

Methods for Introducing Safety Factors into Minimum Time Heating Cycles for Binder Removal from Green Ceramic Bodies

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Heating schedules have been simulated for the minimum time for binder removal from green ceramic components that contain open porosity. To determine such heating schedules, a number of parameters appearing in the model must be specified, including the kinetic parameters of binder degradation, the permeability of the green body, and the temperature and pressure at which the green body fails. Because of uncertainty in these quantities, safety factors can be applied to these model parameters to obtain a more conservative heating cycle that begins at a lower temperature and is longer in duration than the minimum time heating cycle.

Keywords: Binder, Binder Removal, Porosity, Barium Titanate

Introduction

The process of binder removal [1-9] from green ceramic components is a highly coupled problem in that heat transfer, reaction kinetics, and mass transfer all occur, and the net effect of these kinetic and transport processes may be component failure. Exacerbating a quantitative understanding of the binder removal process is that some of the parameters, notably the decomposition kinetics [10] and permeability [11], vary nonlinearly over orders of magnitude during the heating cycle. In addition, both of these quantities are not easy to determine, especially as they depend on the binder loading, which is changing as a function of time and temperature during the heating cycle. Furthermore, little is known or has been reported about the conditions of failure of the green body during binder removal, namely the failure stress, failure pressure, and failure temperature in relation to binder loading [12].

In earlier work [8,9], we have developed an algorithm based on variational calculus for determining the minimum time heating cycle (MTHC) for binder removal from open pore green bodies in which convection is the dominant mode by which the products of binder decomposition exit the green body. To determine the MTHC, the pressure at which the green body fails is needed. Until now, we have always treated the case of a single failure mode, namely a single failure temperature corresponding to a single failure pressure at a certain binder loading. In real green bodies, however, complex and different failure modes may occur, and these may depend on the binder content [12-17]. For example, at high

binder loadings, bloating and delamination may occur while the green body retains some plasticity. At low binder loadings, the green body may fracture into large pieces reminiscent of a brittle failure mode.

The complexity of the coupling between mass transfer, reaction kinetics, and failure modes thus suggests that in practice, the MTHC for binder removal will not be followed exactly, but instead a more conservative heating schedule will be adopted. Such more conservative heating cycles can be developed by modifying model parameters, or in other words, by introducing a safety factor into the heating cycles. Such margins of safety, although leading to longer heating cycles, account for inaccuracies in the kinetic parameters, in the permeability, and in sample to sample variation in mechanical properties of the green components.

In this study, we demonstrate several different ways in which such safety factors can be introduced into heating cycles via a number of model parameters, such as in the kinetics, the permeability, and the conditions at which the body fails. In some instances, however, the introduction of a safety factor leads to counter intuitive heating cycles, i.e., cycles which are shorter and occur at higher temperature, and thus we demonstrate a methodology to circumvent such occurrences, and thereby obtain the desired more conservative heating schedules.

Experimental

The tape samples used in this study were prepared from barium titanate powder (Tamtron X7R 412H, Ferro Electronic Materials, Niagara Falls, NY), which has a mean particle diameter of 1.2 μm and specific surface area of 3.3 m^2/g . The powder at 55.6 wt% was ball milled with 44.6 wt% binder solution (B73305 Ferro

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Corp., San Marcos, CA), which contains approximately 14 wt% poly(vinyl butyral), 8 wt% dioctyl phthalate, 60 wt% toluene, and 18 wt% ethanol. After milling, the slurry was de-aired and then filtered through a 53 μm nylon mesh. The slurry was then tape cast, dried, and cut to obtain samples. The thickness of the dried tapes was approximately 165 μm . The total organic content of the substrates was 10.9% by weight, as determined by thermal gravimetric analysis (TGA) conducted in air flowing at 60 cm^3/min .

To obtain the preexponential factor, A , and activation energy, E , for binder decomposition, TGA data were obtained at different linear heating rates. For binder decomposition occurring as an activated, first-order process, the kinetics of binder decomposition can be expressed in terms of the conversion, α , as:

$$\frac{d\alpha}{dt} = A \exp\left[-\frac{E}{RT}\right] (1-\alpha) \quad (1)$$

where the other symbols are described in the Nomenclature section. For TGA experiments conducted with a linear heating rate, β , A and E can be determined by the method of Lee and Beck [18] from:

$$\ln\left[\frac{-1n(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta(E+2RT)}\right] - \frac{E}{RT} \quad (2)$$

as described in more detail elsewhere [10, 19]. To convert from conversion to volume fraction of binder, ϵ_b , we substitute $\alpha = 1 - \epsilon_b/\epsilon_{bo}$ which then allows the volume fraction of binder at any linear heating rate to be expressed as:

$$\frac{\epsilon_b}{\epsilon_{bo}} = \exp\left[\frac{A}{\beta} \left\{ \frac{\left(\frac{RT^2}{E}\right) \exp\left(-\frac{E}{RT}\right)}{1 + \frac{2RT}{E}} - \frac{\left(\frac{RT_0^2}{E}\right) \exp\left(-\frac{E}{RT_0}\right)}{1 + \frac{2RT_0}{E}} \right\}\right] \quad (3)$$

where ϵ_{bo} is the initial volume fraction of binder and β is the linear heating rate.

