GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 13 NO. 1, JANUARY, 2007 : 77 - 83
 ISSN 1118 - 0579

DRYING CHARACTERISTCIS OF WATER-BASED ALUMINA SUSPENSION FOR TAPE CASTING

Y. T. PUYATE

(Received 25 May, 2005; Revision Accepted 20 January, 2006)

ABSTRACT

Ceramic suspensions for tape casting exhibit a two-stage drying behaviour, where the first stage called the constant-rate period, is followed by a second stage called the falling-rate period. An analysis based on diffusion equation is presented for the drying characteristics of water-based alumina suspension for tape casting. Both the constant-rate period and the falling-rate period are modelled using a constant diffusion coefficient The constant-rate period is long and accounts for about 90% of the moisture lost from the suspension, while the remaining 10% is lost in a short falling-rate period. Predicted length of the constant-rate period, critical moisture content, total drying time, and drying-rate profile of the alumina suspension are compared with experimental data and good agreement is obtained.

KEYWORDS: Drying; Alumina; Suspension; Tape casting ; Diffusion; Solids

INTRODUCTION

Tape casting is a low-cost method for manufacturing large-area, thin, flat sheets of ceramics by making a layer of powdered raw material suspended in a liquid, drying this layer on a temporary support, and cutting the material to proper shape and size (Mistler et al., 1978). The industrial applications of tape cast products include substrates for thin film circuitry, capacitors, solid electrolytes for sensors and solid oxide fuel cells, piezoelectric ceramics for actuators and transducers, and magnesium oxide based materials for photovoltaic solar energy cells (Briscoe et al., 1998). Traditionally, slurries have been thought to dry in a two–stage process; the first stage Is called the constant-rate period, and the second stage is the falling rate period. During the constant-rate period, moisture transport within a body is rapid enough to maintain the moisture level at the surface of the body above that which would be in equilibrium with the ambient gas phase, and the drying rate is constant. During the falling-rate period, the drying rate of a material gradually decreases as the moisture content of the material falls, with the moisture level at the surface maintained at the equilibrium value.

Previous efforts on the use of water based ceramic suspensions for tape casting have been reported in the literature (Hotza and Griel, 1995; Ryu et al., 1993, Nagata, 1993, Puyate, 2003), but very little work has been done on the drying kinetics of water-based ceramic suspensions. Briscoe et al (1998) have reported a detailed experimental study on the formulation and drying kinetics of water-based alumina suspensions for tape casting operation. They developed an empirical model which predicts the weight loss of the suspension as a function of temperature, relative humidity, surface area of sample, and time, in the constant-rate period. However, the paper did not predict the length of the constant-rate period, critical moisture content, total drying time, and drying-rate profile of the suspension. Gilliland and Sherwood (1933) applied diffusion equation to the constant-rate period of drying of hemlock wood. Although the paper predicted the length of the constant-rate period and the critical moisture content, the exact functional relationship between drying rate and time at the critical point was not used, and the falling-rate period was not modelled

Furthermore, alumina suspension exhibits a gradual change from the constant-rate period to the falling-rate period (that is, it does not possess a sharp critical point), which requires a precise method of predicting the critical parameters, as presented here. It is the purpose of this paper to predict the length of the constant-rate period, critical moisture content, total drying time, and drying-rate profile of water-based alumina suspension for tape casting, through exact analyses of the moisture distributions in the constant-rate and falling-rate periods based on Sherwood's diffusion theory.

The two-stage drying model

The equation proposed by Sherwood (1929) to govern mass transport inside all drying media is given in dimensionless form as

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial Y^2} \qquad (1)$$

with the initial and boundary conditions for the constant-rate period as

$$\tau = 0: \qquad \theta = 1 \qquad (2i)$$

$$Y = 0: \qquad \frac{\partial \theta}{\partial Y} = 0 \qquad (2ii)$$

$$Y = 1: \qquad \frac{\partial \theta}{\partial Y} = -\mu \qquad (2iii)$$

The dimensionless variables are given by

$$\theta = \frac{\rho - \rho_{eq}}{\rho_o - \rho_{eq}} \qquad Y = \frac{y}{L} \qquad \tau = \frac{tD}{L^2} \qquad (3)$$

