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Darcy's Law-Based Model for Wicking in Paper-Like Swelling Porous Media

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The wicking of liquid into a paper-like swelling porous medium made from cellulose and superabsorbent fibers was modeled using Darcy's law. The work is built on a previous study in which the Washburn equation, modified to account for swelling, was used to predict wicking in a composite of cellulose and superabsorbent fibers. In a new wicking model proposed here, Darcy's law for flow in porous media is coupled with the mass conservation equation containing an added sink or source term to account for matrix swelling and liquid absorption. The wicking-rate predicted by the new model compares well with the previous experimental data, as well as the modified Washburn equation predictions. The effectiveness of various permeability models used with the new wicking model is also investigated. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2257–2267, 2010
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Introduction

Wicking is the spontaneous absorption of a liquid into a porous medium by the action of capillary pressure. An example of wicking is the imbibition of liquids by towels, paper towels, table napkins, wipes, and sponges. Another important example is that of wicking in commercial wicks used by consumer product companies to dispense volatile substances into the air such as room fresheners or insect repellents.

Capillary pressure during wicking occurs as a result of capillary suction, which is created on the walls of the porous media at the interface of wet and dry matrix.[1,2] These forces originate from the mutual attraction of the molecules in the liquid medium and the adhesion of liquid molecules to those in the solid medium[3]; the wicking phenomenon occurs when the adhesion is greater than the mutual attraction. Wicking is the main cause of absorption in the porous materials, although there may be other factors causing absorbency (Masoodi et al., submitted).

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Wicking performance is an important issue in several industries that deal with liquid-absorbing porous media, including the pulp and paper industry. The most common example is the paper towel, in which water absorption and retention is the primary goal.[1] There are two traditional models for studying the wicking phenomenon mathematically: (1) The older method uses the Washburn (or Lucas-Washburn) equation,[4,5] where the porous medium is assumed to be a bundle of aligned capillary tubes of the same radii; lately, a newer version of this equation has been developed after inclusion of the gravity term.[6] (2) In recent years, a new approach based on Darcy's law has been successfully used to model wicking in porous media such as a sintered polymer wick[7] or bank of fibers.[8] (Darcy' law, a simple formula that relates the average velocity of a liquid to the pressure gradient within a porous medium, was first discovered by Henri Darcy in 1857.[9])

Wicking is a function of the micro- and macro-structure of porous media, the characteristics of liquid, and a function of time.[7] The general relation between the wicking rate, wicking time, and liquid characteristics is clearly described in the aforementioned conventional wicking models. The relation between the wicking rate and structure of a porous

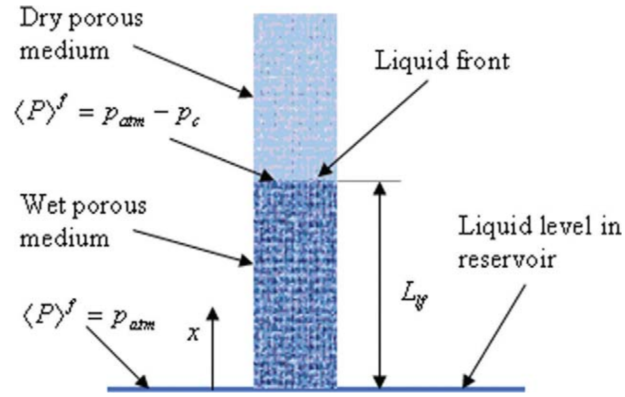

Figure 1. A schematic of the wicking setup and the wicking (or liquid-front) height in a porous wick.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

medium is the most challenging, as the structure of porous media show great variations.[10] Several researchers studied the relationship between the wicking rate and the porous medium structure in fibrous materials by analyzing the wicking rates along the fibers[11–13] and across the fibers.[8,14,15] Recently, the wicking enhancement in multi-ply paper structure was investigated experimentally,[16] where it was shown that this enhancement is most noticeable in the beginning of the wicking process and diminishes gradually. Although several researchers have tried to find a theoretical equation relating the wicking rate to the microstructure of a porous medium, it still remains a poorly understood problem.

Fiber swelling is an important phenomenon that affects wicking in paper,[17] as it is one of the swelling mechanisms that occur during water-fiber interaction in all bio-fiber and plant-based materials such as paper and pulp. As swelling changes the structure and molecular arrangement of materials, it affects both the wettability and "wickability" of the porous media.[18] In fact, the swellability of fibers is an important and useful property of paper for the paper industry—the swelling leads to liquid absorption in the paper matrix, which in turn leads to liquid retention inside the porous paper. In paper industry, this liquid holding capacity, which is related to the moisture content after a paper sheet dries, is called Water Retention Value.[19]

The swelling effect leads to error if the conventional wicking models such as Washburn equation are employed to predict the wicking rate in swelling porous media.[20] Schuchardt and Berg[21] studied the swelling phenomenon experimentally and modified the Washburn equation for application in some swelling materials. This model, built on the assumption that pore radii in a swelling porous medium decrease linearly with time, compares better with the experimental data than the conventional Washburn model.

In this article, we present a new model based on Darcy's law to predict wicking rates in swelling porous media. Using the volume averaging method, the continuity equation for single-phase flow in swelling porous media is modified to include (1) a sink term, which is related to liquid absorption by dry particles; and (2) a source term, which is related to the rate of change of porosity. We also investigate the dependence of permeability upon porosity, expressed through several permeability models, including the Kozeny-Carman model.

The advantage of using Darcy's law to predict wicking rates compared with the Washburn equation is that Darcy's law provides a modern approach that can be extended into modeling two- or three-dimensional wicking flows (Masoodi et al., submitted), while the Washburn equation is limited to one-dimensional wicking due to its origin from the laminar-flow model along a bundle of capillary tubes. By combining the general form of Darcy's law and the continuity equation, any two- or three-dimensional flow in porous media can be modeled. On the basis of such an approach, we developed PORE-FLOW©, a novel, finite element-based numerical simulation, to predict the wicking flow in the three-dimensional and complex geometries (Masoodi et al., submitted). The inclusion of swelling effect in Darcy's law-based model, as proposed in this article, has the added benefit of easy implementation in such flow-modeling codes, based on Darcy's law and the continuity equation, to study three-dimensional wicking in swelling porous materials.

Theoretical Details

Wicking in rigid porous media

In rigid porous media, the sizes of the constituent particles and the pores between them remain constant during the wicking process. The two conventional theories for wicking in rigid porous media, one based on the Washburn equation (also known as the Lucas-Washburn equation) and the other based on Darcy's law, are explained below.

