 14-17].

Whitaker's volumetric average theory is another major study on heat and mass transfer in porous medium developed almost at the same time as Luikov theory[12, 18]. The main difficulty in Luikov theory is that phenomenological coefficient is difficult to obtain. Whitaker's volume average theory overcomes this theoretical defect by describing the thermal mass process in porous medium with the volume average value of real properties[19]. The proposed volume averaging method has become the standard and popular method to establish mathematical model for the drying process of such materials[20]. Whitaker started from the thermal mass balance equation of single phase (solid, liquid and gas), averaged the volume of different phases inside the porous medium, and obtained the continuous equations of thermal mass transfer in the porous medium. Aiming at some mathematical models reflecting "local features", an effective mathematical model applicable to any position of the whole object is derived by means of spatial smoothing. For example, the equation describing the water transfer in porous medium cannot be directly applied to the porous medium as a whole. However, by using the volumetric average technique, a locally effective volumetric average equation around the channel can be established by using the above information about the channel size, and then it can be extended to any spatial position of the object[18, 19].

Ilic and Turner compared Luikov theory and Whitaker theory, and pointed out that the two adopted similar methods[21]. Both equations are based on the conservation of mass, momentum and energy of fluid in porous medium. The establishment of Luikov equation system is based on experiments, while the application of the equation system is limited by the corresponding physical principles. Therefore, in recent years, the drying model based on Luikov theory has been rarely seen.

As the research continues to deepen, the models mentioned above are also questioned, mainly because the above drying models are based on the "continuum hypothesis", and then the "product transport model" which is "applicable" in the whole medium volume domain is further derived. However, under vacuum conditions or when the geometric scale is small enough, the continuum assumption may not apply [1]. In order to further understand the transmission law of wet components in porous medium, the influences of structural parameters and special influencing factors (such as capillary action, adsorption, solid surface effect, vapor pressure reduction, etc.) on the drying process are revealed. Some new theories and methods have emerged, such as the theory of invasive seepage
flow, fractal geometry, multi-scale method and so on. The study of porous medium has entered a new stage.

3. Classification of drying theory of porous medium

Based on the nearly one hundred years of research on drying of porous medium, it can be seen that the research on drying theory can be divided into three stages, with different discussion emphases.

3.1. Single drive potential model

This stage focuses on the dry driving potential. The mass transport mechanism in wet porous medium includes: liquid transport under capillary force and pressure drive, gas transport under diffusion and pressure drive.

Energy transfer mechanisms include thermal diffusion, convection, and evaporation.

In the first half of last century, in the exploration of these driving mechanisms, many scientists successively proposed many theories, such as diffusion theory[22], capillary theory[23], evaporation-condensation theory[24], to describe the laws of heat and mass transfer in wet porous medium.

3.1.1. Diffusion theory. In 1921, American scholar Lewis proposed that solid drying includes two processes: the first was that water evaporation was mainly concentrated on the surface of the material, and the second was that the internal water moved the surface of the material by means of diffusion[3].

In 1929, Sherwood confirmed this view and also proposed that the moisture content gradient provided the driving force for moisture content diffusion and Fick law applied during drying[4, 25]. Sherwood also established a moisture diffusion equation similar to the one-dimensional unsteady heat conduction equation and quantitatively analyzed the fluid migration process.

Babbit believed that the driving force of the internal diffusion of an object should not be the concentration gradient of the moisture content but the pressure gradient[26]. Moreover, due to the complexity of adsorption and desorption, the relationship between concentration and pressure is generally not linear, so the physical validity of the diffusion theory is very questionable. In addition, a single concentration equation cannot distinguish diffusion caused by other migration mechanisms that may exist simultaneously. Babbit demonstrated that the moisture content could even flow in the direction opposite to the concentration gradient under the action of the vapor pressure gradient. In addition, the isothermal diffusion assumption of diffusion theory is also questioned.

However, such factors as shrinkage and surface hardening were not considered in the above diffusion theory. In addition to moisture content and temperature, other factors related to diffusion coefficient were either ignored or confused. But the diffusion theory lays the foundation for the drying theory of porous medium.