Y. T. Puyate, Department of Chemical Engineering, Rivers State University of Science and Technology, P.M.B. 5080, Port-Harcourt, Nigeria

where ρ is the moisture concentration (in mass units), ρ_o is the initial uniform moisture concentration, ρ_{eq} is the equilibrium moisture concentration, D is the moisture diffusion coefficient, y is the distance (and direction) of transport of moisture, t is time, L is the thickness of a flat plate that is dried from only one exposed face, $\mu = \alpha L/(\rho_o - \rho_{eq})D$ is the *drying intensity* which relates the characteristics times for evaporation and liquid diffusion, and α is the rate of drying per unit area in the constant-rate period. The moisture concentration in the body is expressed as a ratio of the "free" moisture concentration to the initial free moisture concentration. The moisture gradient at the exposed face ($y = L$) of the plate is constant during the constant-rate period, while that at the unexposed face ($y = 0$) is zero at all time. When μ is large, evaporation is fast, large concentration gradients occur, and the constant-rate period is short. Conversely, when μ is small, evaporation is slow, the concentration gradients are small, and the constant-rate period is long. Equation (1) can be solved using conditions (2) to obtain the moisture distribution during the constant-rate period as

$$\theta_1(Y,\tau) = 1 - \mu\left[\tau + \frac{Y^2}{2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau)\cos(n\pi Y)\right] \qquad (4)$$

Equation (4) is the one presented by Gilliland and Sherwood (1933) for the constant-rate period of drying of hemlock wood, which is also applied here to the constant-rate period of drying of water-based alumina suspension for tape casting as follows.

Figure 1 shows the moisture distribution during the constant-rate period for $\mu = 1$, indicating that the moisture concentration in the body at any time is higher at the unexposed face than the drying surface. It is assumed that the constant-rate period ends at a dimensionless critical time $\tau = \tau_{cr}$ when the moisture content at the surface of the body has dropped to the equilibrium value corresponding to the humidity of the atmosphere (Gilliland and Sherwood, 1933; Puyate, 1999). Equation (4) provides a relationship between μ and τ_{cr} in the form

$$\mu = \left[\tau_{cr} + \frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty} n^{-2}\exp(-n^2\pi^2\tau_{cr})\right]^{-1} \qquad (5)$$

which is approximated for small μ (or large τ_{cr}) by

$$\tau_{cr} \approx \frac{1}{\mu} - \frac{1}{3} \qquad (6)$$

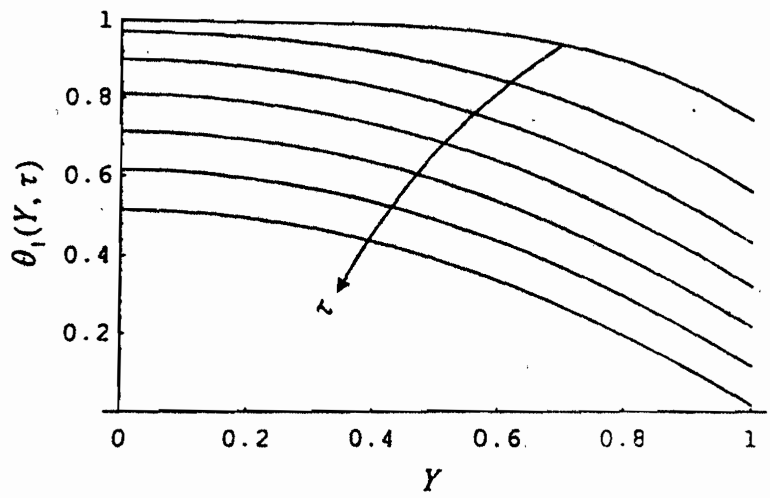

Fig. 1. Moisture distribution during the constant-rate period. Plot of $\theta_1(Y,\tau)$ against Y at $\mu = 1$, $\tau = 0.05$ to 0.65 in steps of 0.1.

Figure 2 shows plots of eqs. (5) and (6) (shown dashed) from which it may be seen that rq. (5) is accurately approximated by eq. (6) when $\mu \leq 1.5$. The inverse relationship simply indicates that τ_{cr} is large if μ, and vice-versa. The total quantity of moisture, Θ, in the body at any time during the constant-rate period is obtained by integrating eq. (4) across the thickness to obtain