Washburn Equation. If a porous medium is assumed to consist of a bundle of parallel capillary tubes of the same size, the governing equation for wicking flow, after assuming the Hagen-Poiseuille flow of liquids through such tubes and neglecting the effect of gravity[6] is,

$$\frac{4\gamma\cos(\theta)}{D_c} = \frac{32\mu L_{lf}}{D_h^2}\frac{dL_{lf}}{dt} \tag{1}$$

where L_{lf} is the height of the rising liquid-front within the porous medium (see Figure 1), μ is the liquid viscosity, γ is the liquid surface tension, θ is contact angle, t is time, D_c is capillary pore diameter, and D_h is hydraulic pore diameter. An integration of Eq. 1 leads to the well-known Washburn equation:

$$L_{lf} = \sqrt{\frac{\gamma D_e\cos(\theta)}{4\mu}t} \tag{2}$$

where D_e, the effective pore diameter, is obtained through

$$D_e = \frac{D_h^2}{D_c} \tag{3}$$

If the capillary and hydraulic diameters are equal, i.e., $D_e = D_h = D_c$, the height of the wicking front changes to

$$L_{lf} = \sqrt{\frac{\gamma D_c\cos(\theta)}{4\mu}t} \tag{4}$$

Darcy's Law. The single-phase flow of a Newtonian liquid in an isotropic and rigid porous medium is governed by Darcy's law and following form of the continuity equation:

$$\text{Darcy's Law}: \quad \langle \vec{V} \rangle = -\frac{K}{\mu} \vec{\nabla} \langle P \rangle^{\mathrm{f}} \tag{5}$$

$$\text{Continuity Equation}: \quad \vec{\nabla} \cdot \langle \vec{V} \rangle = 0 \tag{6}$$

where $\langle \vec{V} \rangle$ and $\langle P \rangle^{\mathrm{f}}$ are volume-averaged liquid velocity and pore-averaged modified pressure, respectively, and K is the permeability of the porous medium. Using the terminology of the well-known volume averaging method used for deriving volume-averaged flow and transport equations in porous media,[22] the volume average (also called the phase average) and the pore average (also called the intrinsic phase average) for any flow related quantity q_f in a porous medium are defined, respectively, as

$$\langle q_f \rangle = \frac{1}{\mathrm{Vol}} \int_{\mathrm{Vol_f}} q_{\mathrm{f}} dV \tag{7}$$

$$\langle q_f \rangle^{\mathrm{f}} = \frac{1}{Vol_f} \int_{\mathrm{Vol_f}} q_{\mathrm{f}} dV \tag{8}$$

where q_{f} is integrated over an averaging volume (Vol) called the representative elementary volume or REV* (see Appendix B). Masoodi et al. have shown[7] that in the case of a one-dimensional flow after neglecting the effect of gravity, the use of Eq. (5) and (6) leads to an equation for liquid-front location in the form of

$$L_{\mathrm{lf}} = \sqrt{\frac{2\,K\,p_{\mathrm{c}}}{\varepsilon_{\mathrm{f}}\,\mu} t^2} \tag{9}$$

where ε_{f}, the porosity of the porous medium, is defined as the ratio of pore volume to the total volume. p_{c} is the capillary pressure obtained through the well-known Laplace equation:

$$p_{\mathrm{c}} = \frac{2\gamma \cos(\theta)}{R_c} \tag{10}$$

Wicking in nonrigid, swelling porous media

To use the aforementioned models in swelling porous media, some modification is necessary as the pore radius, porosity, and permeability change during the course of swelling. In fact, these parameters are functions of both time and space in swelling porous media during wicking. The next section describes two approaches to modify the previous wicking models for application to swelling porous media.

Washburn Equation. Schuchardt and Berg[21] assumed the pore radius in the wetted area of the considered porous medium (a composite of cellulose and superabsorbent fibers) will decrease linearly with time as a result of swelling. They used this assumption to modify the Washburn equation and proposed the relation for the wicking rate as

$$L_{\mathrm{lf}} = \sqrt{\frac{\gamma R_0 \cos(\theta)}{2\mu}} \left[t - \frac{a}{R_0} t^2 + \frac{a^2}{3R_0^2} t^3 \right]^{1/2} \tag{11}$$

while using a decreasing hydraulic radius $R_{\mathrm{h}} = R_0 - at$ behind the flow front due to swelling of fibers constituting the porous medium. In this formulation, R_{h} is hydraulic pore radius, R_0 is the initial value of R_{h}, and a is a constant representing the swelling effect. The details of derivation are presented in Appendix A. Note that upon neglecting the swelling effect (i.e., $a = 0$), Eq. 11 turns to Eq. 4, which is the original Washburn equation for rigid porous media.

Darcy's Law. For a swelling porous medium, the continuity equation modifies to the form,

$$\vec{\nabla} \cdot \langle \vec{\mathrm{V}} \rangle = -S - \frac{\partial \varepsilon_{\mathrm{f}}}{\partial t} \tag{12}$$

using the volume averaging method. (See Appendix B for details of the derivation.) Note that a negative term on the right causes the liquid to 'disappear' from the interconnected pore-space available for the traveling liquid, while a positive term 'creates' liquid in the same space. The first sink term, -S, is created due to the absorption of liquid by the solid matrix. As the porosity ε_{f} decreases in a swelling porous medium, the $\partial \varepsilon_{\mathrm{f}} / \partial t$ terms is $-$ve; thus, the second term on the right is actually a +ve source term.

If we consider the wicking flow to be one-dimensional, the governing equations (Darcy's law and the modified continuity equation) simplify to

$$\langle u \rangle = -\frac{K}{\mu} \frac{d\langle p \rangle^{\mathrm{f}}}{dx} \tag{13}$$

$$\frac{d\langle u \rangle}{dx} = -S - \frac{\partial \varepsilon_{\mathrm{f}}}{\partial t} \tag{14}$$

where $\langle u \rangle$ is the volume-averaged Darcy velocity, also known as the specific discharge in the porous media literature.[9] As S is the rate of liquid absorption by solid matrix and $\frac{d\varepsilon_{\mathrm{s}}}{dt}$ is directly related to the rate of increase of solid-matrix volume, we propose that S is proportional to $\frac{d\varepsilon_{\mathrm{s}}}{dt}$ (ε_{s} defined as the ratio of solid volume to the total volume). In other words, we assume S to be linearly proportional to $\frac{d\varepsilon_{\mathrm{s}}}{dt}$, i.e.,

$$S = b \frac{d\varepsilon_{\mathrm{s}}}{dt} \tag{15}$$

where $b = 0$ case signifies "no absorption of liquid by solid matrix" and $b = 1$ case indicates 'the rate of increase of solid-matrix volume is equal to the volumetric rate of liquid absorption by solid matrix'. Therefore, b, to be referred to as the absorption coefficient, must fall in the range $0 \leq b \leq 1$[†]. We also have the following relation between two porosities:

$$\varepsilon_{\mathrm{s}} + \varepsilon_{\mathrm{f}} = 1 \tag{16}$$

*REV is typically much bigger than the solid constituents (particles or fibers) or a porous medium.

