

Modeling of liquid desiccant drying method for gelcast ceramic parts

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Abstract

Gelcasting is a promising new technology for manufacturing of advanced structural ceramic components. The process involves drying of the “green” gelcast part before densification. Conventional methods in drying green gelcast part, using dry air or gas with a specific condition of humidity and temperature usually are confronted with many difficulties. Non uniform and differential drying in various regions due to the solvent gradient induces structural and residual stresses, that cause defects such as cracking, warping, bending and the other malformations, which make the part useless. Liquid desiccant drying method, as a novel method, has been used for drying green gelcast ceramic parts in the purpose of increasing the drying rate and removing the defects due to the release of residual stresses. In this study, the kinetics of one-dimensional drying of green gelcast ceramic parts through this method is described by a Fickian model, which accounts for the movement of the gel surface. For a constant mutual diffusion coefficient, D_m , the fractional approach to equilibrium, F , is only a function of dimensionless time τ_0^* , and the equilibrium volume ratio, Φ . By using simple method experimental values of D_m which account for the movement of the gel boundary are obtained. Experimental data for alumina gelcast cylinders having diameters of 7 and 9 mm are well fitted by the model, and the amount of ceramic loading was 5, 10, 20, 30 and 35% by volume, respectively. Various concentrations of aqueous solution of PEG1000 were used as liquid desiccants. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Drying; C. Diffusion; D. Al_2O_3 ; Gelcasting

1. Introduction

Gelcasting is a relatively new method for fabricating powder compacts that are used in manufacturing advanced structural ceramic parts for various industries [1–4]. The gelcasting process involves the preparation of an aqueous slurry of ceramic powder [e.g. alumina (Al_2O_3) or silicon (Si)] together with small quantities of monomers, crosslinkers, initiators, catalysts and sintering aids.

Gelation is initiated after pouring the slurry into a simple or complex-shaped mould and increasing the temperature. The macromolecular network that results from this in situ polymerization holds the ceramic particles together. After removal from the mould, the gelled

part contains moisture about one-fourth of its mass, which should then be removed by drying. Then, the part is heated to burn out the polymer gel and is subsequently sintered for densification. The final product is a near-net-shape part that requires very little machining [5].

Drying, i.e. solvent removing from green gelcast part, is an essential step in the gelcasting process. Conventional drying methods generally comprise exposing a formed part to air or a selected gas or gas mixture having a specific condition of temperature and humidity that will cause solvent to evaporate from the gelled part and be carried away by the surrounding medium [6]. Some types of parts having thick and thin regions, sharp edges and/or occluded regions, etc. are difficult to dry properly via conventional methods, because of solvent gradient therein, resulting in significantly non uniform drying of these regions, that induces structural and residual stresses. These stresses can generally cause a complicated situation and make the parts useless [7].

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Nomenclature

D_m	mutual diffusion coefficient
D_p	polymer fixed diffusion coefficient
D_s	solvent fixed diffusion coefficient
F	fractional approach to equilibrium
$J_{i,ref}$	diffusive flux of phase i
r	spatial coordinate
R	radius (cylinder)
R_0	initial radius (cylinder)
t	time
u_{ref}	reference velocity
u_m	volume average velocity
u_p	polymer velocity
u_s	solvent velocity
V	sample volume at time t
V^0	initial sample volume
V^∞	final sample volume
r	dimensionless distance
r^{0*}	dimensionless interface position

Greek letters

τ_0^*	dimensionless time
φ_p	polymer volume fraction
φ_s	solvent volume fraction
φ_p^0	initial polymer volume fraction
φ_p^∞	final polymer volume fraction
φ^*	dimensionless volume fraction
Φ	ratio of final to initial gel (sample) volume

In this work, liquid desiccant drying has been used as a novel method in drying gelcast ceramic parts [8]. The green bodies are brought into contact with an appropriate liquid desiccant, by immersion. The reason for the effect of the liquid desiccant on a gelcast part is the osmotic difference between the liquid desiccant and the gelled polymer in the part [8].

Crosslinked polymer gels, which are three-dimensional network structures, can swell and collapse reversibly when immersed in the solvents. The gel volume change is usually brought about by altering the condition of the solvent: its temperature, composition, pH or salt content [9]. In this investigation, we are concerned with amorphous, covalently crosslinked polymer gels which are filled by ceramic powder (alumina) undergoing one-dimensional drying (collapse) in an isothermal solution of liquid desiccant. Our focus is on rubbery gels; gels which shift between glassy and rubbery states during the course of volume change are not considered [10].

The models describing the kinetics of the gel volume change may be divided into three categories.