3.1.2. Capillary theory. When Cealglske and Hougen studied the drying of granular materials in 1937, they found that the endoplasmic transfer of granular materials was determined by capillary flow rather than diffusion[23]. They pointed out that the water flow was completely determined by the capillary potential and had nothing to do with the moisture content in the particle bed when it was dry[23]. And they have shown experimentally that wet fractions can even flow in the direction of increased concentrations.

Miller et al. believed that the driving force was the surface tension gradient, and both surface tension and viscosity flow were related to pressure[27, 28]. Only when the medium is uniform and self-weight is ignored, the tension will be proportional to the moisture content.

Based on this assumption, a capillary drive model was established, which makes the research on the internal drive mechanism of porous medium a step further and provides a theoretical reference for the future development of multi-drive potential drying models.
3.1.3. Evaporation-condensation theory. Henry introduced the theory of phase transition into the study of water migration in porous medium, and believed that as long as there was a temperature gradient, there would be a corresponding vapor pressure gradient, so water could migrate in the form of vapor diffusion[24]. Apparently Henry proposed another form of the driving force of the wet component migration.

Gurr et al confirmed that there was indeed a wet separation migration in the form of vapor[29]. They found that the unsaturated porous medium such as soil had no liquid flow under the temperature gradient, and the water only moved in the form of vapor. However, when there is a pressure gradient, it is all liquid.

To sum up, the above theories have their own starting points, but only consider the single mechanism of internal wet separation drive. However, the complexity of the internal structure of porous medium determines that the unitary theory cannot reflect the actual situation well. Therefore, these models have great limitations and poor accuracy in application. Later some scholars have made some attempts to improve these models. For example, an effective mass diffusion coefficient $D_m$ is introduced into the liquid diffusion model and it is attempted to be used to cover everything, reflecting the diffusibility transmission of moisture content, capillary potential drive of liquid and molecular diffusion drive of vapor. So many factors are grouped into one physical property that $D_m$ is difficult to determine experimentally.

Therefore, in the later research, people further developed towards the integration of multiple theories, and considered various mechanisms reflecting the moisture content migration.

3.2. Multi-drive potential coupling model
At this stage, the single driving potential can no longer reflect the nature of the drying phenomenon, and this stage is mainly a multi-field driving model based on the continuum hypothesis.

Philip and DE Vries first proposed a two-field driven coupling theoretical model with temperature gradient and moisture content gradient as the driving potential in 1957[8]. Although the two-field driven model is more accurate than the diffusion model, it comes at the expense of increasing the physical properties, which are difficult to be directly measured by experiments, so the model has great inaccuracy.

Most mathematical models before the 1960s regarded materials as continuous media without considering the information of their internal microstructure. Whitaker started from the mass and energy conservation relations of solid, liquid and gas phases, and then adopted volumetric average method for different phases to obtain a series of governing equations[18, 19]. Although the final equation and continuous equation of simple and flow equations do not have too big difference, but he is the creative application of continuum mechanics, from now on will be the study of thermal mass transfer process of porous medium from micro to macro level, from the conservation research of microscopic scales every phase to the characterization of macroscopic scales yuan average conservation research.

The comparison of different moisture migration theories based on the hypothesis of a continuous medium is shown in Table 1.

4. Development trend of drying theory of porous medium
The drying models mentioned in the previous section are based on the continuum hypothesis, and then a product-level transport model "suitable" for the entire medium volume domain is derived. However, when the geometric scale is small enough, the continuum assumption may no longer apply. Such is the case with heat and mass transfer in porous medium and micro structures. Due to geometric dimensions and the difference between the structure and general situation, the flow, heat transfer and mass transfer laws will present different characteristics of the conventional, this involves the discontinuous phase temperature and concentration of non equilibrium mathematical physical model, as well as the transport process of mesoscopic models (both different from the macro, and different from the
microscopic model) of the building, etc. These models need to be able to go deep into the wet porous medium pore description of components (mixture of liquid and vapor phase and gas phase) of the transmission rule, which reveals the channel structure parameters (such as pore radius of porous medium, the size of the porosity, pore diameter distribution, etc.) under the condition of macro/mesoscopic special influence factors (such as capillary action, adsorption, solid surface effect, vapor pressure drop, etc.) on the influence of the drying process. These factors are difficult to consider in conventional continuum models.