$$\Theta_1(\tau) = 1 - \mu\tau \qquad (7)$$

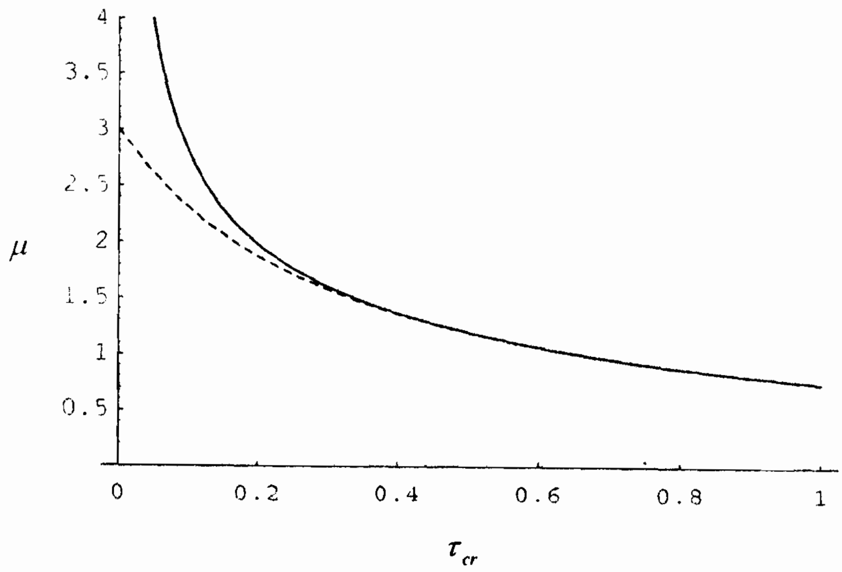

Fig. 2. Plot of μ against τ_{cr}.
________ exact eq. (5); _ _ _ _ _ _ approximate eq. (6).

It is evident by differentiating eq. (7) with respect to time that μ is the dimensionless evaporation rate during the constant-rate period, which can be expressed for an unshrinking material as

$$\mu = \frac{\alpha L}{(X_o - X_{eq}) D \rho_d} \tag{8}$$

where X_o is the initial moisture content (dry basis), X_{eq} is the equilibrium moisture content, and ρ_d is the dry density of the material. Equation (8) holds for a material which does not shrink, but may also be used to describe materials with negligible shrinkage during drying or, with L as the final thickness for a material which shrinks in a brief period at the start of drying while remaining virtually saturated (Puyate, 1999).

Equation (1) still holds in the falling-rate period since the process is controlled by diffusion of free moisture. Sherwood (1931) presented two models for the moisture distribution in the falling-rate period of drying of solids for two cases: (i) the drying rate is very fast such that the constant-rate period is negligible, and the moisture distribution at the beginning of the falling-rate period is approximately the initial uniform moisture concentration of the body, and (ii) the drying rate is very slow and a parabolic moisture distribution is assumed at the start of the falling-rate period. However, the appropriate initial condition of the falling-rate period corresponds to the moisture distribution at the end of the constant-rate period, which is given by eq. (4) at $\tau = \tau_{cr}$. The moisture concentration at the exposed drying surface of the body is the equilibrium moisture content, while the moisture gradient at the unexposed face is zero. Thus, the initial and boundary conditions of eq. (1) for the falling-rate period may be expressed in dimensionless form as

$$\tau = \tau_{cr}: \quad \theta = \theta_1(Y, \tau_{cr}) \tag{9i}$$

$$Y = 0: \quad \frac{\partial \theta}{\partial Y} = 0 \tag{9ii}$$

$$Y = 1: \quad \theta = 0 \tag{9iii}$$

where

$$\theta_1(Y, \tau_{cr}) = 1 - \mu\left[\tau_{cr} + \frac{Y^2}{2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2\pi^2\tau_{cr})\cos(n\pi Y)\right] \tag{10}$$

Equation (1) can be solved (Puyate, 1999) using conditions (9) to obtain the exact model for the moisture distribution during the falling-rate period, which is valid at all drying rate, as

$$\theta_2(Y, s) = \frac{4}{\pi}\sum_{m=1}^{\infty} H_m \exp[-(2m-1)^2\pi^2 s/4]\cos[(2m-1)\pi Y/2] \tag{11}$$

where $H_m = \frac{(-1)^m}{(2m-1)}\left\{\mu\left[\tau_{cr} + \frac{1}{3} - \frac{4}{\pi^2(2m-1)^2} - \frac{2(2m-1)^2}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp(-n^2\pi^2\tau_{cr})}{n^2[(2m-1)^2-4n^2]}\right]-1\right\}$ (12)

and $s = \tau - \tau_{cr}$ is the dimensionless time from the inception of the falling-rate period. Figure 3 shows a plot of $\theta_2(Y, s)$ against Y for a range of values of s for $\mu = 1$ (with a corresponding value of $\tau_{cr} = 0.67$), from which it may be observed that the moisture gradients diminish with time, approaching zero asymptotically through a cosine distribution. The total quantity of moisture in the body at any time during the falling-rate period is obtained by integrating eq. (11) across the thickness as

$$\Theta_2(s) = -\frac{8}{\pi^2}\sum_{m=1}^{\infty}\frac{(-1)^m}{(2m-1)}H_m \exp[-(2m-1)^2\pi^2 s/4] \quad (13)$$

It may be necessary to indicate that Figs. 1 to 3 were plotted in *Mathematica*.

