Drying of porous oil shales

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Rate processes including change of phase are modelled analytically for a half-space porous substance exposed to a jump in external temperature. The model predicts, in a closed form, the pressure build-up and the rate of evaporation of volatiles from a porous matrix. It assumes two distinct regions separated by a moving interface where the change of phase takes place. One region maintains its initial concentration of volatiles while the second is devoid of volatiles. Different thermophysical properties are considered for the two regions. The model was applied for the evaporation of moisture from oil-shale. Results are given in a parametric form

Keywords: *evaporation, rate processes, oil shales*

Growing interest in the utilization of oil shales has led to an attempt to understand the transport phenomena in retorting and combustion processes. These processes differ vastly from those encountered when either liquid oil or coal are burned. The basic difference stems from the physical structure of the shale, an inorganic matrix in which the kerogen (the organic material) is embedded. Thus, during the processing of oil shale particles, their external shape is preserved and product gases and organic matter diffuses through the small pores of the matrix.

Existing shales contain various, non-negligible, amounts of water. When shale particles are introduced into the cumbustor or retorting facility, they experience an instantaneous jump in surface temperature. Water gradually evaporates and flows out from inside the particle. Evaporation within the oil shale particle is assumed to be at local equilibrium, ie the pressure at the evaporation interface is related to the temperature according to the saturation curve. When the shale has a low permeability coefficient, high build-up pressures might occur, resulting in fracture of the inorganic matrix and, hence, change the external shape of the particles. Other processes within the oil shale particle, such as pyrolysis, gasification, combustion etc are affected by diffusion as well as kinetic rate of reaction. However, the solution of the diffusion only, such as applied to the drying process, would be valuable in providing a lower bound for the time needed to complete the process.

The object of this work is to predict rates of drying of oil shale particles and the pressure build-up inside the particles as a function of various non-dimensional parameters based on thermo-physical properties of oil shales, water hold up and pertaining external conditions, ie initial and reactor temperatures and the external pressure. The proposed solution is not limited to oil shales but can handle any infinite kinetic rate process that occurs in a porous matrix.

Luikov[1], in a recent review paper, has described a comprehensive mathematical model for the process of drying porous media. More recently several workers[2-7] have been looking at restricted cases which could be solved analytically. In a recent paper by Cross *et al*, an attempt to predict the pressure build-up in a porous half-space is made. Their basic assumptions were: (a) a distinct moving interface exists between the wet region and the dried region; (b) heat flows through the medium by conduction only and no heat is convected by the outflowing vapour; (c) the vapour is compressible and obeys the ideal gas law. Cross *et al* also assumed that the difference between the external and the evaporation interface temperatures is fixed (20°C) and that the thermal diffusivities of the dry and the wet regions are equal.

In our analysis, the rate of interface motion and the pressure build-up will be calculated without requiring *a priori* assumptions for the value of interface temperature and diffusivities ratio. Indeed, the interface temperature is calculable by the model itself. Since compressible solutions are normally much more difficult to obtain, incompressible solutions are also presented for comparison purposes.

Statement of the problem

When the surface of a slab of oil shale is exposed to a high temperature, heat is transferred into the slab. The liquid within the slab evaporates whenever the temperature reaches local boiling conditions.

The model assumes that two distinct regions exist: region 2 is devoid of liquid while region 1 has the original liquid content. Therefore a definite interface exists between the two regions with discontinuity in liquid content. Initially, the whole slab is in region 1 but with evaporation, the interface moves into the slab, thus increasing region 2. The instantaneous location of the interface is denoted by $s(t)$. The vapour generated at the interface flows through the porous material of region 2 to the slab's boundary. The rate of vapour flow, described by Darcy's Law, is controlled by the pressure gradient and the permeability of the porous region. This flow results from the vapour generation at the interface due to heat transfer from the slab's boundary.

Saturation pressure at the interface is related to the local temperature by Clapeyron's equation.