†One can allow b to be greater than 1 if the increase in solid volume is caused by some other effect other than the migration of volume of the liquid.

Substituting Eq. 15 in Eq. 14, and then using Eq. 16 to eliminate ε_s, leads to the following relation for the continuity equation:

$$\frac{d\langle u\rangle}{dx} = (b-1)\frac{\partial \varepsilon_f}{\partial t} \tag{17}$$

If we substitute Eq. 13 in Eq. 17, and assume the permeability and porosity to be functions of time only, then we obtain

$$\frac{d^2\langle p\rangle^f}{dx^2} = G(t) \tag{18}$$

where

$$G(t) = (1-b)\frac{\mu}{K}\frac{d\varepsilon_f}{dt} \tag{19}$$

Note that in general the porosity and permeability are expected to be functions of both time (t) and space (x coordinate) in swelling materials. If we consider the global values for porosity and permeability throughout the wetted porous medium, then local effects are neglected and the permeability and porosity can then be just functions of time. Neglecting the local spatial dependence in these parameters simplifies the governing Eq. 18 from a nonlinear partial differential equation to an ordinary differential equation that can be solved analytically. Although this assumption reduces the accuracy of our wicking predictions, the resultant simplification in the wicking model makes it worthwhile to neglect the local effects. After neglecting the effect of gravity with $\rho g L_{lf} \ll p_c$, the boundary conditions for Eq. 18 (Figure 1) can be deduced to be

$$\langle p\rangle^f(x=0) = p_{atm} \tag{20a}$$

$$\langle p\rangle^f(x=L_{lf}) = p_{atm} - p_c \tag{20b}$$

After integrating Eq. 18 two times and applying the boundary conditions Eqs. 20a and 20b, the final expression for pressure reduces to

$$\langle p\rangle^f(x,t) = \frac{1}{2}Gx^2 - \left(\frac{1}{2}GL_{lf} + \frac{p_c}{L_{lf}}\right)x + p_{atm} \tag{21}$$

The liquid-front velocity and the Darcy (filtration) velocity are related through the equation (Masoodi et al., submitted)

$$\frac{dL_{lf}}{dt} = \left.\frac{\langle u\rangle}{\varepsilon_{lf}}\right|_{x=L_{lf}} \tag{22}$$

where ε_{lf} is the surface porosity at the liquid front. If we assume the surface and bulk porosities to be identical, then, due to the swelling effect, the porosity will decrease progressively from its initial value of the surface porosity at the liquid front, i.e., $\varepsilon_{lf} = \varepsilon_{f_0} = \varepsilon_f(t=0)$. Substitution of Eq. 13 in Eq. 22 and considering Eq. 21 for pressure term leads to the following differential equation

$$\frac{dL_{lf}}{dt} = G_1 L_{lf} + \frac{G_2}{L_{lf}} \tag{23}$$

where G_1 and G_2 are just functions of time:

$$G_1(t) = -\frac{K(t)\,G(t)}{2\,\varepsilon_{f_0}\,\mu} \tag{24a}$$

$$G_2(t) = \frac{K(t)\,p_c}{\varepsilon_{f_0}\,\mu} \tag{24b}$$

Equation 23 can be converted into a linear differential equation by defining y as

$$y = L_{lf}^2 \tag{25}$$

Using Eq. 25, we can transform Eq. 23 into a differential equation of the form

$$\frac{dy}{dt} = 2G_1 y + G_2 \tag{26}$$

that can be easily integrated using the initial condition $y(t=0)=0$. The final form of the solution is

$$y = 2e^{2\int G_1 dt}\int_0^t e^{-2\int G_1 dt} G_2 dt' \tag{27}$$

SubstitutingG_1, G_2 and y from Eqs. 24a, 24b, 25, respectively, into Eq. 27, results in

$$L_{lf} = \sqrt{2e^{2\int -\frac{KG}{2\varepsilon_{f_0}\mu}dt}\int_0^t e^{-2\int -\frac{KG}{2\varepsilon_{f_0}\mu}dt}\frac{Kp_c}{\varepsilon_{f_0}\mu}dt'} \tag{28}$$

Substituting G from Eq. 19 in Eq. 28, and doing some algebraic operations yields the final relation for liquid front as

$$L_{lf} = \sqrt{\frac{2p_c}{\varepsilon_{f_0}\mu}e^{(b-1)\frac{\varepsilon_f}{\varepsilon_{f_0}}}\int_0^t e^{(1-b)\frac{\varepsilon_f}{\varepsilon_{f_0}}}K(t')dt'} \tag{29}$$

Note that for a rigid porous media with no absorption into fibers/particles ($b = 0$) and with the porosity remaining unchanged behind the liquid front ($\varepsilon_f = \varepsilon_{f_0}$), Eq. 29 reduces to the ordinary porous-media case of Eq. 9. For the special case of $b = 1$ when the swelling rate matches the volumetric absorption rate, the wicking relation (29) simplifies to

$$L_{lf} = \sqrt{\frac{2p_c}{\varepsilon_{f_0}\mu}\int_0^t K(t')dt'} \tag{30}$$

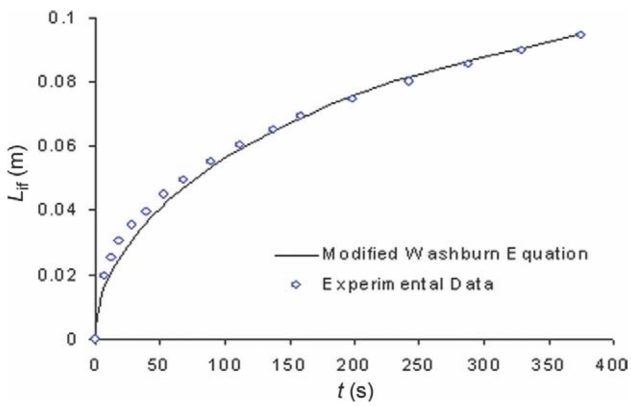

Figure 2. Wicking height vs. time plot for water absorption in the 13%FC CMC/Cellulose composite-paper strip.[21]

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

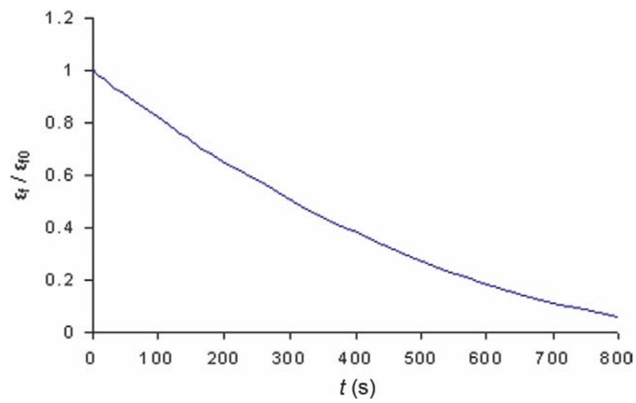

Figure 3. Relative porosity $\varepsilon_f/\varepsilon_{f_0}$ versus time plot for the 13%FC CMC/Cellulose composite-paper.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Our main assumptions in deriving Eqs. 29 and 30 are:

(1) The absorption rate of liquid in the porous medium is linearly proportional to the rate of change of solid volume fraction.