1. Fickian diffusion models; which obey the Fick's law for the distribution of solvent in a gel sample during absorption or desorption of solvent [11]. The movement of the gel boundary, an important feature of large volume change, was taken into account by Singh [12].
2. Collective diffusion models; which are based on the work of Tanaka and coworkers [13,14], who treated the volume change of a gel as the deformation of a network driven by a gradient of stress. These models describe small volume change, furthermore, the parameters estimated by fitting these models to data may be unrealistic [15].
3. Non-Fickian diffusion models; experimental curves (curve of volume change of gel) which are not initially linear are normally considered to indicate non-fickian behaviour. Deviation from the classical behaviour are usually attributed to some of the following phenomena:
 - Variable surface concentration
 - A history-dependent diffusion coefficient
 - Stresses between parts of the gel when volume changes to different extents
 - Polymer relaxation

The first three have been discussed by Crank and Park [16], while the last has been modeled by Berens and Hopfenberg [17] and Joshi and Astarita [18]. Before turning to a more elaborate model, it is crucial to understand the effect of the movement of the boundary on the kinetics of fickian volume change of gel. Recent experimental and theoretical studies of the kinetics of volume change have demonstrated the importance of boundary motion [19–21].

In what follows, we describe the kinetics of gel volume change in pure gel and alumina gelcast cylindrical parts for a one-dimensional geometry, which is valid for large or small volume change. Next, we fit the model to experimental data for cylindrical pure gel and gelcast parts with 5, 10, 20, 30 and 35% by volume of ceramic loading in a pre-mixed solution.

2. Gel volume change equations

Based on the Singh model, gel volume change is modelled as an isothermal two-phase motion of a polymer phase (p) and a low molecular weight solvent phase (s). Both phases are assumed to have constant and equal densities. Each element of volume contains polymer at a volume fraction φ_p and solvent at a volume fraction φ_s , where

$$\varphi_p + \varphi_s = 1 \quad (1)$$

The continuity equations for both phases can be written as follows:

Polymer phase:

$$\frac{\partial \varphi_p}{\partial t} = -\nabla \cdot J_p \quad (2)$$

Solvent phase:

$$\frac{\partial \varphi_s}{\partial t} = -\nabla \cdot J_s \quad (3)$$

where J_i , the volumetric flux density, is the volume of phase i crossing a stationary unit area in unit time and t is the time. The quantity J_i is called the ‘superficial velocity’. The continuity equations for one-dimensional cylindrical geometry are written as follows:

Polymer phase:

$$\frac{\partial \varphi_p}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r J_p) \quad (4)$$

Solvent phase:

$$\frac{\partial \varphi_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (r J_s) \quad (5)$$

The volumetric flux density is related to the linear velocity of phase i , u_i , through

$$J_i = \varphi_i u_i \quad (6)$$

The volumetric flux density is separated into two contributions: a convective flux and a diffusive flux. Let $J_{iu_{ref}}$ be the diffusive flux of the phase i relative to a reference velocity u_{ref} then:

$$J_i = j_{iu_{ref}} + \varphi_i u_{ref} \quad (7)$$

Any reference velocity can be chosen, but the most common choices are the mass, molar, volume average, or the velocities of one of the phases. The polymer and solvent velocities are obtained from Eq. (6) while the volume average velocity is

$$u_m = \varphi_p u_p + \varphi_s u_s \quad (8)$$

Combining Eqs. (1), (4), (5) and (8) yields

$$\frac{\partial}{\partial r} (r u_m) = 0 \quad (9)$$

This equation, which reflects overall continuity, applies within the gel as well as outside the gel where $\varphi_p = 0$ and $u_m = u_s$.

The surface of the gel separates the polymer from the external solution. This interface moves at a velocity, which is equal to the polymer velocity at the surface. Using Eq. (6) for the polymer phase at the surface yields

$$u_p \Big|_{\text{surface}} = \frac{J_p}{\varphi_p} \Big|_{\text{surface}} \quad (10)$$

This equation is referred to as the interface equation.

The description is complicated by a constitutive equation, which defines diffusive flux through a diffusion coefficient. Taking the volume average velocity as the reference velocity and using Fick’s first law, the constitutive equation is

$$J_{pu_m} = D_m \frac{\partial \varphi_p}{\partial r} \quad (11)$$

where, D_m is the mutual diffusion coefficient.