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Mathematical presentation

The governing field equations will be presented for the two regions. For region 1, where no mass flow occurs, the only relevant equation is that of heat conduction, namely:

$$\rho_1 C_1 \frac{\partial T_1}{\partial t} = K_1 \frac{\partial^2 T_1}{\partial x^2} \tag{1}$$

where ρ_1, C_1 and K_1 are the density, specific heat and thermal conductivity, respectively.

For region 2, both heat and mass transfer must be considered. The local temperature of the vapour is assumed identical to that of the matrix. The heat transfer equation is:

$$\rho_2 C_2 \frac{\partial T_2}{\partial t} = K_2 \frac{\partial^2 T_2}{\partial x^2} \tag{2}$$

where the convection of heat due to vapour flow was neglected. The continuity equation describing mass conservation of the vapour is:

$$\varepsilon \frac{\partial \rho_G}{\partial t} + \frac{\partial(\rho_G u_G)}{\partial x} = 0 \tag{3}$$

where ε is the porosity of region 2, and ρ_G and u_G are the gas density and gas apparent velocity respectively. The momentum equation is represented by Darcy's Law:

$$u_G = \frac{\Gamma}{\mu}\left(-\frac{\partial P_G}{\partial x}\right) \tag{4}$$

where P_G is the local pressure and μ and Γ are the gas viscosity and the matrix permeability, respectively.

Two cases for the equation of state of the vapour will be considered: a non-compressible vapour where:

$$\rho_G = \rho_o = \text{const.} \tag{5a}$$

and compressible ideal gas:

$$\rho_G = \frac{P_G}{R T_G} \tag{5b}$$

Initial conditions

Initially only region 1 exists where the liquid content and temperature are uniform so, mathematically:

$$T_1(x,0) = T_i \tag{6}$$

$$\omega_1(x,0) = \omega_1(x,t) \equiv \omega \tag{7}$$

where ω_1 is the volume fraction of the liquid which is assumed to remain constant throughout the process in region 1, while region 2 is devoid of liquid, namely $\omega_2 = 0$.

Boundary conditions

The temperature at the surface of the slab is assumed to equal the outside temperature for all times $t > 0$:

$$T_2(0,t) = T_0 \tag{8}$$

The temperature across the interface, $x = s$, is continuous, namely:

$$T_1(s,t) = T_2(s,t) \triangleq T_s \tag{9}$$

The difference in heat conduction fluxes is equal to the latent heat of evaporation (denoted by L):

$$-K_1\left(\frac{\partial T_1}{\partial x}\right) + K_2\left(\frac{\partial T_2}{\partial x}\right) = \rho_L L \omega \frac{ds}{dt} \tag{10}$$

The conservation of mass at $x = s$ yields:

$$(\rho_L \omega - \rho_G \varepsilon)\frac{ds}{dt} = -\rho_G u_G \tag{11}$$

Finally, the temperature and the pressure at the interface are related by the Clapeyron equation which, when integrated for steam, yields the close approximation[8]:

$$\log_{10}\frac{P_{cr}}{P_s} = \frac{\theta}{T_s}\,\frac{a_1 + a_2\theta + a_3\theta^3 + a_4\theta^4}{1 + a_5\theta} \tag{12}$$

where:

$P_{cr} = 221.1$ bar $= 22.11$ MPa
$T_{cr} = 647.4$ K
$\theta = T_{cr} - T_s$
$a_1 = 3.34613$
$a_2 = 4.14113 \times 10^{-2}$
$a_3 = 7.515484 \times 10^{-9}$
$a_4 = 6.56444 \times 10^{-11}$
$a_5 = 1.3794481 \times 10^{-2}$