Table 1. Comparison of different moisture migration theories based on the hypothesis of a continuous medium

| Theory of types          | Time of first presentation | Representative scholars          | Migration pattern | Migration power               |
|-------------------------|---------------------------|---------------------------------|------------------|------------------------------|
| Diffusion theory[30]    | 1921                      | W. K. Lewis                     | Liquid           | Concentration gradient       |
| Capillary theory[31]    | 1907                      | E. A. Buckingham                | Liquid           | Capillary potential          |
| Evaporation-condensation theory[24] | 1939                | P. S. H. Herry                  | Liquid           | Pressure gradient            |
| Theory of Luikov[32]    | 1934                      | A. V. Luikov                    | Liquid           | Temperature gradient         |
|                         |                           |                                 | Vapor            | Temperature gradient         |
|                         |                           |                                 | Pressure gradient| Concentration gradient       |
| Theory of Philip, De Vires[8] | 1957                  | J. R. Philip, D. A. De Vires    | Vapor            | Temperature gradient         |
|                         |                           | O. Krischer, D. Berger, D. C. T. Pei | Liquid           | Capillary potential          |
| Theory of Krischer, Berger and Pei[17] | 1963               |                                | Vapor            | Concentration gradient       |

On the other hand, the emergence of some new theories and methods in scientific research also provides convenient conditions for the renewal of drying theory, such as the theory of invasive seepage flow, fractal geometry, multi-scale method and so on.

4.1. Model of channel network for drying porous medium

The theory of channel network drying is a completely discrete method, which can directly consider the microscopic influence of the dried substance into the model.

At present, the theoretical researches on drying based on pore network can be divided into two categories: one is the research on pore network on the unit body. The other is based on the product level channel network research.

Nowicki et al. first attempted to conduct researches on the drying of porous medium by using pore network on a globally representative "representational volume unit" (REV) demarcated from the dried substance[30]. The initial research is to obtain macroscopic transmission parameters and related characteristic data in the continuous model. They will REV internal pore space, is expressed by the channel network that drying process in porous medium channel fluid and gas phase flow and distribution in the space can use the statistical parameters of the equivalent channel network to describe the rules, and molecular dynamics method is applied to compute the average volume unit on the effective transmission of parameters. After the establishment of the channel network, the migration model of steam and liquid in the channel was further established, and the position of the meniscus in the drying process, that is, the position of the drying front, was determined through calculation, so as to obtain other characteristic parameters and data about drying. The channel network method provides a new way for the study of porous medium drying and indicates a new direction for the further development of the study.
Prat first applied the theory of invasive seepage to study the microscopic transmission of rigid porous medium from the product level, and obtained the data of dynamic drying characteristics of porous medium drying[33]. This research can make full use of the current computer science and technology to study the drying problem.

Porous medium pore network model on the channel level study of drying process, thus it can be get more drying characteristic data, including the dynamic distribution of each phase in the porous medium, the instantaneous drying rate and drying period of the critical value, and can be directly observed drying process (simulation or experimental), at the same time also can analyze the influence of channel structure parameters on the drying rate. The pore network model represents a new development direction of drying theory.

Due to the complexity of porous medium itself, the existing researches on porous medium channel network assume that porous medium is rigid, ignoring many micro-structures, as well as adsorption, deformation and other possible phenomena in practice. Therefore, the current channel network model cannot accurately describe the drying process of materials. However, as a relatively new drying theory, pore network theory has considerable development potential. What needs to be strengthened in this respect are:

(1) explore new methods of network construction;
(2) Increase the amount of information in the channel network, shorten the distance from the actual drying process, and make it more realistic to describe the actual drying process;
(3) To seek a more reasonable information extraction method.

4.2. Multiscale method

In the early 1990s, some scholars put forward the theory of multi-scale system[34], which has now developed into a science.

Multi-scale method is used to dry porous medium can according to the characteristics of the space geometric scale medium (capillary channel and gravity channel) to establish the space subsystem, according to Fick's Law and Fourier law establish concentration and temperature time subsystem, and then studies the system internal and mutual relationship, finally solve the problem of the total system, such as drying efficiency, etc.

