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Thermal conductivity of a microporous particulate medium: moist silica gel

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Abstract— A systematic study of the thermal conductivity of beds of moist silica gel is presented. The influence of porosity, water content, total gas pressure and temperature is determined through measurements under transient conditions with the transient hot-strip (THS) method and under static conditions in a bench-scale reactor. The predictions of the effective thermal conductivity of the beds from four different simple models (Russell, geometric mean value, unit-cell model and stochastic model) agree reasonably well with the experimental results. The unit-cell model is extended in order to account for the water sorbed in the micropores and describes satisfactorily the dependency of the effective thermal conductivity on the water content.

1. INTRODUCTION

THE CHEMICAL heat pump is a new name recently given to the periodically operating absorption heat pump, in order to stress the heat storage function that is not commonly associated with an absorption heat pump or absorption refrigerating machine [1]. Gas–solid sorption reactions are attractive in such processes. The gas–solid reactor consists of a bed of particles sandwiched between a heat exchanging surface and a vapour adduction channel. An important point of its design is the transfer of heat in the fixed bed.

The adsorption system water vapour–silica gel was previously studied in an investigation of the factors influencing the heat power output of a chemical heat pump during sorption and heat power input during desorption [2]. The results could be analysed in terms of a pseudo-homogeneous heat conduction model. The important entities in the time-dependent heat conduction equation are the thermal conductivity of the bed and its thermal mass, which also includes the heat turned over in the reaction.

The present study is undertaken in order to measure and analyse the thermal conductivity properties of silica gel beds in more detail, which includes finding both appropriate techniques to measure the thermal conductivity and reliable models for its prediction.

Silica gel is a rather well-known adsorbent, widely used in industry for desiccation purposes or as a catalyst support. In fact, silica gel is a generic name for a variety of materials with different physical characteristics. This makes the direct use of published thermal conductivity data rather difficult (see Table 1). Only Andrianov *et al.* [7] present data at various water content. Nowhere are data available for moist silica gel in an atmosphere of only water vapour.

In the present study, two different techniques to measure the thermal conductivity of beds of particles are considered. Measurements are performed in one technique under transient conditions (the THS method) and in the other under static conditions. Both kinds of techniques are necessary to evaluate the influence from the different parameters determining the thermal conductivity.

A great number of equations predicting the heat conductivity of a heterogeneous medium (e.g. a solid dispersed in a continuous fluid) exist in the literature. Several approaches to the task of modelling are possible [14] yielding different equations with mathematical properties that depict the physical reality with varying accuracy. The basic mechanisms for the transmission of heat in a particulate medium are clear (see e.g. Luikov *et al.* [15]). The geometrical structure of the system is, of course, important, but the contact between the elements of the discontinuous phase (the particles) seem to play an essential role.

The computation of an effective thermal conductivity of a bed of particles requires knowledge of the thermal conductivity of the particles themselves. It is seldom possible to obtain a particle of a microporous sorbent large enough for a measurement of its thermal transport properties. To overcome this difficulty, however, the calculation can be done in two steps as by Harriott [16], i.e. first compute the thermal conductivity of the particle using the properties of the materials and second that of the aggregate of particles.

2. EXPERIMENTAL

2.1. *The silica gels*

Two types of silica gel from W. R. Grace Ltd. are used: (a) the Davison gel, Grace type 125 and (b) the Grace type 119 of lower density. Material data are summarized in Table 2. The first gel has a particle size of 1–3 mm and is used as such in the bench-scale experiments but ground to DIN 12 sieve size (< 0.5 mm) for the THS measurements. Samples with varying water content for the THS measurements are prepared by storing them in exsiccators over solutions

NOMENCLATURE

A	parameter in equation (3)
a	thermal diffusivity [$m^2 s^{-1}$]
c_p	heat capacity at constant pressure [$J kg^{-1} K^{-1}$]
E	Young's modulus [$N m^{-2}$]
H	characteristic dimension of a bed [m]
h	skeleton thickness [m]
h_r	height of a microroughness [m]
k_c	empirical coefficient in equation (A3) [$(N m^{-2})^{3/2}$]
k_k	adhesion coefficient in equations (A2) and (A3)
L	height of the reactor in equation (1), and particle size otherwise [m]
l	pore width [m]
m	thickness of water film [m]
P	pressure [Pa]
Q	heat flow [W]
R	thermal resistance [$K W^{-1}$]
r	radius [m]
S	area of the contact spot, equation (A3) [m^2]
T	temperature [K]
V	volume [m^3]
w	water content [$g(H_2O) g^{-1}$(dry gel)].