2.1. Volume change equations

Combining Eqs. (1)–(11) gives the gel diffusion equation

$$\frac{\partial \varphi_p}{\partial t} = \frac{1}{r} \left[\frac{\partial}{\partial r} \left(D_m r \frac{\partial \varphi_p}{\partial r} \right) \right] \quad (12)$$

and the interface equation

$$\frac{\partial R}{\partial t} = - \frac{D_m}{\varphi_p} \frac{\partial \varphi_p}{\partial r} \Big|_{r=R} \quad (13)$$

By choosing any reference velocity, we have different gel diffusion and interface equations. Since each equation must yield the same polymer velocity at the gel interface $u_p|_{\text{interface}}$ we have:

$$D_m = \varphi_p D_p = \varphi_s D_s \quad (14)$$

2.2. Initial and boundary conditions

The initial polymer volume fraction is uniform at φ_p^0 and at the surface of the gel the polymer volume fraction gets its equilibrium value, φ_p^∞ , instantaneously upon exposure to solvent:

$$t = 0, \quad \varphi_p = \varphi_p^0 \quad \text{for } 0 \leq r \leq R \quad (15)$$

$$r = R \quad \varphi_p = \varphi_p^\infty \quad \text{for } t > 0 \quad (16)$$

where R is the time-variable radius of cylinder. The remaining boundary condition for Eq. (12) arises from symmetry:

$$r = 0, \quad \frac{\partial \varphi_p}{\partial r} = 0 \text{ for } t \geq 0 \quad (17)$$

The initial conditions for Eq. (13) is

$$t = 0 \quad R = R_0 \quad (18)$$

where R_0 is the initial (as cast) radius of a cylinder.

2.3. Dimensionless volume change equations

Dimensionless time, distance, volume fraction and interface position are defined as follows:

$$\tau_0^* = \frac{D_m t}{R_0^2} \quad (19)$$

$$r^* = \frac{r}{R} \quad (20)$$

$$\varphi^* = \frac{\varphi_p^0 - \varphi_p}{\varphi_p^0 - \varphi_p^\infty} \quad (21)$$

$$r^{0*} = \frac{R}{R_0} \quad (22)$$

Assuming D_m as a constant, Eqs. (12)–(18) have the following dimensionless forms:

$$\frac{\partial \varphi^*}{\partial \tau_0^*} = \frac{r^*}{r^{0*}} \frac{\partial \varphi^*}{\partial r^*} \frac{dr^{0*}}{d\tau_0^*} + \left(\frac{1}{r^{0*}} \right)^2 \left(\frac{1}{r^*} \left(\frac{\partial \varphi^*}{\partial r^*} \right) + \frac{\partial^2 \varphi^*}{\partial r^{*2}} \right) \quad (23)$$

$$\frac{dr^{0*}}{d\tau_0^*} = [\Phi - 1] \frac{1}{r^{0*}} \frac{\partial \varphi^*}{\partial r^*} \Big|_{r^*=1} \quad (24)$$

subject to

$$\tau_0^* = 0, \quad \varphi^* = 0 \text{ for } 0 \leq r^* \leq 1 \quad (25)$$

$$r^* = 1, \quad \varphi^* = 1 \text{ for } \tau_0^* > 0 \quad (26)$$

$$r^* = 0, \quad \frac{\partial \varphi^*}{\partial r^*} = 0 \text{ for } \tau_0^* \geq 0 \quad (27)$$

$$\tau_0^* = 0 \quad r^{0*} = 1 \quad (28)$$

where

$$\Phi = \frac{\varphi_p^0}{\varphi_p^\infty} \quad (29)$$

The volumetric fractional approach to equilibrium, F , is given by

$$F = \frac{V - V^0}{V^\infty - V^0} \quad (30)$$

where V is the gel volume at time t , V^0 is the initial gel volume and V^∞ is the equilibrium (final) gel volume. Since the volume of the polymer is the same in the initial and final states, Φ may also be written as the ratio of the final to initial volumes:

$$\Phi = \frac{V^\infty}{V^0} \quad (31)$$

Combining Eqs. (22), (30) and (31) yields

$$F = \frac{r^{0*2} - 1}{\Phi - 1} \quad (32)$$

For constant D_m , the fractional approach to equilibrium is a function only of the dimensionless time τ_0^* and the volume ratio, Φ .

3. Experimental details

3.1. Materials

The specification of the materials used in this work are summarized in Table 1.

3.2. Experimental procedure

The experiments that have been performed in this study showed, as expected, that lower ceramic loading in the gel binder creates higher drying potentials (and higher drying rates), whereas relatively higher ceramic loading creates lower drying potentials. Thicker samples correspond to longer transport distances and hence result in drying rates that are much smaller than those for thin gelcast parts. Concentration of liquid desiccant is another parameter which affects on the drying rate of the gelcast parts. Higher concentration of the liquid desiccant creates higher drying rates. Three sets of drying experiments have been conducted on cylindrical shaped alumina gelcast samples and pure acrylamide gels. In each set, one of the parameters (i.e. ceramic loading, thickness, or liquid desiccant) varies while the other two parameters were kept constants. These experiments revealed the relative sensitivity of the drying rates to the above parameters and helped to determine the model parameter (D_m).