Basic idea of multi-scale study of porous medium drying: Firstly, scale division is carried out. Possible scales are divided into: molecular scale - mesoscopic scale (particle and pore scale)- material scale - dryer scale. The molecular scale and the dryer scale are extensions of the microscopic and macroscopic scales. In the field of basic physics, the "mesoscopic scale" between macro and micro is defined as 0.1 nm ~ 1 m, and the "mesoscopic scale" here is defined by the material model, namely 0.1 m ~ 1 mm. Such a scale is much larger than the free path of molecular motion, but it may invalidate some of the laws of fluid motion and heat and mass transfer.

The methods used to conduct the study vary from scale to scale. The Monte Carlo model is often used to study the microscopic phenomena of transfer process[35]. Lattice Boltzmann model for mesoscopic phenomena[36-39]. In the study of macroscopic phenomena, it is the traditional continuum model based on the continuum hypothesis. Although the latter method (including partial differential equation description and numerical method) ignores some process characteristics, the continuum hypothesis is still quite effective for multi-scale studies of porous medium in many cases. The lack of macro - scale multi - scale research is incomplete.

4.3. Application of fractal theory in drying porous medium

Fractal geometry has developed rapidly in modern and modern times. The structure and shape of porous medium with different properties (such as desiccant, catalyst, mudstone, coal rock, soil and gas gel, etc.) have fractal characteristics. Therefore, fractal theory can be used to study the porous medium with fractal characteristics. At present, the research on analysis mainly includes the following aspects[40]:

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(1) to describe the physical properties of porous medium, such as volume density, pore size distribution, pore surface area, particle size distribution, aggregate size distribution, soil natural structure shape, etc.;

(2) to conduct quantitative research on spatial variability of porous medium;

(3) to simulate the physical process of porous medium: seepage, pressure pump process, heat transfer, absorption, diffusion, water and solution transmission, crushing, etc.

In the research field of heat and mass transfer in porous medium, Chen Y et al. described the geometric structure of soil by using the image of actual porous medium, figured out the integral dimension of section surface, and established the thermal conductivity model of actual porous medium[41]. Shi M and Zhang D obtained the fractal expression of the thermal conductivity of porous medium, studied the heat conduction process in porous medium, and found that the thermal conductivity process in fractal media was related to the fractal dimension and porosity of the skeleton[42, 43]. Other scholars have made a variety of researches on fractal theory, which have opened a new window on the drying of porous medium[44-47].

5. Conclusion

In this paper, the main viewpoints and their respective characteristics of various continuum hypothesis models for the wet separation and migration of solid matter in the drying process are described. The defects and defects of the continuum hypothesis theory are pointed out.

Compared with the wet separation migration theory based on the continuum hypothesis, the pore network model method can be said to be a revolution in the dry theory research process. Aiming at the mesoscopic structure scale of porous medium, it tries to explore the relationship between the microstructure characteristics of porous medium and the macroscopic transfer phenomenon.

With the deepening of the research, the pore network method will play a greater role. Multi-scale method has been applied in many fields, especially in solving complex system problems, which has incomparable advantages compared with other methods. Based on the analysis of the morphological characteristics and internal heat and mass transfer characteristics of porous medium, it is considered feasible to introduce the multi-scale method in the study of porous medium drying. The multi-scale study of drying should be based on the division of the scales and the representative methods of each scale, and adopt the comprehensive scale method with the ultimate goal of multi-scale information fusion.

Fractal geometry is also a new method that has made great achievements in many fields of application. It also has a broad application prospect in the field of drying of porous medium. Channel network theory and fractal theory will be effective methods for scale synthesis.

