



**HEAT AND MASS TRANSFER IN HYGROSCOPIC POROUS MEDIA:
ALGEBRAIC RELATIONSHIPS AND MATLAB® SCRIPT**

Graham R. Thorpe
Institute for Sustainable Industries and Liveable Cities
Victoria University, Melbourne, Australia

**HEAT AND MASS TRANSFER IN HYGROSCOPIC POROUS MEDIA:
ALGEBRAIC RELATIONSHIPS AND MATLAB® SCRIPT**

Contents

ABSTRACT.....	2
PREFACE	3
BACKGROUND.....	4
SOME USEFUL IDENTITIES.....	6
ALGEBRAIC RELATIONSHIPS WHEN THE SORBABILITY APPROACHES ZERO AND INFINITY	11
FINDING THE DWELL, OR PLATEAU STATE, P, USING MATLAB®	16
DISCONTINUITIES.....	17
NOMENCLATURE.....	20
REFERENCES.....	21
MATLAB® SCRIPT	22

ABSTRACT

Several authors have suggested that published mathematical descriptions of heat and mass transfer that occur in ventilated beds of hygroscopic porous media are complicated. Furthermore, they are sometimes presented in a terse style. In this work algebraic expressions that govern the rates at which transfer waves propagate through beds of hygroscopic porous media are derived in detail. Expressions that govern the behaviour of ventilated beds of porous media that display no, or a high degree of hygroscopy are similarly derived. The governing equations comprise functions of only three parameters that completely describe systems in which thermodynamic equilibrium between the solid and fluid phases exist, and there are no dispersive processes. Significantly, the work includes an annotated MATLAB[®] script that enables the performance of systems described by Freundlich and Tóth isotherms to be compared. This is in keeping with an objective of the work, namely to make the analysis of heat and mass transfer in beds of hygroscopic media readily accessible to neophytes.

Key words: Porous media, hygroscopic, heat and mass transfer, Freundlich, Tóth

PREFACE

Heat and mass transfer processes that occur in ventilated beds of hygroscopic porous media are governed by mass and energy conservation equations. When referring to their solution, Ingram [1] stated that it is ‘difficult to interpret their physical significance’. Similarly, Close [2] suggests that aspects of the analysis of heat and mass transfer ‘cause difficulties in comprehension’, and Hunter [3] writes that the analysis is ‘necessarily complicated’. Both Close [2] and Hunter [3] noted that empirical equations formulated to capture the sorption properties can give rise to the prediction of anomalous behaviour of ventilated beds of hygroscopic media. Thorpe [4] noted that this occurs when the Tóth isotherm is employed to model the performance of ventilated beds of RD silica gel. This work enables the results of applying Tóth’s and Freundlich’s isotherms to be contrasted.

The theoretical framework of the study was developed by Banks [5], but his presentation is quite terse. In order to help students and researchers new to this field the present work has three objectives, namely to present:

1. Derivations of expressions first stated by Banks [5] that govern the behaviour of ventilated beds of solid desiccants. The expressions account for two extremes, namely when the solids approach being non-hygroscopic, and when they are highly hygroscopic.
2. Derivations of useful algebraic relationships that govern the behaviour of beds of hygroscopic porous media when they are ventilated with air.
3. An annotated MATLAB[®] script that plots the trajectories of temperature in the temperature-humidity plane. The script enables users to extract other data that may be of interest to them.

This work may be used as supplementary material to the following papers:

Thorpe, G. R. (2024) Heat and mass transfer in hygroscopic porous media: Significance of the sorption isotherm presented at the 9th Thermal and Fluids Engineering Conference, 2024 [6].

Thorpe, G. (2023) Heat and Mass Transfer in Hygroscopic Porous Media: Consequences of Invoking Tóth’s Sorption Isotherm. *Transp Porous Med* 148, 137–156 (2023). [4] <https://doi.org/10.1007/s11242-023-01931-7>

Further details can be found in the papers and accompanying supplementary information provided by Thorpe [4] [6] [7]. The author expresses his gratitude to Dr Julian van Leersum for assistance with developing Eqn (29).

Graham Thorpe
Melbourne, Australia

BACKGROUND

When a bed of warm, dry desiccant is ventilated with cool, dry air it is conventionally assumed that two transfer waves traverse the bed, as indicated in Fig 1. Velocities on the slower wave,

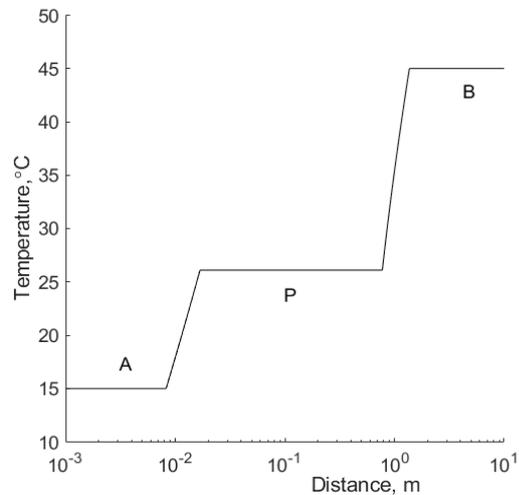


Fig. 1. The initial thermodynamic state of a bed of silica gel is defined by its initial temperature of 45°C, and it is equilibrium with interstitial air that has a humidity of 0.017 kg water/kg dry air, state B. The bed is ventilated with air that has a temperature and humidity of 15°C and 0.01 kg/kg respectively, state A. The plateau state, P, has a temperature and humidity of 26.1°C and 0.00555 kg/kg respectively. The interstitial velocity of air through the bed is 0.1 m/s and after 10,000s operation the distances penetrated trailing and leading edges of the moisture wave, AP, are 8.26 mm and 16.83 mm respectively. The corresponding distances for the temperature wave, PB, are 775 mm and 1369 mm.

AP, are associated with moisture being adsorbed by the hygroscopic medium, and the liberation of heat of sorption reduces the cooling capacity of the interstitial air. Heat and mass transfer are inextricably intertwined, and the slow progress of this wave is associated with the high-density solid phase adsorbing moisture from air that has a low density. The slow moving wave is dubbed the ‘moisture’ wave. According to Banks’ [5] nomenclature, points along the moisture wave lie on a line of constant F_1 . Figure 2 shows loci of points on this wave in the $T-w$ plane.

Heat and mass transfer processes along the faster moving wave, PB, are governed by the solids being cooled by exchanging sensible heat with the interstitial air. The rate of cooling is enhanced because latent heat is extracted from the solid phase because this phase loses water with the passage of the wave. This faster travelling wave is dubbed the ‘temperature’ wave, or lines of constant F_2 in Banks’ [5] nomenclature. Loci in the $T-w$ plane of this wave are depicted in Figure 2.

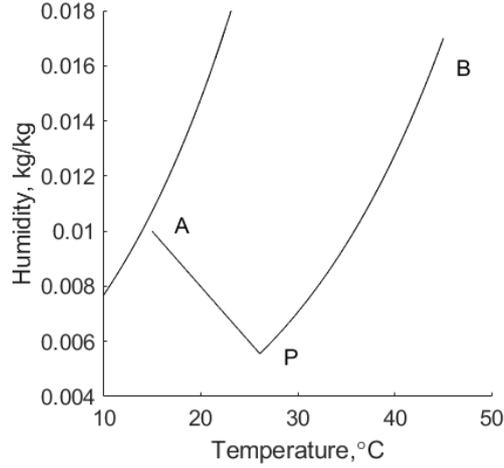


Fig. 2. Lines of constant F_1 and F_2 in the T - w plane for the case considered are shown as AP and PB respectively. The figure also depicts the saturation temperature as a function of humidity.

