Heat and Mass Transfer in Hygroscopic Porous Media: Consequences of Invoking Tóth's Sorption Isotherm

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Abstract

The thermal performance of ventilated beds of hygroscopic porous media depends strongly on the sorption properties of the solid phase. Furthermore, the published literature shows that the predicted performance of ventilated beds of hygroscopic porous media is extremely sensitive to the form and accuracy of the sorption isotherm. This is particularly apparent under idealized conditions when thermodynamic equilibrium is deemed to exist between the solid and fluid phases. When Tóth's isotherm is invoked in an equilibrium model used to analyse the performance of a bed of initially warm and dry silica gel ventilated with cool, humid air, it is predicted that a shock wave develops downstream of air entering the bed. In contrast, it is shown that non-equilibrium solutions result in a transfer wave, the width of which decreases as the velocity of the interstitial air decreases. The Tóth isotherm gives rise to erroneous values of the integral heat of wetting of silica gel. Previously published studies of simultaneous heat and mass transfer in beds of hygroscopic materials refer to conceptual difficulties in interpreting the results, and some published mathematical analyses are somewhat terse. A secondary aim of this work is to assuage these difficulties by detailing the analyses in Supplementary Information.

Article Highlights

- The behaviour of ventilated beds of hygroscopic porous media is extremely sensitive to the form of isotherm.
- Shock fronts form in beds of hygroscopic porous media when Tóth's isotherm is invoked by equilibrium models.
- Corresponding non-equilibrium models result in the propagation of steep transfer waves.

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1 Introduction

Ventilated packed beds of hygroscopic porous media constitute a central component of several industrial processes. For example, they are used to dry compressed air (Daghooghi-Mobarakeh et al. 2022). Because they can be regenerated using low-grade heat, they form components of environmentally sustainable systems. De Antonellis et al. (2021) have proposed that beds of desiccant be used in cold climates to humidify air before it is introduced into buildings, and Strong et al. (2022) suggest that ventilated beds of desiccant be used to store thermal energy. A solar thermal, open-cycle desiccant bed cooling system for preserving stored food grains has been developed by Thorpe and Chen (2002). Stored grains are themselves hygroscopic porous media. A sound appreciation of the heat and mass transfer processes that occur within them is essential if they are to be protected from the depredations of insects, fungi and other biota (Panigrahi et al. 2020).

Figure 1 illustrates the temperature profile along a bed of RD silica gel. The physical properties and the parameters in and the form of Tóth's isotherm are given by Chua et al. (2002). The thermodynamic states of the silica gel and that of the air used to ventilate the bed have been chosen to ensure that two heat and mass transfer waves propagate through the bed. Initially, the temperature and moisture content of the silica gel are 50 °C and 0.121 kg water/kg dry silica gel, respectively, and the bed is ventilated with air that has a temperature and specific humidity of 25 °C and 0.0094 kg water kg/dry air. The Darcian or superficial velocity of the air is 80 mm/s and the system has been operating for 3600 s. It is observed that there are three distinct zones, A, P and B, which are separated by two waves that lengthen over time. The silica gel in Zone A is in thermodynamic equilibrium with the incoming air, whilst that in zone C is at its initial state. Zone P is at the so-called plateau, or dwell state that has a temperature of about 34.7 °C. The distance scale is logarithmic, and it is seen that the trailing edge of the moisture wave has travelled a mere 5 mm from the inlet of the bed, whereas the leading edge of the temperature wave has penetrated the bed to a depth of almost 1.5 m.

The behaviour portrayed in Figs. 1 and 2 represents a special case. In general, the loci of points along the moisture wave in the temperature-humidity, T-w, plane approach two extremes. If the solid phase is non-hygroscopic then no mass transfer occurs, and loci of points along the transfer wave, AP, are parallel to the temperature axis, i.e. $\partial w / \partial T = 0$. The other extreme occurs when all of the heat liberated by adsorption of water raises the

Fig. 1 The temperature profile along a bed of ventilated silica gel with psychometric properties described by Tóth's isotherm. The silica gel in Zone A is in thermodynamic equilibrium with the air entering the ventilated bed, and that in Zone B is at its state before ventilation commenced. Zone P is the plateau state. The transfer wave between states A and P is designated the moisture wave, and that between states P and B is the temperature wave. Note that the distance scale is logarithmic
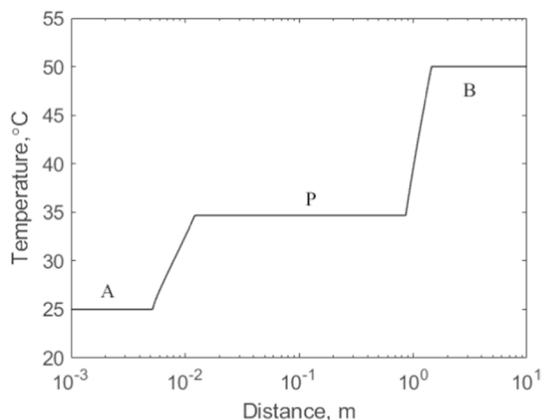
Fig. 2 The ventilation process in the temperature-humidity. *T-w*, plane. The air entering the bed of silica gel is at state A, and the initial state of the bed is at state B. The loci of points on the moisture and temperature waves lie on AP and BP, respectively, where P is the plateau state. The dotted line traces the loci of constant adiabatic wet bulb temperatures
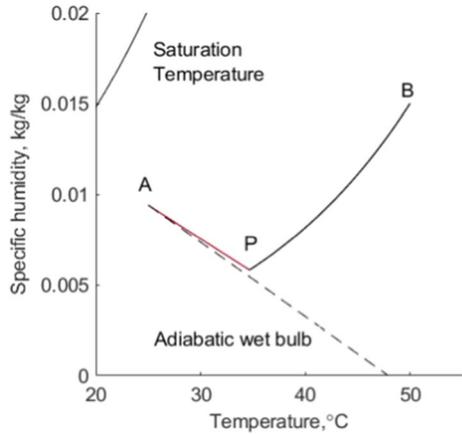
temperature of the air as it flows through the interstices of the bed of silica gel. In this limiting case, the line AP is coincident with that of a constant adiabatic wet bulb temperature. Hygroscopic materials lie between these two extremes. Figure 2 shows that the loci of points on the moisture wave, AP, follow a similar trajectory to those on a line of constant adiabatic wet bulb temperature. This suggests that an exchange of latent heat between the air and silica gel dominates the exchange of sensible heat. In this work, it is shown that when beds of hygroscopic porous media are ventilated with air that has a relative humidity approaching unity, and Tóth's isotherm is invoked, the predicted behaviour of beds of silica gel is quite different from that portrayed in Figs. 1 and 2.