Commercial-grade alumina powder that consists of particles of 30 μm in size was used to produce the gelcast parts. The gelation system which was used to form

Table 1
Characteristics of materials

Material	Function	Chemical formula	Characteristics	Supplier
Alumina	Ceramic powder	Al_2O_3	Mean particle size 30 μ	Good Fellow ^a
Acrylamide	Monofunctional monomer	$\text{C}_2\text{H}_3\text{CONH}_2$	–	Merck ^b
<i>N,N'</i> -Methylene bisacrylamide	Difunctional monomer (cross linker)	$(\text{C}_2\text{H}_3\text{CONH}_2)_2\text{CH}_2$	–	Sigma ^c
Ammonium persulfate	Initiator	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	–	Merck ^b
<i>N,N,N',N'</i> -Tetra methyl ethyl diamine	Accelerator (catalyst)	$\text{C}_6\text{H}_{16}\text{N}_2$	–	Merck ^b
Poly(ethylene glycol)	Liquid desiccant	$\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$	Mw. 950–1050	Merck ^b

^a Cambridge Science Park, Cambridge CB4 4DJ, UK.

^b E. Merck, D6100 Darmstadt, F.R., Germany.

^c Sigma Chemical Co., PO Box 14508, St. Louis, MO 63178, USA.

the test samples has been described in detail elsewhere [1–3]. The system consists of a monomer (acrylamide) and a crosslinker (*N,N'*-methylene bis acrylamide) as the major constituents, accompanied by small amounts of initiator and catalyst, which are added to support the thermally activated free-radical polymerisation reaction.

After gelation, the sample was remoulded and immersed in an aqueous solution of PEG1000 as liquid desiccant solution. Each 30 min, sample was removed from the con-

tainer and washed with deionized water. Excess water on the surface of the sample was drained off with tissue and then weighed. Sample was weighed based on above procedure until a state of equilibrium was reached.

The six experiments in the first set (set 1) were conducted at ceramic loading of 0, 5, 10, 20, 30 and 35% by volume, respectively. The thickness was 7 or 9 mm and concentration of the aqueous solution of liquid desiccant was 20% by weight. Three experiments in second

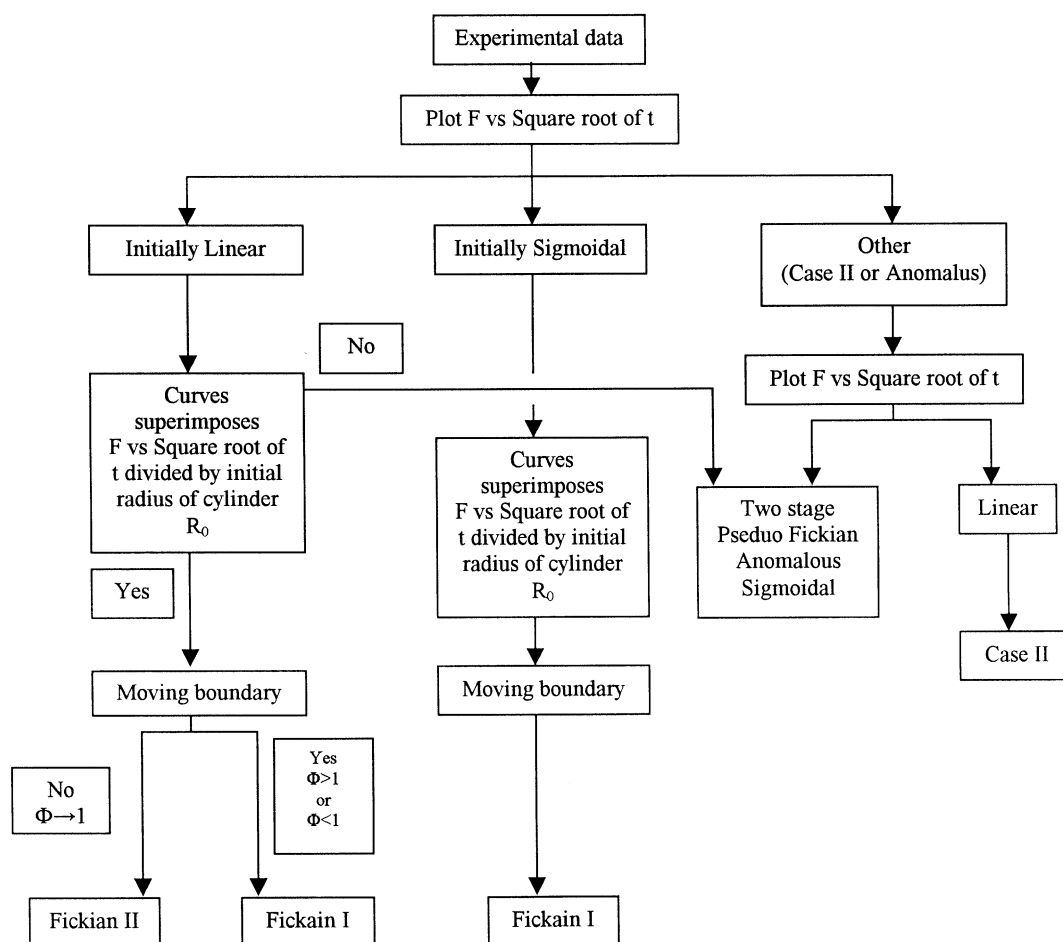


Fig. 1. Determination of diffusion type from experimental data [22].