References

[1] X Liu and B Yang 2005, *J. China. Agric. Univ.* 04 81-92
[2] Hubbert M K 1957 *J. Int. Assoc. Sci. Hydrol. Bull.* 2(1) 23-59
[3] Lewis W K 1921 *J. Ind. Engr. Chem.* 13(5) 427-432
[4] Sherwood T K 1929 *J. Ind. Engr. Chem.* 21(1) 12-16
[5] Sherwood T K and Comings E W 1934 *J. Ind. Engr. Chem.* 25 1134-36
[6] Fortes M and Okos R 1980 *J. Adv. Drying*. 1 119-154
[7] Ding X 2003 *D, China. Agric. Univ.*
[8] Philip J R and De Vries D A 1957 *J Trans. A. Geophys. Union.* 38(2) 222-232,594
[9] De Vries D A 1958 *J Trans. A. Geophys. Union.* 39(5) 909-916
[10] Luikov A V 1980 *M Heat and Mass Transfer*. Moscow: Mir Publishers 541-542
[11] Luikov, A V 1975 *J. Int. J. Heat. Mass. Transfer.* 18(1) 1-14
[12] Ferguson W J and Lewis R W 1993 *J. Numer. Heat. Transfer. Part B.* 23(1) 91-110
[13] Wei Q and Lin J 1995 *J.Sichuan. Ind. Acad.* 02 121+123-124
[14] Yang S and Wei Q 1994 *J. Eng. Thermophys.* 01 68-72
[15] Li Y, Zeng D and Wu S 2001 *J. Eng. Thermophys.* 01 5-8
[16] Wang X, Wang H, Shi M and Yu W 2001 J. Appl. Sci. 03 257-260
[17] Berger D and Pei D C T. 1973 J. Int. J. Heat. Mass. Transfer. 16(2) 293-302
[18] Whitaker, S 1977 M. Simultaneous Heat, Mass, and Momentum Transfer in Porous medium: A Theory of Drying, in Advances in Heat Transfer.119-203
[19] Whitaker, S 1999 M. The Method of Volume Averaging
[20] Quintard, M. and S. Whitaker1993 J. Chem. Eng. Sci. 48(14) 2537-2564
[21] Ilic M and Turner I W. 1986 J. Appl. Math. Modell. 10(1) 16-24
[22] Sherwood T K1932 J. Ind. Engr. Chem. 24(3) 307-310
[23] Ceaglske N H. and Hougen O A 1937 J. Ind. Engr. Chem. 29(7) 805-813
[24] Henry P S H. and Pickard R H 1939 J. Proc. R. Soc. London. 171(A) 215-241.
[25] Sherwood T K1929 J. Ind. Engr. Chem., 21(10) 976-980
[26] Babbitt J D1950 J.Can. J. Res. 28a(4) 449-474
[27] Miller E E and Miller R D 1955 J. Proc. Soil. Sci. Am. 19(3) 267-271
[28] Miller E E and Miller R D 1955 J. Proc. Soil. Sci. Am. 19(3) 271-275
[29] Gurr C G, Marshall T J and Hutton J T 1952 J. Soil. Sci. 74(5) 335-346
[30] Nowicki S C, Davis H T and Scriven L E 1992 J. Drying Technol. 10(4) 925-946
[31] Buckingham E A 1907 J U. S. Dept. Agr. Bull. 38
[32] Luikov A V 1986 M. Drying Theory
[33] Prat M 2002 J. Chem. Engr. 86(1-2) 153-164
[34] Zhao W, Pan Q, Dai G and Zhang H 2001 J. Electron. Inf. 12 1427-33
[35] Zhang L 2015 D. Liaoning. Engr Tech. Univ.
[36] Du Y, Shu X and Zhang J 2014 J Petrochem. Ind. Appl. 33(04) 17-20
[37] Gan Y 2012 D, China. Min. Univ
[38] Wang X, Suo L, Lui D and Cheng Y 2002 J. Hohai. Univ. 06 61-66
[39] Xiang R 2015 D. China. Jiling. Academy
[40] Perfect E and Kay B D 1995 J. Soil. Tillage.Res. 36(1) 1-20.
[41] Chen Y and Shi M 2000 J. Appl. Sci. 03 263-266
[42] Zhang D and Shi M 2004 J. Eng. Thermophys. 01 112-114
[43] Shi M and Chen Y 2001 J. Nanning. Norm. Univ. 01 6-12
[44] Ziaei S, Lorente S and Bejan A 2015 J. Appl. Phys. 117(22) 5
[45] Sciacovelli A, Gagliardi F and Verda V 2015 J. Appl. Energy. 137
[46] Zhang S, Chen J and Liu X 2013 J. Mater. Rep. 27(10) 161-164
[47] Zhang J, Zhang Y and Wang S 2019 J. South. Agric. Mach. 50(02) 62-63+105