(2) The porosity and permeability are considered globally for the whole wet area; thus, they are functions of time only.

(3) The effect of gravity on the wicking phenomenon is negligible.

Results and Discussions

An experimental study

Schuchardt and Berg[21] conducted experiments to compare the predictions of their modified Washburn model, Eq. 11, with the experimental results. Figure 2 shows the experimental data and predictions of the modified Washburn equation for wicking water in a composite paper strip of 13%FC‡ CMC§/Cellulose (i.e., 13% of FC consists of CMC fibers and the rest is made of cellulose fibers). Although there is a minor deviation at the beginning, the theoretical predictions match well with the experimental results as the time passes on. Schuchardt and Berg[20] used two different liquids in their wicking experiments: one that causes swelling in the composites paper during wicking, and one that does not. They compared the measured values for pore radii under swelled and non-swelled conditions at various times, and thus estimated the values of R_0 and a in Eq. 11. The characteristics of their test liquids, and the measured values of R_0 and a are listed in Table 1. Although the modified Washburn equation predicts well in Figure 2, it has some limitations-it assumes the hydraulic radius continually reduces, which means the fiber swelling must continue during the wicking time. Therefore, Schuchardt and Bergs' model works as long as the wicking time is not greater than the maximum-permitted swelling time (depending upon the void space between fibers) for individual fibers.

Changes in Porosity During Wicking. The porosity was not measured in the above-mentioned experiment. As the pore radius and its rate of change were measured, we can derive an expression for porosity versus time, as follows. In the capillary model, the areal porosity is defined as

$$\varepsilon_f = n\pi R_c^2 \tag{31}$$

where n is the number of assumed capillary tubes passing through a unit area of the porous medium. Note, we assumed area-based porosity to be equal volume-based porosity. The capillary (pore) radius, R_c, decreases linearly with time as a result of swelling as

$$R_c = R_0 - at \tag{32}$$

The initial porosity ε_{f_0} can be similarly defined as

$$\varepsilon_{f_0} = n\pi R_0^2 \tag{33}$$

Comparing Eqs. 31 and 33 while including Eq. 32 leads to the following relation for porosity

$$\varepsilon_f = \varepsilon_{f_0}\left(\frac{R_0 - at}{R_0}\right)^2 \tag{34}$$

Figure 3 plots the relative porosity $\varepsilon_f/\varepsilon_{f_0}$ against time for the composite paper strip of 13%FC CMC/Cellulose using Eq. 34; it is clear that the porosity and the rate of change of porosity decrease with time.

Changes in Fiber Size During Wicking. If we assume 13%FC CMC/Cellulose to consist entirely of fibers, we can also derive an expression for fiber size as a function of time from the data presented in the above-mentioned experiment.

Table 1. The Characteristics of Test Liquid (distilled water) and the Values of R_0 and a measured by Schuchardt[20]

Characteristic	Value	Unit
Viscosity of test liquid	0.000911	Kg/m s
Surface tension of test liquid	0.0723	N/m
Pore radius reduction rate a	8.40E-10	s^{-1}
Initial pore radius R_0	8.80E-07	m

‡FC (or Aquasorb FC) is a type of superabsorbent fiber made by the Hercules Chemical Company (which may now be known as DuPont).
§CMC is an acronym for Carboxymethylcellulose.

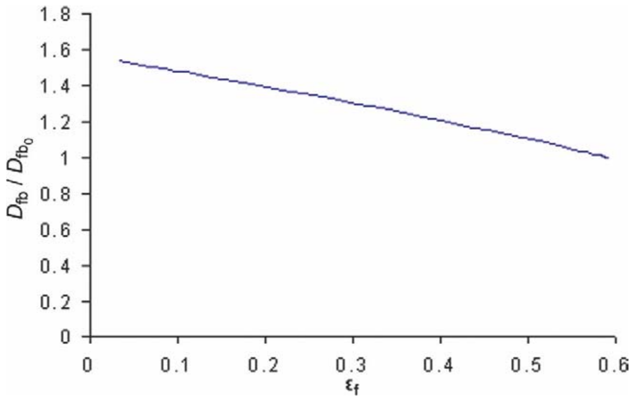

Figure 4. Dimensionless fiber diameter D_{fb}/D_{fb_0} versus porosity plot for the 13%FC CMC/Cellulose composite-paper.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

If we assume the porous medium to consist entirely of parallel fibers, the solid volume fraction ε_s can be formulated as

$$\varepsilon_s = \frac{1}{4} m\pi D_{fb}^2 \tag{35}$$

where m is the total number of fibers in a unit cross-sectional area, and D_{fb} is the diameter of fibers. As a result, the initial solid volume fraction ε_{s_0} is given by

$$\varepsilon_{s_0} = \frac{1}{4} m\pi D_{fb_0}^2 \tag{36}$$

On dividing Eq. 34 with Eq. 36 while using Eq. 16 results in the following relation for fiber diameter:

$$D_{fb} = D_{fb_0}\sqrt{\frac{1-\varepsilon_f}{1-\varepsilon_{f_0}}} \tag{37}$$

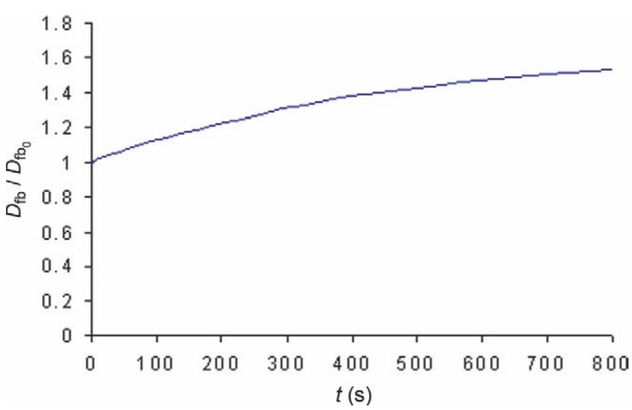

Figure 5. Dimensionless fiber-diameter D_{fb}/D_{fb_0} versus time plot for the composite 13%FC CMC/Cellulose paper.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Different Suggested Relations for $\phi(\varepsilon_f)$ for Porous Media Consisting of Packed Particles, Where *c* is an Arbitrary Constant that Depends on the Structure of Porous Media

