## CHAPTER FIVE

# A COMPARATIVE ANALYSIS OF MULTIPHASE TRANSPORT MODELS IN POROUS MEDIA

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## ABSTRACT

This chapter presents a critical review and comparison of a carefully selected set of models for heat and mass transfer in the presence of phase change in porous media. The selected models represent the most generally applicable classical models of this subject. This study examines the details of the transport phenomena and the relevant terms appearing in each model and makes qualitative comparisons among the models. It poses the main assumptions and the consecutive simplifications employed in each model. It is aimed to serve as a useful tool for researchers in this area as a number of assumptions and simplifications employed in some models have not been discussed clearly if mentioned at all. Based on analysis of the assumptions and transport details, the advantages and deficiencies of each model are pointed out and the general applicability of each model is discussed. The development of models with non-thermal-equilibrium assumption, which is a requirement for some problems, is discussed. Conclusive comments are made on the present status of general formulation of transport processes in the presence of phase change in porous media. And recommendations are made on ways to cope with common difficulties encountered.

## NOMENCLATURE

| | |
|---|---|
| $a$ | volumetric air content |
| $a_{m1}$ | diffusion coefficient of vapor, $\mathrm{m}^2\ \mathrm{s}^{-1}$ |
| $a_{m1}^T$ | thermal vapor diffusivity, $\mathrm{m}^2\ \mathrm{s}^{-1}\ \mathrm{K}^{-1}$ |
| $a_{m2}$ | diffusion coefficient of liquid, $\mathrm{m}^2\ \mathrm{s}^{-1}$ |
| $a_{m2}^T$ | thermal liquid diffusivity, $\mathrm{m}^2\ \mathrm{s}^{-1}\ \mathrm{K}^{-1}$ |

| | |
|---|---|
| $c_s$ | specific heat of moist porous medium per unit dry mass, J kg$^{-1}$ K$^{-1}$ |
| $D$ | apparent mass diffusion coefficient of vapor in air, m$^2$ s$^{-1}$ |
| $D_{\mathrm{eff}}$ | gas-phase total effective diffusivity tensor, m$^2$ s$^{-1}$ |
| $D_{T1}$ | thermal liquid diffusivity, m$^2$ s$^{-1}$ K$^{-1}$ |
| $D_{Tv}$ | thermal vapor diffusivity, m$^2$ s$^{-1}$ K$^{-1}$ |
| $D_{\theta 1}$ | isothermal liquid diffusivity, m$^2$ s$^{-1}$ |
| $D_{\theta v}$ | isothermal vapor diffusivity, m$^2$ s$^{-1}$ |
| $E$ | rate of evaporation, s$^{-1}$ |
| $g$ | gravitational constant, m s$^{-2}$ |
| $h$ | relative humidity |
| $h_l$ | specific enthalpy of liquid, J kg$^{-1}$ |
| $h_{lv}$ | specific latent heat of vaporization, J kg$^{-1}$ |
| $h_v$ | specific enthalpy of vapor, J kg$^{-1}$ |
| $j$ | mass flux, kg m$^{-2}$ s$^{-1}$ |
| $K$ | thermal conductivity, W m$^{-1}$ K$^{-1}$ |
| $\mathbf{k}$ | unit vector in the vertical direction, m |
| $k_f$ | filtration coefficient, kg m$^{-1}$ s$^{-1}$ Pa$^{-1}$ |
| $k_{\langle T \rangle}$ | $-\partial\langle P_c\rangle/\partial\langle T\rangle$, N m$^{-2}$ K$^{-1}$ |
| $k_\varepsilon$ | $-\partial\langle P_c\rangle/\partial\varepsilon_\beta$, N m$^{-2}$ |
| $K$ | unsaturated hydraulic conductivity, m s$^{-1}$ |
| $K_C$ | liquid conductivity, m$^{-1}$ s |
| $K_L$ | liquid conductivity, m$^2$ s$^{-1}$ |
| $K_V$ | vapor diffusivity, m$^2$ s$^{-1}$ |
| $K_\beta$ | single scalar component of permeability tensor for the liquid phase, m$^2$ s$^{-1}$ |
| $K_\gamma$ | single scalar component of permeability tensor for the gas phase, m$^2$ s$^{-1}$ |
| $\langle \dot{m} \rangle$ | mass rate of evaporation per unit volume, kg s$^{-1}$ m$^{-3}$ |
| $m_{\mathrm{ev}}$ | rate of evaporation, kg s$^{-1}$ m$^{-3}$ |
| $P$ | pressure, Pa |
| $P_0$ | reference pressure, Pa |
| $P_c$ | capillary pressure, Pa |
| $S$ | porosity |
| $t$ | time (Luikov), s; temperature (Eckert), K |
| $u$ | total moisture content of body (Luikov); liquid content (Berger and Pei) |
| $\bar{\mathbf{v}}$ | velocity vector defined as the volume flow rate per unit soil cross section, m s$^{-1}$ |
| $\bar{v}_\beta$ | velocity of the liquid phase, m s$^{-1}$ |
| $\bar{v}_\gamma$ | velocity of the gas phase, m s$^{-1}$ |
| $w$ | ratio of vapor mass to mixture (air and vapor) mass |
| $x$ | length coordinate, m |
| $z$ | length coordinate, m |