Greek symbols

ε	volume fraction
λ	thermal conductivity [$W m^{-1} K^{-1}$]
ρ	density [$kg m^{-3}$].

Subscripts

c	solid contact between two particles
con	continuous phase
dis	discontinuous phase
eff	effective value
g	gas phase
o	dry gel
p	particle, or pore equations (7) and (8)
s	solid phase
w	water.

of sulphuric acid at appropriate concentrations. The water content is determined by drying the sample in a vacuum oven at *ca* 100°C.

The other gel is almost nonhygroscopic. Its particle size is *ca* 1 mm and the gel is used as such in all experiments.

2.2. *Thermal conductivity measurements with the THS method*

The THS method, recently developed at the Chalmers University of Technology [17], is used for simultaneously measuring the thermal conductivity and the thermal diffusivity of solids and liquids with a low electrical conductivity. In this method a flat metal strip is used both as a continuous plane heat source and as a sensor for the temperature increase in the strip itself. By supplying a constant current to the metal strip (the output of power is then very nearly constant) and by monitoring the subsequent voltage increase over a short period of time after the start of the experiment, it is possible to get precise information on the thermal transport properties of the material surrounding the heat source. The recorded voltage change is originally due to the temperature increase which causes an increase in the electrical resistance of the strip. When the width of the strip is well chosen it is possible to obtain both heat conductivity and diffusivity in a single experiment. A detailed description of the method is given in ref. [17].

For the present investigations two sample cells

Table 1. Literature values of the thermal conductivity of a bed of dry silica gel

Author	Particle density $\rho_{p,o}$($kg m^{-3}$)	Bed density ρ($kg m^{-3}$)	Effective thermal conductivity λ($W m^{-1} K^{-1}$)	Mean temperature T(°C)
Mantell [3]	1201	720	0.144	
W. R. Grace Ltd. [4]				
Niebergall [5]			0.198	
Vasilev *et al.* [6]		850	0.153	20
		998	0.182	20
		865	0.160*	20
Andrianov *et al.* [7]		510	0.045	
Sharma *et al.* [8]	891†	452–750 [9]	0.128–0.168	ambient to 135.0
Sharma and Hughes [10]		428–690†	0.116–0.148	48.7
Blasinski and Heim [11]	870 [12]	461–609†	0.106–0.135	140
Simonova [13]		634†	0.151	20
		838†	0.179	20

* Extrapolated from data at higher temperatures.
† Calculated by us.

Table 2. Some material data for the 119 and 125 silica gels from W. R. Grace Ltd. [4]

	Type 119	Type 125
Density (kg m^{-3})	689	1201
Microporosity	0.69	0.45
Pore diameter (nm)	11.5	2.1
Specific surface ($m^2 g^{-1}$)	400	750

were constructed with the sample space dimensions $40 \times 60 \times 10$ mm and $10 \times 60 \times 10$ mm (volumes: 24 and 6 ml, respectively). Platinum strips 3.79×59.3 mm, or 3.57×53.3 mm with a thickness of 0.0125 mm are placed vertically in the sample space and soldered to the leads. The electric circuit is shown in Fig. 1. The silica gel particles are poured into the cells. The density of the sample beds is determined by weighing the cells and different densities are obtained by shaking the cell gently or by applying a mild pressure.