To obtain the permeability of the green bodies, tape samples were laminated in a press with heated platens at 7 MPa at 85°C for 10 minutes. Samples of disk geometry were then inserted into a sample holder with an open area of 1.56 cm in diameter and sealed with a flexible o-ring. A steady-state flux across the substrate was obtained by adjusting the pressures P_1 and P_2 across the sample thickness, L , and the volumetric flow rate was recorded and then converted to a molar flux, N_m . Using a procedure described in more detail elsewhere [11], the permeability, κ , was then determined from Darcy's Law as:

$$\kappa = -2RTN_m \mu \frac{L}{P_2 - P_1} \quad (4)$$

where μ is the viscosity of the gas. To obtain samples of lower binder content, the binder was removed by

oxidation in air at temperatures of 150-200°C for times of 0.5-24 h.

Model

The governing equations for the thermal removal of binder by minimum time heating cycles have been derived elsewhere, and so we simply summarize here the main results [8,9]. In order to determine the MTHC for open pore green compacts, we represent the rate of binder decomposition, r , as an activated process:

$$r = -\frac{d\epsilon_b}{dt} = A \exp\left(\frac{-E}{RT}\right) \epsilon_b \quad (5)$$

The permeability in the green body, κ , is modeled by:

$$\kappa = \frac{\epsilon^3}{k(1-\epsilon)^2 S^2} \quad (6)$$

where ϵ is the porosity, k is a constant, and S is the surface area per unit volume. From conservation of volume:

$$\epsilon = 1 - \epsilon_s - \epsilon_b \quad (7)$$

where ϵ_s is volume fraction of solid.

We next describe the pressure distribution in a 3-D porous medium of parallelepiped geometry for the thermal decomposition of binder by first order kinetics where convective flow is the transport mechanism by which the product gases exit the body. The pressure distribution is derived by assuming: 1) the temperature distribution in the body is uniform [20]; 2) the viscosity, μ , of the decomposition products is constant during the heating cycle; and 3) the dimensions, L_x , L_y , and L_z , of the green body do not change during the heating cycle. Under these circumstances, the normalized maximum pressure occurs in the center of the body, $(P/P_o)_o$, and is given by:

$$\left(\frac{P}{P_o}\right)_o = \left(1 + 0.8365 \frac{1}{2\rho_o^2 \kappa R M T_o^2} \frac{\mu r \rho_b T}{L_x^2 L_y^2 L_z^2} \right)^{1/2} \\ = \left(1 + G \frac{r T}{\kappa}\right)^{1/2} \quad (8)$$

Equation 8 thus describes the pressure in the center of the body in terms of the reaction rate, r , permeability, κ , temperature, T , and component dimensions. The quantity G in Eq. 8, in light of the model assumptions, is a constant given as:

$$G = 0.8365 \frac{\mu \rho_b}{2\rho_o^2 R M T_o^2} \frac{L_x^2 L_y^2 L_z^2}{L_x^2 L_y^2 + L_x^2 L_z^2 + L_y^2 L_z^2} \quad (9)$$

The minimum time, t^* , to remove completely binder from an initial binder loading ϵ_{bo} is then expressed as:

$$t^* = G T_s \int_0^{\epsilon_{bo}} \frac{d\epsilon_b}{(P_t^2 - 1) \kappa(\epsilon_b)} \quad (10)$$

where T_s is the starting temperature for the binder

removal cycle, and P_b , the threshold pressure, is the value of $(P/P_o)_o$ in Eq. 8 corresponding to when failure in the body occurs. For a single failure mode at a constant value of P_b , the term in Eq. 10 can be taken outside of the integral.

Equation 10 is thus the approximate analytical solution for the minimum time for binder removal in terms of all of the dimensional and transport parameters appearing in the problem. Although the minimum time in Eq. 10 does not explicitly depend on the kinetic decomposition parameters A and E , the starting temperature, T_s , of the binder removal cycle does, however, depend on the specifics of the kinetic expression, as given by:

$$T = -\frac{E}{R} \left[1 - \frac{\kappa(P_b^2 - 1)}{\epsilon_b G T_s A} \right]^{-1} \quad (11)$$

Equations 10 and 11 are thus the primary expressions used to obtain the MTHC, and thus the quantities appearing in the constant G must be known, as well as the kinetic parameters, the permeability, and the threshold pressure.

Results and Discussion

Figure 1 shows the decomposition behavior of the binder in the presence of barium titanate as obtained from TGA experiments conducted at different heating rates in air. The kinetic parameters obtained from Eq. 2 by the method of Lee and Beck at each heating rate, along with the range of conversion evaluated, are shown in Table 1. Although the kinetic parameters obtained at each heating rate are different, these parameters do describe well the early decomposition data at each heating rate in Fig. 1, but then deviate at higher conversion. When one set of parameters, say those from a heating rate of $0.2 \text{ K minute}^{-1}$, is used to predict the kinetics at all of the other heating rates, however, discrepancies between the predicted and observed decomposition kinetics arise, as seen in Fig. 2. This deviation becomes more pronounced as the difference increases between the heating rate at which the kinetic parameters were acquired and were applied, *i.e.*, the discrepancy is worse at a heating rate of 10 K minute^{-1} as compared to 1 K minute^{-1} when the kinetic parameters obtained at a heating rate of $0.2 \text{ K minute}^{-1}$ are used. This lack of agreement, which is discussed in more detail elsewhere [10,19], arises because the decomposition mechanism, which is a complicated, multi-step process, is not precisely