**Greek Symbols**

| | |
|---|---|
| $\varepsilon$ | void fraction of solid |
| $\varepsilon_2$ | phase-conversion coefficient for the liquid phase |

| | |
|---|---|
| $\varepsilon_\beta$ | volume fraction of the liquid phase |
| $\theta_l$ | volumetric liquid content |
| $\theta_v$ | volumetric vapor content |
| $\mu_\beta$ | coefficient of dynamic viscosity for the liquid phase, kg $m^{-1}$ $s^{-1}$ |
| $\mu_\gamma$ | coefficient of dynamic viscosity for the vapor phase, kg $m^{-1}$ $s^{-1}$ |
| $\xi$ | a function of the topology of the liquid phase |
| $\rho$ | density, kg $m^{-3}$ |
| $\rho_d$ | density of dry soil, kg $m^{-3}$ |
| $\rho_0$ | density of saturated water vapor, kg $m^{-3}$ |
| $\tau$ | time, s |
| $\phi_c$ | capillary potential, $m^3$ $s^{-2}$ |

**Subscripts**

| | |
|---|---|
| $l$ | liquid |
| $v$ | vapor |
| 1 | vapor |
| 2 | liquid |

**Special Symbol**

| | |
|---|---|
| $\langle\ \rangle$ | volume-averaging symbol |

## 1 INTRODUCTION

The pioneering works in the area of fluid transport as well as some aspects of heat transport in porous media go back to the beginning of this century [1–6]. The subject of transport processes with change of phase in porous media has been studied extensively during the past two decades. Some of the current problems involving transport processes in porous media include drying phenomena of porous materials such as wood and food products, nuclear waste disposal processes, heat pipe applications, and phase change (condensation) in fibrous building-insulation materials. The subject has applications in hydrological, petroleum, and geothermal engineering [7–14].

The early works of chemical engineers in drying processes were characterized by representing the fluid motion by diffusion equations [2, 4, 15–17], while researchers in other disciplines such as hydrology, colloid chemistry, and ceramics were the first to recognize that surface tension forces (capillary action) are also important in explaining moisture movement in porous media [1, 5, 18].

In the initial phases of research on drying, heat transport was not considered to have a significant influence on drying processes. Krischer [6,19] and Krischer and Rohnalter [20] were the first to seriously consider the effect of energy transport in drying processes.

Relatively complete studies considering both heat and mass transfer with phase change and capillary action in porous materials started in the 1950s. Among the classical studies are the works of Philip and DeVries [21] and DeVries [22], who modeled moisture movement in porous materials under temperature gradients, and formulated simultaneous heat and mass transfer in porous media. Berger and Pei [7] improved the pioneering work of Krischer with a model for drying of hygroscopic capillary porous solids. In Soviet research, Luikov [23, 24] established a system of equations for heat and mass transfer in capillary porous media; this work included considerable detail. Papers by Eckert and Pfender [25] and Eckert and Faghri [26] reported studies on combined heat and mass transfer with phase change in porous media and migration of moisture due to temperature gradients in unsaturated porous media. The model describing drying processes in porous media, developed by Whitaker [27], uses volume-averaging technique and provides a systematic way of obtaining the governing equations.

In all the abovementioned investigations, as is the case for most work in this area, local thermal equilibrium among the different phases at any location within the system was assumed. The same emphasis is given to such models in this chapter. However, one class of problems does not allow the local-thermal-equilibrium assumption; fixed-bed heat-storage systems and catalytic reactors in packed-bed form as well as packed beds used for heat transfer, adsorption, and absorption processes fall into this category. Most of the relevant investigations in this category use experimental methods, and this area lacks rigorous models and numerical simulation work. Almost all the analytical work in which no local-thermal-equilibrium assumption is made uses rather simplified models, mostly for comparing experimental data with analytical results.

The main difficulties encountered in the modeling of transport processes in porous media are due to the large number of transport coefficients required for formulation of the physical phenomena. Experimental findings show that these coefficients may vary to different orders of magnitude within the range of temperature and the range of moisture content of interest for any particular problem. For instance, the hydraulic conductivity depends not only on the liquid content but also on the temperature of the system. Likewise, the thermal conductivity of each phase depends on the temperature, and the effective thermal conductivity of the moist porous system depends on both the temperature and the volume fractions of the different phases. Moreover, for an accurate representation, the effective thermal conductivity should also include dispersion effects. These reasons make it difficult, if not impossible for some cases, to determine such transport coefficients.

Due to the complexity of the structure and the internal transport processes, a number of simplifying assumptions are usually made in modeling heat and mass transfer in porous media. The most common assumptions are

- The solid matrix is incompressible and free of chemical reaction.
- No liquid or gaseous component is contained in the solid phase, that is, the system contains no bound moisture.
- Local thermodynamic equilibrium exists between the different phases in the multiphase porous system.
- Viscous dissipation and compressional work are negligible.
- Water vapor and noncondensable gas components can be treated as ideal gases.