set (set 2) were performed at concentrations of aqueous solution of PEG1000 of 20, 40 and 60% by weight. The thickness was 7 mm and ceramic loading of 35% by volume. Six experiments in the final set (set 3) were performed at a various ceramic loading and concentration of 20% by weight of aqueous solution of PEG1000 on samples having a thickness of 7 and 9 mm. In all the experiments, concentration of liquid desiccant on the surface of sample remained constant during the drying cycle.

4. Results and discussion

By using experimental data, one could determine the kinetics of gel drying and also the possible mechanism of diffusion of solvent through the gel as follows: (Fig. 1) [22]. As shown in Fig. 1, with plot of F against square root of t , one could make an initial guess about type of diffusion of the solvent through gel and its kinetic behaviour, but for a complete consideration of this behaviour, experiments were developed based on various sample thicknesses. A gel is regarded as Fickian (Fickian I or Fickian II), if all of the curves of the F verses square root of t divided by R_0 are superimposed.

Fig. 2 shows that, for pure gel (ceramic loading of zero) the curves of different R_0 superimpose on each other and they are linear in their initial time portion (generally 40–60% of the equilibrium time). Therefore, based on our pervious discussion (Fig. 1), the kinetic behavior of drying of pure gel is a Fickian diffusion with volume change.

Change in the amount of ceramic loading of the gel at a constant concentration of liquid desiccant solution has no effect on the type of diffusion and drying of gel in constant concentration of liquid desiccant, which are

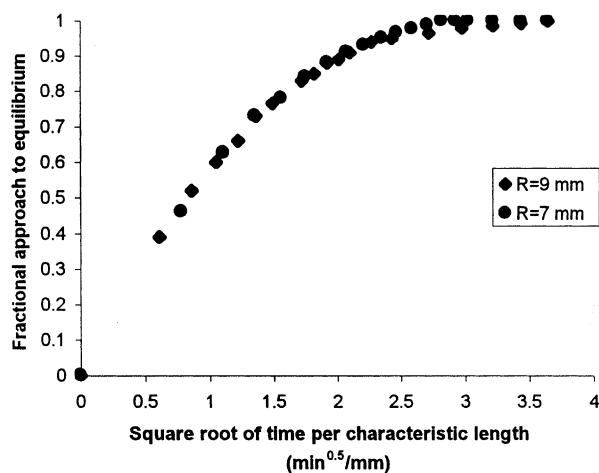


Fig. 2. Pure cylinder gel dried in 20% by weight of aqueous solution of PEG1000.

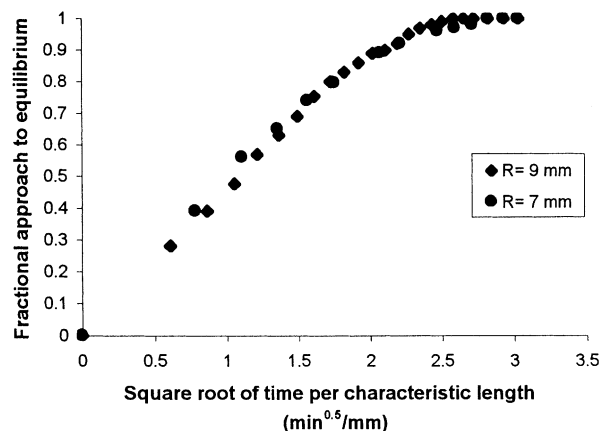


Fig. 3. Alumina (10 vol.%) gelcast part (cylinder) dried in 20% by weight of aqueous solution of PEG1000.