If systems that comprise beds of ventilated hygroscopic porous media are to be optimised, we require detailed mathematical models of the heat and mass transfer processes that occur within them. The governing mass and energy conservation equations can be readily solved using numerical methods. However, numerical solutions do not provide explicit mathematical relationships between the rate and degree of heating and cooling of ventilated beds of hygroscopic porous media and other physical properties. In contrast, the method of characteristics enables these phenomena to be described explicitly in terms of physical variables. As a result, deep insights into the performance of such systems can reveal anomalous behaviour that is not evidenced by numerical solutions.

The predicted performance of ventilated beds of hygroscopic porous media is extremely sensitive to the mathematical form of the isotherm that represents experimental data on the sorption of water vapour by the solid phase. For example, Hunter (1988) observed that the mathematical form of the sorption isotherm has a profound effect on the predicted velocities of transfer waves that propagate through ventilated, or aerated, beds of wheat, a hygroscopic material. In particular, he compared the predicted performance of ventilated beds of wheat when two different forms of isotherms are invoked, namely those proposed by Sutherland et al. (1971) and Hunter (1987).

Anomalous results can ensue when isotherms that accurately fit experimental data are employed to model heat and mass transfer in beds of porous media. For example, Close and Banks (1972) studied heat and mass transfer in ventilated beds of silica gel. To capture fine details of measured sorption properties of silica gel, they initially described the isotherm by means of a series of polynomials with 27 free parameters. Their resulting model of heat and mass transfer produced discontinuities in the predicted velocities of the transfer waves.

Furthermore, the predicted velocities are highly irregular in that they do not vary monotonically with the humidity of the interstitial air as expected. However, when Close and Banks (1972) reduced the number of free parameters to 14, some smoothing of the experimental sorption data occurred, and the predicted velocities of the transfer waves became more regular, although some discontinuities remained. The underlying problem arose because of inaccuracies and inconsistencies in the sorption data modelled by Close and Banks (1972). Driscoll's (1985) results on the rate of drying of paddy rice, a hygroscopic material, also displayed irregular behaviour, although he left this phenomenon unremarked.

Close and Banks (1972) demonstrate that their sorption isotherm for silica gel results in two widening cooling waves propagating through the bed, as indicated in Fig. 1. However, in this work, it is demonstrated that when Tóth's isotherm is invoked, the moisture wave between states A and P collapses into a shock front. The widening temperature wave between zones P and B persists. When the restriction of thermodynamic equilibrium is relaxed, it is shown that the shock front is replaced by a transfer wave that does not increase in wavelength as it propagates through the bed a silica gel.

Ventilated beds of desiccant are used typically to produce dry air. Under these conditions air used to generate Fig. 1 leaving a 1-m long bed of ventilated silica gel would be at the plateau state, P, for about 100 h. Air at the plateau state is required for technological purposes because its relative humidity is low, and in the case shown it is cooler than that of its initial state, B. A slow moving moisture wave propagates through a ventilated bed. It widens as it propagates because, *ceteris paribus*, a reduction of the relative humidity of the interstitial air along a moisture wave is accompanied by a reduction in the sorptivity of the solid phase. As a result, the relative humidity of the interstitial air decreases as a moisture wave exits a bed of hygroscopic porous media. If the technological objective is to dry air, this slow decline in performance is undesirable. In this work, it is shown that desiccants with isotherms of the form of Tóth's generate slow moving, but steep moisture fronts.

Close (1983) declared that the abstract nature of the solution of the governing heat and mass conservation equations by the method of characteristics "causes difficulties in comprehension". This sentiment is echoed by Ingram (1979). When discussing an analysis of heat and mass transfer in beds of stored food grains he opined of characteristics, "it is difficult to interpret their physical significance". In a similar vein, Hunter (1988) expressed the view that "The analysis of heat and mass transfer in porous hygroscopic media is necessarily complicated". A secondary objective of this work is to assuage some of these perceived difficulties by presenting a comprehensive and detailed account of the analysis in Supplementary Information.

2 Mathematical Background

Dispersive effects may obscure the underlying mechanisms of heat and mass transfer in beds of porous media: dispersive phenomena are essentially aleatory. In this work, it is initially assumed that the interstitial air and solid phase are in thermodynamic equilibrium throughout the bed, and there are no dispersive effects. Although these assumptions appear to be limiting, they nonetheless bring to the fore, and make explicit, the effects of physical properties on the performance of ventilated beds of hygroscopic porous media. Sutherland et al. (1983) demonstrate that the assumption of equilibrium accurately displays the key features of heat and mass transfer phenomena in beds of ventilated stored grains. Along with Ingram (1979), they demonstrate that the effects of dispersive phenomena may be

superimposed on the results developed here. Close and Banks (1972) also report that the equilibrium model of heat and mass transfer in ventilated beds of silica gel provides reasonable agreement with experimental results. The assumption of thermodynamic equilibrium between the solid and fluid phases will be subsequently relaxed, and its effects quantified.

The equation that governs the conservation of water in a bed of ventilated hygroscopic porous medium at a distance x downstream of the air inlet at time t presented by Banks (1972) may be stated as

$$v\frac{\partial w}{\partial x} + \frac{\partial w}{\partial t} + \mu\frac{\partial W}{\partial t} = 0 \tag{2.1}$$

in which w represents the specific humidity of the interstitial fluid, and W is the moisture content of the solid phase expressed on a dry basis, and v is the mean velocity of air within the interstices of a packed bed of porous media. The volume-weighted density, μ, is given by

$$\mu = \frac{\rho_s(1-\varepsilon)}{\rho_a\varepsilon} \tag{2.2}$$

The corresponding equation for the conservation of enthalpy is

$$v\frac{\partial h}{\partial x} + \frac{\partial h}{\partial t} + \mu\frac{\partial H}{\partial t} = 0 \tag{2.3}$$

where h and H are, respectively, the specific enthalpies of moist air and solids expressed on a dry basis. The hygroscopic nature of the solid phase results in $W = W(w, T)$ where T is temperature. The specific enthalpy, H, of moist silica gel is a function of its moisture content and temperature; hence, it follows that $H = H(w, T)$. Under a condition of constant pressure the specific enthalpy, h, can be expressed as $h = h(w, T)$ and by employing the chain rule of partial differentiation, Eqs. 2.1 and 2.3 become

$$\mu\left(\frac{\partial W}{\partial T}\right)_w \frac{\partial T}{\partial t} + \left(1 + \mu\left(\frac{\partial W}{\partial w}\right)_T\right)\frac{\partial w}{\partial t} + v\frac{\partial w}{\partial x} = 0 \tag{2.4}$$

and

$$\left(\left(\frac{\partial h}{\partial T}\right)_w + \mu\left(\frac{\partial H}{\partial T}\right)_w\right)\frac{\partial T}{\partial t} + v\left(\frac{\partial h}{\partial T}\right)_w \frac{\partial T}{\partial x} + \left(\left(\frac{\partial h}{\partial w}\right)_T + \mu\left(\frac{\partial H}{\partial w}\right)_w\right)\frac{\partial w}{\partial t} + v\left(\frac{\partial h}{\partial w}\right)_T \frac{\partial w}{\partial x} = 0 \tag{2.5}$$