- The liquid component is incompressible.
- Radiative heat transfer and free convection are negligible.

Depending on the physical conditions, the following assumptions are also frequently made:

- Gravity effects are negligible.
- Noncondensable gas components are stagnant.
- The vapor-phase moisture content is negligible compared to that of the liquid phase.
- Boundary and inertia terms are negligible in momentum transport.

## 2 ANALYSIS AND COMPARISON OF MULTIPHASE TRANSPORT MODELS IN POROUS MEDIA

A large number of studies dealing with specific problems related to heat and mass transport with phase change in porous media may be found in the literature. A considerable number of these studies analyze drying of different porous materials. Some examples are those reported by Plumb et al. [8], Harmathy [28], and Haber et al. [29]. Studies on phase change with simultaneous heat and mass transport in porous insulation materials have been reported by Vafai and Sarkar [30], Vafai and Whitaker [10], and Ogniewicz and Tien [9]. Recent studies on heat pipe applications were reported by Udell [11] and Udell and Fitch [31], and studies on boiling and two-phase flow in a porous medium have been reported by Chuah and Carey [32]. Most recently, White and Tien [33, 34] reported analytical and experimental studies on film condensation in porous media.

It is possible to extend the list of references in which practical applications of heat and mass transfer with phase change in porous media have been modeled and analyzed. Each specific problem has different dominant physical phenomena (e.g., diffusion, capillary action) due to different physical conditions (e.g., large or small pressure and/or temperature gradients, funicular or pendular state for liquid). According to the prevailing physical conditions of the problem considered, a number of transport terms may be neglected with respect to others. Moreover, the constitutive equations used for the mass-flux terms may be different depending on the transport mechanism (e.g., diffusion, capillary absorption). In addition, different thermodynamic relations may be used as coupling relations in different models. Consequently, the modeling of the governing equations for each specific application may differ to some extent from the modelings used in other applications.

The fundamental conservation laws are the same for each practical application. Therefore, a general model of simultaneous heat and mass transfer with phase change in a porous medium should reduce to the form used in each application after the relevant assumptions, transport mechanisms, and coupling relations used in that particular problem are employed.

Only a limited number of studies on the general formulation of heat and mass transfer with phase change in porous media are available. Five models were selected to be analyzed in this section. They were chosen because they represent the most significant and classical models, the ones that are the fundamental backbone of most of the work related to heat and mass transport with phase change in porous materials. Although some of these models might be considered as being related to particular applications, their different versions are used so widely that they can be considered classical models. Each model is based on several references; however, only the most pertinent references for each model are cited. The models considered are those by Whitaker [27], Luikov [23, 24], DeVries [21, 22], Berger and Pei [7], and Eckert [25, 26]. In the cases of DeVries's and Eckert's models, the references cited for each case are complementary to each other for that case. In the case of Luikov model, the second reference summarizes the first, with some differences.

Table 1 depicts the representations of the liquid and vapor mass-flux terms as well as the phase-change term in each model with respect to the notations used in each work.

A qualitative comparison of the details of momentum transport processes in different models is summarized in Table 2. A similar comparison for heat transport processes is given in Table 3. The differences between different models usually arise either from simplifying assumptions made for actual physical phenomena, which are stated explicitly or invoked implicitly, or from the combination of physically different transport components into a single term by utilizing different heuristic definitions for transport coefficients, for example, combining molecular diffusion and capillary absorption into a single term and conditionally describing the two transport processes as diffusion [23].

A question might arise as to whether it is possible to establish a correspondence between the transport coefficients listed in Table 1 for different models. Unfortunately, this is not possible for several reasons. First, selection of the proper transport potentials depends on the transport mechanism assumed to prevail (e.g., diffusion, capillary action). This leads to different constitutive equations with entirely different transport potentials (e.g., pressure, density), and thus, the physical meanings and representations of the transport coefficients are different in each case. Second, the effect of some transport potentials (e.g., temperature, gravity) has been neglected in some models. Therefore, the flux terms in different models are not exactly equivalent to each other, and hence, it is not possible to establish a one-to-one correspondence between the transport coefficients of the models analyzed.

Whitaker's model, which applies volume-averaging technique on the governing point equations, is rigorous. It consists of a total thermal energy equation, continuity equations for liquid and gas phases, equations of motion for liquid and gas phases, a diffusion equation for the gas phase, a volume-constraint equation, and five thermodynamic relations that yield 12 equations for 12 unknowns. These are strongly coupled equations, and they must be solved simultaneously. As may be seen from Tables 2 and 3, Whitaker's model considered a larger number of transport details than did the others. His model takes into account diffusion, dispersion, convective flow, and gravity effects in all phases in addition to capillary motion in the liquid phase. By a systematic definition of the effective diffusion coefficient, dispersion is