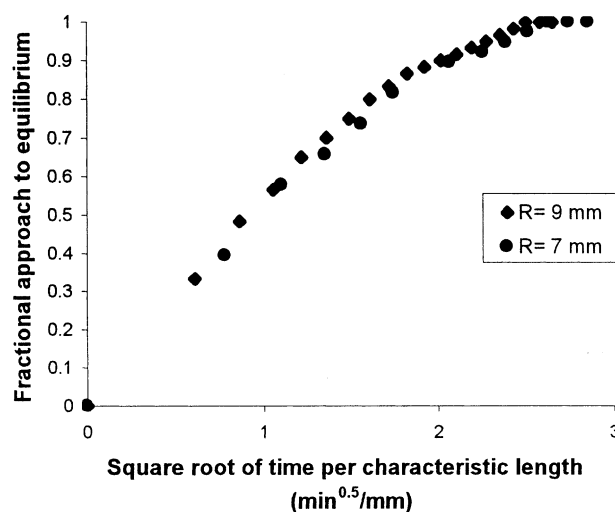


Fig. 4. Alumina (20 vol.%) gelcast part (cylinder) dried in 20% by weight of aqueous solution of PEG1000.

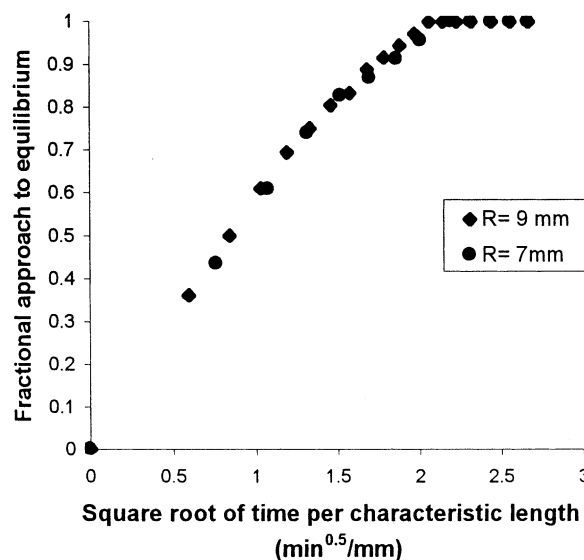


Fig. 5. Alumina (30 vol.%) gelcast part (cylinder) dried in 20% by weight of aqueous solution of PEG1000.

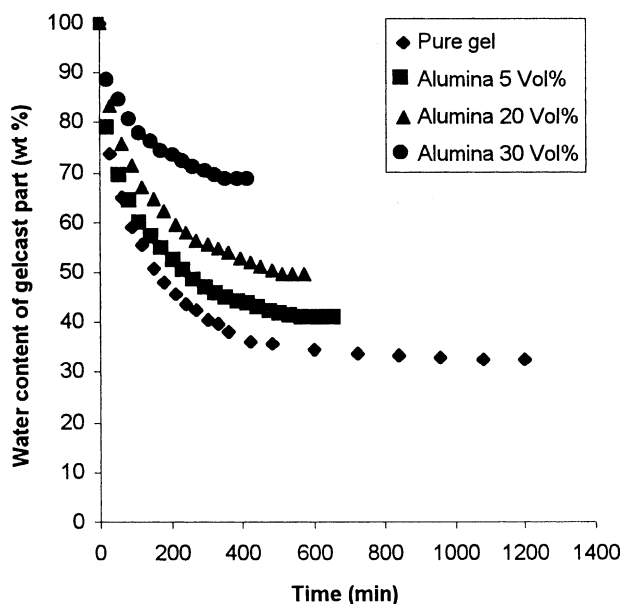


Fig. 6. Comparing rate of drying of gelcast parts in various loading of ceramic at 20% by weight of PEG1000 and thickness of 9 mm.

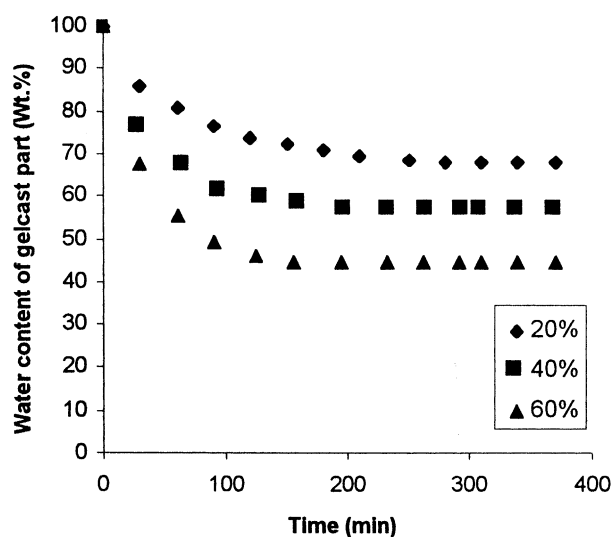


Fig. 7. Comparing rate of drying of gelcast parts in various concentration of liquid desiccant at ceramic loading of 30% by volume and thickness of 7 mm.

typically shown in Figs. 3–5. But for a given amount of ceramic in the gel as a neutral component, the rate of drying decreases with increasing the ceramic loading of the gel, Fig. 6, which is reasonable.