Notation

a_1, a_2, a_3, a_4, a_5	Coefficients (Eq (12))
A_1, A_2	Coefficients (Eqs (18), (19))
C_j	Specific heat
Q	Porosity parameter (Eq (20))
H	Permeability parameter (Eq(22))
K_j	Thermal conductivity
K	Thermal conductivity ratio K_1/K_2
L	Latent heat
P_j	Pressure
R	Gas constant
$s(t)$	Instantaneous location of the interface
t	Time
T_j	Temperature
u_G	Gas apparent velocity
x	Coordinate, normal to surface
α	$(\alpha_1/\alpha_2)^{1/2}$
α_j	Thermal diffusivity
Γ	Permeability
ε	Porosity
η	Similarity parameter (Eq (16))
λ	Interface locator parameter (Eq (17))
μ	Gas viscosity
ρ_j	Density
θ	$T_{cr} - T_s$
ω	Volume fraction of liquid

Subscripts

1	Region 1, with initial concentration of volatiles
2	Region 2, devoid of volatiles
G	Gas
L	Liquid
s	Interface
o	External, ambient
cr	Critical point
i	Initial

The second boundary condition for region 1 is:

$$T_1(\infty,t)=T_i \qquad (13)$$

for a semi-infinite slab.

Solution for semi infinite case

The general solution of the heat equation for region 1 (Eq (1)) which satisfies the boundary condition at infinity (Eq (13)) is:

$$T_1=T_i+A_1\,\mathrm{erfc}\,(\eta) \qquad (14)$$

The solution for region 2, which satisfies the boundary condition at $x=0$ (Eq (8)) is:

$$T_2=T_0+A_2\,\mathrm{erf}\,(\eta(\alpha_1/\alpha_2)^{1/2}) \qquad (15)$$

where η is a similarity parameter defined as:

$$\eta=\frac{x}{2(\alpha_1 t)^{1/2}} \qquad (16)$$

and A_1, A_2 are parameters to be determined. The motion of the interface is taken, and later justified, to be proportional to $(\alpha_1 t)^{1/2}$:

$$s=2\lambda(\alpha_1 t)^{1/2} \qquad (17)$$

where λ is the interface locator parameter to be determined.

A_1 and A_2 are determined as a function of λ by introducing the temperature profiles (Eqs (14) and (15)) and the interface location (Eq (17)) into the boundary conditions (Eqs (9) and (10)):

$$A_1=-T_0\frac{1-\dfrac{T_i}{T_0}[1-Q\lambda e^{\lambda^2}\,\mathrm{erfc}(\lambda)]}{\mathrm{erf}(\lambda\alpha)+\dfrac{\alpha}{K}\mathrm{erfc}(\lambda)\exp[\lambda^2(1-\alpha^2)]} \qquad (18)$$

and:

$$A_2=T_0\frac{1-\dfrac{T_i}{T_0}\left[1+Q\dfrac{K}{\alpha}\lambda e^{\lambda^2\alpha^2}\mathrm{erf}(\lambda\alpha)\right]}{\mathrm{erfc}(\lambda)+\dfrac{K}{\alpha}\mathrm{erf}(\lambda\alpha)\exp[\lambda^2(\alpha^2-1)]} \qquad (19)$$

where α, K and:

$$Q=\sqrt{\pi}\,\omega\frac{L}{C_1 T_i}\frac{\rho_L}{\rho_1} \qquad (20)$$

are known quantities.

The vapour velocity in region 2 is determined from continuity (Eq (3)) and the boundary condition (Eq (11)). The local time variation of the vapour density within region 2 can be neglected in Eq (3) from order of magnitude considerations, even for the case of compressible vapour, (Eq (5b)):

$$u_G=-\frac{\rho_L-[\rho_G]_{x=s}}{\rho_G}\omega\lambda\sqrt{\alpha_1}\frac{1}{\sqrt{t}}$$

$$\cong-\frac{\rho_L}{\rho_G}\omega\lambda\sqrt{\alpha_1}\frac{1}{\sqrt{t}} \qquad (21)$$

since $\rho_L \gg \rho_G$.