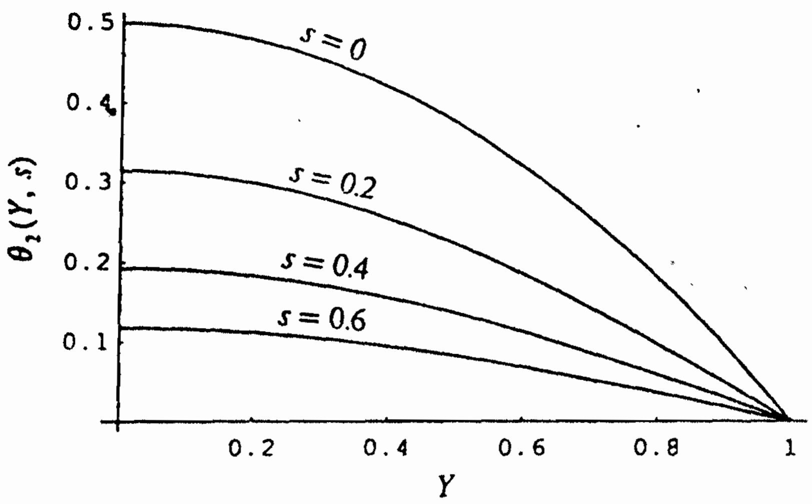

Fig. 3. Moisture distribution during the falling-rate period. Plot of $\theta_2(Y, s)$ against Y for a range of values of s for $\mu = 1$ and $\tau_{cr} = 0.67$

Prediction of drying parameters

Here, the length of the constant-rate period, the critical moisture content, and the total drying time of the alumina suspension are predicted using the models presented above. Table 1 shows the key drying parameters required.

Table 1. Key drying parameters of alumina suspension (Puyate, 1999)

Parameter	Experimental value
Material thickness (L), m	0.0006
Drying rate in the constant-rate period (α), kg/m^2s	1.51×10^{-5}
Initial moisture content (X_o), kg/kg	0.296
Equilibrium moisture content (X_{eq}), kg/kg	0.05
Moisture diffusion coefficient (D), m^2/s	1.75×10^{-10}
Dry density (ρ_d), kg/m^3	1700

Length of the constant-rate period and critical moisture content

The alumina suspension was dried from only one face, so L is the total thickness. The values of the parameters in Table 1 can be used in eq. (8) to give $\mu = 0.124$, which since $\mu < 1.5$, can be used in eq. (6) to obtain $\tau_{cr} = 7.73$ Equations (6) and (8) can be combined to estimate the duration of the constant-rate period of the suspension as

$$t_{cr} = \frac{(X_o - X_{eq})\rho_d L}{\alpha} - \frac{L^2}{3D} = 15900\,\text{s}\,(4.42\ \text{hours}) \tag{14}$$

The critical moisture content, X_{cr}, of the suspension is obtained by subtracting the quantity of water lost during the constant-rate period from the initial moisture content using eq. (7) in the form

$$X_{cr} = X_o - \frac{\alpha t_{cr}}{L\rho_d} = 0.06\ (\text{dry basis}) \tag{15}$$

Total drying time

It may be seen from eq. (13) that the moisture concentration of a body approaches the equilibrium value only if $s \to \infty$ The first order terms of eq. (13) gives

$$\Theta_2(s) \approx -\frac{8}{\pi^2}\exp(-\pi^2 s/4)\left\{\mu\left[\tau_{cr} + \frac{1}{3} + \frac{2}{3\pi^2}[\exp(-\pi^2\tau_{cr}) - 6]\right] - 1\right\} \tag{16}$$