3 The Velocities of Moisture and Temperature Waves

Thorpe (2022) provides a detailed demonstration of the solution of Eqs. 2.4 and 2.5 by means of a classical application of the method of characteristics presented by Rhee et al. (2013). This provides a simple expression for estimating the velocities $\mathcal{V}_i$ of temperature and moisture waves that travel through the bed, namely

$$\mathcal{V}_i = \mathcal{A}_i v, \quad i = 1, 2 \tag{3.1}$$

in which $i = 1, 2$ refer to the moisture and temperature waves, respectively, and $\mathcal{A}_i$ are velocity ratios that depend on the local thermodynamic state within the bed. They are given by

$$\mathcal{A}_i = \frac{1}{1 + \mu\gamma_i}, \quad i = 1, 2 \tag{3.2}$$

Thorpe (2022) demonstrates that

$$\gamma_i = \frac{\left(c_s + Wc_W + \frac{\partial}{\partial T}\int_0^W h_w(T, W)dW\right) + \left(c_W T + h_w(T, W)\right)(\partial W/\partial T)_j}{(c_a + wc_v) + \left(c_W T + h_v|_T\right)(\partial w/\partial T)_j} \quad i = 1, 2; j \neq i \tag{3.3}$$

in which $h_w(T, W)$ is the isothermal differential heat of wetting of the solid phase. c_a, c_s, c_v and c_W are, respectively, the specific heats of dry air, dry solid, water vapour and liquid water, and $h_v|_T$ is the latent heat of vapourisation of free water at the temperature T. γ_i is the ratio of the derivatives with respect to temperature of the specific enthalpies of the solid and fluid phases, and it is expressed by

$$\gamma_i = (\partial H/\partial h)_j, \quad i = 1, 2, \ i \neq j \tag{3.4}$$

γ_i is analogous to the ratio, σ, of the specific heats of the solid and fluid phases in beds of non-hygroscopic solids, but the numerator and denominator in Eq. 3.4 incorporate terms that account for the hygroscopic nature of silica gel. The subscript j indicates that the differentials are evaluated as tangents to the line in the T-w domain other than that designated by i, as indicated in Eq. 3.3. The ratio, $(\partial H/\partial h)_j$, provides an indicator of the importance of the hygroscopy of the solid phase. For example, along AP indicated in Fig. 1. $(\partial H/\partial h)_1 > \sigma$, and the high ratio of the effective specific heat of the solids to air is associated with the low velocity of the moisture wave. Conversely, $(\partial H/\partial h)_2 < \sigma$ corresponds to the temperature wave propagating with a relatively high velocity through beds of hygroscopic porous media, and this occurs along the more rapidly travelling temperature wave, PB. Along moisture and temperature waves Thorpe (2022) shows that

$$\left(\frac{\partial H}{\partial h}\right)_i = \left(\frac{\partial W}{\partial w}\right)_i, \quad i = 1, 2 \tag{3.5}$$

Equation 3.3 has a simple form that provides insights into the behaviour of ventilated beds of hygroscopic porous media. However, it is necessary to evaluate $(\partial w/\partial T)_j$ and $(\partial W/\partial T)_j$ which lie along the lines AP and BP in Fig. 2.

4 Characteristic potentials

The transport equation that governs the nondispersive flow of a scalar, F, may be written as

$$\mathcal{A}\frac{\partial F}{\partial t} + \mathcal{\ell}\frac{\partial F}{\partial x} = 0 \tag{4.1}$$

where $\mathcal{A}$ and $\mathcal{\ell}$ are constants, or functions of F, x and t. Importantly, the velocity, $\mathcal{V}$, with which the scalar is transported is the ratio $\mathcal{\ell}/\mathcal{A}$. Consider a system in which the solid and fluid phases are in thermodynamic equilibrium. In this case, the temperature, T, the humidity, w, and the moisture content, W, of the solids at a point on a transfer wave remain constant as the point transits the bed, that is the three quantities travel with the same speed. Hence, the key to solving Eqs. 2.4 and 2.5 is to recognise that the ratio of the coefficients

of $\partial T/\partial t$ and $\partial T/\partial x$ are the same as those of $\partial w/\partial t$ and $\partial w/\partial x$. It is shown in Supplementary Information that this leads to an expression of the form

$$\left(\frac{\partial T}{\partial t} + \alpha_i \frac{\partial w}{\partial t} \right) + A_i v \left(\frac{\partial T}{\partial x} + \alpha_i \frac{\partial w}{\partial x} \right) = 0 \tag{4.2}$$

Banks (1972) introduced the concept of characteristic potentials that drive heat and mass transfer in beds of porous hygroscopic media, such as silica gel. Since there are two waves, we replace F in Eq. 4.1 with F_i which are termed characteristic potentials and which constitute a potential driving force that captures the effects of both heat and mass transfer. This is achieved by defining α_i in Eq. 4.2 as

$$\alpha_i = \frac{\left(\frac{\partial F_i}{\partial w} \right)_T}{\left(\frac{\partial F_i}{\partial T} \right)_w} = -\left(\frac{\partial T}{\partial w} \right)_{F_i} \tag{4.3}$$

which implies that values of F_i are constant along lines in the w-T plane that result from the integration Eq. 4.3. By inserting Eqs. 4.3 into 4.2, it is shown in Supplementary Information that implementation of the rules partial differentiation yields the desired result, namely

$$\frac{\partial F_i}{\partial t} + \mathcal{A}_i v \frac{\partial F_i}{\partial x} = 0, \quad i = 1, 2 \tag{4.4}$$

Numerical values of F_i are generally considered arbitrary, although Close (1983) attempted to assign values to them. The nature of characteristic potentials is discussed in further detail in Supplementary Information.

We make use of the method of characteristic potentials to evaluate $(\partial w/\partial T)_j$ and $(\partial W/\partial T)_j$ in Eq. 3.3. Banks' (1972) analysis is somewhat terse; hence, it is elucidated in some detail in Supplementary Information, where it is shown that

$$\alpha_i = \frac{(\sigma v + \lambda \alpha_h + \alpha_W) - (-1)^i \left(\left(\sigma v + \lambda \alpha_h - \alpha_W \right)^2 + 4 \alpha_W \lambda \alpha_h \right)^{0.5}}{2}, \quad i = 1, 2 \tag{4.5}$$

where $(\partial w/\partial T)_i = -1/\alpha_i$, and variables such as σ, v, λ defined by Banks (1972) are given in Supplementary Information. In practice, we know the initial conditions required to integrate Eq. 4.5. They are those that correspond to those in equilibrium with the air entering the silica gel bed, A, and the initial condition of the silica gel, B. Integration enables the loci of points along AP and BP to be determined.