The pressure field in region 2 depends on the type of equation of state that is employed. For non-compressible vapour (Eq (5a)) it is:

$$P_G/P_0=1+\lambda H\eta \qquad (22a)$$

For 'ideal gas' compressible vapour (Eq (5b)) the pressure is:

$$(P_G/P_0)^2=1+2\lambda H\eta\left\{1+\frac{A_1}{T_0}\left[\mathrm{erf}(\eta\alpha)-\right.\right.$$

$$\left.\left.-\frac{1}{\eta\alpha\sqrt{\pi}}(1-\mathrm{e}^{-\eta^2\alpha^2})\right]\right\} \qquad (22b)$$

where H is a nondimensional parameter:

$$H=\frac{2\mu\alpha_1\omega(\rho_L-\rho_0)}{\Gamma P_0\rho_0}$$

and ρ_0 and P_0 are the ambient density and pressure, respectively. The pressure at interface, P_s, is then:

$$P_s/P_0=1+\lambda^2 H \qquad (23a)$$

for the incompressible vapour (Eq (5a)) and:

$$(P_s/P_0)^2=1+2\lambda^2 H\left\{1+\frac{A_1}{T_0}\left[\mathrm{erf}(\lambda\alpha)-\right.\right.$$

$$\left.\left.-\frac{1}{\lambda\alpha\sqrt{\pi}}(1-\mathrm{e}^{-\lambda^2\alpha^2})\right]\right\} \qquad (23b)$$

for the 'ideal gas' vapour (Eq (5b)).

The temperature at the interface is calculated from Eq (14) or (15):

$$T_s=T_i+A_1\,\mathrm{erfc}(\lambda) \qquad (24)$$

It can clearly be seen that the interface temperature stays constant throughout the process and depends only on the phenomenological coefficients. Its value can be calculated once the interface locator parameter is determined.

Introduction of the expressions for the interface temperature (Eq (24)) and the pressure (Eq (23a) or (23b)) into the Clapeyron equation (Eq (12)), results in a transcendental algebraic equation for λ, for both the incompressible and the compressible cases. The explicit solution for λ can easily be derived when a bi-section computer program is employed for various values of the seven non-dimensional parameters α, K, Q, H, T_0/T_i, P_{cr}/P_0 and T_{cr}/T_i. It should be noted that the procedure by which water vapour pressures and temperatures were obtained is equally valid for any other evaporating substance provided the kinetics of phase change reach equilibrium at an infinite rate. The only equation that must be altered is Eq (12).

Results and discussion

The analysis presented here was applied to calculate the rate of drying and the pressure build up for Israeli oil shales. Two sample sets of conditions were considered:

(a) $T_0=150°\mathrm{C}$, $T_i=20°\mathrm{C}$ simulating predrying of shales.

(b) $T_0=500°\mathrm{C}$, $T_i=50°\mathrm{C}$ simulating drying in a retort.

The thermophysical properties, used in the calculations, and the results are given in Table 1. An average value for the location of the interface as a function of time is $s=0.28(t)^{1/2}$ for Set a and $s=0.82(t)^{1/2}$ for Set b, where s is in mm and t in seconds.

Table 1 Drying and pressure build-up of Israeli oil shales

	Set a			Set b		
	T_0 = 150°C p_0 = 1 bar	T_i = 20°C		T_0 = 500°C p_0 = 1 bar	T_i = 50°C	
Conductivity ratio, K_1/K_2		1.0			1.0	
Diffusivity ratio, α_1/α_2		1.086			1.086	
Initial moisture, ω	0.5	0.10	0.15	0.05	0.10	0.15
Permeability parameter, H	5.16	10.3	15.5	5.16	10.3	15.5
Porosity parameter, Q	0.569	1.13	1.70	0.516	1.03	1.547
Interface locator, λ	0.278	0.223	0.192	0.767	0.653	0.582
Pressure build-up, P_s/P_0	1.33	1.40	1.44	2.34	2.74	2.97