Figure 2 shows the corresponding lines of constant F_2 and F_2 in the T - w plane. Tangents to these curves are given by

$$-\left(\frac{\partial w}{\partial T}\right)_i = \alpha_i = \frac{(\sigma v + \lambda \alpha_h + \alpha_w) - (-1)^i ((\sigma v + \lambda \alpha_h - \alpha_w)^2 - 4 \alpha_w \lambda \alpha_h)^{0.5}}{2} \quad i = 1, 2 \quad (1)$$

An alternative expression for α_i can be obtained by recognising that $(\sigma v + \lambda \alpha_h + \alpha_w)^2 - 4 \alpha_w \lambda \alpha_h$ can be rearranged to form $(\sigma v + \lambda \alpha_h - \alpha_w)^2 + 4 \alpha_w \sigma v$ so Eqn (1) can be expressed as

$$-\left(\frac{\partial w}{\partial T}\right)_i = \alpha_i = \frac{(\sigma v + \lambda \alpha_h + \alpha_w) - (-1)^i ((\sigma v + \lambda \alpha_h - \alpha_w)^2 + 4 \alpha_w \sigma v)^{0.5}}{2} \quad i = 1, 2 \quad (2)$$

The speeds, \mathcal{V}_i , of points on the transfer waves, F_1 and F_2 . are given by

$$\mathcal{V}_i = \mathcal{A}_i v \quad (3)$$

where \mathcal{A}_i is the ratio of the speed of small changes in F_i on a transport wave to the speed, v , of the interstitial air, \mathcal{A}_i is given by

$$\mathcal{A}_i = \frac{1}{1 + \mu \gamma_i} \quad (4)$$

in which the volume weighted density, μ , is defined by $\mu = (1 - \rho_s \varepsilon) / \rho_a \varepsilon$ and

$$\gamma_i = v^{-1}(\sigma v + \lambda\alpha_h - \alpha_i) \quad (5)$$

γ_i is an analogue of the ratio of the specific heats of the solid and fluid phases in bed of non-hygroscopic material. However, γ_i accounts for exchanges of heat of sorption between the solid and fluid phases which is made explicit by Thorpe [7].

SOME USEFUL IDENTITIES

To show that

$$\frac{\gamma_i}{\sigma} = \frac{\alpha_W}{\alpha_W - \alpha_i} \quad (6)$$

Equation (5) may be expressed in the form

$$\frac{\gamma_i}{\sigma} = 1 - \frac{\alpha_i - \lambda\alpha_h}{\sigma v} \quad (7)$$

which when multiplied by $(\alpha_W - \alpha_i)$ becomes

$$\begin{aligned} \frac{\gamma_i}{\sigma}(\alpha_W - \alpha_i) &= \left(1 - \frac{\alpha_i - \lambda\alpha_h}{\sigma v}\right)(\alpha_W - \alpha_i) \\ &= \alpha_W - \frac{\alpha_i(\alpha_W + \lambda\alpha_h + \sigma v) - \alpha_i^2 - \alpha_W\lambda\alpha_h}{\sigma v} \end{aligned} \quad (8)$$

Let

$$A = \alpha_W + \lambda\alpha_h + \sigma v \quad (9)$$

and

$$C = -4\alpha_W\lambda\alpha_h \quad (10)$$

in which case

$$\alpha_i = \frac{A - (-1)^i(A^2 + C)^{0.5}}{2} \quad (11)$$

which when substituted into Equation (8) enables us to write

$$\frac{\gamma_i}{\sigma}(\alpha_W - \alpha_i) = \alpha_W - \frac{1}{\sigma v} \left\{ A \frac{A - (-1)^i(A^2 + C)^{0.5}}{2} - \left(\frac{A - (-1)^i(A^2 + C)^{0.5}}{2} \right)^2 - \alpha_W\lambda\alpha_h \right\} \quad (12)$$

Consider

$$\begin{aligned}
& A \frac{A - (-1)^i (A^2 + C)^{0.5}}{2} - \left(\frac{A - (-1)^i (A^2 + C)^{0.5}}{2} \right)^2 \\
&= \frac{2A^2 - (-1)^i 2A(A^2 + C)^{0.5} - A^2 + (-1)^i 2A(A^2 + C)^{0.5} - (-1)^{2i} (A^2 + C)}{4} \quad (13)
\end{aligned}$$

Collecting terms in Eqn (13) results in

$$A \frac{A - (-1)^i (A^2 + C)^{0.5}}{2} - \left(\frac{A - (-1)^i (A^2 + C)^{0.5}}{2} \right)^2 = -\frac{C}{4} \quad (14)$$

Substituting Eqn (10) into Eqn (12) we see that the terms in braces sum to zero, hence we obtain

$$\frac{\gamma_i}{\sigma} (\alpha_W - \alpha_i) = \alpha_W \quad (15)$$

or the desired result, Eqn (6).

To show that

$$\frac{\gamma_i}{\sigma} = \frac{\alpha_j - \alpha_W}{\sigma \nu} \quad i, j = 1, 2; \quad i \neq j \quad (16)$$

Retaining the definitions of A and B in equations (9) and (10) enables us to write

$$2\alpha_i = A - (-1)^i (A^2 + C)^{0.5} \quad (17)$$

And from Eqn (5)

$$\alpha_i = \lambda \alpha_h + \sigma \nu - \gamma_i \nu \quad (18)$$

Adding $\alpha_W - \alpha_W$ to Eqn (18) gives

$$\alpha_i = \lambda \alpha_h + \sigma \nu + \alpha_W - \alpha_W - \gamma_i \nu \quad (19)$$

or

$$\alpha_i = A - \alpha_W - \gamma_i \nu \quad (20)$$

Hence

$$2\alpha_i = 2A - 2\alpha_W - 2\gamma_i \nu \quad (21)$$

Making use of Eqn (17) in Eqn (21) yields

$$A + (-1)^i (A^2 + C)^{0.5} - 2\alpha_W - 2\gamma_i \nu = 0 \quad (22)$$

Observe that $+(-1)^i = -(-1)^j$ when $i, j = 1, 2$ and $i \neq j$ hence

$$2\alpha_j = A + (-1)^i(A^2 + C)^{0.5} \quad (23)$$

Eqn (21) becomes

$$2\alpha_j - 2\alpha_w - 2\gamma_i\nu = 0 \quad (24)$$

which when divided by σ can be written as

$$\frac{\gamma_i}{\sigma} = \frac{\alpha_j - \alpha_w}{\sigma\nu} \quad (25)$$

which is the desired result.

To show that

$$\alpha_1\alpha_2 = \alpha_w\lambda\alpha_h \quad (26)$$

Firstly, we determine an expression for $\alpha_1\alpha_2$ in terms of the nomenclature introduced in equation (11) and write

$$\alpha_1\alpha_2 = \frac{(A - (-1)^1(A^2 + C)^{0.5})(A - (-1)^2(A^2 + C)^{0.5})}{4} \quad (27)$$

$$= -\frac{C}{4} \quad (28)$$

Hence from the definition of C in Equation (10) we find the required result, namely Eqn (26).

To show that

$$\alpha_1\alpha_2 = \alpha_r\alpha_a \quad (29)$$

in which α_a is defined as

$$\alpha_a = \left(\frac{\partial T}{\partial w}\right)_a \quad (30)$$

where the subscript 'a' signifies that the moist air is flowing along an adiabatic saturator, and it leaves with a temperature, a.

$$\alpha_r = \left(\frac{\partial T}{\partial w}\right)_r \quad (31)$$

where the subscript 'r' signifies a line of constant relative humidity in the T - w plane.

Eqn (29) is a remarkable relationship between the slopes of lines of constant F_i and the thermodynamic properties of moist air, and it was stated without proof by Banks [5].

Over a small element of length in an adiabatic saturator, $m_a dw$ water evaporates into the air stream. This increases its humidity by an amount, dw , and so that the specific enthalpy of the air stream increases by $h_v dw$. Hence, all other things being equal we have

$$\left(\frac{\partial h + h_v dw}{\partial w}\right)_a = \left(\frac{\partial h}{\partial w}\right)_a + h_v = \left(\frac{\partial h}{\partial w}\right)_T \quad (32)$$

Now

$$dh = \left(\frac{\partial h}{\partial w}\right)_T dw + \left(\frac{\partial h}{\partial T}\right)_w dT \quad (33)$$

from which we obtain

$$\left(\frac{\partial h}{\partial w}\right)_a = \left(\frac{\partial h}{\partial w}\right)_T \left(\frac{\partial w}{\partial w}\right)_a + \left(\frac{\partial h}{\partial T}\right)_w \left(\frac{\partial T}{\partial w}\right)_a \quad (34)$$

or

$$\left(\frac{\partial h}{\partial w}\right)_a = \left(\frac{\partial h}{\partial w}\right)_T + \left(\frac{\partial h}{\partial T}\right)_w \left(\frac{\partial T}{\partial w}\right)_a \quad (35)$$