5 Discontinuities

A discontinuity forms when the trailing edge of a transfer wave has a higher velocity than its leading edge. This typically occurs when a bed of hygroscopic porous medium with a high moisture content is dried with air that has a low relative humidity. However, we shall observe that Toth's isotherm predicts the formation of a discontinuity in the moisture wave. Thorpe (2022) demonstrates that the thermodynamic states on either side of a discontinuity in a ventilated bed of hygroscopic porous media are governed by the following relationship

$$\frac{\Delta H}{\Delta h} = \frac{\Delta W}{\Delta w} \tag{5.1}$$

in which Δ represents the difference in the quantities across a discontinuity. We can express the difference in the enthalpies of the air between the plateau state and the air entering the system, by designating their subscripts p and in, respectively, thus

$$\Delta h = c_a\left(T_p - T_{in}\right) + c_w\left(w_p T_p - w_{in} T_{in}\right) + w_p h_v\big|_p - w_{in} h_v\big|_{in} \tag{5.2}$$

and the difference in the enthalpy of the solid phase across the discontinuity is given by

$$\Delta H = c_s\left(T_p - T_{in}\right) + c_w\left(W_p T_p - W_{in} T_{in}\right) + H_W\big|_p - H_W\big|_{in} \tag{5.3}$$

To ensure that Eq. 5.1 is satisfied we define a function

$$\phi\left(T_p, w_p\right) = \Delta h \Delta W - \Delta H \Delta w \tag{5.4}$$

and search for values of T_p and w_p such that $\text{abs}\left(\phi\left(T_p, w_p\right)\right)$ approaches zero to within a pre-defined tolerance.

The values of T_p and w_p are constrained to lie on a line of constant F_2 that passes through the initial state of the bed of porous media. A fourth order Runge–Kutta method is used to integrate the first-order differential equation

$$\left(\frac{\partial T}{\partial w}\right)_{F_2} = -\alpha_2 \tag{5.5}$$

The Nelder–Mead method is used to determine w_p such that $\left|\phi\left(T_p, w_p\right)\right| \le 10^{-4}$ given that the integration of Eq. (5.5) provides values of T_p and w_p at the plateau state.

Equations 3.2 and 3.5 indicate that the velocity ratio, $\mathcal{A}_i$, at points along the transfer waves is closely related to the ratio $(\partial W/\partial w)_j$ which is evaluated along a line of constant F_i, i.e. along a transfer wave. It convenient to designate this quantity the characteristic sorbability, $\beta_{c,i}$, of hygroscopic materials defined by

$$\beta_{c,i} = \left(\frac{\partial W}{\partial w}\right)_i \tag{5.6}$$

6 Physical Properties

The principal aim of this work is to investigate the effect of the form of Tóth's isotherm on the performance of ventilated beds of hygroscopic porous media. This study makes use of the physical properties of RD silica gel reported by Chua et al. (2002) who give the following form of Tóth's isotherm

$$W = \frac{K_p}{\left(1 + \left(\frac{K_p}{W_m}\right)^t\right)^{1/t}} \tag{6.1}$$

where

$$K_p = K_0 p_v \exp\left(\frac{Q_{st}}{\mathcal{R}_v T_{abs}}\right) \tag{6.2}$$

in which K_0 and Q_{st} are, respectively, an empirical constant and the differential heat of sorption. R_v is the gas constant specific to water vapour, T_{abs} is the absolute temperature, and W_m is the saturated moisture content of the solid that occurs when the relative humidity of the surrounding air is unity, and t is the Tóth constant. T_{abs} is the absolute temperature, K. Chua et al (2002) provide the following values for the empirical constants for RD silica gel: $K_0 = 7.3 \times 10^{-13}$ kg.kg^{-1}.Pa^{-1}, $Q_{st} = 2.693 \times 10^6$ J.kg^{-1}, $t = 12$, $W_m = 0.45$ and $\mathcal{R}_v = 461.5$ J.kg^{-1}.K^{-1}.

Thorpe (2001) points out that the differential heat of sorption is functionally related to the temperature, T, and the fractional relative humidity, r, of the interstitial air, and the moisture content, W, of the solids through

$$\frac{h_s}{h_v} = 1 + \frac{p_s}{r}\frac{dT}{dp_s}\left(\frac{\partial r}{\partial T}\right)_W \tag{6.3}$$

in which p_s is the saturation vapour pressure of water, Pa. It is shown in Supplementary Information that in the case of Tóth's isotherm

$$\frac{h_s}{h_v} = p_s \frac{dT}{dp_s}\frac{Q_{st}}{\mathcal{R}_v T_{abs}^2} \tag{6.4}$$

Equation 6.4 is somewhat tautological because h_s and Q_{st} represent the same quantity, namely the differential heat of sorption. According to Tóth's isotherm, h_s/h_v is independent of the moisture content of silica gel, and this is reflected by Eq. 6.4. When Eq. 6.3 is evaluated, it is found that h_s also varies little with temperature. For example, h_s is 2.691×10^6 when the temperature is 5 °C and 2.683×10^6 when the temperature is 50 °C. These values are consistent with the value of Q_{st} given Chua et al. (2002), namely 2.693×10^6 J/kg.

The isothermal differential heat of wetting, h_w, is liberated when water is adsorbed by the solid substrate of the silica gel. In keeping with the convention of thermodynamics it is deemed to be a negative quantity. The latent heat of sorption, h_s, is the total quantity of energy required to liberate adsorbed moisture, and it comprises the latent heat of vapourisation of free water, h_v, and the negative of differential heat of wetting, and it is defined thus

$$h_s = h_v - h_w \tag{6.5}$$

The integral heat of wetting is defined as

$$H_W = \int_0^W (h_v - h_s)\,dW \tag{6.6}$$

Which when combined with Eq. (6.3) becomes

$$H_W = h_v\left(1 - p_s\frac{dT}{dp_s}\frac{Q_{st}}{\mathcal{R}_v T_{abs}^2}\right)W \tag{6.7}$$

If we accept the assumption implicit in Tóth's isotherm that Q_{st} is indeed constant we have

$$\frac{\partial H_W}{\partial T} = \frac{d}{dT} \int_0^W (h_v - Q_{st}) dW \approx W \frac{dh_v}{dT} \tag{6.8}$$