Author	Suggested Relation for $\phi(\varepsilon_f)$
Blake (1922), Kozeny (1927), Carman (1937)[9]	$c\frac{\varepsilon_f^3}{(1-\varepsilon_f)^2}$
Zunker (1920)[10]	$c\frac{\varepsilon_f}{(1-\varepsilon_f)^2}$
Terzaghi (1625)[10]	$c\frac{(\varepsilon_f-.13)^2}{(1-\varepsilon_f)^{1.3}}$
Fehling (1939)[10]	$c\varepsilon_f^4$
Rose (1945)[10]	$c\varepsilon_f^{4.1}$
Rumpf and Gupte (1971)[10]	$c\varepsilon_f^{5.5}$

Figure 4 plots the dimensionless fiber diameter D_{fb}/D_{fb_0} against porosity for the tested material using Eq. 37; it is clear that the average fiber diameter increases as the porosity decreases during the swelling of the material. As porosity is a function of time through Eq. 34, the fiber diameter is also a function of time. Figure 5 shows how the fiber diameter is expected to increase with time in 13%FC CMC/Cellulose composite paper, a swelling porous media.

Permeability

To predict the Darcy's law-based wicking length given by Eqs. 29 or 30, we need to know how the permeability of the composite paper changes with time. In the capillary model, where the porous medium is assumed to be a bundle of capillary tubes, the permeability can be obtained by comparing Eq. 4 with Eq. 9 (after using Eq. 10). Note that porosity in Eq. 9 refers to the porosity at liquid front, which is the porosity under the non-swelled, initial state, i.e., $\varepsilon_f = \varepsilon_{f_0}$. The relation thus obtained with this assumption is referred to as the capillary-model permeability[10]:

$$K = \frac{1}{8}\varepsilon_{f_0} R_c^2 \tag{38}$$

As the capillary pore radius changes with time (Eq. 32), this permeability is also a function of time only.

Table 3. Different Suggested Relations for $\phi(\varepsilon_f)$ for Porous Media Consisting of Packed Fibers, where *c* is an Arbitrary Constant that Depends on the Structure of Porous Media

Author	Suggested Relation for $\phi(\varepsilon_f)$
Davies (1952)[10]	$c\frac{1}{(1-\varepsilon_f)^{1.5}[1+56(1-\varepsilon_f)^3]}$
Chen (1955)[10]	$c\frac{\varepsilon_f}{1-\varepsilon_f}\ln\frac{0.64}{(1-\varepsilon_f)^2}$
Bruschke and Advani (1993)[23]	$c\frac{(1-\eta)^2}{\eta^3}\left(\frac{3\eta.\tan^{-1}\sqrt{(1+\eta)/(1-\eta)}}{\sqrt{1-\eta^2}}+\frac{\eta^2}{2}+1\right)^{-1}$ where $\eta = \frac{4}{\pi}(1-\varepsilon_f)$
Gebart (1992)[24]	$c\left(\sqrt{\frac{1-\varepsilon_{f_{min}}}{1-\varepsilon_f}}-1\right)^{5/2}$ where $\varepsilon_{f_{min}} = 1-\frac{\pi}{2\sqrt{3}}$

Table 4. The Final Forms of Permeability Relations (Obtained Using $\phi(\varepsilon_f)$ and Eq. 36) for Porous Media Consisting of Packed Particles

Author	Suggested Relation for $\phi(\varepsilon_f)$
Blake (1922), Kozeny (1927), Carman (1937)[9]	$K_0\left(\frac{\varepsilon_f}{\varepsilon_{f0}}\right)^3 \frac{1-\varepsilon_{f0}}{1-\varepsilon_f}$
Zunker (1920)[10]	$K_0 \frac{\varepsilon_f}{\varepsilon_{f0}} \frac{1-\varepsilon_{f0}}{1-\varepsilon_f}$
Terzaghi (1625)[10]	$K_0\left(\frac{\varepsilon_f-0.13}{\varepsilon_{f0}-0.13}\right)^2\left(\frac{1-\varepsilon_{f0}}{1-\varepsilon_f}\right)^{0.3}$
Fehling (1939)[10]	$K_0\left(\frac{\varepsilon_f}{\varepsilon_{f0}}\right)^4 \frac{1-\varepsilon_f}{1-\varepsilon_{f0}}$
Rose (1945)[10]	$K_0\left(\frac{\varepsilon_f}{\varepsilon_{f0}}\right)^{4.1} \frac{1-\varepsilon_f}{1-\varepsilon_{f0}}$
Rumpf and Gupte (1971)[10]	$K_0\left(\frac{\varepsilon_f}{\varepsilon_{f0}}\right)^{5.5} \frac{1-\varepsilon_f}{1-\varepsilon_{f0}}$

We may also use some empirical and theoretical formulas for estimating the permeability, which are well-established in the literature on porous media. These formulas are generally in the form

$$K = D_f^2 \phi(\varepsilon_f) \tag{39}$$

where $\phi(\varepsilon_f)$ is a function of porosity. We have used different empirically obtained or theoretically derived formulas for ϕ, which are listed in Tables 2 and 3. Table 2 shows different suggested relations for $\phi(\varepsilon_f)$for porous media consisting packed particles, while Table 3 displays similar formulas for porous media consisting of packed fibers. There is a constant factor c in each formula for $\phi(\varepsilon_f)$, which plays an important role and may depend on other aspects of flow through porous media, including the particle-based Reynolds number.[25] As we have the exact value of K_0, the permeability of the composite paper at $t = 0$ for the case of no swelling, we have used the ratio of K/K_0 to eliminate the constant c. As we also used Eq. 37 to express pore diameter as a function of porosity, the final expression of the permeability is just a function of porosity. Tables 4 and 5 list the final forms of the theoretical and empirical formulas for permeability of swelling porous media.