Table 1 Representations of the liquid and vapor mass flux terms and phase-change terms

| | Vapor flux | Liquid flux | Phase change |
|---|---|---|---|
| Whitaker | $-\frac{1}{\mu_\gamma} K_\gamma \langle \rho_\gamma \rangle^\gamma \cdot (\nabla \langle P_\gamma - P_0 \rangle^\gamma - \rho_\gamma \bar{g}) - \langle \rho_\gamma \rangle^\gamma D_{\text{eff}} \cdot \nabla \left( \frac{\langle \rho_v \rangle}{\langle \rho_\gamma \rangle} \right)$[a] | $-\left( \frac{\varepsilon_\beta \xi K_\beta}{\mu_\beta} \right) [k_\varepsilon \nabla \varepsilon_\beta + k_{\langle T \rangle} \nabla \langle T \rangle - (\rho_\beta - \rho_\gamma) \bar{g}]$ | $\langle \dot{m} \rangle$ |
| Luikov | $-a_{m1} \rho_0 \nabla u - a_{m1}^T \rho_0 \nabla T - k_f \nabla P$[b] | $-a_{m2} \rho_0 \nabla u - a_{m2}^T \rho_0 \nabla T - k_f \nabla P$[c] | $-\varepsilon_2 \rho_0 \frac{\partial u}{\partial t}$ |
| DeVries | $-\rho_l D_{Tv} \nabla T - \rho_1 D_{\theta v} \nabla \theta_l$ | $-\rho_l D_{\theta l} \nabla \theta_l - \rho_l D_{Tl} \nabla T - \rho_l K \hat{\mathbf{k}}$ | $E$ |
| Berger[d] and Pei | $-K_V(\varepsilon - u) \frac{\partial \rho_v}{\partial x}$ | $-K_L \rho_L \frac{\partial u}{\partial x}$ | $m_{\text{ev}}$ |
| Eckert | $-D\rho w + \rho w \bar{v}$ | $-\rho_l K_C (\nabla \phi_c + g \bar{z})$ | |

[a] Includes flux of noncondensable gases in the first term.
[b] Includes infiltration flux of liquid phase.
[c] Includes infiltration flux of vapor phase.
[d] This model is based on an improved version of Krischer's model.

**Table 2 Momentum transport details in different models**

| | Whitaker | Luikov | DeVries | Berger and Pei | Eckert |
|---|---|---|---|---|---|
| Vapor | | | | | |
| Molecular transport (diffusion) | Yes | Yes | Yes | Yes | Yes |
| Dispersion | Yes | No | No | No | No |
| Darcy's flow (convective) | Yes | Yes[a] | No | No | No |
| Gravity | Yes | No | Yes[b] | No | No |
| Liquid | | | | | |
| Molecular transport (diffusion) | Yes | Yes | Yes | No | Yes |
| Dispersion | Yes | No | No | No | No |
| Capillary motion | Yes | Yes[c] | Yes | Yes | Yes |
| Darcy's flow (convective) | Yes | Yes[a] | Yes | No | Yes |
| Gravity | Yes | No | Yes | No | Yes |
| Noncondensables | | | | | |
| Molecular transport (diffusion) | Yes | Yes | No | No | No |
| Dispersion | Yes | No | No | No | No |
| Darcy's flow | Yes | No | No | No | No |
| Gravity | Yes | No | No | No | No |

[a] In the final formulation, the Darcy's flow for both liquid and vapor is given in combined form in terms of the external pressure gradient.

[b] This is taken care of indirectly in the density gradient term for the vapor phase.

[c] The capillary motion of liquid is accounted for in combined form with molecular diffusion.

accounted for in the diffusion term. Likewise, the effective thermal-diffusion tensor represents conduction in all phases as well as thermal dispersion in liquid, vapor, and noncondensable gas phases, that is, thermal dispersion is modeled in a diffusive term.

Luikov, in establishing the set of transport equations, described the molecular diffusion and capillary diffusion as a single diffusive term, which is then decomposed

**Table 3 Heat transfer details in different models**

| | Whitaker | Luikov | DeVries | Berger and Pei | Eckert |
|---|---|---|---|---|---|
| Conduction | | | | | |
| Solid phase | Yes | Yes | Yes | Yes | Yes |
| Liquid phase | Yes | Yes | Yes | No | Yes |
| Vapor phase | Yes | Yes | Yes | No | Yes |
| Noncondensables | Yes | Yes | No | No | No |
| Convection | | | | | |
| Liquid phase | Yes | Yes | Yes | No | No[a] |
| Vapor phase | Yes | Yes | Yes | No | No[a] |
| Noncondensables | Yes | Yes | No | No | No |
| Dispersion | Yes | No | No | No | No |
| Heat sources or sinks | Yes | No | No | No | No |

[a] These terms have been taken into account in Eckert and Faghri [26].

into temperature-gradient and moisture-content-gradient components. Although the model is capable of accounting for noncondensable gas constituents, the assumption stating that no chemical conversion is connected with producing noncondensable gas components and the assumption stating that the mass of noncondensables is negligible compared to the mass of liquid phase eliminate the need for considering noncondensables in the system of equations. Another major assumption made by Luikov in deriving a definition for the liquid-phase conversion factor is that in addition to the mass of noncondensables, the mass of water vapor is negligible compared to the mass of liquid in the porous medium. Hence, the rate of change of vapor content is approximated by 0, and the set of governing equations is based on total moisture content, which is approximated by the liquid content only. Although molecular diffusion and capillary motion in all phases except the inert-gas phase are considered, dispersion and gravity effects are neglected. There seems to be a discrepancy and some ambiguity in the infiltration terms defined in [23] and [24]. While in [23] it is stated that a pressure gradient causes filtration of vapor and liquid, in [24] it is stated that filtration of vapor and inert gases takes place. Both of these formulations, however, seem to be misleading since Darcy's law should be applied to the liquid and gas or vapor components separately, and the Darcy's flux term for each component should be proportional to the negative pressure gradient of that individual component only.