Another parameter which affects the rate of drying, is the concentration of aqueous solution of liquid desiccant. Three levels of concentrations were considered (i.e. 20, 40, 60% by weight). As shown in Fig. 7, with increase in the concentration of aqueous solution of liquid desiccant, the rate of drying decreased considerably. This could be attributed to the difference

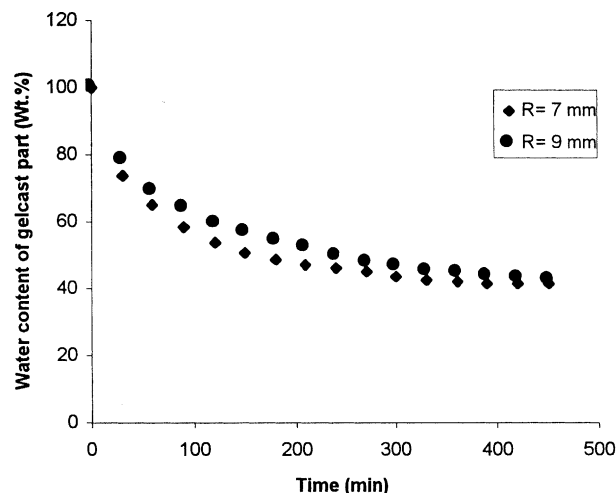


Fig. 8. Comparing rate of drying of gelcast parts in different thickness of sample at ceramic loading of 5% by volume and 20% by weight of PEG1000.

between the concentration of solvent (water) in the gel and the bath (liquid desiccant solution). This difference results in a gradient of chemical potential between the two media. Higher the gradients, cause more diffusion of solvent from gel to the bath. As a result, the rate of drying increases accordingly.

The thickness of sample is another factor that has considerable effect on the time and the rate of drying. As seen in Fig. 8, rate of drying decreases with increase in sample thickness. The thickness of the sample will increase the length of solvent diffusion through the sample, and its equilibrium time.

Since an exact solution of Eqs. (23)–(29) is available only for the collapse of slabs [23], these equations were solved numerically by the finite difference method of Sparrow and Chuck [24]. Results are presented here as the fractional approach to equilibrium, F , versus the square root of dimensionless time τ_0^* .

Figs. 9–11 show drying curves for cylinder of pure gel and alumina gelcast at 7 mm thickness with several values of ceramic loading in gel at various concentration of liquid desiccant in the bath. With increasing ceramic loading or decreasing concentration of liquid desiccant solution, sample needs much more time to reach the equilibrium. Therefore, the rate of drying decreases. The same result is obtained for pure gel in the bath with similar solvent within the gel (water), when Φ increases (up to 1). Eq. (31) shows that Φ may also be written as the ratio of the final to initial volume of sample. Based on this equation and with considering shrinkage of sample during drying, one could relate effect of ceramic loading and concentration of liquid desiccant of the sample to Φ . Φ is the only input parameter to program for computing numerically the kinetic of gelation at these states. As seen in Figs. 9–11, the volume change

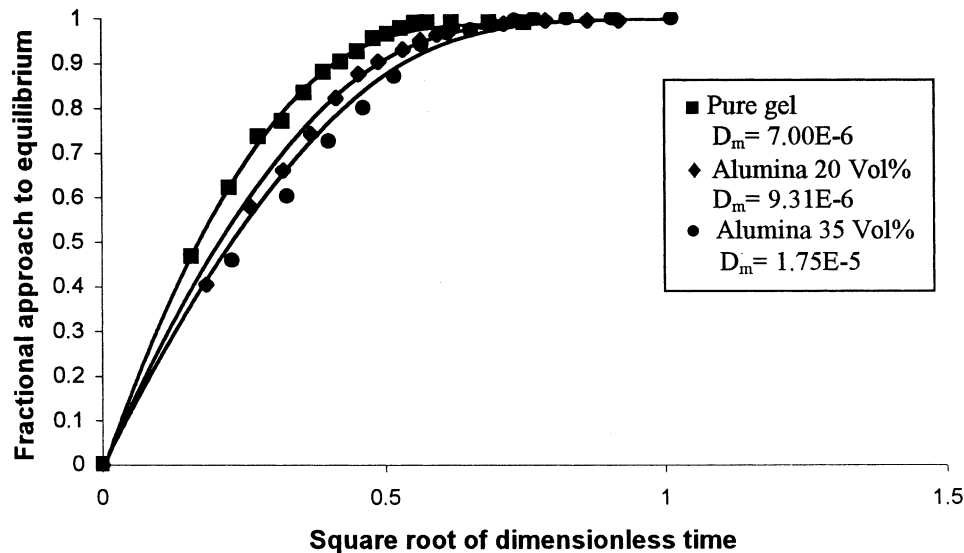


Fig. 9. Validation of the drying model at various ceramic loading with experimental data on samples 7 mm thick and 20% by weight of solution of PEG1000.