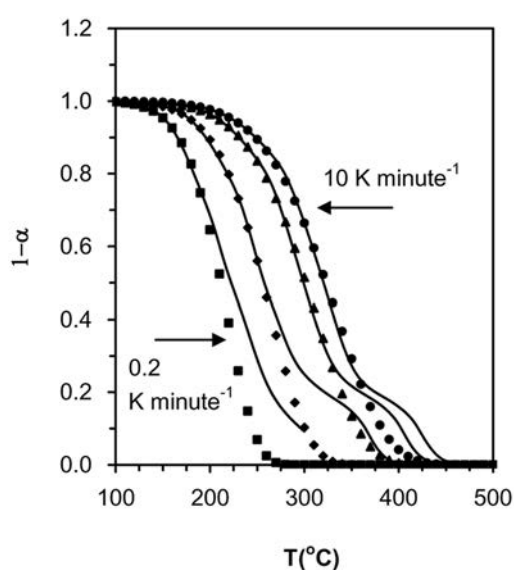


Fig. 1. Thermogravimetric weight loss data (solid lines) for binder in the presence of barium titanate heated at different linear heating rates of 0.2, 1, 5, and 10 K minute^{-1} . The predicted kinetics (symbols) by a first-order decomposition mechanism obtained for the first region of weight loss are also shown.

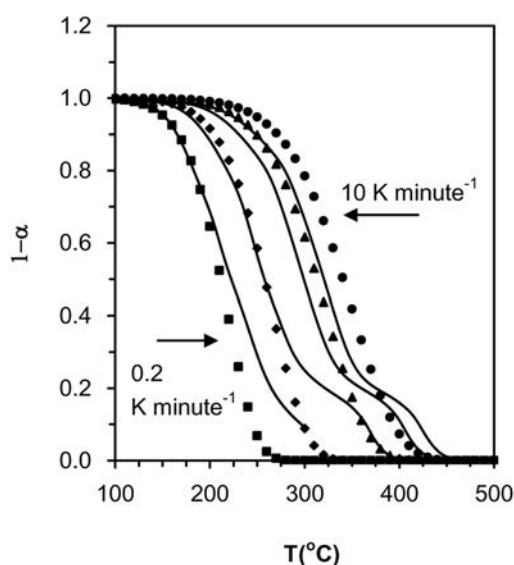


Fig. 2. Thermogravimetric weight loss data (solid lines) for binder in the presence of barium titanate heated at different linear heating rates of 0.2, 1, 5, and 10 K minute^{-1} . The predicted kinetics (symbols) by a first-order decomposition mechanism using a single set of kinetic parameters ($E = 66.7 \text{ kJ/mol}$, $A = 1358 \text{ s}^{-1}$ obtained at a heating rate of $0.2 \text{ K minute}^{-1}$ for the first region of weight loss) are also shown.

Table 1. Kinetics parameters, regression coefficients, and range of conversion determined from the first region of weight loss at different heating rates for barium titanate and binder using a first-order decomposition mechanism.

β (K minute^{-1})	A (s^{-1})	E (kJ/mol)	R^2 (-)	$1-\alpha$ (-)
0.2	1358	66.72	0.997	0.987~0.697
1	258	59.58	0.997	0.991~0.448
5	190	56.53	0.999	0.991~0.241
10	215	56.15	0.999	0.986~0.227

known.

The uncertainty in the kinetic parameters illustrated above has an important ramification in the development of the MTHC. Figure 3 shows that for a single heating rate of 10 K minute^{-1} , the evolution of the predicted pressure in the center of the body varies depending on which set of kinetic parameters is used. Thus for a given temperature, the corresponding pressure may vary by 10-25%. The arrows in Fig. 3 also illustrate that for failure observed at say $T_f = 200^\circ\text{C}$, the value of P_t depends on the kinetic parameters, which in turn will influence the MTHC from Eqs. 10 and 11. Figures 1-3 thus illustrate that because of uncertainty in one of the model parameters, in this case the kinetics, which arises because the decomposition mechanism is not precisely known, a safety factor may have to be incorporated when determining the MTHC.

Figure 4 shows the measured permeability of the green tapes, determined from Eq. 4, as a function of porosity. The permeability shows a complex dependence on porosity, and no permeability data are reported for low binder contents, *e.g.*, high porosity, because of the brittle nature, and hence fracture, of the samples at these conditions. Figure 4 also shows the predicted permeability from three versions of the Kozeny-Carman model (Eq. 6): a best fit model, and two models that better bound the upper and lower values of the permeability. Thus once again we see that uncertainty exists in parameters that appear within the model for