In a THS experiment the thermal conductivity λ and the thermal diffusivity a are determined as parameters in a curve-fit of the recorded resistance history of the strip. Of these two parameters, the thermal diffusivity is very sensitive to the nature of the contact area whereas the thermal conductivity is not. The heat capacity c_p then calculated from these two values is a good indicator of whether a measurement yields erroneous results (i.e. if any imperfections in the contact exists or if desorption of moisture occurs). To check the validity of the THS results the heat capacity for the samples investigated are measured independently using a Perkin–Elmer DSC-II differential scanning calorimeter. Large volume capsules (75 μl), that are sealed with O-rings, are used for the samples. The heating rate is 10°C min^{-1}. The heat capacities from DSC measurements are good approximations to the heat capacities at constant pressure. The contributions from the differences in conditions: constant total volume, a sorption equilibrium, desorption of water to adjust its partial vapour pressure to equilibrium, are a couple of orders of magnitude lower.

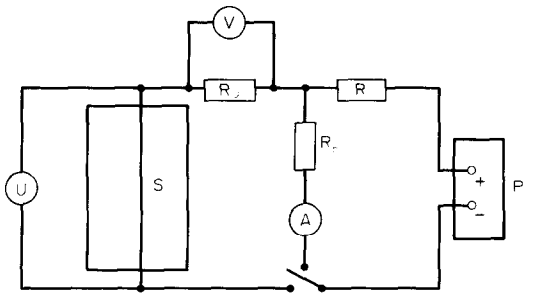

FIG. 1. Electrical circuit for the thermal transport studies by the THS technique: S, P, power supply, R_0, R_b and R, standard resistors, current limiting resistor and balancing resistor, respectively, A, ammeter to adjust the balancing current, U and V, digital voltmeters HP 3456A and HP 3437A, respectively.

When applying the THS technique to measurements on powders the particle size must be small enough in relation to the width of the strip. Measurements on particles with a 1–3 mm diameter failed to give values of the heat capacities in agreement with the DSC values. Only when having reduced the size of the particles, by crushing them to diameters below 0.5 mm, is agreement between the two sets of data obtained.

The heat capacities calculated from the THS measurements on moist silica gel agree well with the DSC values. The desorption of water does thus not interfere. The 15–20 s of an experiment are much less than the half-time of the desorption and sorption process even in vacuum, i.e. when water vapour is the only gas present, which is approximately 3 min at the actual temperature [2]. This half-time is considerably increased in the presence of stagnant air. The temperature increase in the strip during an experiment is of the order of 1°C.

Reducing the pressure in the THS sample cell leads not only to incorrect heat capacities but also to obviously unreasonable thermal conductivities and thermal diffusivities. This can be ascribed to the so-called skin effect, i.e. the Smoluchowski temperature discontinuity arising below a threshold pressure. This inconvenience is, however, shared with most static and transient methods utilizing the conditions close to the heat source. This difficulty is avoided by measuring the temperature gradient in the bulk of a sample during the experiments, cf. Section 2.3.

2.3. *Thermal conductivity measurements of a bed of dry silica gel under static conditions*

Steady-state measurements of the heat conductivity of dry silica gel beds are performed with an apparatus designed for studying sorption and desorption processes of water vapour, see Fig. 2 [2]. It is a 250 mm high cylindrical reactor with a jacket and an inner heat exchanger, leaving an annular space with inner and outer diameters of 60 and 125 mm, respectively, for the sample. The heat flow through the annulus is measured as a temperature rise in the water flowing through the inner heat exchanger. The temperature gradient in the bed is measured with thermocouples. The heat flows in the experimental set-up were calibrated by filling the reactor with a paraffin, the heat conductivity of which was measured with the THS technique as 0.247 W m^{-1} K^{-1}.

The jacket is kept at 40°C and the inner heat exchanger at 20°C during all the measurements. Experiments are carried out under air at different pressures between 2 and 10^5 Pa (16 mTorr to atmospheric pressure).