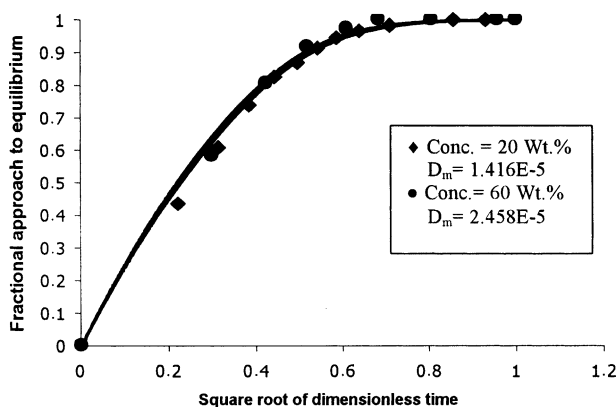


Fig. 10. Validation of the drying model at various concentration of liquid desiccant with experimental data on samples 7 mm thick and ceramic loading of 30% by volume.

model for constant D_m with several values of Φ was fitted to the data by adjusting D_m to minimize the sum of the squared deviation between the experimental and the computed values of F . The solid curves in these figures are the best fit, which were obtained with different values of D_m for different values of Φ .

5. Conclusions

In this work, the kinetics of drying of gelcast part for one-dimensional drying in various ceramic loading and concentration of liquid desiccant were modeled. For a constant D_m , the fractional approach to equilibrium, F , is only a function of dimensionless time, τ_0^* , and the equilibrium volume ratio, Φ . The equilibrium volume ratio, Φ , contains the effect of ceramic loading in the

gel and the concentration of the liquid desiccant. Therefore, it is the only parameter that is needed to input to the program for computing numerically the kinetic behaviour of gelation. Numerical computations for one-dimensional cylindrical geometry with constant D_m demonstrate a significant effect of the boundary movement on the kinetics of the drying of the gel. Higher ceramic loading, lower concentration of liquid desiccant solution and higher thickness of sample, decrease the rate of drying and increase the time which is needed for sample to reach the equilibrium.

This engineering model predicts drying rates with reasonable accuracy over a sufficiently broad range of part thicknesses, ceramic loading and concentration of liquid desiccant. However, there is a significant possibility of extending this work to two-dimensional (axisymmetric) or three-dimensional drying for other geometries such as slab and sphere. Such a model could conceivably be coupled with drying stress and shrinkage models, to present a more unified and, hence, very useful means of modeling gelcast drying via liquid desiccant method.

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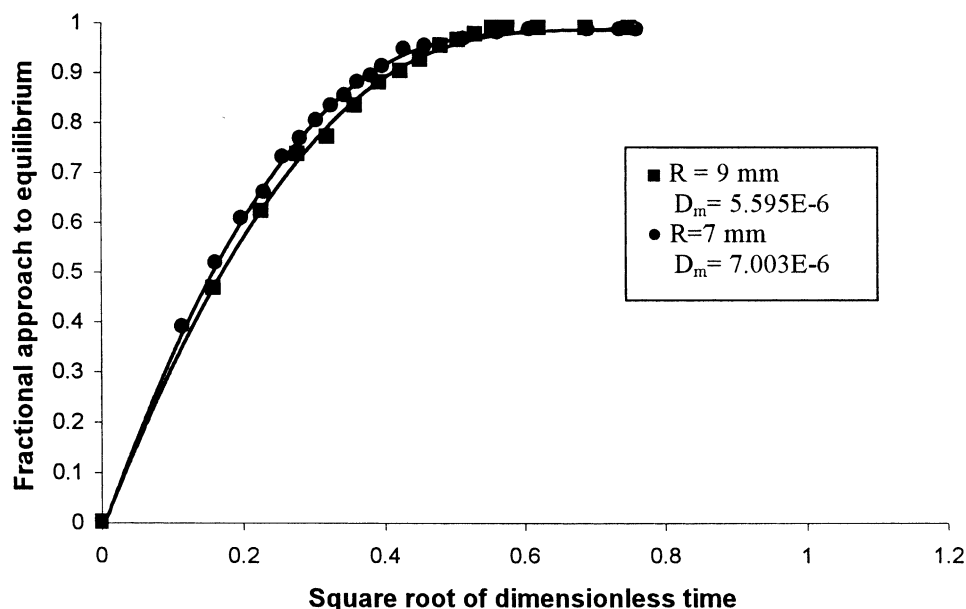


Fig. 11. Validation of the drying model on samples 7 and 9 mm thick at 20% by weight solution of PEG1000 and 0% by volume of ceramic loading.

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