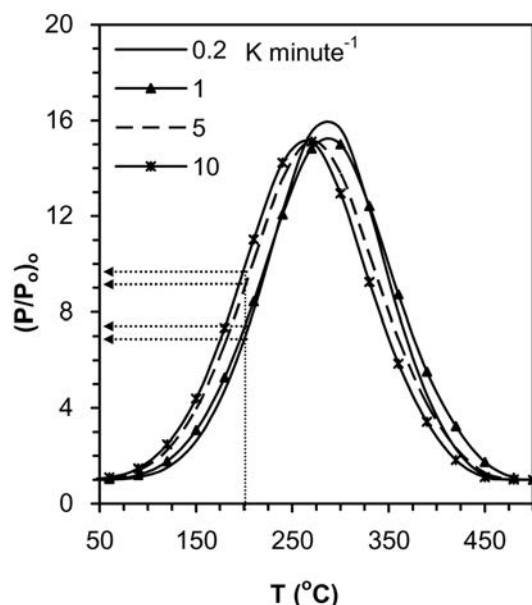


Fig. 3. Profiles of the normalized pressure, $(P/P_o)_o$, versus temperature predicted by the model at a heating rate of $\beta = 10 \text{ K minute}^{-1}$. Each profile was calculated by using the kinetic parameters obtained at a different heating rate (see Table 1 for the values of A and E). For a failure temperature, T_f , of 200°C , the failure pressures, P_t , corresponding to the different kinetics are indicated by the arrows.

predicting the MTHC.

Further uncertainty arises from the method used to determine the failure temperature and the failure pressure. To the best of our knowledge, no method has been reported on directly measuring the failure pressure within a porous body, especially for the case where the average pore size is less than $1 \mu\text{m}$. To circumvent this difficulty, we have developed a procedure where components of parallelepiped geometry are subjected to rapid linear heating rates during which we visually monitor the sample and record the temperature, T_f , at which failure occurs. This procedure leads to some uncertainty in T_f , as the defects must be large enough to be observed and also not occur in a location on a sample hidden from the observer. To determine P_t , we then use Eqs. 3, 5, 6, 7, and 8 with the known heating rate and calculate $(P/P_o)_o$ as a function of temperature using values for the kinetics and for the permeability. Then, as is schematically illustrated in Fig. 3, the observed T_f is used to obtain a value for P_t . Thus, while T_f is directly observed, P_t is a calculated quantity, the value of which is subject to all of the uncertainty in the other model parameters.

As a consequence of the sources of uncertainty described above, we therefore need to introduce some type of safety factor into the MTHC. To this end, we use the parameters in Table 2, and systemically investigate how modifying the kinetics, the permeability, the failure temperature, the failure pressure, and also how directly modifying Eqs. 10 and 11 influences the resultant MTHCs.

For the first case, we attempt to modify the kinetics in such a manner as to ultimately lead to a more

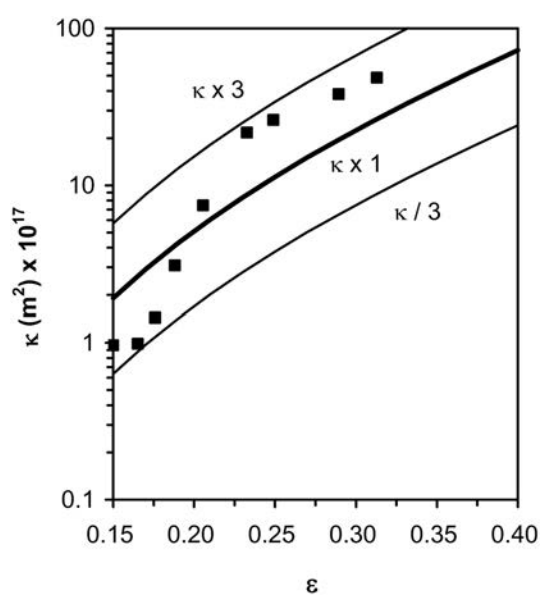


Fig. 4. Permeability versus porosity obtained from measured flux data using Darcy's law. The permeability is also shown as predicted by three different sets of parameters for the Kozeny-Carman model.

Table 2. Parameters used in the simulations.

Symbol	Value	Units
P_o	0.1	MPa
T_o	300	K
M	0.044	kg/mol
R	8.314	$\text{m}^3 \text{ Pa/mol K}$
μ	0.000025	Pa s
S	7.0×10^6	m^{-1}
k	5	(-)
ρ_b	1000	kg/m^3
ρ_o	40.09	mol/m^3
ε_s	0.53	(-)
ε_{bo}	0.32	(-)
L_x	0.04	m
L_y	0.04	m
L_z	0.04	m
A	1358	s^{-1}
E	66.72	kJ/mol

conservative heating cycle. In Fig. 5a, we show how increasing or decreasing the rate of decomposition by a factor of three influences the evolution of pressure in the center of the body for a constant heating rate of 10 K minute^{-1} . With increasing rate of reaction, the pressure profiles are shifted to lower temperature and the maxima in the profiles increase slightly. For a fixed failure temperature of say 130°C , the failure pressures corresponding to the different kinetics increase with increasing reaction rate. Thus, as Fig. 5b indicates, for a failure temperature of 130°C , decreasing the reaction kinetics leads to more conservative heating cycles, and in addition, we note that the start temperatures are not a strong function of the reaction kinetics.