If $dh_v/\partial T$ is taken to be -2376.2 J/(kg °C) the above formulation suggests that $\partial H_W/\partial T = O(10^2)$, and it is a negative quantity. This is inconsistent with values implied by the work of Close and Banks (1972) who demonstrate that the differential heat of sorption, h_s, is expressed as

$$h_s = h_v \varphi(W) \tag{6.9}$$

where $\varphi(W)$ is an empirical function of the moisture content, W, of silica gel, and it has a value of about 1.1. When Q_{st} is replaced by h_s defined by Eq. 6.9 in Eq. 6.6 we have

$$\frac{\partial H_W}{\partial T} = \frac{d}{dT} \int_0^W (h_v - h_v \varphi(W)) dW \approx -0.1 W \frac{dh_v}{dT} \tag{6.10}$$

i.e., according to this formulation $\partial H_W/\partial T$ is of an order of magnitude of 10^1 in a typical working range. Furthermore, that value of $\partial H_W/\partial T$ given by Eq. 6.10 is positive. The numerator in Eq. 3.3 contains a term $c_s + W c_W + \frac{\partial}{\partial T} \int_0^W h_w(T, W) dW$, and since $\frac{\partial}{\partial T} \int_0^W h_w(T, W) dW \ll c_s + W c_W$ we neglect the differential of the integral heat of wetting with respect to temperature. This approximation makes no material difference to the arguments presented in this work, and in practice $\partial H_W/\partial T$ is subsumed into the specific heat of the solid phase. Chakraborty et al. (2009) demonstrate how the sorption properties influence the apparent specific heat of silica gel (Type 125). When considering heat and mass transfer in stored food grains Thorpe (2022) noted that subsuming $\partial H_W/\partial T$ into the specific heat of the solid phase is necessary when sorption data are incomplete, or internally inconsistent.

7 Solution of the Governing Heat and Mass Conservation Equations

Given the initial conditions the loci of points along the F_1 and F_2 characteristics in the T-w plane are calculated by implementing a fourth order Runge–Kutta algorithm (Shampine and Reichelt 1997) to integrate the following equation.

$$T_i = - \int_{T_{k,i}, w_{k,i}}^{w_p} \alpha_i dw \quad i = 1, 2; k = 1, 2, i \neq k \tag{7.1}$$

in which the subscripts $i = 1, 2$ refer to the loci of points along the moisture and temperature waves, respectively, and $k = 1, 2$ refers to the thermodynamic states at the inlet to the bed, state A, and the initial conditions, state B, respectively. A value of the humidity, w_p, is sought at the point of intersection of the lines of constant F_1 and F_2, which corresponds to the plateau, or dwell state. The intersection is deemed to occur when $|T_2 - T_1| < 10^{-4}$, which is determined by the Nelder-Mead simplex method (Lagarias, et al. 1998).

8 Results

Consider an element of a bed of hygroscopic porous medium, as shown in Fig. 3. The element travels through the bed with the same velocity as that of a point on a transfer wave such that its thermodynamic state remains constant. In this case, each point, F_i, located along a transfer wave along which F_j is constant has a different velocity $\mathcal{V}_i$. The velocity, v, of the interstitial air is several orders of magnitude greater than that of transfer waves, and its velocity relative to the moving element is $v - \mathcal{V}_i$. Because the element travels with a velocity $\mathcal{V}_i$, the solid phase effectively enters the element at its downwind face and leaves from its upwind face. During this process, the solid exchanges mass and energy with the air stream, and the net result is that it loses enthalpy to the interstitial air. Since the process is isenthalpic, the enthalpy gained by the air stream is extracted from the hygroscopic porous medium. The situation is discussed in more detail in Supplementary Information.

The performance of a ventilated bed of RD silica gel is investigated under the operating conditions given in Table 1.

8.1 The Moisture Wave

When the relative humidity of the interstitial air is high, and Tóth's isotherm is invoked it can be seen in Fig. 4 that the behaviour of silica gel exhibits characteristics that approach those of a non-hygroscopic material, i.e. $(\partial w/\partial T)_{F_1} \to 0$. We shall observe

Fig. 3 Air with a velocity v enters an element of a bed of hygroscopic porous medium that has a velocity $\mathcal{V}_i$, at a point on the transfer wave, j. Cool air enters the element from upstream and exchanges energy and moisture with silica gel that enters the moving element through its downstream face. No energy or mass accumulates in the element
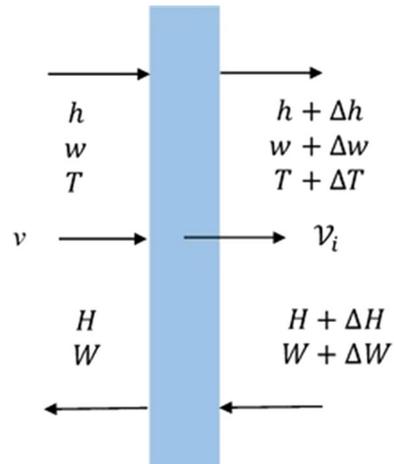
Table 1 The operating conditions of a ventilated bed of silica gel. A shock front forms between the inlet and plateau states, AP

	Inlet State, A	Plateau, P	Initial state, B
Temperature, °C	25	34.86	50
Humidity, kg water/kg dry air	0.019	0.01535	0.040
Moisture content, kg water/kg dry solid	0.44979	0.3007	0.3105
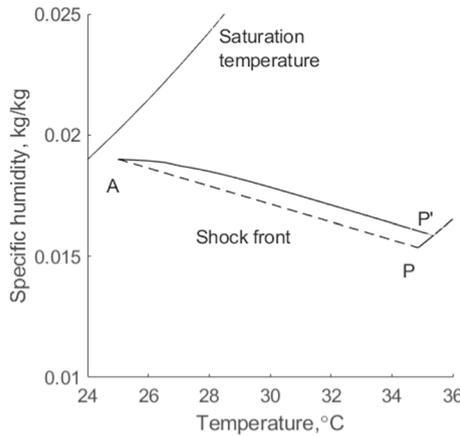
Fig. 4 Air at state A enters a bed of silica gel. When Eq. 4.5 is integrated, the resulting moisture wave intersects the temperature wave at P´. In the vicinity of A, the gradient $(\partial w/\partial T)_{F_1}$ calculated using Tóth's isotherm is low which indicates that the silica gel adsorbs little moisture, hence the velocity of the moisture wave is high. The reverse is true in the vicinity of P´, so the velocity of trailing edge of the moisture wave notionally has a higher velocity than the leading edge. Hence, a shock wave forms, depicted by the dotted line AP

that as the sorptivity increases, the speed of the moisture wave, $\mathcal{V}_1$, decreases, and since the trailing edge cannot overtake the leading edge a shock wave forms, indicated by the dotted line in Fig. 4. We shall now quantify the factors that lead to these phenomena.