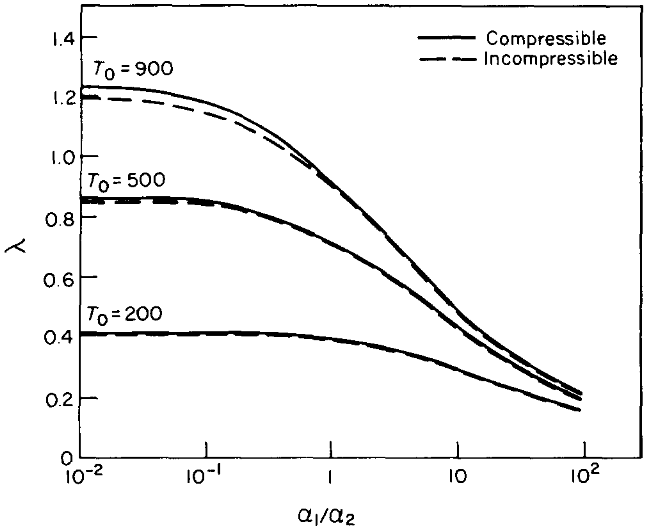

Fig 1 Interface locator versus thermal diffusivity ratio for $K_1/K_2 = Q = H = 1$

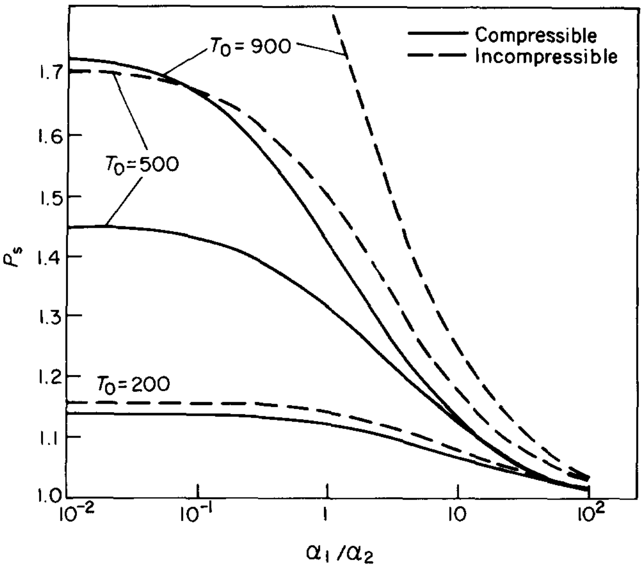

Fig 2 Interface pressure versus thermal diffusivity ratio for $K_1/K_2 = Q = H = 1$

Since the analysis may be applied to many other conditions a parametric study was carried out to obtain the interface locator λ, which determines the interface propagation rate, as a function of various thermophysical properties and environmental parameters. Comparisons between the compressible and incompressible results for the interface locator and the interface pressure of water vapour are given in Figs 1 to 8 for drying at an initial temperature $T_i = 50°C$ and ambient pressure $P_0 = 1$ bar.

Figs 1 and 2 illustrate the influence of thermal diffusivity ratio α_1/α_2 on λ and P_s for vaious temperatures T_0 (all other non-dimensional parameters constant). Figs 3 and 4 show the effects of the conductivity ratio K on λ and P_s. Figs 5 and 6 demonstrate the dependence of λ and P_s on the permeability parameter H for various external temperatures T_0, and Figs 7 and 8 the interface locator and pressure dependence on the porosity parameter Q.

Since a direct relationship exists between the interface pressure and the temperature (Eq (12)), Figs 2, 4, 6 and 8 can also be used to obtain the interface temperature.

Analysis of Figs 1, 3, 5 and 7, which show the dependence of the interface locator λ on the various thermophysical parameters, indicate that:

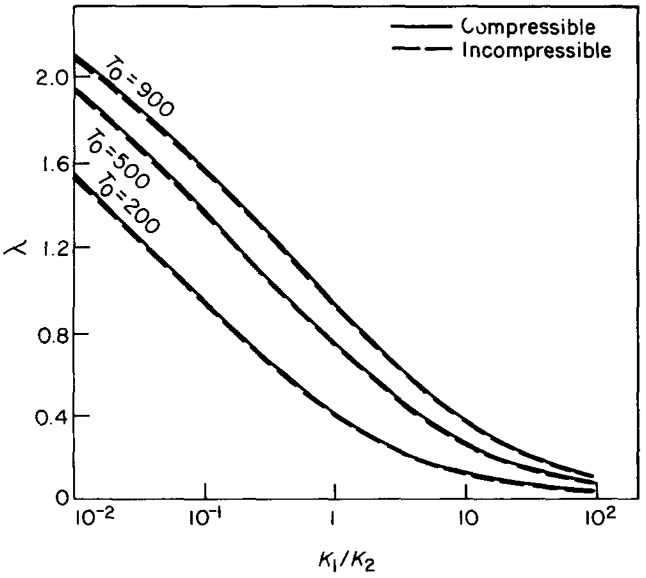

Fig 3 Interface locator versus thermal conductivity ratio for $\alpha_1/\alpha_2 = Q = H = 1$

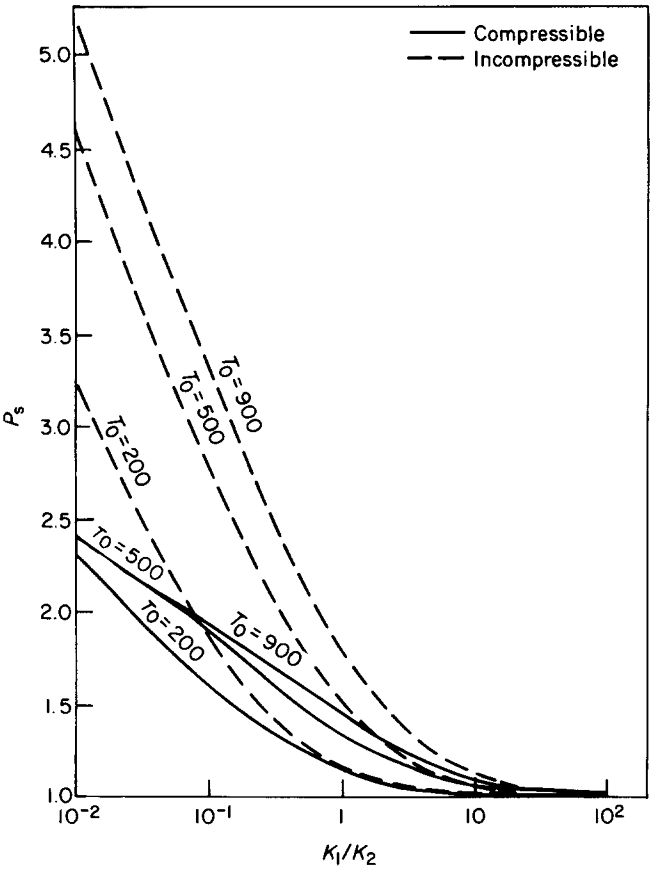

Fig 4 Interface pressure versus thermal conductivity ratio for $\alpha_1/\alpha_2=Q=H=1$

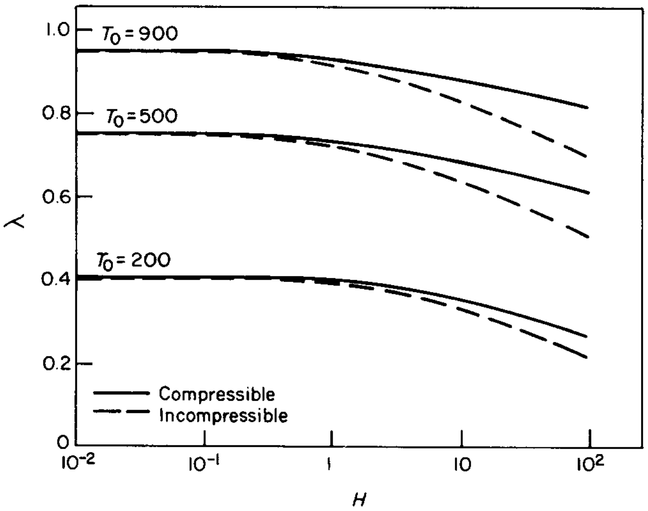

Fig 5 Interface locator versus permeability parameter for $\alpha_1/\alpha_2=K_1/K_2=Q=1$

(a) The values of the interface locator λ, vary between approximately 0.1 to 2.0 while the thermophysical parameters vary substantially (between 10^{-2} to 10^2).