If the failure temperature in Fig. 5a is at 280°C , however, the ordering in the threshold pressures varies in a different manner with the reaction kinetics, as compared to the case of $T_f = 130^\circ\text{C}$. The cycles are now substantially shorter, because P_t is larger, and furthermore, the ordering in the heating cycles shown in Fig. 5c differs from what was observed in Fig. 5b. We also see that the start temperatures for the cycles in Fig. 5c are now a strong function of the kinetics and do not vary in a simple manner with modifications to the reaction kinetics.

We now summarize the above case for applying a safety factor into the kinetics. For any variation or uncertainty in the kinetics, the MTHC length, as seen from Eq. 10, will be inversely proportional to the failure pressure. The cycle start temperature, however, will depend on both P_t and the values of A and E (see Eq. 11). The results in Fig. 5 thus indicate that modifying the kinetics does always not lead to a straightforward method for obtaining more conservative heating cycles.

A similar exercise can be performed when the permeability is selected as the parameter to adjust. Figure 6a shows that as the permeability is increased by a

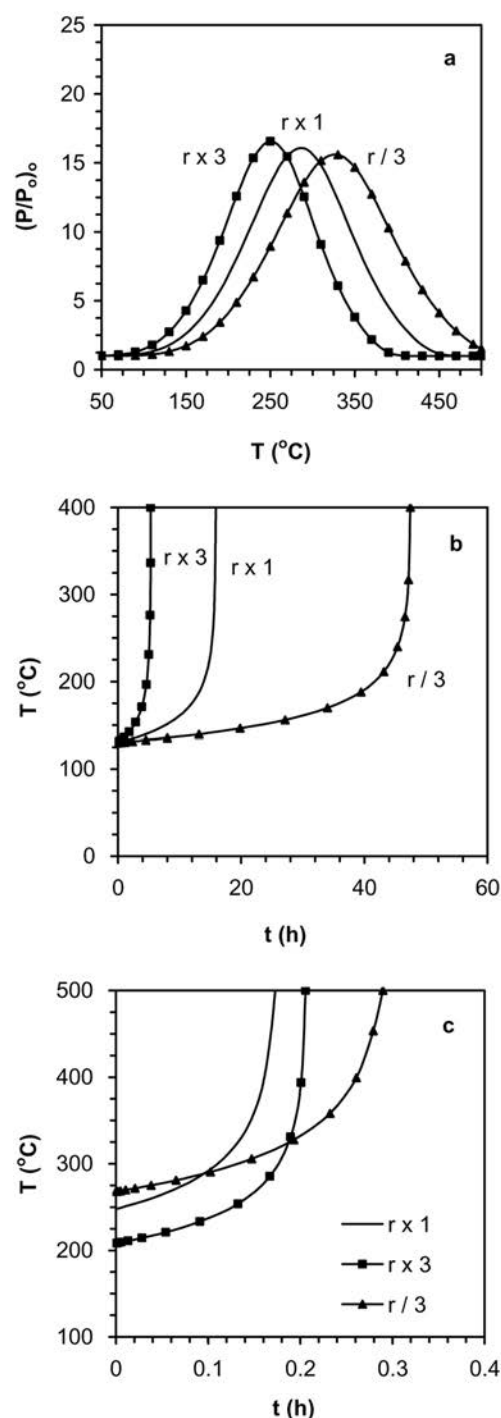


Fig. 5. a) Profiles of $(P/P_o)_o$ versus temperature for $\beta = 10 \text{ K minute}^{-1}$ obtained by applying safety factors to the kinetics. b) Temperature profiles with time obtained by applying safety factors to the kinetics with the failure pressures obtained from Fig. 5a for $T_f = 130^\circ\text{C}$. c) Temperature profiles with time obtained by applying safety factors to the kinetics with the failure pressures obtained from Fig. 5a for $T_f = 280^\circ\text{C}$.

factor of three, the magnitude of the pressure decreases, but the pressure profiles, and thus the maxima in each profile, are not shifted along the temperature axis. Under these circumstances, the ordering in the failure pressures will remain unchanged for any failure tem-

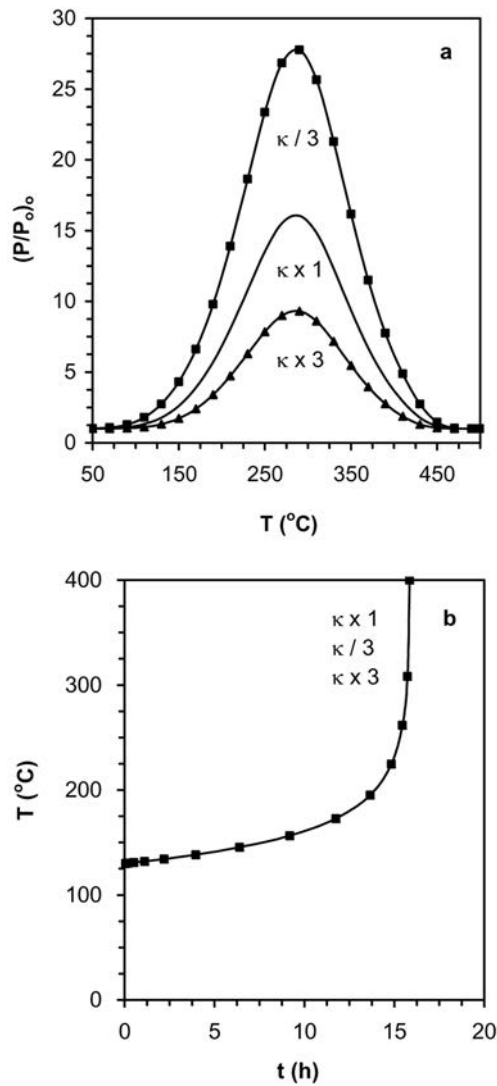


Fig. 6. a) Profiles of $(P/P_o)_o$ versus temperature for $\beta = 10$ K minute^{-1} obtained by applying safety factors to the permeability. b) Temperature profiles with time obtained by applying safety factors to the permeability with the failure pressures obtained from Fig. 6a for $T_f = 130^\circ\text{C}$.