In Luikov's model, the energy transport equation was essentially derived by an energy balance on a control volume. With further simplified definitions for combined transport coefficients, Luikov obtained a system of coupled differential equations for three dependent variables, namely, total moisture content, temperature, and pressure. An additional thermodynamic relation was given for the vapor pressure in the system by a sorptional isotherm relation for the case when the moisture content of the porous matrix was less than the maximum sorptional value, and by the Clausius–Clapeyron equation for the case when the moisture content of the body was greater than the maximum sorptional value.

DeVries's model includes two mass-balance equations for liquid and vapor phases, an energy equation, a volume-constraint relation, and a thermodynamic relation relating vapor density to saturation vapor density, pressure, and temperature. The unknown parameters are $\theta_l$, $\theta_v$, $E$, $T$, and $\rho_v$. The liquid mass flux is defined by Darcy's law. The breakdown of the pressure component of the total liquid-flux potential into temperature-gradient and liquid moisture-content-gradient parts in the capillary condensation region allows description of the liquid motion in terms of thermal-diffusion and isothermal-diffusion components in addition to the gravity component. The vapor flux is also defined in a diffusion equation as being proportional to the vapor-density gradient. A thermodynamic relation for the vapor density leads to breakdown of the density gradient into temperature- and moisture-content-gradient parts. Gravity effects for the vapor phase are taken into account in an indirect way by the vapor-density-gradient term. Although this is not seen directly as in Darcy's law, in which pressure and gravity components are defined explicitly, the thermodynamic relation used for defining the vapor density implicitly takes care of the gravity effects in the vapor motion. There is also an implicit assumption that considers the noncondensables to be immobile. The energy equation is derived by an energy balance on a control volume after the heat-flux density and the total heat content per unit volume of the moist porous system have been described. The definition of the heat-flux density is based on a hypothetical conduction term for the case when no moisture is moving in the system, a latent heat transfer term due to vapor movement, and sensible heat transfer terms due to vapor and liquid motion. However, no quantitative definition is provided for the thermal conductivity of the system for the hypothetical conduction case considered in defining the heat flux. The approach in defining the total heat content per unit volume of the moist porous system is different from the corresponding definitions of all other methods. In this approach, the concept of differential heat of wetting is introduced to distinguish between the heat of vaporization at saturation vapor pressure and the heat of vaporization at a vapor pressure different from the saturation vapor pressure.

Berger and Pei defined the motion of both liquid and vapor by Fick's law. Vapor flow is taken to be proportional to the gradient of the partial vapor pressure. With the assumption of small temperature changes, the gradient of partial vapor pressure is expressed in the form of the gradient of vapor density by invoking the ideal gas equation of state. The motion of liquid is defined to be capillary flow and is expressed by a term that is proportional to the liquid-content gradient. The additional assumption of constant transport coefficients, the vapor diffusivity $K_V$, and the liquid conductivity $K_L$, simplifies the approach significantly. In Berger and Pei, gravity effects are not considered, and noncondensables are not taken into account. In establishing the energy equation, it is assumed that the heat-transport processes in the porous medium consist only of conduction through the solid matrix and transfer of latent heat by phase change. These also simplify the energy equation since no convective heat transfer or heat dispersion are considered. Also, no need arises for defining an effective thermal conductivity for the multiphase porous system. For the unknown parameters $u$, $\rho_v$, and $T$, two coupling equations are suggested for use. These are the Clausius–Clapeyron equation and the equation of sorptional isotherm; respectively, these equations define the vapor density at the regions of higher than maximum sorptional liquid content and lower than maximum sorptional liquid content.

Eckert defines the liquid motion with an equation that looks like Darcy's equation by taking the liquid mass flux to be proportional to the negative gradient of liquid pressure. The assumption of constant air pressure in the system allows the liquid-pressure gradient to be replaced by the gradient of the capillary potential. Further manipulation with the assumption of homogeneous porous medium yields a liquid-flux term proportional to the moisture-content gradient. Hence, the capillary motion of the liquid is expressed by a diffusionlike equation. Gravity effects are also taken into account in the liquid phase. The motion of the vapor is based on the bulk motion of vapor and air as well as on diffusion of vapor, which is caused by the gradient of the vapor pressure caused by a gradient in temperature. Another simplification is the neglect of the difference between the vapor pressure over a curved surface when air is also present and the saturation vapor pressure of pure vapor over a plane liquid surface. Hence, the vapor pressure is assumed to be the saturation vapor pressure at that temperature. Gravity effects are neglected in the vapor phase. Reference [25] does not provide a complete energy equation but gives a definition for the heat flux per unit area of the system. This definition does not take into account the transfer of sensible heat due to liquid and vapor motion. The energy equation given in [26] seems to be incorrect; the correct form of this equation should read

$$\rho_d c_s \frac{\partial t}{\partial \tau} = \nabla(k\,\nabla t) - \nabla\cdot[(h_{lv} + h_l)\vec{J}_v + h_l\vec{J}_l]$$

A mass-balance equation is not provided in [25], but definitions of liquid- and vapor-flux terms are available.