Table 5. The Final Forms of Permeability Relations (Obtained Using $\phi(\varepsilon_f)$ and Eq. 36) for Porous Media Consisting of Packed Fibers

Author	Suggested Relation for $\phi(\varepsilon_f)$
Davies (1952)[10]	$K_0\left(\frac{1-\varepsilon_{f0}}{1-\varepsilon_f}\right)^{0.5} \frac{1+56\,(1-\varepsilon_{f0})^3}{1+56\,(1-\varepsilon_f)^3}$
Chen (1955)[10]	$K_0 \frac{\varepsilon_f}{\varepsilon_{f0}} \ln\frac{0.64}{(1-\varepsilon_f)^2} / \ln\frac{0.64}{(1-\varepsilon_{f0})^2}$
Bruschke and Advani (1993)[23]	$K_0 \dfrac{\psi(\eta)}{\psi(\eta_0)} \dfrac{\eta}{\eta_0}$ where $\eta_0 = \dfrac{4}{\pi}(1-\varepsilon_{f0})$ and $\psi(\eta) = \dfrac{(1-\eta)^2}{\eta^3}\left(\dfrac{3\eta.\tan^{-1}\sqrt{(1+\eta)/(1-\eta)}}{\sqrt{1-\eta^2}} + \dfrac{\eta^2}{2} + 1\right)^{-1}$
Gebart (1992)[24]	$K_0 \dfrac{1-\varepsilon_f}{1-\varepsilon_{f0}}\left[\left(\sqrt{\dfrac{1-\varepsilon_{f_{min}}}{1-\varepsilon_f}}-1\right)/\left(\sqrt{\dfrac{1-\varepsilon_{f_{min}}}{1-\varepsilon_{f0}}}-1\right)\right]^{5/2}$ where $\varepsilon_{f_{min}} = 1 - \dfrac{\pi}{2\sqrt{3}}$

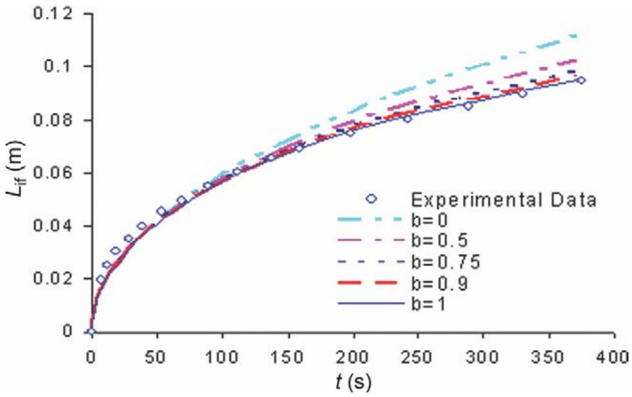

Figure 6. Wicking height vs. time plot for water absorption in the 13%FC CMC/Cellulose composite-paper strip using the capillary-model permeability and different values for the absorption coefficient *b*.

Experimental data are from Ref. 21. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Wicking predictions

The derived formula for the height of wicked liquid, Eq. 29, has the absorption coefficient b, which is directly related to the absorption of liquid by solid matrix of a porous medium. Figure 6 plots the growth of wicking height for water using the capillary-model permeability (Eq. 38) for different values of b and compares such predictions with Schuchardt and Berg's experimental data.[21] According to the figure, predictions of Darcy's law employing the capillary-model permeability improve with an increase in b: a value of b between 0.9 and 1.0 leads to a very good match with the data. A reason for the increase in the average wicking height can be proffered as follows. Based on Figure 6, as b increases from 0 to 1, the distance traveled by the wicking front or the wicking height decreases. Note that as b

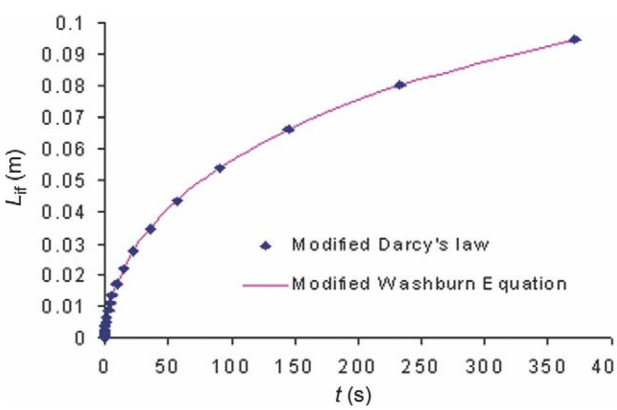

Figure 7. A comparison of predictions by the modified Washburn equation (Eq. 10) and the modified Darcy's law with "*b*=1" (Eq. 29) while using the capillary-model permeability.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

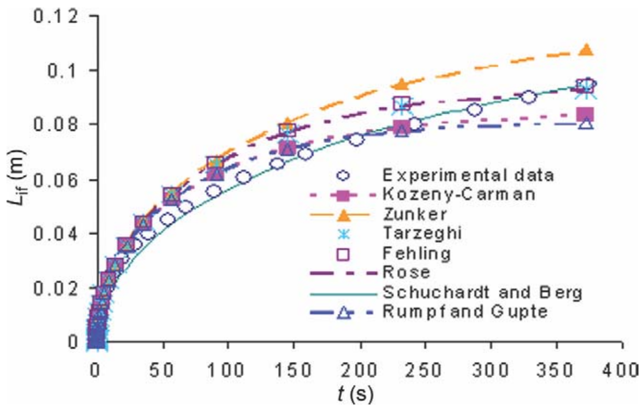

Figure 8. Wicking height vs. time predictions for the wicking of water in the 13%FC CMC/Cellulose composite-paper strip using the Darcy's law-based model with different formula for the permeability of particulate porous media.

The predicted values are compared with the modified Washburn-equation predictions and the experimental data of Schuchardt and Berg.[21]

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

approaches unity, the net value of the volumetric source term on the right hand side of Eq. 17 goes to zero, meaning that less liquid is available in the pores to push the liquid-front forward.

Figure 7 compares the wicking height predictions by the modified Washburn equation with the modified Darcy's law (Eq. 30 with the absorption coefficient $b = 1$ and the capillary-model permeability Eq. 38); we note that both the models predict identical growth in wicking heights. It is not surprising to obtain the same predictions from the two models, as the capillary-model permeability is used in the modified Darcy's law approach, while the modified Washburn equation is based on the capillary model.[7] However, as the modified Washburn equation is an accepted model for wicking in a class of swelling porous material, the flawless comparison verifies our key assumption of Eq. 15. In essence, using the capillary model for permeability, and considering b to be unity, leads to the same prediction from Eq. 30, as given by using Eq. 9. This indicates that in the newly proposed wicking model based on Darcy's law, the value of "b" should be either one or very close to one.