If h is constant such that $dh = 0$ we obtain from Eqn (33)

$$\left(\frac{\partial h}{\partial T}\right)_w = -\frac{\left(\frac{\partial h}{\partial w}\right)_T}{\left(\frac{\partial T}{\partial w}\right)_h} \quad (36)$$

By inspection of Eqn (32), we observe that

$$-h_v = \left(\frac{\partial h}{\partial T}\right)_w \left(\frac{\partial T}{\partial w}\right)_a \quad (37)$$

Inserting Eqn (36) into Eqn (37) yields

$$-h_v = -\frac{\left(\frac{\partial h}{\partial w}\right)_T}{\left(\frac{\partial T}{\partial w}\right)_h} \left(\frac{\partial T}{\partial w}\right)_a = -\left(\frac{\partial h}{\partial w}\right)_T \frac{\alpha_a}{\alpha_h} \quad (38)$$

We wish to demonstrate that $\alpha_1 \alpha_2 = \alpha_r \alpha_a$, which from Eqn (26) is equivalent to showing that

$$\alpha_r \alpha_a = \alpha_w \lambda \alpha_h \quad (39)$$

At this point we make use of identities stated by Banks [5], and developed in more detail in the Supplementary Information that accompanies Thorpe [4]. (Note that the latter work is available Open Access). We define the function, ψ , by

$$\psi = \frac{\left(\frac{\partial h}{\partial w}\right)_T}{h_v} \quad (40)$$

Hence from Eqns (38) and (40)

$$\alpha_a = -\frac{\left(\frac{\partial T}{\partial w}\right)_h}{\psi} = \frac{\alpha_h}{\psi} \quad (41)$$

It is demonstrated by Thorpe [4] (after being stated by Banks [5]) that

$$\alpha_r = -\frac{\Omega}{wS} \quad (42)$$

and that

$$\alpha_w = -\frac{\Omega}{w\lambda\psi S} \quad (43]$$

From Eqns (41) and (42)

$$\alpha_a\alpha_r = -\frac{\alpha_h}{\psi} \frac{\Omega}{wS} \quad (44)$$

This may be expressed as

$$\alpha_a\alpha_r = \alpha_w\lambda\alpha_h \quad (45)$$

which is equivalent to the desired result, namely Eqn (29).

To show that

$$\gamma_1\gamma_2 = -a_w\sigma/v \equiv \sigma\beta \quad (46)$$

From Eqn (7) we have

$$\frac{\gamma_1\gamma_2}{\sigma^2} = \left(1 - \frac{\alpha_1 - \lambda\alpha_h}{\sigma v}\right) \left(1 - \frac{\alpha_2 - \lambda\alpha_h}{\sigma v}\right) \quad (43)$$

which when expanded can be expressed as

$$\gamma_1\gamma_2 = \left\{ \sigma^2 - \frac{\sigma(\alpha_1 - \lambda\alpha_h)}{v} - \frac{\sigma(\alpha_2 - \lambda\alpha_h)}{v} + \frac{\alpha_1\alpha_2 - \lambda\alpha_h(\alpha_1 + \alpha_2) + (\lambda\alpha_h)^2}{v^2} \right\} \quad (44)$$

By making use of Eqn (26) for $\alpha_1\alpha_2$ and recognising that

$$\alpha_1 + \alpha_2 = \frac{A - (-1)(A^2 + C)^{0.5} + A - (-1)^2(A^2 + C)^{0.5}}{2} \quad (45)$$

Hence

$$\alpha_1 + \alpha_2 = A = \alpha_w + \lambda\alpha_h + \sigma v \quad (46)$$

Substituting Eqn (26) and Eqn (46) into Eqn (44) yields

$$\gamma_1\gamma_2 = \left\{ \sigma^2 - \frac{\sigma A}{\nu} + \frac{2\sigma\lambda\alpha_h}{\nu} + \frac{\alpha_w\lambda\alpha_h - A\lambda\alpha_h + (\lambda\alpha_h)^2}{\nu^2} \right\} \quad (47)$$

which simplifies to

$$\gamma_1\gamma_2 = -a_w\sigma/\nu \quad (48)$$

The sorbability, β , can be expressed as $-a_w/\nu$ [4],[5] hence

$$\gamma_1\gamma_2 = \sigma\beta \quad (49)$$

Eqn (48) and Eqn (49) furnish the desired results. It should be noted that the definition of sorbability, β , is

$$\beta = \left(\frac{\partial W}{\partial w} \right)_T \quad (50)$$

ALGEBRAIC RELATIONSHIPS WHEN THE SORBABILITY APPROACHES ZERO AND INFINITY

Intuitive reasoning

A bed of porous medium containing a non-hygroscopic solid lies at one end of a continuum. At the other end is a bed comprising an idealised solid that adsorbs an infinite quantity of sorbate. Real hygroscopic systems fall somewhere within these two extrema. Recognising the behaviour at these extreme provides useful insights into the heat and mass transfer processes that occur in ventilated beds of hygroscopic porous media.

We can intuitively predict the behaviour of a system comprising a non-hygroscopic medium. For example, if we consider such a bed that is ventilated with air at a constant state and which has come to a quasi-steady state and we impose a step-change on the specific humidity and temperature of the air entering the bed we can intuit the following:

- i. Heat and mass transfer processes are decoupled.
- ii. It is possible that air entering a bed of non-hygroscopic medium has a different humidity from the interstitial air within the bed. A moisture front will form, with air on the downstream side having the initial humidity within the bed. It will be replaced with air that has the humidity of the air entering the system. The front travel with the velocity of the interstitial air.

- iii. A temperature wave will traverse the bed, and in this case $\gamma = \sigma$, the ratio of the specific heats of the solid phase and moist air. Hence from Eqn (4) the velocity of the ‘temperature’ wave, \mathcal{V} , is

$$\mathcal{V} = \frac{v}{1 + \mu\sigma} \quad (51)$$

In the case of a highly sorbent solids such that $\beta = (\partial W / \partial w)_T \rightarrow \infty$ we might intuitively expect that:

- iv. The speed of a moisture transfer wave is zero, because as moisture vapour in the interstitial air flows towards a point in the bed of porous hygroscopic medium it is completely adsorbed by the solid. As a result, we anticipate that $\gamma_2 \rightarrow \infty$ and $A_2 \rightarrow 0$.
- v. The total amount of heat liberated by water vapour that is adsorbed by the highly ($\beta \rightarrow \infty$) hygroscopic is much greater than any changes of enthalpy of the solid phase. As a result, the heat liberated by the moisture being adsorbed is used solely for increasing the sensible heat of the interstitial air. Hence, the behaviour of the air tends to follow that of the adiabatic wet bulb temperature, which is close to that of a line of constant enthalpy on a psychrometric chart. In other words, lines of constant F_1 are similar to lines of constant enthalpy of moist air.
- vi. We have noted in vi above that the enthalpy of the bed across a temperature wave changes, but the moisture content remains constant. The rate of cooling of a desiccant material by the exchange of sensible heat between cool air and warmer solids is enhanced by an exchange of latent heat. The latter arises because water evaporates from the solid phase. We can state that $\gamma_1 < \sigma$.
- vii. The sorbability, β , of a hygroscopic material is defined by Eqn (50) which indicates the rate at which the moisture content of a substance increases with the humidity of the interstitial air. The difference in the humidity of air at states P and B along a temperature wave approaches a constant value as the sorbability of the solid increases. *Ceteris paribus*, the amount of water removed from the solid phase tends to a constant value. However, as the sorbability increases so does the amount of water adsorbed, hence the removal of a fixed amount of water across the temperature wave becomes an increasingly small fraction of the total adsorbed moisture. This leads to the moisture content of the solids tending to being constant along a temperature wave as the sorbability increases.

A more rigorous approach

The intuitive reasoning presented above has been put on a sound footing by Banks [5]. An objective of the present work is to fill in some of the algebraic details of his analysis. The equations that govern α_i and γ_i , Eqns (1), (2) and (5) do not rely on any specific physical properties of the sorbate/sorbent system. They are quite general. However, they govern the quantities F_i and A_i that specify the performance of a ventilated sorbent/sorbate system. Lines of constant F_i determine the thermodynamic state paths of a system, and the values of A_i determine the speed at which changes in the thermodynamic state are transported. As pointed out by Banks [5] F_i and A_i depend on three terms, namely σv , $\lambda\alpha_h$ and α_w . A defining property of a sorbing medium is its sorbability, β , and from Eqns (48) and (49) we note that

$$\frac{\sigma v}{\alpha_w} = -\frac{\sigma}{\beta} \quad (52)$$

Hence, if the sorbability is low then σv dominates α_w , and vice versa if the sorbability is high. After the manner of Banks [5] we shall consider the extrema of α_i and γ_i/σ as the sorbability tends to zero (the non-hygroscopic case) and to infinity (the idealised infinitely sorbing case). The behaviour of real systems lies in this range.