8.1.1 Conditions at Point A

The terms in Eqs. 3.2 and 3.4 that govern the rate at which a moisture wave traverses a ventilated bed of silica gel are shown in Table 2. Under the conditions at point A where

Table 2 Terms in Eq. 3.3, that with Eq. 3.2, govern the rate at which transfer waves propagate through beds of silica gel, the psychrometric properties of which is described by Tóth's isotherm

	Moisture wave, $i=1$		Temperature wave, $i=2$	
	Inlet: A	Plateau: P	Plateau: P	Initial: B
$(\partial W/\partial T)_{F_i}$	-1.7151×10^{-4}	-0.02541	5.858×10^{-4}	7.125×10^{-4}
$c_s + Wc_W$	2804.18	2177.32	2177.32	2221.24
$c_W T(\partial W/\partial T)_\pm$	-17.95	-3709.31	85.51	149.16˘
$h_w(T, W)(\partial W/\partial T)_{F_i}$	42.35	6821.69	-157.26	-214.09
$(\partial H/\partial T)_{F_i}$	2828.58	5289.70	2105.57	2156.31
$(\partial w/\partial T)_{F_i}$	-5.4685×10^{-5}	-3.725×10^{-4}	9.981×10^{-4}	2.478×10^{-3}
$c_a + wc_v$	1039.20	1032.58	1032.58	1077.22
$c_W T(\partial w/\partial T)_{F_i}$	-5.71	-54.37	145.7	518.70
$h_v|_T(\partial w/\partial T)_{F_i}$	-133.27	-900.65	2413.5	5902.28
$(\partial h/\partial T)_{F_i}$	900.22	77.57	3591.78	7498.20
$(\partial H/\partial T)_{F_j}/(\partial h/\partial T)_{F_i}$	3.14	68.2	0.586	0.287
$\mathcal{A}_{F_i}$	2.141×10^{-4}	9.88×10^{-6}	1.145×10^{-3}	2.335×10^{-3}

the silica gel is in thermodynamic equilibrium with air entering the bed $(\partial W/\partial T)_{F_1}$ and $(\partial w/\partial T)_{F_1}$ are -1.7151×10^{-4} J·(kg·°C)$^{-1}$ and -5.4685×10^{-5} J·(kg·°C)$^{-1}$ respectively. Hence, according to Eq. 5.6 the characteristic sorptivity, $\beta_{c,1}$, is 3.14, which is relatively low, and it demonstrates that only a small quantity of water vapour is adsorbed by the silica gel. The velocity ratio, $\mathcal{A}_2$, at point A is 2.141×10^{-4}.

The heat and mass transfer processes are intertwined. Moist air at point A gains 1039.20 J·(kg·°C)$^{-1}$ of sensible heat as it cools the silica gel. During this process, moisture condenses on the internal and external surfaces of the solid phase, and 133.3 J·(kg·°C)$^{-1}$ of latent heat of condensation of water is liberated. This reduces the capacity of the air to cool the silica gel, which results in the velocity of the transfer wave being lower than if the solid phase was not hygroscopic. Because the humidity of the air falls as it traverses the moisture wave, it loses 5.71 J·(kg·°C)$^{-1}$ of sensible heat associated with the reduction of humidity.

The silica gel cools as it traverses the moving element, and it can be seen in Table 2 that it *loses* 2804.18 J·(kg·°C)$^{-1}$ of sensible heat. As the silica gel passes through the moving element, its moisture content *increases* which increases its enthalpy by 17.95 J·(kg·°C)$^{-1}$. The increase in moisture content of the silica gel results in its *losing* 42.35 J·(kg·°C)$^{-1}$ arising from its heat of wetting.

The net result of the heat and mass transfer processes is that the Tóth isotherm predicts that at point A moist air with a cooling capacity of 900.2 J·(kg·°C)$^{-1}$ has the duty of cooling silica gel that has an effective specific heat of 2826.58 J·(kg·°C)$^{-1}$, hence $(\partial H/\partial h)_{F_1}$ is 3.14. As anticipated from Eq. 3.5, this is identical to the characteristic sorptivity, $\beta_{c,1}$. Significantly, about 87% of the cooling capacity of the moist air arises from an increase in its sensible heat, and the transfer of latent heat is relatively small.

8.1.2 Conditions at the Plateau State, P

At the plateau state, P, it is shown in Table 2 that along a line of constant F_1 the moisture characteristic sorptivity, $\beta_{c,1}$, of silica gel is 68.2. As a result, a large volume of air must flow to increase the moisture content of silica gel, and the velocity ratio, $\mathcal{A}_2$, at this point is 9.88×10^{-6}, i.e. it is slower by a factor of 21.7 than at point A. Hence, a shock front forms.

On passing through a moving element of solid at point P the silica gel would lose 2177.32 J·(kg·°C)$^{-1}$ which is somewhat less than that at point A because its moisture content is lower. However, the higher characteristic sorptivity increases its rate of adsorption of moisture, hence it gains 3709.31 J·(kg·°C)$^{-1}$ as a result of its moisture content increasing. However, the silica gel loses 6821.69 J·(kg·°C)$^{-1}$ because heat of wetting is liberated. The net change in the enthalpy of silica gel at the plateau state as it traverses the moving element shown in Fig. 3 is a *loss* of 2828.58 J·(kg·°C)$^{-1}$.

We observe that the air extracts 1032.6 J·(kg·°C)$^{-1}$ of sensible heat from the silica gel. The humidity of the air falls as it traverses the bed because water vapour in the interstitial air condenses on the external and internal surfaces of the silica gel. Hence, the air loses 900.61 J·(kg·°C)$^{-1}$ of latent energy. The latent energy is liberated as heat of condensation, and most of this energy is used to heat the air stream as it flows through the bed of silica gel: this reduces the cooling capacity of the air. We observe from Table 2 that the air is capable of extracting only 77.57 J·(kg·°C)$^{-1}$ of energy from the silica gel, whereas the energy of the silica gel is reduced by 5285.5 J·(kg·°C)$^{-1}$. As a result $(\partial H/\partial h)_{F_1}$ is 68.2, so the velocity ratio is 9.88×10^{-6}, as anticipated by the analysis of mass transfer.

Contours of equal velocity ratios, $\mathcal{A}_2$, along the moisture waves predicted by Tóth's isotherms are shown in Fig. 5. It is striking that Tóth's isotherm predicts that $\mathcal{A}_2$ exhibits minimum values. This follows from the above discussion, which indicates that the isotherm implies that little sorption takes place when the relative humidity of the interstitial air is high at point, A; hence, the velocity ratio is high. The characteristic sorptivity subsequently increases, liberating heat of sorption which lowers the rate of cooling of the silica gel. However, the sorptivity of water along a line of constant F_1 subsequently decreases as the system approaches the plateau state, P. Hence, less heat of sorption is liberated and the speed of the moisture wave increases.