Figure 8 shows the predictions of wicking height against time for water absorption in the 13%FC CMC/Cellulose composite-paper strip using the different models for permeability for porous media made from particles. Here, Eq. 30 based on the modified Darcy's law model is used for the wicking prediction, where b is unity. The empirical formulas for permeability as a function of porosity are listed in Table 4, while the porosity changes with time according to Eq. 34 or Figure 3. The prediction of the modified Washburn equation is also shown in Figure 8 for comparison. It is clear that Schuchardt and Bergs' model matches with the experimental data better that any other models (this is not surprising because the model gets its values of parameters R_o and a after fitting the experimental data[21]); however, among the empirical formulas used for permeability in the proposed Darcy's law-based model, the Terzaghi, Fehling, and Rose formulas fare the best against the experimental data, although the predictions from other formulas are also reasonable.

Figure 9 shows the wicking predictions using the different permeability models for fibrous porous media. (The empirically obtained or theoretically derived formulas for these permeability models are listed in Table 5.) It is clear that prediction using the capillary model for permeability best agrees with the experimental data. As we have the measured pore-radius values as a function of time for this specific experiment from,[21] it is not surprising that the capillary model, which relies on these values, performs the best. If we had measured the porosity separately, then we could have seen better predictions from the other models. Among the empirical formulas for permeability, the Davies and Chen models seem to fare well against the experimental data.

Summary and Conclusions

In this article, the wicking of liquid into a paper-like swelling porous medium (a composite paper made formed from a network of cellulose and superabsorbent fibers), is studied theoretically. This work is built on a previous study by Schuchardt and Berg,[21] in which a modified Washburn equation was used to predict liquid absorption in the composite paper. Here, we propose a new theoretical approach in which Darcy's law is coupled with a modified continuity equation, characterized by sink and source terms representing the effects of liquid absorption into fibers and their subsequent swelling.

The wicking predictions obtained from the newly proposed wicking model compare well with the previous theoretical predictions of the modified Washburn equation, as well as the experimental data of Schuchardt and Berg.[20,21] It

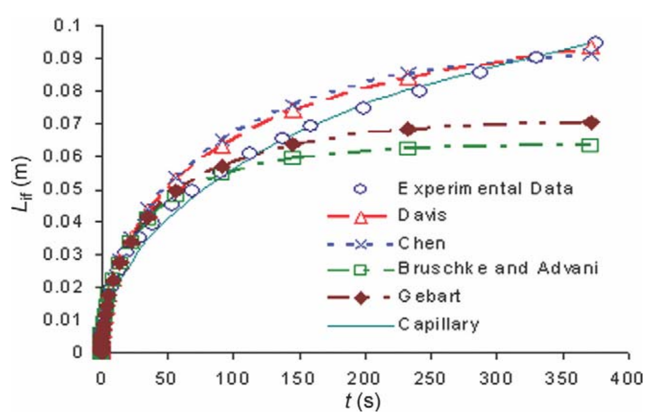

Figure 9. Wicking height vs. time predictions for the wicking of water in the 13%FC CMC/Cellulose composite-paper strip using the proposed Darcy's law-based model with different formula for the permeability of fibrous porous media.

The predicted values are compared with the modified Washburn-equation predictions and the experimental data of Schuchardt and Berg.[21]

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is observed that the proposed model performs the best when it is assumed that the volume of liquid absorbed into the fibers is equal to their volumetric expansion. An estimate of change in porosity with time for the proposed model is obtained from the published data on changes in hydraulic radius with time during wicking in the composite paper. This porosity change, when fed to several pre-existing permeability models, with their permeability values being a function of porosity, gives an estimate of changes in permeability in the paper. Of the several permeability models considered, the models by Terzaghi, Fehling, and Rose for porous media formed from particles, and the models by Davies and Chen for porous media formed from fibers perform the best when coupled with the proposed wicking model.

The new Darcy's law-based approach has an important advantage over the Washburn equation-based approach, as the former can be extended into two- and three-dimension wicking situations, while the latter Washburn model is restricted to one-dimensional flows (Masoodi et al., submitted). The Darcy's law-based approach has some advantages over other wicking models based on multi-phase flows, as well. The proposed model, as it harnesses the simplicity of single-phase flow, has fewer property values and parameters to be measured; moreover, the property and parameter values for single-phase flows are relatively simpler to measure.

Another advantage of the proposed Darcy's law-based model is its versatility. We have used the model in a preliminary study of liquid absorption in a porous bed of particles made from superabsorbent polymer,** and it seems that this model can improve wicking predictions in such extremely-swelling materials, as well.[28] We have also applied this theory to model flow in natural-fiber performs used in the liquid composite molding process for making bio-based composites, and our first attempt showed that it also works well for this material.[29] We plan to extend this theory, especially considering other values for the parameter b of Eq. 15, and study its effectiveness in modeling 2D and 3D flows in the swelling, liquid-absorbing porous media made from natural-fibers.

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Notation

A = area (m^2)
a = a constant ratio related to the rate of decreasing pore radius (1/s)
b = absorption coefficient (proportional to liquid absorption into matrix) (1/s)
D = diameter (m)
G = a set of defined function (Eqs. 24a, 24b, 18)
H = total length of porous media (m)
K = permeability (m^2)
L = length (m)
m = number of fibers per unit area in a porous medium
n = number of pores per unit area in a porous medium
P = modified pressure ($P = p + \rho g h$) (Pa)
p = liquid pressure (Pa)
q = any flow related quantity (Eqs. 7, 8)
R = radius (m)
S = sink term in the modified continuity equation (1/s)
t = time (s)
u = x-component of velocity (m/s)
V = velocity vector (m/s)
Vol = volume of REV (m^3)
x = x-coordinate
y = a defined variable (Eq. 25)

Greek letters

θ = contact angle (degree)
γ = surface tension of liquid (N/m)
μ = viscosity of liquid (kg/m s)
ε = porosity
η = A parameter in Bruschke and Advanis' model (Table 3)
ϕ = a function of porosity in an empirical formula for permeability (Eq. 39)
∇ = gradient operator

Superscripts

$'$ = dummy variable

Subscripts

0 = initial value
1 = an assigned number (Eq. 24a)
2 = an assigned number (Eq. 24b)
atm = atmosphere
c = capillary
e = effective
f = corresponding to fluid phase
fb = fiber
fs = corresponding to fluid-solid interface
h = hydraulic
lf = liquid front
nsw = nonswelling parameter
s = corresponding to solid phase
sw = swelling parameter

Other symbols

$\langle\rangle$ = volume-averaged quantities (Eq. 7)
$\langle\rangle^{f}$ = pore-averaged quantities (Eq. 8)

**Superabsorbent polymers are used as extreme water-absorbing substances that swell to many times their original particle dimensions while absorbing many times their weight of water.