Low sorbability, $\beta \rightarrow 0$

In this case $\sigma v \rightarrow \infty$, hence $\lambda\alpha_h$ and α_w become negligibly small compared with σv in Eqns (1) and (2) from which we conclude that

$$\alpha_1 \rightarrow \sigma v \rightarrow \infty \quad (53)$$

Hence $(\partial T/\partial w)_{F_1} \rightarrow -\infty$, or $(\partial w/\partial T)_{F_1} \rightarrow 0$ which indicates that lines of constant F_1 tend to lines of constant w as the sorbent becomes non-hygroscopic.

When we divide the numerator and denominator of Eqn (6) by α_w there obtains

$$\frac{\gamma_1}{\sigma} = \frac{1}{1 - \frac{\alpha_1}{\alpha_w}} \rightarrow \frac{\alpha_w}{\sigma v} \text{ as } \beta \rightarrow 0 \text{ and } v \rightarrow \infty \quad (54)$$

This implies that as the sorbability β tends to zero, $\gamma_1 \rightarrow 0$. As a result, we observe from Equation (4) that $\mathcal{A}_1 \rightarrow 1$. Hence, changes in F_2 , along lines of constant F_1 tend to travel with same velocity of the fluid. This was presaged in the section on the non-hygroscopic/hygroscopic continuum.

Turning our attention to α_2 and γ_2 we see that if $\sigma\nu \gg \alpha_w$ and $\sigma\nu \gg \lambda\alpha_h$ then from Eqn (1) we have

$$2\alpha_2 \approx \sigma\nu - ((\sigma\nu)^2 - 4\alpha_w\sigma\nu)^{0.5} = \sigma\nu[1 - (1 - 4\alpha_w/\sigma\nu)^{0.5}] \quad (55)$$

Expanding $(1 - 4\alpha_w/\sigma\nu)^{0.5}$ in terms of a Maclaurin series, and recognising that $4\alpha_w/\sigma\nu \ll 1$ enables us write

$$(1 - 4\alpha_w/\sigma\nu)^{0.5} \approx 1 - 2\alpha_w/\sigma\nu \quad (56)$$

Which when substituted into Equation (55) results in

$$\alpha_2 = \frac{\alpha_w\lambda\alpha_h}{\sigma\nu} \rightarrow 0 \text{ as } \nu \rightarrow \infty \quad (57)$$

Hence $(\partial T/\partial w)_{F_2} \rightarrow 0$ in the case of non-sorbent materials which implies that lines of constant F_2 are coincident with lines of constant temperature, T .

We determine γ_2/σ by substituting (57) into (54) when $i = 2$ gives the result

$$\frac{\gamma_2}{\sigma} = 1 - \frac{\alpha_w\lambda\alpha_h/\sigma\nu - \lambda\alpha_h}{\sigma\nu} \rightarrow 1 \text{ as } \nu \rightarrow \infty \quad (58)$$

Hence $\gamma_2 \rightarrow \sigma$. This is in keeping with our intuitive reasoning that the equivalent of an F_2 wave in a non-hygroscopic porous medium, a temperature wave, would travel with a velocity governed by

$$\mathcal{A}_2 = \frac{1}{1 + \mu\sigma} \quad (59)$$

High sorbability, $\beta \rightarrow \infty$

We now turn our attention to the case in which the sorbability is high, i.e. $\beta \rightarrow \infty$ and $\nu \rightarrow 0$. In this case we observe from Eqn (2) that

$$2\alpha_1 \rightarrow (\lambda\alpha_h + \alpha_w) - (-1)^1((\lambda\alpha_h - \alpha_w)^2)^{0.5} \text{ as } \nu \rightarrow 0 \quad (60)$$

Hence $\alpha_1 = -(\partial T/\partial w)_{F_1} \rightarrow \lambda\alpha_h$. From the definitions of λ and α_h , Eqns (6.12) and (6.13) in the Supplementary Information respectively accompanying [4]

$$\lambda\alpha_h = \left\{ 1 - \frac{(\partial H/\partial W)_T}{(\partial h/\partial w)_T} \right\} \cdot \frac{(\partial h/\partial w)_T}{(\partial h/\partial T)_w} \quad (61)$$

so

$$\lambda\alpha_h = \frac{\left\{ \left(\frac{\partial h}{\partial w} \right)_T - \left(\frac{\partial H}{\partial W} \right)_T \right\}}{\left(\frac{\partial h}{\partial T} \right)_w} \quad (62)$$

This takes the form of Eqn (7.3.4) derived in the Supplementary Information presented in [4] as

$$\lambda\alpha_h = \frac{h_s}{c_a + w \left(\left. \frac{\partial \lambda_v}{\partial T} \right|_T + c_w \right)} \quad (63)$$

i.e.

$$\left(\frac{\partial T}{\partial w} \right)_{F_i} = - \frac{h_s}{c_a + w \left(\left. \frac{\partial \lambda_v}{\partial T} \right|_T + c_w \right)} \quad (64)$$

A line of constant enthalpy on a T - w plot is defined as

$$\left(\frac{\partial T}{\partial w} \right)_h = - \frac{\left(\frac{\partial h}{\partial w} \right)_T}{\left(\frac{\partial h}{\partial T} \right)_w} = - \frac{c_w(T - T^o) + h_v}{c_a + w \left(\left. \frac{\partial \lambda_v}{\partial T} \right|_T + c_w \right)} \quad (65)$$

Now $c_w(T - T^o) + h_v \cong h_s$ (depending on the selection of the reference temperature, T^o , which is typically 0°C). Hence, it is observed that when hygroscopic materials have a high sorbability a line of constant F_1 is closely coincident with a line of constant enthalpy.

To determine γ_1 we divide the numerator and denominator of Eqn (6) by α_w , and make use of Eqn (60) to obtain

$$\frac{\gamma_1}{\sigma} = \frac{1}{1 - \frac{\alpha_1}{\alpha_w}} = \left(1 - \frac{\lambda\alpha_h}{\alpha_w} \right)^{-1} \text{ as } \beta \rightarrow \infty \quad (66)$$

The numerator of Eqn (63) is the differential heat of sorption, h_s , of water by silica gel, and we know that $h_s > 0$. The denominator of Eqn (63) is the differential of the enthalpy of moist air, and this is greater than zero. As a result, we have

$$\lambda\alpha_h > 0 \quad (67)$$

If we consider a line of constant moisture content, W , of silica gel in the T - w plane the humidity of the air, w , increases monotonically with temperature, T , i.e. $(\partial T / \partial w)_W > 0$.

The definition of α_W is

$$\alpha_W = -\left(\frac{\partial T}{\partial W}\right)_W \quad (68)$$

hence $\alpha_W < 0$. We can deduce from the above reasoning that $(1 - \lambda\alpha_h/\alpha_W) > 1$ so from Eqn (66) we find that

$$\gamma_1 < \sigma \quad (69)$$

The physical consequence of this result is that the speeds of F_1 waves through beds of highly adsorbent porous media are greater than those through beds in which heat transfer alone occurs.

When $\beta \rightarrow \infty$ and $\nu \rightarrow 0$ is quite trivial to determine an expression for α_2 from Eqn (2), but for completeness we note that

$$2\alpha_2 = \lambda\alpha_h + \alpha_W - (-1)^2(\lambda\alpha_h - \alpha_W) \quad (70)$$

from which $\alpha_2 = \alpha_W$. From the definition of α_W it follows that a line of constant F_2 becomes coincident with a line of constant moisture content, W , on a T - w plot as the sorbability of the sorbent increases.