At the plateau state, the loci of points along the cooling wave are closely aligned with an adiabatic wet bulb line, as most of the heat of adsorption raises the temperature of the air as it flows through the bed, and there is little capacity for the air to cool the silica gel.

The distance, x, travelled by points on the moisture and temperature waves is given by the product of the interstitial velocity of the air, v, elapsed time, t, and the velocity ratio, $\mathcal{A}_i$. The variation of the velocity ratio against temperature along the fictional moisture wave and the temperature wave is shown in Fig. 6. It can be seen that the situation is absurd because the displacement of a given temperature along the moisture wave would have two values simultaneously. The situation is resolved by recognising that Eqs. 2.4 and 2.5 that govern heat and mass transfer demand the formation of a shock front.

8.2 The Temperature Wave

There is a striking difference between the moisture and temperature waves. In the former case, water is adsorbed by the silica gel, which reduces its rate of cooling, whereas some
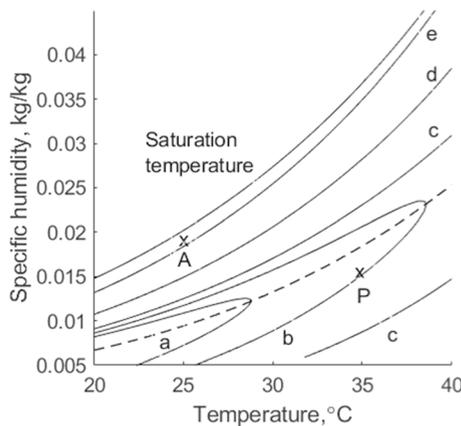
Fig. 5 Contours of velocity ratios, $\mathcal{A}_2$, along the moisture wave (F_1 is constant) that exhibit minimum values indicated by the dashed line. This arises because at a given temperature when the relative humidity of the interstitial air is high, the sorptivity of silica gel is low; and as the sorptivity increases the velocity ratio, $\mathcal{A}_2$, decreases to a minimum. A further reduction in the relative humidity results in $\mathcal{A}_2$ increasing. The thermodynamic states across the moisture shock front are indicated by points A and B. Key: Values of $\mathcal{A}_2$ are a=8, b=10, c=14, d=60e, e=200 (all values to be multiplied by 10^{-6})

Fig. 6 Air enters a bed of silica gel at thermodynamic state A, given in Table 1. When Eq. 4.5 is integrated, the loci of the transfer waves in the $\mathcal{A}_i$-T plane are obtained. However, Tóth's isotherm demands that the velocity of the trailing edge exceeds that of the leading edge, hence a fictitious moisture wave is predicted. In this case, the plateau state is designated by P′. The situation is resolved by the formation of a shock front, in which case a corrected plateau state exists, designated by P. The initial state of the silica gel is denoted by B
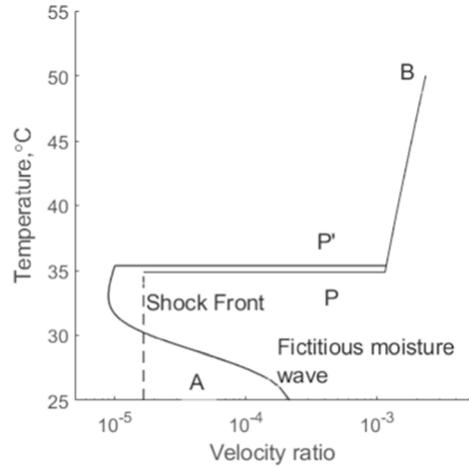
drying of the silica gel occurs with the passage of the temperature wave. Although the amount of drying is relatively small, the latent heat of vapourisation of water supplements the transfer of sensible heat from the silica gel to the interstitial air. Table 2 shows that at the plateau state, P, Tóth's isotherm predicts that at the trailing edge of the temperature wave the air gains 2413.5 J·(kg·°C)$^{-1}$ of energy associated with the latent heat of water vapour in the interstitial air. In addition, 1032.6 J·(kg·°C)$^{-1}$ of sensible heat is extracted from the silica gel. A further 145.7 J·(kg·°C)$^{-1}$ of sensible heat is required to increase the temperature of the water vapour added to the air by evaporation.

The net result of the above processes is that at the trailing edge of the temperature wave the enthalpy of the air increases by 3591 J·(kg·°C)$^{-1}$: this energy is extracted from the silica gel as it cools. It can be seen from Table 2 that 2177 J·(kg·°C)$^{-1}$ of sensible heat is removed from the silica gel, and a further 85.5 J·(kg·°C)$^{-1}$ is required to cool the moisture adsorbed by the gel. However, the energy required to cool the silica gel is offset somewhat by the heat of adsorption, 157.26 J·(kg·°C)$^{-1}$ liberated by the formation of weak chemicophysical between the water and the solid substrate of the silica gel (Fig. 7).

Fig. 7 Contours of velocity ratios, $\mathcal{A}_1$, along the temperature wave calculated using Tóth's isotherm. It is observed that $\mathcal{A}_1$ increases monotonically along the temperature wave from the plateau state, P, to that at the initial conditions. B. Hence, the leading edge of the wave has a higher velocity that the trailing edge. The values of the contours are multiplied by 10^{-3} to obtain the velocity ratios
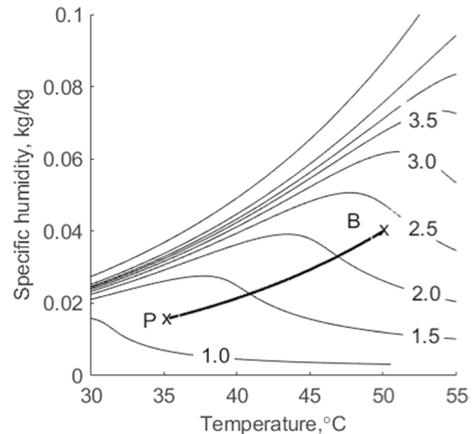
The vapour pressure of water adsorbed by silica gel increases rapidly with temperature. Again considering the Tóth isotherm we observe in Table 2 that $(\partial w / \partial T)_{F_2}$ at the leading edge of the temperature wave, point B in Fig. 8, is 2.48 times higher than at the trailing edge. At the leading edge of the wave the rapid increase in the moisture content of the air requires that 7498 J·(kg·°C)$^{-1}$ of latent heat be extracted from the silica gel. In addition, 1077 J·(kg·°C)$^{-1}$ of sensible heat must be extracted from the moist silica gel along with 518.7 J·(kg·°C)$^{-1}$ required to heat the additional water vapour in the interstitial air.

The velocity ratio of the leading edge of the temperature wave is 2.334×10^{-3}, which is over twice, that at the plateau state. As a result, the temperature wave widens as it traverses the bed of silica gel. Figure 8 indicates that the silica gel dries as the temperature wave traverses the bed of silica gel.