perature. As seen in Fig. 6b, however, the heating cycles determined in this manner are identical, which can be rationalized from the structure of Eqs. 8 and 10. Thus modifying the permeability does not lead to a method for obtaining more conservative heating cycles.

A third option to modify the MTHC is to introduce a safety factor directly into the failure temperature. This is shown in Figure 7a for two cases: for failure at temperatures below and above the maximum in $(P/P_o)_o$. For a given failure temperature below the maximum in $(P/P_o)_o$ of say 130°C , a modified failure temperature can be obtained by either increasing or decreasing T_f by 20°C . Figure 7b illustrates that by decreasing the failure temperature, which in turn leads to smaller values of P_o , longer heating cycles are obtained, whereas shorter cycles are obtained when the failure temperature is increased. This behavior, however, is reversed for

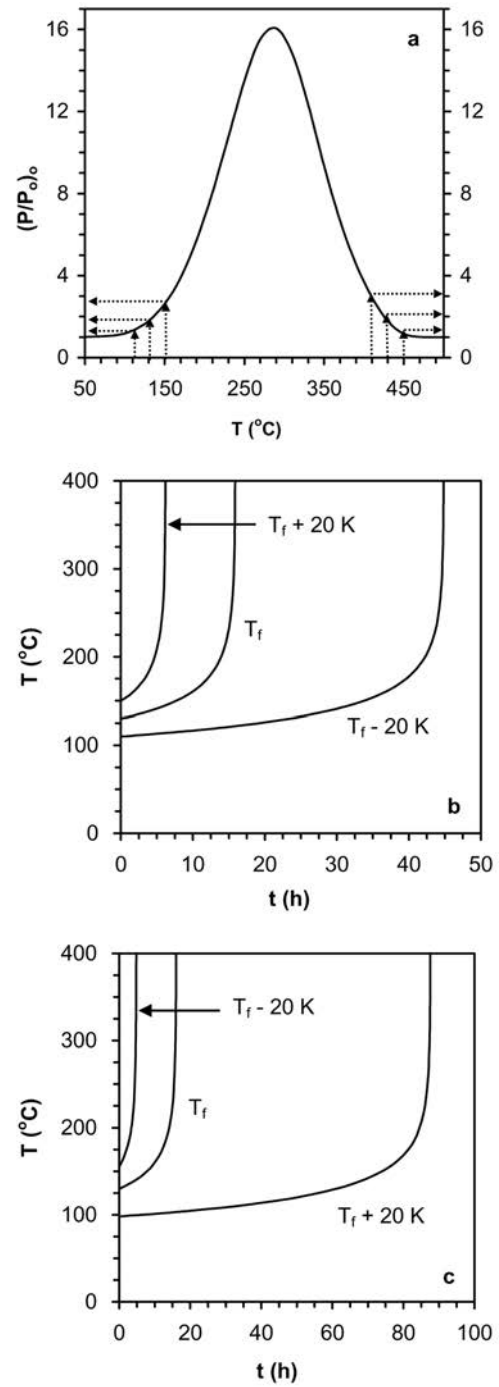


Fig. 7. a) Profile of $(P/P_o)_o$ versus temperature for $\beta = 10$ K minute^{-1} . Failure temperatures of 130°C and 430°C with safety factors of $\pm 20^\circ\text{C}$, along with the corresponding failure pressures, are also shown. b) Temperature profiles with time obtained by applying safety factors to a failure temperature of 130°C with the failure pressures obtained from Fig. 7a. c) Temperature profiles with time obtained by applying safety factors to a failure temperature of 430°C with the failure pressures obtained from Fig. 7a.

failure to the right of the maximum in the pressure profile, as seen in Figs. 7a and 7c. Thus, as was seen for the kinetics, modifying the failure temperature does not lead to a straightforward manner to obtain a more conservative heating cycle. For both cases, however,

variations in the failure temperature that do lead to longer heating cycles also lead to lower starting temperatures.

Another approach to obtain more conservative MTHCs is to use the best, *e.g.*, unmodified, values for the kinetics, permeability, and failure temperature and then determine P_t from these values. A safety factor (see Fig. 8a) can then be introduced to decrease directly P_t , and Fig. 8b then shows that heating cycles determined in this manner are unambiguously longer and start at lower temperature. Thus, this procedure of directly decreasing P_t provides a means to achieve in a straightforward manner more conservative heating schedules in both the time and temperature domains.