The determination of γ_2 as $\beta \rightarrow \infty$ is readily determined from Eqn (25) and recognising that $\alpha_1 \rightarrow \lambda\alpha_h$. Re-arranging Eqn (25) leads to

$$\gamma_2 = \frac{1}{\nu}(\alpha_1 - \alpha_W) \quad (71)$$

or

$$\gamma_2 = \beta \left(1 - \frac{\lambda\alpha_h}{\alpha_W}\right) \quad (72)$$

We have shown that $\lambda\alpha_h/\alpha_W > 0$ hence $\gamma_2 \rightarrow \infty$ as $\beta \rightarrow \infty$. As a result, the speed of passage of an F_2 wave is infinitely small in hygroscopic media the sorbability of which approaches infinity.

FINDING THE DWELL, OR PLATEAU STATE, P, USING MATLAB®

The user specifies:

- a. The thermodynamic state of the air entering the system, shown as A, in Figure 1
- b. The initial state of the bed. This is also specified by the user in terms of its initial temperature and the humidity of interstitial air in equilibrium with the solid, state B.
- c. The isotherm to be used by specifying `model`. If `model = 1` the Tóth isotherm invoked, otherwise the Freundlich isotherm is invoked if `model = 2`.

The user should be aware that the MATLAB[®] script is designed for research purposes, and to enable readers to reproduce the results presented by Thorpe [4]. The script does not have checks to ensure that the operating conditions result in the formation of shock fronts, or otherwise. It is operational under the default conditions supplied.

The objective is to make use of the above-mentioned thermodynamic states as initial conditions, and integrate Eqs (1) and (2) to the point P at which the lines of constant F_1 and F_2 intersect. This is the plateau state.

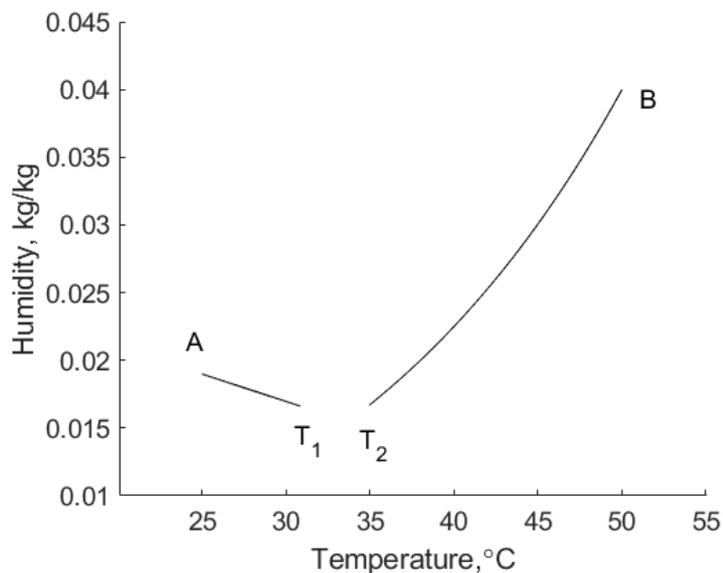


Figure 3. The thermodynamic state, A, of the air entering the bed is specified by the user and it is specified by T_{in} and w_{in} . Similarly, the initial state of the interstitial air in the bed of hygroscopic medium at B is specified by the user.

With A and B known Eqns (1) and (2) are integrated to an upper integration limit of humidity, w_P . The integration is carried out by means of a Runge-Kutta algorithm out using `dTbydw_RK(w, T, model, i)`. `model` specifies which isotherm is to be used, and `i` refers to lines of constant F . This parameter, `i`, is built into the script, and the user does not need to manipulate it.

The idea is to determine a value of w_P such that the two lines intersect, and $\text{abs}(T_1 - T_2)$ is minimised. The minimisation is achieved using the `fminsearch` function.

DISCONTINUITIES

Thorpe [4] demonstrates that a discontinuity may form when the velocity of the trailing edge of a transfer wave is higher than its leading edge. This situation is expected to occur when cool

moist silica gel is dried by ventilating them with warm air that has a low relative humidity [8]. However, shock fronts are predicted to form when the Tóth isotherm is invoked to predict the performance when warm, dry silica gel is ventilated with cool, moist air.

Consider the ‘shock’ wave propagating with a velocity, \mathcal{V} , through a bed of silica gel as shown in Fig 4. Properties such as the humidity, w , of the interstitial air, and moisture content, W , of the silica gel display discontinuities Δw and ΔW respectively across the moving front. The relative velocity of the interstitial air sensed by an observer travelling with the shock front is $v - \mathcal{V}$, and the humidity entering the shock front from upstream is w . The observer also perceives that the silica gel is approaching the shock front with a velocity of \mathcal{V} , and its moisture content is $W + \Delta W$. The observer, moving with the shock front, senses that the silica gel is flowing upstream at a velocity \mathcal{V} , and with a moisture content, W . Air with humidity $w + \Delta w$ is perceived by the observer to be travelling downstream of shock with a velocity $v - \mathcal{V}$ relative to the front. Since moisture is conserved across the front we have

$$\begin{array}{l} \text{Rate of moisture approaching} \\ \text{the discontinuity} \end{array} = \begin{array}{l} \text{Rate of moisture leaving} \\ \text{the discontinuity} \end{array}$$

$$\rho_a \varepsilon (v - \mathcal{V}) w + \mathcal{V} \rho_s (1 - \varepsilon) (W + \Delta W) = \rho_a \varepsilon (v - \mathcal{V}) (w + \Delta w) + \mathcal{V} \rho_s (1 - \varepsilon) W \quad (73)$$

Collecting terms

$$\mathcal{V} (\rho_s (1 - \varepsilon) \Delta W + \rho_a \varepsilon \Delta w) = \rho_a \varepsilon v \Delta w \quad (74)$$

so the speed of the front is given by

$$\mathcal{V} = \frac{v}{1 + \mu \frac{\Delta W}{\Delta w}} \quad (75)$$

where

$$\mu = \frac{\rho_s (1 - \varepsilon)}{\rho_a \varepsilon} \quad (76)$$

The system portrayed in Fig 4 is considered to be adiabatic. Hence, the conservation of enthalpy is accounted for by replacing w and W with h and H respectively, in which case

$$\mathcal{V} = \frac{v}{1 + \mu \frac{\Delta H}{\Delta h}} \quad (77)$$

Comparing Eqns (75) and (77) enables us to write

$$\frac{\Delta H}{\Delta h} = \frac{\Delta W}{\Delta w} \quad (78)$$

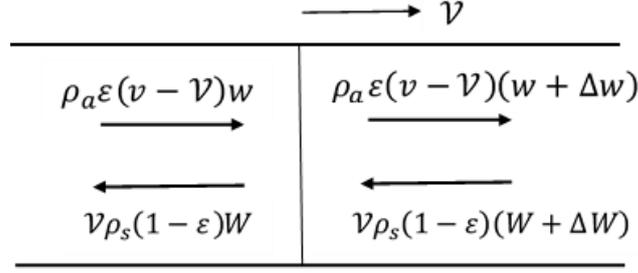


Fig. 4. A bed of silica gel is ventilated with air that has a velocity v , and a shock wave propagates through a bed with a velocity \mathcal{V} . Hence the relative velocity of the air flowing through the discontinuity is $v - \mathcal{V}$. Upstream of the shock, the humidity of the air is w , and that downstream is $w + \Delta w$. To an observer travelling with the shock wave, it appears that silica gel with a moisture content $W + \Delta W$ is approaching the shock front with a velocity \mathcal{V} , whilst it leaves upstream with a moisture content W .

Conservation equations across a shock front

If we define the discontinuities across the shock front that forms between the air inlet and the plateau state

$$\Delta H = H_p - H_{inlet}$$

$$\Delta h = h_p - h_{inlet}$$

$$\Delta W = W_p - W_{inlet}$$

$$\Delta w = w_p - w_{inlet}$$

we are able to 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 $inlet$ respectively, thus

$$\Delta h = c_a(T_p - T_{inlet}) + c_w(w_p T_p - w_{inlet} T_{inlet}) + w_p h_v|_p - w_{in} h_v|_{inlet} \quad (79)$$

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

$$\Delta H = c_s(T_p - T_{inlet}) + c_w(W_p T_p - W_{in} T_{inlet}) + H_W|_p - H_W|_{inlet} \quad (80)$$

Cross multiplying Eqn (78), and to ensure it is satisfied we define a function

$$\phi(T_p, w_p) = \Delta h \Delta W - \Delta H \Delta w \quad (81)$$

and search for values of T_p and w_p such that $\text{abs}(\phi(T_p, w_p))$ approaches zero to within a pre-defined tolerance. The function used to determine $\phi(T_p, w_p)$ is `Obj_fn_Shock_ToTh`

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

$$\left(\frac{\partial T}{\partial w}\right)_{F_2} = -\alpha_2 \quad (82)$$

The integration is carried out in the MATLAB script by `dTbydw_RK_ToTh` and w_p is adjusted by `fminsearch` until $\phi(T_p, w_p)$ approaches zero, within the default limit set by MATLAB.