where $\Theta_2(s) = (X_2(s) - X_{eq})/(X_o - X_{eq})$ is the ratio of the free moisture content during the falling-rate period to the initial free moisture content (dry basis). Since $\Theta_2(s)$ varies from unity (initial wet condition) to zero (dry condition at equilibrium), it is necessary to select an arbitrary value for the dryness of a body in order to predict the total drying time. Equation (16) is used to predict the total drying time of the suspension based on the time at which $\Theta_2(s)$ falls to a small value, say 0.001 (99.9% dry). The suspension sample will be 99.9% dry when $\Theta_2(s) = 0.001$. Equation (16) is easily solved as shown in Appendix A using appropriate values of the parameters in Table 1 with $\Theta_2(s) = 0.001$ to obtain $s = 1.5$ The dimensionless total drying time becomes $\tau = \tau_{cr} + s = 9.23$ to give the total drying time of the suspension as $t = \tau L^2 / D = 18987\text{s}$ (5.27 hrs).

RESULTS AND DISCUSSION

Table 2 summarizes the observed and predicted drying parameters of the alumina suspension

Table 2. Observed and predicted drying parameters of alumina suspension

Parameter	Observed	Predicted
Constant-rate period (hrs)	3.75	4.42
Critical moisture content (kg/kg)	0.09	0.06
Total drying time (hrs)	5.28	5.27

In order to compare predicted and experimental drying-rate profiles for the suspension, the drying rates from eq. (7) and (13) were expressed in terms of moisture content (dry basis) and used together with $\mu = 0.124$ and $\tau_{cr} = 7.73$ (predicted) for the duration of the experiment. The bone-dry mass of the suspension was used to convert the units of the predicted drying rate from moisture content per unit time to mass of moisture per unit time. Figure 4 shows the measured and predicted drying-rate profiles, from which, it may be seen that eqs. (7) and (13) compare reasonably well with the experimental data. The major difference between the measured and predicted profiles is that the predicted profile does not really capture the trend of the measured profile near the critical point. This is because the alumina suspension exhibits a gradual change from the constant-rate period to the falling-rate period, which makes accurate location of the critical point quite difficult. This also explains the slight over-prediction of the length of the constant-rate period, and the slight under-prediction of the critical moisture content in Table 2. As may be observed from Fig. 4(a), the drying rate of the suspension sample falls dramatically to zero at around $t = 19000\text{s}$, and the quantity of moisture lost in the region $t > 19000\text{s}$ is negligible. The predicted total drying time may then be seen to compare reasonably well with the experimentally observed value.