(b) The diffusivity ratio α_1/α_2 has a mild effect on λ. An increase of the ratio α_1/α_2 causes a decrease in λ.

(c) The conductivity ratio K has the largest effect on λ. An increase in K causes a decrease in λ, since, for high K_1 values, the flux of heat into region 1 increases at the expense of the heat provided to evaporate the liquid.

(d) The permeability factor H has little effect on λ and its value remains practically constant for $H<0.1$ (large permeabilities). This is accounted for by the small pressure build up resulting in a low interface temperature.

(e) The porosity parameter Q has a similar effect on λ to that of the diffusivity ratio α_1/α_2. An increase of Q means a porosity increase which has a similar effect as an increase in the latent heat of the liquid. Thus larger Q is equivalent to larger amount of heat needed to evaporate the liquid causing decrease in λ.

(f) The incompressible solution proves to be a good approximation in predicting λ and just slightly underestimates it. Thus, a conservative result for the interface progress can easily be obtained utilizing the simpler solution for incompressible vapour.

(g) An increase of the external temperature, obviously, causes a higher rate of interface progress.

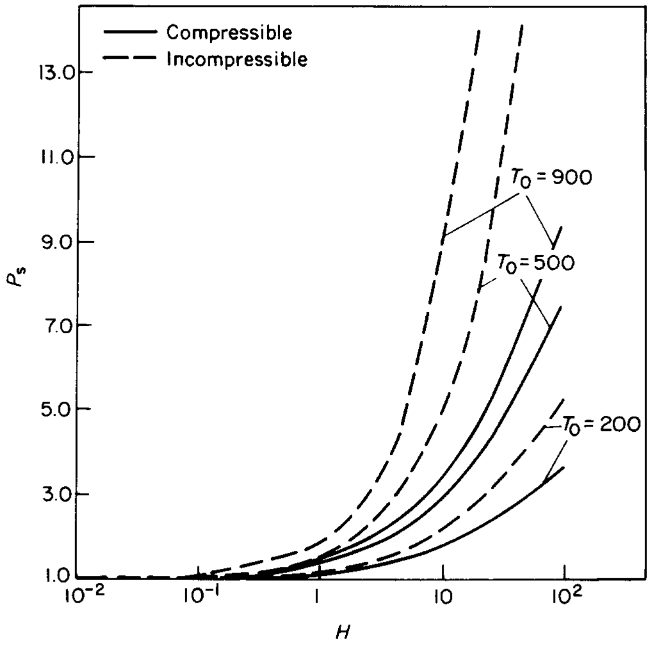

Fig 6 Interface pressure versus permeability parameter for $\alpha_1/\alpha_2=K_1/K_2=Q=1$

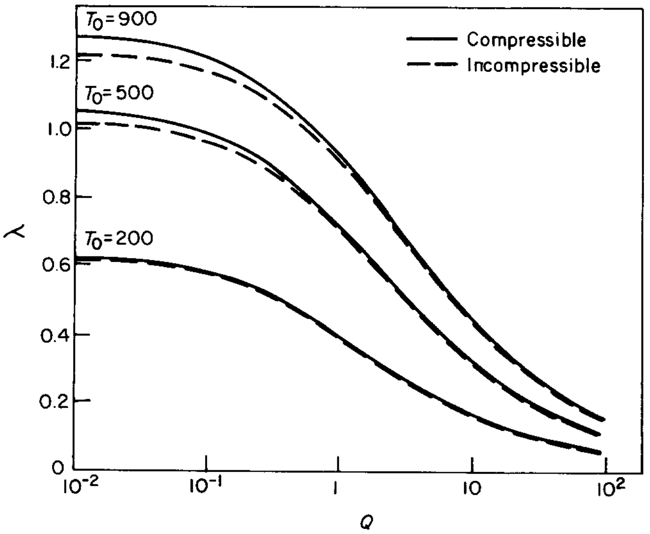

Fig 7 Interface locator versus porosity parameter for $\alpha_1/\alpha_2=K_1/K_2=H=1$