Physical properties used in the MATLAB script are based on those presented by Chua et al. [9]

NOMENCLATURE

\mathcal{A}	Ratio of velocities	t	Time, s
c_a	Specific heat of dry air, J (kg °C) ⁻¹	T	Temperature, °C
c_s	Specific heat silica gel, J (kg °C) ⁻¹	T^o	Reference temperature, °C
c_w	Specific heat of liquid water, J (kg °C) ⁻¹	T_{abs}	Absolute temperature, K
F	Characteristic potential	v	Mean interstitial velocity, m s ⁻¹
h	Specific enthalpy of air, J (kg dry air) ⁻¹	\mathcal{V}	Velocity of a transfer wave, m s ⁻¹
h_s	Heat of sorption, J kg ⁻¹	w	Specific humidity of air, kg.kg ⁻¹
h_v	Latent heat of vaporisation of water, J kg ⁻¹	W	Moisture content of silica gel, kg.kg ⁻¹
h_w	Isothermal differential heat of wetting, J kg ⁻¹	W_0	Empirical constant, kg.kg ⁻¹
H	Specific enthalpy of moist solid, J (kg dry) ⁻¹	W_m	Empirical constant, kg.kg ⁻¹
H_W	Integral heat of wetting, J kg ⁻¹	x	Distance along the bed, m
K_0	Constant in Tóth's sorption isotherm, Pa ⁻¹	Greek symbols	
K_p	A function of temperature	α_h	$-(\partial T/\partial w)_h, ^\circ\text{C}$
p	Vapour pressure of water, Pa	α_i	$-(\partial T/\partial w)_{F_i}, i = 1, 2, ^\circ\text{C}$
p_s	Saturation vapour pressure of water, Pa	α_w	$-(\partial T/\partial w)_w, ^\circ\text{C}$
p_v	Vapour pressure of water, Pa	β	Sorbability $(\partial W/\partial w)_T$
p_{atm}	Atmospheric pressure, Pa	ε	Void fraction of the silica gel bed
q	Tóth constant	γ	Ratio of effective specific heats
r	Relative humidity of air	λ	$1 - (\partial H/\partial W)_T/(\partial h/\partial w)_T$
\mathcal{R}_v	Gas constant for water, J.(kg K) ⁻¹	μ	Volume-weighted ratio of solids and air
		ν	$-(\partial T/\partial W)_w, ^\circ\text{C}$
		ρ_a	Density of dry air, kg m ⁻³
		ρ_s	Density of dry silica gel, kg m ⁻³
		σ	Ratio of specific heats
		Subscript	
		i, j	Designates the transfer wave

REFERENCES

- [1] Ingram, G. W.: Solution of grain cooling and drying problems by the method of characteristics in comparison with finite difference solutions. *Journal of Agricultural Engineering Research* 24(3), 219-232 (1979). [https://doi.org/10.1016/0021-8634\(79\)90065-9](https://doi.org/10.1016/0021-8634(79)90065-9)
- [2] Close, D. J.: Characteristic potentials for coupled heat and mass transfer processes. *Chemical Engineering Science*, 26(7), 1098-1102 (1983) [https://doi.org/10.1016/S0017-9310\(83\)80138-0](https://doi.org/10.1016/S0017-9310(83)80138-0)
- [3] Hunter, A. J.: Temperature and moisture front movement in an aerated seed bulk. *Journal of Agricultural Engineering Research*, 40, 113-127 (1988). [https://doi.org/10.1016/0021-8634\(88\)90109-6](https://doi.org/10.1016/0021-8634(88)90109-6)
- [4] Thorpe, G. (2023) Heat and Mass Transfer in Hygroscopic Porous Media: Consequences of Invoking Tóth's Sorption Isotherm. *Transp Porous Med* 148, 137–156 (2023). [4] <https://doi.org/10.1007/s11242-023-01931-7>
- [5] Banks, P.J.: Coupled equilibrium heat and single adsorbate transfer in fluid flow through a porous medium - I Characteristic potential and specific capacity ratios. *Chemical Engineering Science*, 27(5), 1143-1155 (1972). [https://doi.org/10.1016/0009-2509\(72\)80025-3](https://doi.org/10.1016/0009-2509(72)80025-3)
- [6] Thorpe, G. R. (2024) Heat and mass transfer in hygroscopic porous media: Significance of the sorption isotherm presented at the 9th Thermal and Fluids Engineering Conference, 2024.
- [7] Thorpe, G. R. (2022). On the rate of cooling of aerated food grains. *Biosystems Engineering*, Volume 222, October 2022, Pages 106-116. <https://doi.org/10.1016/j.biosystemseng.2022.08.001>
- [8] Close, D. J. and Banks, P. J.: (1972) Coupled equilibrium heat and single adsorbate transfer in fluid flow through a porous medium – II Predictions for a silica-gel air-drier using characteristic charts. *Chemical Engineering Science*, 27, 1157-1169 (1972) [https://doi.org/10.1016/0009-2509\(72\)80026-5](https://doi.org/10.1016/0009-2509(72)80026-5)
- [9] Chua, H.T., Ng, K.C., Chakraborty, A., Oo, N.M. and Othman, M.A.: Adsorption characteristics of silica gel+ water systems. *Journal of Chemical & Engineering Data*, 47(5), 1177-1181 (2002). <https://doi.org/10.1021/jc0255067>

MATLAB® SCRIPT

```
% To find the dwell state of ventilated beds of
% hygroscopic porous media and trajectories of
% heat and mass transfer waves in the temperature-humidity (T-w) plane.

% G. R. Thorpe
% Institute for Sustainable Industries and Liveable Cities
% Victoria University
% Melbourne, Australia

% DISCLAIMER

% This script is written for scientific research and teaching purposes
% only. The author does not warrant that the script is free from
% errors. The software is offered with the intention that it assists
% researchers. They are solely responsible for the use to which any
% results are put.

% LIMITATIONS

% This script has been developed in the interest of transparency to
% demonstrate how data presented by Thorpe (2024) are obtained. It is
% anticipated that the analysis is likely to be robust over a
% wide range of operating conditions. However, adjustments
% to graphical outputs may have to be made to ensure that the data
% can be portrayed properly. It does not have GUI, but the script
% is easy to use.

% REFERENCES

% SI refers to Supplementary Information provided in [4]
% Thorpe, G., 2023.
% "Heat and Mass Transfer in Hygroscopic Porous Media:
% Consequences of Invoking Tóth's Sorption Isotherm."
% Transport in Porous Media, 148(1), pp.137-156

% ASTFE 24 refers to HEAT AND MASS TRANSFER IN HYGROSCOPIC POROUS MEDIA:
% SIGNIFICANCE OF THE SORPTION ISOTHERM, ASTFE CONFERENCE 2024.

clear all
global T_dwell w1 w2 T1 T2
format long
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

% SPECIFY THE CONDITIONS UNDER WHICH THE SYSTEM OPERATES

% Condition of the air entering the bed:
T_in=25; % Inlet temperature, deg. C
w_in=0.019; % Humidity of air

% Initial state of the bed
T_initial=50; % Initial temperature of the silica gel
w_initial=0.04; % Humidity of air inequilibrium with the solid

% CHOOSE THE SORPTION ISOTHERM TO BE INVESTIGATED
```

```

% model = 1      Toth
% model = 2      Freundlich

model=2;

%
% End of main script
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Toth isotherm with discontinuity
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
w0=0.007; % Estimated value of the humidity at dwell/plateau state.
if model == 1

% This function is called when the governing equations are discontinuous,
% and a shock front forms

% Note that for a shock front to form the velocity ratio at
% the trailing edge must be greater than at the leading edge.

[w_dwell]=fminsearch(@(w_dwell)
dwell_find_shock_Toth(w_dwell,T_in,w_in,T_initial, ...
w_initial,model),w0);

% Plot results in the T-w plane
Toth_plots(w_dwell,T_dwell,w_in,T_in);

end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Freundlich isotherm
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
if model == 2
% This function is called when the governing equations are continuous.
% fminsearch is called to estimate the value of wP, the value of the
% humidity at the dwell, or plateau state. This is achieved by
% integrating SI 6.2.1 along lines of constant F1 and F2 and finding
% the value of wP when the two lines intersect, i.e. when the
% temperatures at the end of each line are equal. To labour a point at
% the intersection of the two lines the humidities and temperatures
% are equal.

[w_dwell]=fminsearch(@(w_dwell) dwell_find_Freundlich(w_dwell,T_in, ...
w_in,T_initial,w_initial,model),w0);

% Plot results in the T-w plane
Freundlich_plots(w_dwell,T_dwell,w_in,T_in,w_initial,T_initial)
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% End of main program %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

function [hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
% Physical properties of silica gel/air/water system

hv0 = 2500900;
dhvdT = -2376.2;