It should be noted that in all of the models discussed in this section, local thermal equilibrium was a major assumption employed. Therefore, these models are applicable to problems in which fluid motion and thermal transport processes are relatively slow so that the assumption of local thermal equilibrium between different phases in the porous medium does not cause considerable inaccuracy. Problems with relatively faster fluid motion and heat transfer processes with local temperature-jump conditions between different phases cannot be modeled by the local-thermal-equilibrium assumption. Therefore, this class of problems deserves special attention and treatment since the models previously discussed in this section will fail to solve these problems unless they are modified for the non-thermal-equilibrium condition.

The earlier examples of problems requiring no local-thermal-equilibrium assumption were those analytical and experimental investigations on heat transfer in packed beds. The experimental work undertaken by a number of researchers was aimed primarily at determining the fluid-to-particle heat transfer coefficient in packed beds. This continues to be a fundamental issue. The mathematical modeling of such problems requires more than one energy equation due to the different temperature distributions in different phases, and the transfer of heat due to the temperature-jump condition between the solid and fluid phases is modeled as a convective heat transfer term that requires the fluid-to-particle heat transfer coefficient. Numerous experimental investigations have been carried out for determining the fluid-to-particle heat transfer coefficient in packed beds with a single phase of fluid. The majority of these experiments were carried out with air or water as the working fluid for different geometrical shapes and packing configurations for the solid particles, including randomly oriented spheres, beds of spheres oriented in cubic or rhombohedral arrays, cubes, cylinders, granular materials, and commercial packings. The results of most of these studies have been presented in the form of empirical or semiempirical correlations. For a limited review of the literature on heat transfer between fluids and particulate solids in a packed bed, see Barker [35].

More recent investigations in this category of problems are aimed at rather specific applications that mostly use packed beds. One work aimed at the theoretical formulation of volume-averaged energy equations for a fluid flow in a saturated porous medium utilizing the non-thermal-equilibrium assumption is that of Wong and Dybbs [36]. An analytical and numerical investigation on the performance of a heat exchanger containing a conductive porous medium that was used as a coolant passage in simulating the convection cooling of a high-temperature environment was reported by Koh and Colony [37]. Spiga and Spiga [38] also conducted an analytical study on the heat transfer in porous media and packed beds for the non-thermal-equilibrium case; they obtained analytical solutions for some simplified cases for constant transport coefficients and for a constant fluid-to-particle heat transfer coefficient. Studies on modeling of fixed-bed heat-storage systems using phase-change materials, reported by Pitts and Hong [39] and Ananthanarayanan et al. [40], are among the most recent investigations in this category. To our knowledge, however, no analytical/numerical or experimental investigations have been carried out for analyzing the problems of the non-thermal-equilibrium case in the presence of phase change in the working fluid of the porous medium.

The modeling of any problem dealing with transport processes in porous media, whether with the local-thermal-equilibrium assumption or the non-thermal-equilibrium assumption, will not be complete without the specification of proper boundary conditions.

The choice of boundary conditions is an essential part of the mathematical modeling for any specific problem since they are used to formulate the physical conditions at the boundaries of the system. The boundary conditions, however, depend on the nature of the problem under consideration. Their choice depends on selection of the transport potentials used in the governing equations of the model.

The boundary conditions commonly employed in the problems dealing with transport phenomena in porous media can be broadly divided into two categories: permeable or impermeable boundaries. Three common types of boundary conditions are used for energy equations: constant temperature, constant heat flux, and convective heat transfer. The application of these conditions to impermeable boundaries is relatively simpler. In the case of permeable boundaries in which there may be a mass flux at the boundary, the proper boundary condition must be formulated from an energy balance at the surface. For the governing mass transfer equation(s) in the case of impermeable boundaries, the mass-flux term(s) should be equal to 0 at the boundaries. For permeable-boundary cases, the boundary condition should be established from a mass balance at the surface. Depending on the problem, this can be a constant mass flux or a convective mass transfer condition. For instance, a convective boundary condition is commonly employed in the drying of a porous material. This is done by equating the total moisture flux, expressed in the form of the gradient of the moisture content or saturation depending on which is used in the governing conservation equation, to the product of the convective heat transfer coefficient and the difference in the vapor density of the porous system and the surrounding drying medium. For the momentum equation, the constant-pressure boundary condition is commonly employed. In some models, such as Whitaker's, in which equations such as thermodynamic relations and volume-constraint relations have been used in addition to the conservation equations, additional boundary conditions, such as pressure, density, or volume fraction, may be needed.