For the methods to modify MTHCs treated above in Figs. 5-8, coupling may occur between the cycle length and start temperature whereby varying a parameter may

lead to substantial changes in both quantities. Such coupling may be advantageous in that more conservative heating cycles, in both the time and temperature domains, are obtained or may be deleterious. To avoid this coupling—or in other words to independently vary the cycle length and temperature range of the cycle—the modified heating cycle can be obtained by first establishing the MTHC with the most accurate model parameters available and then to modify the resulting times and temperatures empirically and independently. Figure 9 shows that when a factor of two is introduced directly into Eq. 10, the cycle time can be directly modified without changing the temperature ranged spanned by the heating cycle. In a similar manner, the cycle time can be left unchanged, but the cycle start temperature can be decreased by introducing the safety factor into the temperatures obtained from Eq. 11. Thus, these two constants allow the heating cycle to varied independently in both the time and temperature domains. Of course, the same or different safety factors can be applied to achieve more conservative heating cycles in both the time and temperature domains, and an example of utilizing this approach for the same factor of two is also shown in Fig. 9.

To summarize the above section, the removal of binder is a complex process with tight coupling between kinetics, permeability, and failure criteria. In addition, several of the parameters that appear within the model vary over orders of magnitude and nonlinearly during the heating cycle. The uncertainty in the model parameters suggests that it is advantageous to modify the MTHC in order to obtain a more conservative heating cycle. This paper has indicated a number of parameters that

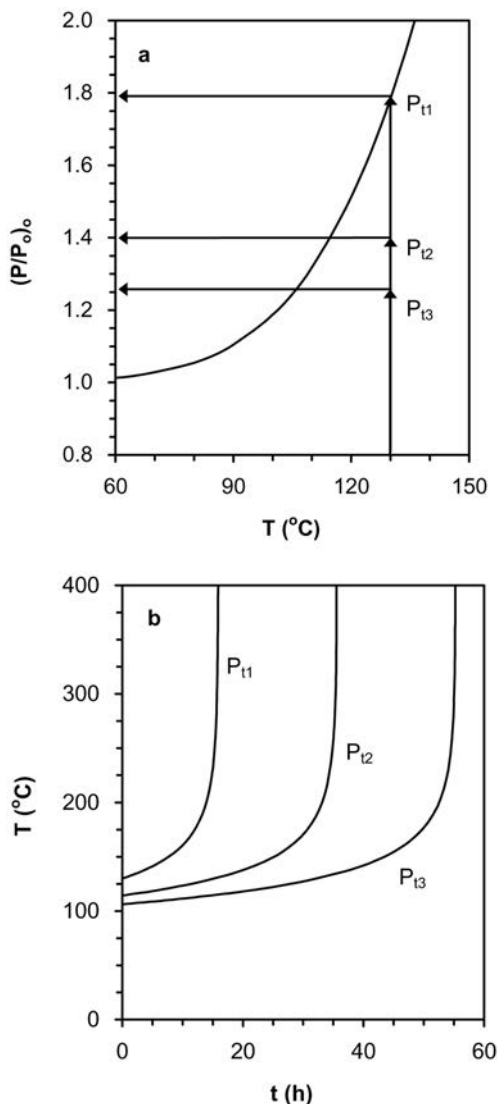


Fig. 8. a) Section of the profile of $(P/P_o)_o$ versus temperature for $\beta = 10 \text{ K minute}^{-1}$ with safety factors applied to the failure pressure for $T_f = 130^{\circ}\text{C}$. b) Temperature profiles with time obtained by applying safety factors to the failure pressure obtained from Fig. 8a for $T_f = 130^{\circ}\text{C}$.

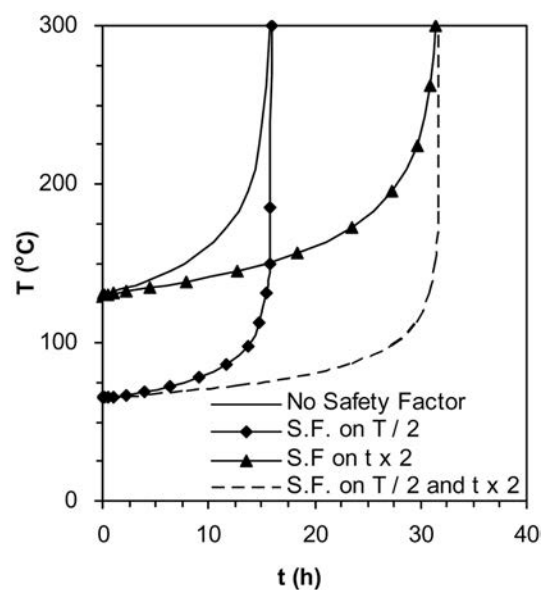


Fig. 9. Temperature profiles with time using a safety factor (S.F.) of 2 applied directly to the results of time (Eq. 10), to the temperature (Eq. 11), and to both the time and temperature (Eqs. 10 and 11, respectively).

may be varied, and has shown how these parameters influence the resultant heating cycle. When parameters in the model such as the kinetics and failure temperature are adjusted, no *a priori* safety factor can be specified for obtaining more conservative heating cycles. For changes made to the permeability, the cycles remain unchanged. For decreases to the threshold pressure, the resultant heating cycles are longer and exhibit a change in the range of temperatures spanned. To achieve maximum flexibility in obtaining more conservative heating cycles, it is also possible to vary the cycle time or temperature independently of each other.