```

```

ca = 1004.8;
cw = 4186.8;
cs = 921;
N = 0.622;
pt = 101325;
rho = 1.169;
eps = 0.4;
P = 1158.0;
mu = P*(1-eps)/(rho*eps);
end

```

```

function [T_diff] = dwell_find_Freundlich(wP, T_in, w_in, T_initial,
w_initial,model)
global T_dwell w1 w2 T1 T2
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

```

```

% This function integrates Eqn (1) of this work. The limits of
% integration are w0 to wP. In the case of the line of constant F1,
% the moisture wave, the initial humidity, w0, and temperature of
% the air entering the bed of silica gel and the temperature are
% w0=w_in and T0=T_in.
% Along the line of constant F2, the initial conditions are w0=w_initial
% and T0=T_initial.
% At the end of the two integrations the humidity is set to wP. However,
% the corresponding temperature are TF1 and TF2. At the point of
% intesection of the F1 and F2 lines these temperatures are equal.
% Hence to objective is to search for a value of wP that ensures
% that abs(TF1-TF2) < some limit. In this case it is the default value
% 10-6.
% The required value of wP is determined by the function fminsearch.
%

```

```

% Constant F1
w0=w_in;
T0=T_in;
i=1;
[w,T]=ode45(@ (w,T) dTbydw_RK(w,T,model,i), [w0 wP], T0);
w1=w;
T1=T;
nT1=length(T);
TF1=T(nT1);

```

```

% Constant F2
w0=w_initial;
T0=T_initial;
i=2;
[w,T]=ode45(@ (w,T) dTbydw_RK(w,T,model,i), [w0 wP], T0);
w2=w;
T2=T;

```

```

nT2=length(T);
TF2=T(nT2);
% The variable to be minimised by fminsearch manipulating the value
% of wP.
T_diff=abs(TF1-TF2);
T_dwell=0.5*(TF1+TF2);
end

```

```

function dTbydw=dTbydw_RK(w,T,model,i)

```

```

% Integrate Eqn (1) of this work and SI 6.20 by means of ode45
% function dTbydw_RK calculates values of dT/dw along
% lines of constant Fi, i=1,2.
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

p=pt*w/(w+N);
Omega=1-p/pt;
[ps,dpsbydT] = Psat_Huang1(T);
hv = latent_heat(T,hv0,dhvdT);
r = rel_hum(w,ps,pt,N);

% model = 1      Toth
% model = 2      Freundlich

if model == 1
    Weq=Weq_Toht(w,T);
end
if model == 2
    Weq=Weq_Freundlich(r);
end

W=Weq;

if model==1
    hsbyhv=hsbyhv_Toht(W,T);
end
if model==2
    hsbyhv=1;
end

hs = Heat_of_sorption(hsbyhv,hv);

if model == 1
    zeta=zeta_Toht(W,T);
end
if model == 2
    zeta=zeta_Freundlich(r);
end

beta=zeta*Omega/w; %SI 7.5.15
dhbydT = ca+w*(cw+dhvdT);
lamda_alphah=hs/dhbydT; %SI By definition 7.2.3
S=dpsbydT/ps; %SI By definition 7.7.9
alphaW=-Omega/(w*(hs/hv)*S); %SI 7.9.8
dHbydT=dH_by_dT1(cs,cw,W);
dhbydT = dh_by_dT(ca,cw,w,dhvdT);
sigma=dHbydT/dhbydT; %SI 7.1.1
nu=1.0/(zeta*(hs/hv)*S); %SI 7.7.10
nu_sigma=nu*sigma;
A=lamda_alphah+nu_sigma+alphaW;
C=-4*alphaW*lamda_alphah;
alpha(1)=(A+sqrt(A^2+C))/2; %SI 6.20
alpha(2)=(A-sqrt(A^2+C))/2; %SI 6.20
gamma(1)=sigma*alphaW/(alphaW-alpha(1)); %This work 6 & 15
gamma(2)=sigma*alphaW/(alphaW-alpha(2)); %This work 6 & 15
if i==1

```

```

    dTbydw=-alpha(1);    %Definition of alpha Eqn 1
end
if i==2
    dTbydw=-alpha(2);    %Definition of alpha Eqn 1
end

end

function [psat,dpsatbydT] = Psat_Huang1(T)
% Saturation vapour pressure of water using Huang's formula
% SI 13.1

[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
e_f=1.0053; % Enhancement factor calculated at atmospheric pressure
           % using Huang's approximation.
psat=e_f/(T+105)^1.57*exp(34.494-4924.99/(T+237.1));
dpsatbydT=psat*(4924.99/(T+237.1)^2-1.57/(T+105));
end

function [hv] = latent_heat(T,hv0,dhvdT)
% Latent heat of vaporization of water
% hv0 at 0 degC
% dhvdT is dhv/dT
hv = hv0+dhvdT*T;
end

function [r] = rel_hum(w,ps,pt,N)
% Relative humidity of air given its humidity,w, and psat.
p = pt*w/(w+N);
r = p/ps;
end

function W=Weq_Freundlich(rh)
% Equilibrium moisture content, W,as a function of relative
% humidity, rh, according to Freundlich's isotherm.
W=0.444*rh^(1/1.342);
end

function [Weq]=Weq_Toth(w,T)

% The Toth isotherm for RD silica gel to find
% the moisture content, Weq, of silica gel
% in equilibrium with air that has a humidity of w and a temperature, T.
% Data from Chua et al. (2002)
% SI 9.1 et seq.

[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

Tabs=T+273.15;
K0=7.3e-13;
Qst=2693.0e3;
W0=0.45;
t=12;    % Toth constant
Rwater=461.5;
pvap=pt*w/(N+w);
K=K0*exp(Qst/(Rwater*Tabs));    %SI 9.3
KP=K*pvap;    %SI 9.2
Weq=KP/(1+(KP/W0)^t)^(1/t);    %SI 9.3
end

```

```

function hsbyhv=hsbyhv_Toht(W,T)
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

hv=hv0+dhvdT*T; % Latent heat of vaporization of water
Qst=2693.0e3; % Differential heat of sorption
hsbyhv=Qst/hv;
end

function[zeta]=zeta_Toht(W,T)

% Calculate zeta using Toht isotherm.
% Annotations provide the principal equations used.

[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

Tabs=T+273.15;
K0=7.3e-13;
Qst=2693.0e3;
W0=0.45;
t=12; % Toht constant
Rwater=461.5;

K=K0*exp(Qst/(Rwater*Tabs));
pv=W/(K*(1-(W/W0)^t)^(1/t));
KP=K*pv;

% To find dpv/dW at constant temperature

[psat,dpsbydT] = Psat_Huang1(T);
rh=pv/psat;
V=K*(1-(W/W0)^t)^(1/t); %SI 9.5
U=1-(W/W0)^t; %SI 9.7
dpbydW=(1/(K*U^(1/t)))*(1+1/(U)*(W/W0)^t); %SI 9.9
dWbydr=psat/dpbydW; %SI 9.12
zeta=pv/dpbydW; %SI 9.13
end

function zeta=zeta_Freundlich(rh)
% zeta defined by SI 7.5.3
dWbydr=0.444/1.342*rh^(-0.342/1.342);
zeta=rh*dWbydr;
end

function [rh1,rh2]=rh_find
global T_dwell w1 w2 T1 T2
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

% Plot lines of constant F1 and F2.
% Calculate values of relative humidities
% along lines of constant F1 and

L_w1=length(w1);
L_w2=length(w2);
for i=1:L_w1
T=T1(i);
[ps,dpsbydT] = Psat_Huang1(T);