## 3 DISCUSSION

Whitaker's model is rigorously formulated and quite comprehensive. It contains a great deal of detailed information on the physical phenomena and their formulations. The approach of establishing the local volume-averaged conservation equations as well as the volume-constraint and thermodynamic relations for the unknown parameters of the system is reasonable and quite systematic. By this model, detailed studies of transient distribution of all different phases and the rate of phase change can be accomplished. This is possible since many details of the physical phenomena are formulated and a comprehensive system of coupled equations is formed. Thus, the solution for many different phase variables is possible in contrast to the other models, in which the solution of a limited number of variables is possible. Provided that sufficient information is available on transport coefficients, a comprehensive analysis can be accomplished by this model. By neglecting different transport terms in turn, the effect of each transport phenomenon for the given specific problem may be determined. Thus, this will enable one to invoke the appropriate simplifying assumptions without significant loss of accuracy. The most important drawback of this model, however, is perhaps the determination of the numerous transport coefficients some of which are in the form of second-order tensors in the case of nonhomogeneous and anisotropic media (e.g., effective thermal-conductivity tensor, gas-phase total effective diffusivity tensor). Whitaker's work does not include information on determination of the transport coefficients. It should be noted that determination of some of the transport coefficients given in Whitaker's model is very difficult and may be impossible for some cases. Therefore, complete applicability of this model is not warranted at this time due to the lack of information on a number of transport coefficients.

Luikov's model is also a comprehensive one when the primitive forms of the governing transport equations established in the model are considered. In this model too, provided that the primitive forms of the transport equations are used for all phases with relevant information on transport coefficients and sufficient coupling constraints and thermodynamic relations, a comprehensive analysis of transient solution for distribution of different phases as well as rate and location of phase change will be possible.

Luikov, after some simplifying assumptions, reduces the whole system of governing equations to three coupled differential equations on temperature, total moisture content, and pressure. This system of equations, however, may not be sufficient for a detailed and accurate analysis of the actual physical phenomena. One cannot compute the distribution of liquid and vapor phases or determine the rate and locations of phase change by this system of equations. The assumption of constant transport coefficients for a small range of temperature and moisture content may not be reasonable for all problems. Rather than neglecting the value of $\partial u_1/\partial t$ compared with $\partial u_2/\partial t$ in order to define $\varepsilon_2$ (the phase-conversion factor for liquid), $\varepsilon_2$ should be kept as one of the unknown parameters to be determined. Nevertheless, a simplified analysis of moisture migration due to a temperature gradient in a porous medium, in which the noncondensables have a negligible effect, may be carried out by this system of equations provided that the transfer coefficients, including the phase-conversion coefficient, are known.

It should also be noted that some of the transport coefficients used in this system of equations have rather ambiguous physical meanings due to the combination of the liquid and vapor-flux terms by heuristic definitions for combined transport coefficients. For a more accurate study, the primitive conservation equations should be used simultaneously with relevant thermodynamic relations such as the Clausius–Clapeyron and Kelvin equations as well as the volume-constraint relation in order to form a more complete coupled system of governing equations. Luikov's work contains limited information on empirical correlations for some of the transport coefficients. However, a definition for effective thermal conductivity of the moist porous medium is not given in his work.

Although DeVries's model does not consider noncondensables, it still forms a complete, solvable system of equations for problems in which capillary condensation is the dominant mode of transport in the liquid phase. It is possible to solve numerically for the liquid and vapor distributions as well as the phase-change rate and location. For practical cases in which either no noncondensables are available or the noncondensables are present but have no significant influence on the transport phenomena, DeVries's model is reasonable. In the relation between $\theta_l$ and $\theta_v$ given in Eq. (7) of [22], a factor seems to be missing. With the implicit assumption that $S = \theta_l + \theta_v$, the correct form of the equation should read

$$\frac{\theta_v \rho_v}{\rho_l} = (S - \theta_l)\frac{\rho_v}{\rho_l} = (S - \theta_l)\frac{\rho_0 h}{\rho_l}$$

However, this is still not quite correct since $S = a + \theta_l + \theta_v$, and therefore $\theta_v = S - a - \theta_l$ should have been used rather than $\theta_v = S - \theta_l$. Although some empirical correlations are provided for the transport coefficients for the specific problem considered, those for the liquid phase are based on the capillary condensation region only. Therefore, these cannot be generalized for any problem since, depending on whether the liquid in the system is in the pendular or the funicular state, diffusion or capillary action, respectively, will be the dominant transport mechanism. The differential heat of wetting introduced in this model does not appear in any other model. This term is introduced as a correction for the latent heat of vaporization. It is required due to the fact that the heat of vaporization in a porous medium with a certain amount of liquid, where the vapor pressure is different from the saturation vapor pressure at that temperature, will be different from the latent heat of vaporization of free pure water evaporating at the same temperature. In other models, either this detail is not mentioned or the dependence of the heat of vaporization on vapor pressure has been neglected.