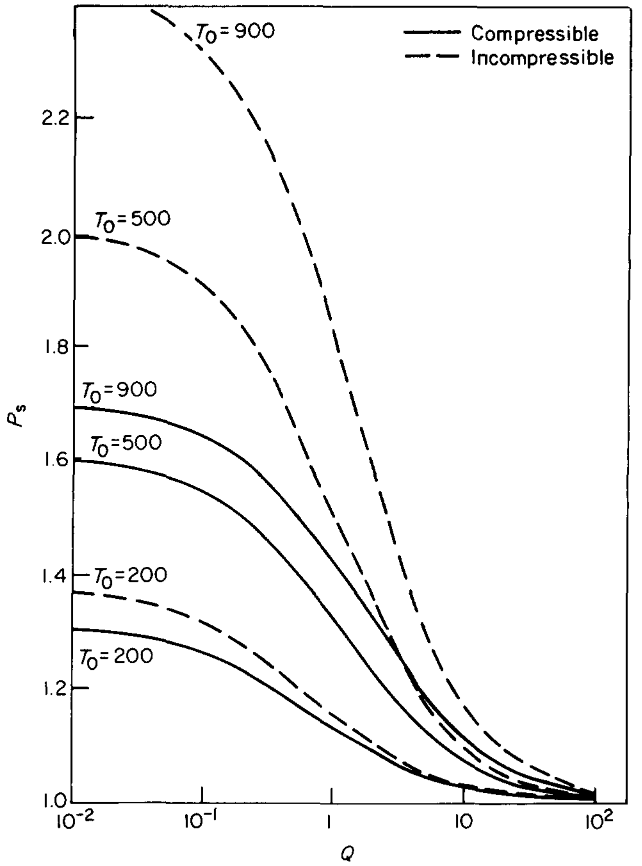

Fig 8 Interface pressure versus porosity parameter for $\alpha_1/\alpha_2 = K_1/K_2 = H = 1$

Analysis of Figs 2, 4, 6 and 8 for the interface pressure, show that:

(1) The parameters Q, K and α only affect the pressure build up mildly. Values of these parameters larger than 10 result in almost no pressure build up.

(2) A large pressure build up can be created for values of H higher than unity (namely small permeabilities), as expected.

(3) An increase of external temperature obviously causes an increase of pressure build-up.

(4) Predictions of pressure build-up using the incompressible solution always result in substantial overestimates, especially when the material is exposed to a high external temperature.

The solution may be invalid for elevated temperatures and low permeabilities since a pressure build-up can result in material fracture.

Cross *et al* assumed *a priori* the temperature difference, $T_0 - T_s$ at 20°C. In our solution that is not necessary. Indeed, the Clapeyron equation provides the means to calculate the interface temperature. From the results shown in Figs 2, 4, 6 and 8, the interface temperature can easily be derived. The temperature difference, $T_0 - T_s$ may be as high as 750°C, for an external temperature of 900°C. Only for very low external temperatures it could be of the order of 20°C.

The results may deviate from the practical case on two counts:

(i) the convection by the outflowing vapour was neglected.

(ii) a semi-infinite model was assumed, rather than a slab or a sphere.

The first tends to reduce the pace of the moving interface, while the converse is true for the second. For low external temperatures, below 200°C, the temperature variations within the particle do not exceed 100°C. Thus the heat convected by the vapour is relatively small. Under these conditions the solution, as presented here, yields a lower bound for the rate of drying. At higher external temperatures, further research is required to determine either lower or upper bound for the drying process.

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