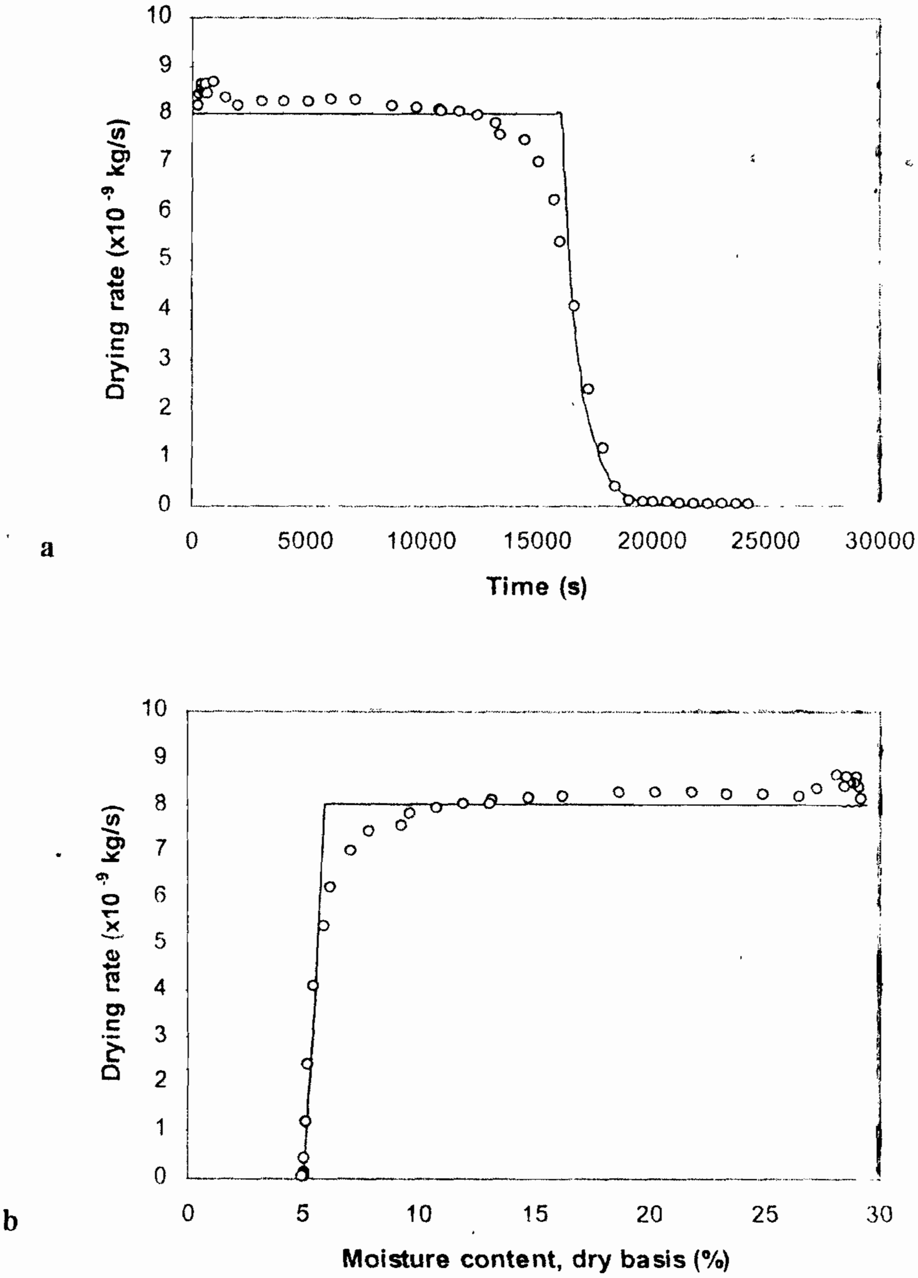

Fig. 4. Measured and predicted drying-rate profiles for the alumina suspension: (a) Plot of drying rate against time, (b) Plot of drying rate against moisture content.
o measured values; _______ eq. (7) for the constant-rate period, and eq (13) for the falling-rate period.

CONCLUSION

The drying of water-based alumina suspension for tape casting is a two-stage process consisting of a long constant-rate period during which the bulk of free moisture is lost by evaporation, and a short falling-rate period which accounts for the remaining moisture loss due to diffusion. During the constant-rate period, the process is evaporation-controlled and the drying rate can be influenced by air flow, ambient humidity and temperature, depending upon the operating conditions of the process. During the falling-rate period, diffusion of vapour from the interior of the material to the surface controls the drying process. Although the suspension does not exhibit a sharp critical point, and the predicted length of the constant-rate period and the critical moisture content are slightly different from the experimentally observed values, the predicted total drying time is in good agreement with the experimental value, and the predicted drying-rate profile also compares reasonably well with the measured profile. On the whole, the analysis presented here for the drying characteristics of the alumina suspension is based on Sherwood's diffusion theory of a two-stage drying process, and may be applied to the drying of solids and related materials.

Appendix A

Determination of s from eq. (16) for the suspension

For the alumina suspension, $\mu = 0.124$ and $\tau_{cr} = 7.73$, which when substituted into eq (16) gives

$$\Theta_2(s) = -\frac{8}{\pi^2}\exp(-\pi^2 s/4)\left\{0.124\left[7.73 + \frac{1}{3} - \frac{12}{3\pi^2}\right] - 1\right\} \quad \text{(A1)}$$

$$= -\frac{8}{\pi^2}\exp(-\pi^2 s/4)[0.124(7.66) - 1]$$

$$= -\frac{8}{\pi^2}\exp(-\pi^2 s/4)[0.95 - 1]$$

$$= -\frac{8}{\pi^2}\exp(-\pi^2 s/4)[-0.05]$$

$$\Theta_2(s) = \frac{0.4}{\pi^2}\exp(-\pi^2 s/4) \quad \text{(A2)}$$

The suspension will be 99.9% dry when $\Theta_2(s) = 0.001$, and eq. (A2) becomes

$$0.001 = \frac{0.4}{\pi^2}\exp(-\pi^2 s/4) \quad \text{(A3)}$$

Taking the natural logarithms of both sides of eq. (A3) gives

$$-6.91 = \ln(0.4/\pi^2) - \frac{\pi^2 s}{4} \quad \text{(A4)}$$

$$-6.91 = -3.21 - \frac{\pi^2 s}{4} \quad \text{(A5)}$$

$$-3.7 = -\frac{\pi^2 s}{4} \quad \text{(A6)}$$

to obtain

$$s = \frac{4 \times 3.7}{\pi^2} = 1.499$$

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