Berger and Pei's model seems to be oversimplified. The assumption of small temperature changes in the system limits the applicability of this model to more general physical processes. Another major simplification is the neglect of heat conduction in the liquid and vapor phases as well as the neglect of transport of sensible heat by the liquid and vapor movement. Moreover, the noncondensables are not considered in this model. Another important deficiency of the model is that it mentions nothing about the dependency of the liquid conductivity $K_L$ and the vapor diffusivity $K_V$ on either the moisture content or the temperature. The assumption of constant $K_L$ and $K_V$ cannot be generalized since these transport coefficients depend very much on the temperature and the moisture content in the medium as well as on capillarity. The mass-flux terms should generally consist of a temperature-gradient term and a mass-concentration-gradient term to account for the so-called thermal and isothermal diffusion processes. This model too, although very much simplified by the assumptions made, forms a solvable system of equations. It will be reasonable to use this model for the practical applications in which there are no large temperature gradients and no significant noncondensable effects. Solutions for distribution of the liquid and vapor phases and the rate of evaporation are possible.

Eckert's model, like Berger and Pei's, uses the limiting assumption of small temperature changes in the system. This is easily seen with the absence of a temperature-gradient term in both the liquid and vapor mass-flux terms. For this reason, the model should not be applied to processes with relatively high temperature changes. As for the energy equation, the approach in [25] neglects sensible heat transport in the liquid and vapor phases. It should be noted that [25] presents only the definitions of heat- and mass-flux terms and not the conversation equations. The effect of phase change in the heat-flux term is taken into account. On the other hand, in [26] the model is developed for the case where there is no phase change and the porous matrix is bound by impermeable walls so that the total amount of moisture (liquid and vapor) in the system remains unchanged. This model is useful for simultaneous heat and mass transfer analysis of problems with no phase change. By this model, one can study the effect of temperature gradient on moisture movement in a porous medium.

Of the models discussed, Whitaker's seems to be the most rigorously formulated and complete one from the theoretical point of view. Luikov's model, on the other hand, gives considerable insight as to what kind of simplifying assumptions may be made in formulating multiphase transport processes in porous media. The other three models discussed are classical examples of simplified models that are encountered mostly in the literature.

In modeling the problems with the non-thermal-equilibrium assumption, the main difference occurs in the conservation of energy. Due to the different temperature distributions in solid and fluid phases, there will be an additional mode of heat transfer from the warmer phase to the cooler phase. This transfer mode can be conceived of as convective heat transfer that can be formulated via a fluid-to-particle heat transfer coefficient. One of the difficulties encountered in doing so is that safe application of the empirical and semiempirical relations found for the fluid-to-particle heat transfer coefficient is questionable because of the inconsistencies among the existing results of many investigations. Moreover, if the fluid phase is undergoing a phase change (e.g., condensation), the heat transfer phenomena will be much more complicated. An assumption of local thermal equilibrium between the liquid and gaseous phases may be reasonable and will simplify the modeling to some extent. However, empirical relations will still be needed for the fluid-to-particle heat transfer coefficients in the presence of two different fluid phases as will an acceptable method of determining the surface areas subject to heat transfer among different phases. In the presence of liquid and gaseous phases in the porous medium, determining the effective thermal conductivity for the fluid phases will be complicated too.

To our knowledge, no work has been done to determine an effective fluid-to-particle heat transfer coefficient for the case when a vapor flowing through a porous medium undergoes condensation or for the case when a vapor flows through a porous medium that already contains some condensate. Likewise, no theoretical or experimental investigation has been carried out to establish a reliable method of determining the effective thermal conductivity for the fluid phases in a porous medium containing a vapor and its condensate. At this time, numerical modeling of such problems in porous media cannot be carried out very accurately due to lack of the abovementioned quantities. However, parametric studies may be performed with reasonable assumptions for these quantities.

## 4 CONCLUDING REMARKS

It can be seen from the models reviewed that the nature and extent of the simplifying assumptions made in modeling heat and mass transfer with phase change in porous media may vary widely. These assumptions are usually the consequences of the prevalent physical conditions, which allow the neglect of certain transport terms from an order-of-magnitude analysis, or the lack of information on transport coefficients or their functional dependencies, which forces the researchers to make some assumptions such as treating the transport coefficients as constants. As a result of the need for the latter type of assumptions, the model that appears to be the most attractive one from the theoretical point of view may be of little value from a practical point of view.

In multiphase transport processes in porous media, although the physical phenomena are relatively well understood, further work to establish a more generalizable formulation of the transport processes in porous media is still needed. Universal methods of definition of the transport coefficients will definitely facilitate the realization of a generalized model. This requires proper identification of the transport potentials. The adoption of such universal methods is strongly recommended; otherwise, great difficulties may be encountered in distinguishing between the interaction of different physical phenomena expressed by gradient terms. At this juncture, further theoretical and experimental work directed at establishing generalized empirical correlations for transport coefficients seems to be a very pressing issue in the multiphase transport in porous media.

For the class of problems in porous media that have liquid and gaseous–vapor phases available as fluid phases and in which the non-thermal-equilibrium assumption is required, the abovementioned points are equally crucial. Moreover, effective thermal conductivity for the fluid phases and the effective fluid-to-particle heat transfer coefficient are crucial quantities that need to be explored further.

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