The methodology presented above treats a complex process in a limited fashion in the sense that only one failure condition is treated in terms of single failure temperature and failure pressure. In reality, the strength of a ceramic green body is a strong function of binder content and thus instead of a constant threshold failure

pressure, it may be more appropriate to use a failure pressure which is a function of the binder content. Unfortunately, however, no data are available summarizing the threshold strength of ceramic green bodies versus binder content.

In light of this absence of data, we simply express the functional relationship between threshold pressure and binder content as:

$$P_t = \left[\left(\frac{1 - \epsilon_{bo} - \epsilon_s}{\epsilon} \right)^a (P_{to}^2 - 1) + 1 \right]^{1/2} \quad (12)$$

where a is an arbitrary parameter and P_{to} is the initial threshold pressure of the green body, which is 2 for the case under consideration here. Figure 10a shows that the value of a determines how the threshold pressure decreases with decreasing binder content. Figure 10b shows how the corresponding MTHCs vary for selected values of a between 0-5. In general, the heating cycles become substantially longer as the pressure corresponding to failure of the green body decreases with decreasing binder content. If the value of P_t decrease too rapidly, as in the case of $a = 5$, then the heating cycle has an initial segment of nearly constant temperature (actually a slight decrease in temperature) so as to not decompose binder too quickly and thereby exceed the threshold pressure in the green body. In the limit of a failure pressure of unity, the cycle length becomes infinity long as well, or in other words, the green body cannot sustain the buildup of internal pressure.

Conclusions

Methods have been evaluated for introducing safety factors into minimum time heating cycles for the removal of binder from green ceramic bodies containing open porosity. Such safety factors can be applied to the kinetics, the permeability, the failure temperature, and the failure pressure. In some instances, modifications to the model parameters do not lead unambiguously to more conservative heating cycles, and this was especially apparent for modifications applied to the kinetics, permeability, and failure temperature. Direct modification to the equations for determining the evolution of the cycle time and cycle temperature, however, always leads to more conservative heating cycles, and in addition the heating cycles can be independently varied in both the time and temperature domains. We have also shown that when the failure pressure in the green body is a decreasing function of binder content, longer heating cycles are obtained as compared to when a constant failure pressure, independent of binder content, is assumed.

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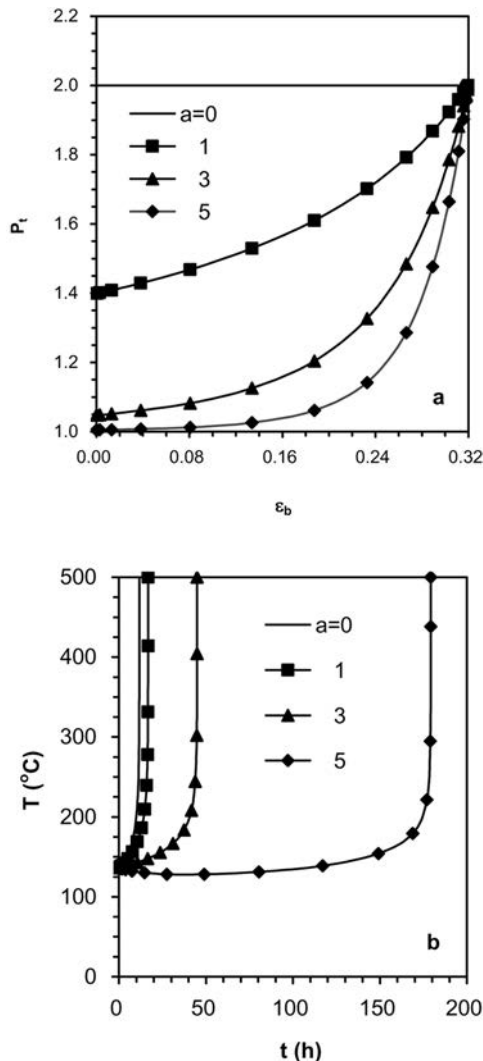


Fig. 10. a) Four profiles of how the failure pressure depends on binder content. b) Temperature profiles with time obtained from the four models in Fig. 10a for describing how the failure pressure depends on binder content.

Nomenclature

A , preexponential factor
 E , activation energy
 f , as subscript, denoted quantity at the failure temperature
 k , Kozeny-Carman parameter
 L_i , $i = x, y, z$ dimensions of the body
 M , average molecular weight of gas products
 N_m , molar flux
 P , pressure
 P_o , ambient pressure
 P_t , threshold pressure in the center of the body
 R , gas constant
 r , rate of binder decomposition
 S , surface area per unit volume
 t , time
 t^* , minimum cycle time for binder removal
 T , temperature
 T_o , initial temperature
 T_s , starting temperature of binder removal cycle
 α , binder conversion
 β , heating rate
 ε , porosity
 ε_s , volume fraction of solid
 ε_b , volume fraction of binder
 ε_{bo} , initial volume fraction of binder
 ρ_b , binder density
 ρ_o , initial gas density at T_o and P_o
 κ , permeability
 μ , gas viscosity

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