```

```

    psat1(i)=ps;
    p(i)=w1(i)*pt/(N+w1(i));
    rh1(i)=p(i)/psat1(i);
end
for i=1:L_w2
    T=T2(i);
    [ps,dpsbydT] = Psat_Huang1(T);
    psat2(i)=ps;
    p(i)=w2(i)*pt/(N+w2(i));
    rh2(i)=p(i)/psat2(i);
end
hold on
plot(T1,w1)
hold on
plot(T2,w2)
ylabel('Humidity, kg/kg','FontSize',14)
xlabel('Temperature, {\circ}C','FontSize',14)
end

function [hs] = Heat_of_sorption(hsbyhv,hv)
hs = hsbyhv*hv; %Definition of hs/hv
end

function [dhbydT] = dh_by_dT(ca,cw,w,dhvdT)
dhbydT = ca+w*(cw+dhvdT); %SI 7.1.6
end

function [dHbydT] = dH_by_dT1(cs,cw,W)
% In this work dHW/dT is subsumed in the specific heats.
% i.e. dHW/dT = 0. This is the subject of 5. CLOSING REMARKS
% of the ASTFE 24 paper.
dHbydT = cs+cw*W; %SI 7.1.2
end

function r = r_Freundlich(W)
% An expression of Freundlich's isotherm used in ASTFE 24 paper.
r=(W/0.444)^1.342;
end

function [Obj_fn] = dwell_find_shock_Toht(wP, T_in, w_in, T_initial,
w_initial,model)
global T_dwell w1 w2 T1 T2
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
% Given the initial conditions of a bed of silica gel, defined by
% w_initial and T_initial Eqn SI 6.20 is integrated using
% the Runge-Kutta algorithm.
% Values of the humidity, w-p, at the plateau are adjusted
% by fminsearch to render Obj_fn a minimum within the default
% accuracy of MATLAB. This gives the temperature, T_p,
% at the plaeau state.

w0=w_initial;
T0=T_initial;
i=2;
[w,T]=ode45(@ (w,T) dTbydw_RK_Toht(w,T,model,i),[w0 wP],T0);
w2=w;
T2=T;
nT2=length(T);
T_p=T(nT2);
w_p=w(nT2);

```

```

Obj_fn=Obj_fn_Shock_Toht(w_in,T_in,w_p,T_p,model);
T_dwell=T_p;
end

function dTbydw=dTbydw_RK_Toht(w,T,model,i)
% Integrate Eqn SI 6.20 using the Runge-Kutta algorithm
% The three parameters alphaW, lamda-alphah and nu-sigma
% are calculated.

[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
p=pt*w/(w+N); %SI A form of 7.5.8
Omega=1-p/pt; %SI By definition 7.5.16
[ps,dpsbydT] = Psat_Huang1(T);
hv = latent_heat(T,hv0,dhvdT);
r = rel_hum(w,ps,pt,N);

Weq=Weq_Toht(w,T);

W=Weq;

hsbyhv=hsbyhv_Toht(W,T);

hs = Heat_of_sorption(hsbyhv,hv);

zeta=zeta_Toht(W,T);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
beta=zeta*Omega/w; %SI 7.5.15
dhbydT = ca+w*(cw+dhvdT);
lamda_alphah=hs/dhbydT; %SI By definition 7.2.3
S=dpsbydT/ps; %SI By definition 7.7.9
alphaW=-Omega/(w*(hs/hv)*S); %SI 7.9.8
dHbydT=dH_by_dT1(cs,cw,W);

dhbydT = dh_by_dT(ca,cw,w,dhvdT);
sigma=dHbydT/dhbydT; %SI 7.1.1
nu=1.0/(zeta*(hs/hv)*S); %SI 7.7.10
nu_sigma=nu*sigma;
A=lamda_alphah+nu_sigma+alphaW;
C=-4*alphaW*lamda_alphah;
alpha(1)=(A+sqrt(A^2+C))/2; %SI 6.20
alpha(2)=(A-sqrt(A^2+C))/2; %SI 6.20
gamma(1)=sigma*alphaW/(alphaW-alpha(1)); %k 6 % 15
gamma(2)=sigma*alphaW/(alphaW-alpha(2)); %This work 6 & 15
if i==1
dTbydw=-alpha(1); %Definition of alpha Eqn 1 This work
end
if i==2
dTbydw=-alpha(2); %Definition of alpha Eqn 1 This work
end
end

function Obj_fn=Obj_fn_Shock_Toht(w_in,T_in,w_p,T_p,model)
% To estimate the conditions across a shock wave. Obj-fn
% is defined.

% The idea is to minimise the objective function
% which Eqn 81 in the ASTFE 24 paper

[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;

```

```

Qst=2693.0e3;
Rwater=461.5;

hv_in=hv0+dhvdT*T_in;
hv_p=hv0+dhvdT*T_p;
[ps_in,dpsbydT_in] = Psat_Huang1(T_in);
[ps_p,dpsbydT_p] = Psat_Huang1(T_p);

[W_in]=Weq_Toht(w_in,T_in);
[W_p]=Weq_Toht(w_p,T_p);

Tabs_in=T_in+273.15;
Tabs_p=T_p+273.15;

HW_in=hv_in*(1-hsbyhv_Toht(W_in,T_in))*W_in;
HW_p =hv_p*(1-hsbyhv_Toht(W_p,T_p))*W_p;

h_in=ca*T_in+w_in*(cw*T_in+hv_in);
h_p=ca*T_p+w_p*(cw*T_p+hv_p);
H_in=cs*T_in+W_in*cw*T_in+HW_in;
H_p=cs*T_p+W_p*cw*T_p+HW_p;

Dh=h_in-h_p;
DH=H_in-H_p;
Dw=w_in-w_p;
DW=W_in-W_p;
Obj_fn=abs(Dh*DW-DH*Dw);
end

function [rh2]=rh_find_shock
global T_dwell w1 w2 T1 T2
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
L_w1=length(w1);
L_w2=length(w2);

for i=1:L_w2
    T=T2(i);
    [ps,dpsbydT] = Psat_Huang1(T);
    psat2(i)=ps;
    p(i)=w2(i)*pt/(N+w2(i));
    rh2(i)=p(i)/psat2(i);
end

%plot(T1,w1)
hold on
    plot(T2,w2)
hold on
T_plot=linspace(20,55,46);
LT=length(T_plot);
for i=1:LT
    T=T_plot(i);
    [ps,dpsbydT] = Psat_Huang1(T);
    wsat(i)=0.622*ps/(101325-ps);
end
plot(T_plot,wsat)
ylabel('Humidity, kg/kg','FontSize',14)
xlabel('Temperature, {\circ}C','FontSize',14)
pbaspect([1 1 1])
end

```

```

function Toth_plots(w_dwell,T_dwell,w_in,T_in)
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
w_dwell
T_dwell
Weq_dwell_Toht=Weq_Toht(w_dwell,T_dwell);
Weq_inlet_Toht=Weq_Toht(w_in,T_in);
[rh2]=rh_find_shock;

T_plot=linspace(20,40);
LT=size(T_plot);
for i=1:LT
    T=T_plot(i);
    [ps,dpsbydT] = Psat_Huang1(T);
    wsat(i)=0.622*ps/(101325-ps);
end
hold on
plot(T_plot,wsat,'k')

T_shock=linspace(T_in,T_dwell,30);
w_shock=linspace(w_in,w_dwell,30);
hold on
plot(T_shock,w_shock)
    DW=Weq_inlet_Toht-Weq_dwell_Toht;
    dw=w_in-w_dwell;
    V_shock=1/(1+mu*DW/dw)
end

function Freundlich_plots(w_dwell,T_dwell,w_in,T_in,w_initial,T_initial)
[hv0,dhvdT,ca,cw,cs,N,pt,eps,rho,P,mu]= phys_properties_SG;
w_dwell
T_dwell

    p=pt*w_dwell/(w_dwell+N);
    [ps,dpsbydT] = Psat_Huang1(T_dwell);
    r = p/ps;
    W_dwell=Weq_Freundlich(r)

    [rh1,rh2]=rh_find;

% Conditions at initial state
T=T_initial;
w=w_initial;

    p=pt*w/(w+N);
    [ps,dpsbydT] = Psat_Huang1(T);
    r=p/ps;
    Weq_F=Weq_Freundlich(r)

end

```