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Appendix A: Derivation of the Modified Washburn Equation for Swelling Media

Schuchardt and Berg [21] assumed that the radius of parallel tubes decreases linearly with time as a result of swelling. On the basis of this assumption, the capillary and hydraulic radii were proposed to be:

$$R_c = R_0 \tag{A1a}$$

$$R_h = R_0 - at \tag{A1b}$$

Note that the capillary radius is taken to be a constant, as it is in the incoming dry part of the porous medium where the liquid front is just beginning to wet the matrix during wicking, while the hydraulic radius is deemed to decrease as a result of swelling. Substituting of Eqs. A1a and A1b in Eq. 1 leads to

$$\frac{2\gamma\cos(\theta)}{R_0} = \frac{8\mu L_{lf}}{(R_0 - at)^2}\frac{dL_{lf}}{dt} \tag{A2}$$

On separating the variables and rearranging, we have

$$\frac{\gamma\cos(\theta)}{4\mu R_0}(R_0 - at)^2 dt = L_{lf} dL_{lf} \tag{A3}$$

Integrating Eq. A3 while using the initial condition of $L_{lf}(t=0) = 0$ results in the modified Washburn equation of the form proposed by Schuchardt and Berg [21]:

$$L_{lf} = \sqrt{\frac{\gamma R_0\cos(\theta)}{2\mu}}\left[t - \frac{a}{R_0}t^2 + \frac{a^2}{3R_0^2}t^3\right]^{1/2} \tag{A4}$$

Appendix B: Derivation of the Volume-Averaged Continuity Equation for Liquid-Absorbing, Swelling Porous Media

For a single-phase flow in a porous medium, the point-wise continuity equation for fluid flow through the pores of the porous medium can be written as

$$\frac{\partial\rho_f}{\partial t} + \vec{\nabla}.(\rho_f\vec{V}_f) = 0 \tag{B1}$$

where ρ_f and $\vec{V}_f$ are density and velocity of fluid, respectively. The volume averaging of Eq. B1 in a term-by-term fashion within a representative elementary volume (REV) [22] leads to

$$\left\langle\frac{\partial\rho_f}{\partial t}\right\rangle + \langle\vec{\nabla}.(\rho_f\vec{V}_f)\rangle = 0 \tag{B2}$$

Two averaging theorems are used to convert the average of time and space derivatives to the derivatives of time and space. Using any fluid-flow related quantity q_f in a porous medium, the first and second averaging theorems,[26,27] respectively, can be described as

$$\langle\nabla q_f\rangle = \nabla\langle q_f\rangle + \frac{1}{\mathrm{Vol}}\int_{A_{fs}} q_f\vec{n}_{fs}\,dA \tag{B3}$$

$$\left\langle\frac{\partial q_f}{\partial t}\right\rangle = \frac{\partial\langle q_f\rangle}{\partial t} - \frac{1}{\mathrm{Vol}_f}\int_{A_{fs}} q_f\vec{V}_{fs}.\vec{n}_{fs}\,dA \tag{B4}$$

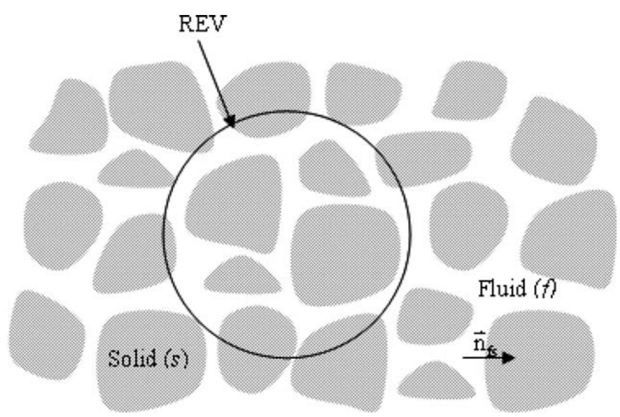

Figure B1. A schematic showing a spherical representative elementary volume (REV), the solid particles, the fluid region, and the unit normal vector $\vec{n}_{fs}$ (which is on the fluid-solid interface and is directed from the fluid phase to the solid phase) in a porous medium.

Here, A_{fs} is fluid-solid interface area, $\vec{n}_{fs}$ is the unit normal vector on the fluid solid interface pointing from fluid phase to the solid phase, and $\vec{V}_{fs}$ is the velocity of fluid-solid interface (see Figure B1). The first and second terms on the right hand side of Eq. B2 can be expanded using the first and second average theorems, Eqs. B3 and B4, as

$$\frac{\partial\langle\rho_f\rangle}{\partial t} - \frac{1}{\text{Vol}}\int_{A_{fs}} \rho_f \vec{V}_{fs}.\vec{n}_{fs}\, dA + \vec{\nabla}.\langle\rho_f \vec{V}_f\rangle + \frac{1}{\text{Vol}}\int_{A_{fs}} \rho_f \vec{V}_f.\vec{n}_{fs}\, dA = 0 \quad \text{(B5)}$$

Rearranging Eq. B5 gives the following form for the volume-averaged continuity equation.

$$\frac{\partial\langle\rho_f\rangle}{\partial t} + \vec{\nabla}.\langle\rho_f \vec{V}_f\rangle + \frac{1}{\text{Vol}}\int_{A_{fs}} \rho_f(\vec{V}_f - \vec{V}_{fs}).\vec{n}_{fs}\, dA = 0 \quad \text{(B6)}$$

The term $\vec{V}_f - \vec{V}_{fs}$ is the relative velocity of fluid with respect to the solid surface of the particles. In the other words, the surface integral, which is evaluated at the fluid-solid interface, is the rate of absorption of a liquid by the porous-medium fibers (or particles). In superabsorbent-fiber networks undergoing swelling, the liquid is absorbed by the fibers. Eq. B6 is the general continuity equation for flow in a deforming porous media undergoing liquid absorption by solid fibers or particles.

For an incompressible liquid, the density can be removed from the terms of Eq. B6 and the continuity equation reduces to

$$\frac{\partial\langle 1\rangle}{\partial t} + \vec{\nabla}.\langle\vec{V}_f\rangle + S = 0 \quad \text{(B7)}$$

with

$$S = \frac{1}{\text{Vol}}\int_{A_{fs}} (\vec{V}_f - \vec{V}_{fs}).\vec{n}_{fs}\, dA \quad \text{(B8)}$$

such that the sink term S is defined to be the ratio of volumetric rate of liquid absorption within an REV to the total volume of REV. Using Eq. 7, it is easy to see that $\langle 1\rangle = \varepsilon_f$. As a result, Eq. B7 can be simplified to the following final form for the flow of an incompressible liquid in a swelling, liquid-absorbing porous medium.

$$\vec{\nabla}.\langle\vec{V}_f\rangle = -S - \frac{\partial\varepsilon_f}{\partial t} \quad \text{(B9)}$$

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