9 Non-Equilibrium Conditions

We have noted that Tóth's isotherm results in the formation of a shock front when warm dry silica gel is ventilated with cool air that has a high relative humidity, which has not been reported previously. The trailing edge of the moisture wave is calculated to have a higher velocity than the leading edge. In practice, dispersive effects such as finite resistances to heat and mass transfer between the air and the silica gel, thermal conduction between beads of silica gel, and the dispersion of water vapour and heat within the interstices formed by the solid phase. Thorpe and Whitaker (1992a, b) demonstrated that thermal equilibrium between the solid and fluid (air) phases may be assumed, but mass equilibrium is not necessarily attained. This is to be expected because the response of beads of silica gel to changes in temperature is on the order of 10 s, which is several orders of magnitude less than the rate at which temperature changes occur along the length of the bed. The rate of mass transfer between RD silica gel and its surrounding atmosphere is taken as being driven by the mean moisture content, W, within beads of silica gel and the moisture content, W_e, in thermodynamic equilibrium with the interstitial atmosphere, i.e.

Fig. 8 Constant moisture contents, W, of silica gel are shown as dashed lines in the T-w plane. The silica gel dries with the passage of a temperature wave, which is consistent with the air at the leading edge of the wave, at point B, having a higher humidity than that at the trailing edge, point P
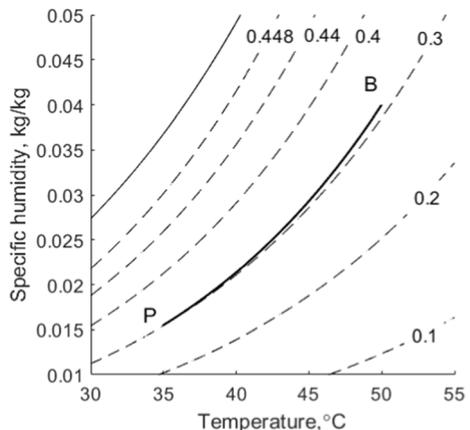
$$\frac{\partial W}{\partial t} = -k(W - W_e) \tag{9.1}$$

where k is a rate constant. The expression for $\partial W/\partial t$ given by Eq. 9.1 is substituted into the conservation equations, Eqs. 2.4 and 2.5 which yield values of the temperature, T, and interstitial humidity, w, along ventilated beds of silica gel

The silica gel is assumed to be in the form of spherical beads with a radius of R_p which enables the rate constant to be calculated by means of the equation proffered by Mohammed (2018), namely

$$k = \frac{15\mathcal{D}_s}{R_p^2} \tag{9.2}$$

in which the surface diffusivity, $\mathcal{D}_s$, is given by

$$\mathcal{D}_s = 2.65 \times 10^{-4} \exp\left(-\frac{E_a}{\mathcal{R}T_{abs}}\right) \tag{9.3}$$

where E_a is an activation energy, $\mathcal{R}$ is the universal gas constant, and T_{abs} is absolute temperature. Dispersive effects are included in Eqs. 2.4 and 2.5 which are solved numerically, as outlined in Supplementary Information. There is a gratifyingly high degree of consilience between the analytical and numerical solutions of the heat and mass conservation equations, although the techniques used to obtain them are quite different.

The temperature wave is rapidly expelled from the bed, and the time it taken for the moisture wave to break out from the bed is generally technologically important. Figure 9 contrasts the shock front predicted by the equilibrium model, and temperature waves predicted to occur when dispersive effects are included. It is notable that the numerical and the method of characteristic potentials provide the same average speed of the moisture front and wave. Figure 9 shows that the plateau conditions predicted by the equilibrium and numerical models are in very close agreement.

Fig. 9 The effects of the interstitial velocity on the form of the moisture wave. The velocities are 0.1 **a** and 0.2 m/s **b** and the time of operation is 150000 s and 300000 s, respectively. It can be observed that the wave is narrower when the velocity is lower because the beads of silica gel have a longer time to attain equilibrium with their local environment
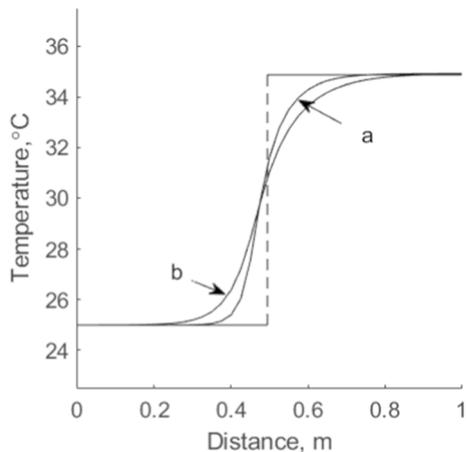
10 Conclusions

Previous authors suggest that the predicted behaviour of ventilated beds of hygroscopic porous media is highly sensitive to the form of isotherm adopted in their analyses. This also applies when isotherms with different mathematical forms are fitted to the same data.

In this work, it is shown that Tóth's isotherm implies that silica gel has a low sorptivity in regions of ventilated beds of silica gel in which the relative humidity is high. As a result, little water is adsorbed by the solid phase and an exchange of sensible heat between the interstitial air and the silica gel plays a dominant role in the rate of cooling. It is shown that as the relative humidity of the interstitial air decreases the sorptivity of silica gel increases and the ratio of the velocities of the interstitial air and that of a moisture wave decreases to a minimum. After attaining a minimum value, the velocity ratio increases as the relative humidity of the interstitial air falls further.

Because the velocity ratio is high when the relative humidity of the interstitial is high, but it subsequently decreases a shock front is predicted to form. This occurs when thermodynamic equilibrium is assumed to exist between the silica gel and the interstitial air. However, when the restriction of equilibrium is relaxed, it is observed that under the conditions studied in this work that a moisture transfer wave forms, the wavelength of which decreases as the interstitial velocity of the air decreases.

An explicit relationship is presented that enables the velocities at which transfer waves propagate along beds of ventilated hygroscopic porous media. The equation contains a term for the derivative of the integral heat of wetting with respect to temperature. The magnitude of this term is typically two orders of magnitude less than other terms in the equation, and its effect may be subsumed in the specific heat of the moist solid phase. However, it has been shown in previous work that if this term is incorrectly formulated it can give rise to significant errors in calculating the velocities of transfer waves. This appears to be the case when calculating the derivative, $\partial H_W / \partial T$, When Tóth's isotherm is used to evaluate $\partial H_W / \partial T$ it appears that the result is an order of magnitude higher than results presented by previous authors.

In this work, the two simultaneous equations that govern heat and mass transfer in ventilated beds of hygroscopic porous media have been solved by the method of characteristic potentials. This enables the equations to be reduced to an equation that assumes the form of the nondispersive transport equation. The method is elaborated in Supplementary Information.

Declarations

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