The thermal conductivity of the bed is calculated from the heat flow through the bed by

$$\lambda = \frac{Q}{2\pi L(\mathrm{d}T/\mathrm{d}\ln r)} \qquad (1)$$

where Q is the heat flow, L the height of the bed, and

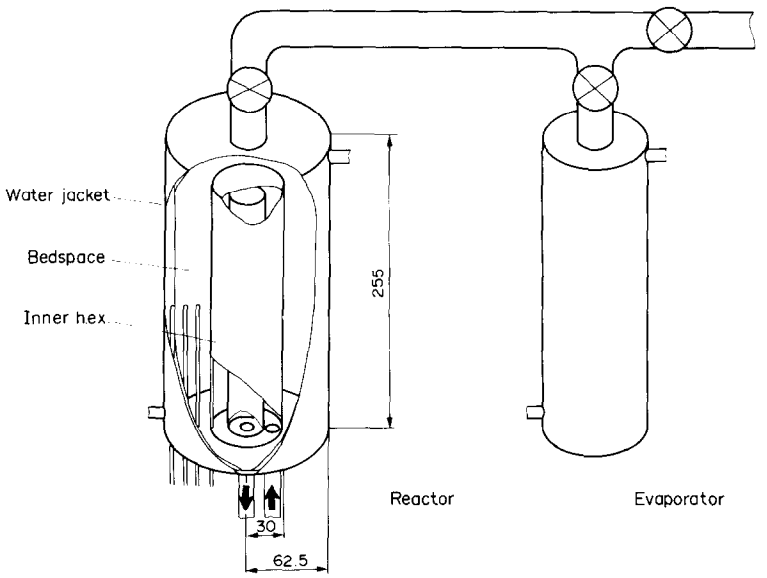

FIG. 2. Schematic drawing of the bench-scale reactor system [2].

$dT/d\ln r$ is the mean temperature gradient in the bed. The skin effect (temperature discontinuity) at the contact surface between the gel and the heat exchanger observed at low total pressures could thus be disregarded.

3. EXPERIMENTAL RESULTS

The experimental results obtained with the THS method are listed in Table 3. The thermal conductivities for the Grace 125 gel are plotted in Fig. 3(a) vs the macroporosity, ε_g of the dry gel, in Fig. 3(b) vs the water content at $\varepsilon_g = 0.325$, and in Fig. 3(c) vs the temperature at $\varepsilon_g = 0.274$ for the dry gel.

The swelling of the gel upon sorption of water is considered to be negligible and the macroporosity of the bed is calculated as

$$\varepsilon_g = 1 - \frac{\rho}{\rho_{p,0}(1+w)} \tag{2}$$

Table 3. Heat conductivities of silica gel beds as obtained with the THS technique

Nr	T(K)	w	ρ(kg m^{-3})	λ(W m^{-1} K^{-1})	a(10^{-6} m^2 s^{-1})	c_p(kJ kg^{-1} K^{-1})
1	295	0	700	0.147	—	—
2	295	0	836	0.165	0.232	0.85
3	295	0	852	0.168	0.237	0.84
4	295	0	872	0.170	0.235	0.83
5	295	0	964	0.179	0.223	0.84
6	295	0	978	0.184	0.227	0.83
7	295	0.008	868	0.164	0.220	0.86
8	295	0.104	994	0.195	0.160	1.22
9	295	0.117	768	0.173	0.155	1.46
10	295	0.117	879	0.177	0.152	1.32
11	295	0.117	883	0.178	0.143	1.38
12	295	0.117	899	0.188	0.154	1.36
13	295	0.142	993	0.205	0.172	1.20
14	295	0.144	967	0.202	0.164	1.27
15	295	0.153	928	0.205	0.160	1.38
16	295	0.204	912	0.213	0.153	1.52
17	295	0.204	912	0.214	0.158	1.48
18	295	0.204	973	0.219	0.154	1.51
19	295	0.239	1017	0.214	0.142	1.48
20	295	0.310	920	0.230	0.162	1.55
21	295	0.310	1045	0.273	0.164	1.60
22	295	0.310	1090	0.269	0.153	1.62
23	295	0.329	1073	0.254	0.145	1.63
24	295	0.329	1113	0.265	0.144	1.65
25	314	0	872	0.175	0.235	0.86
26	336	0	872	0.188	0.245	0.88

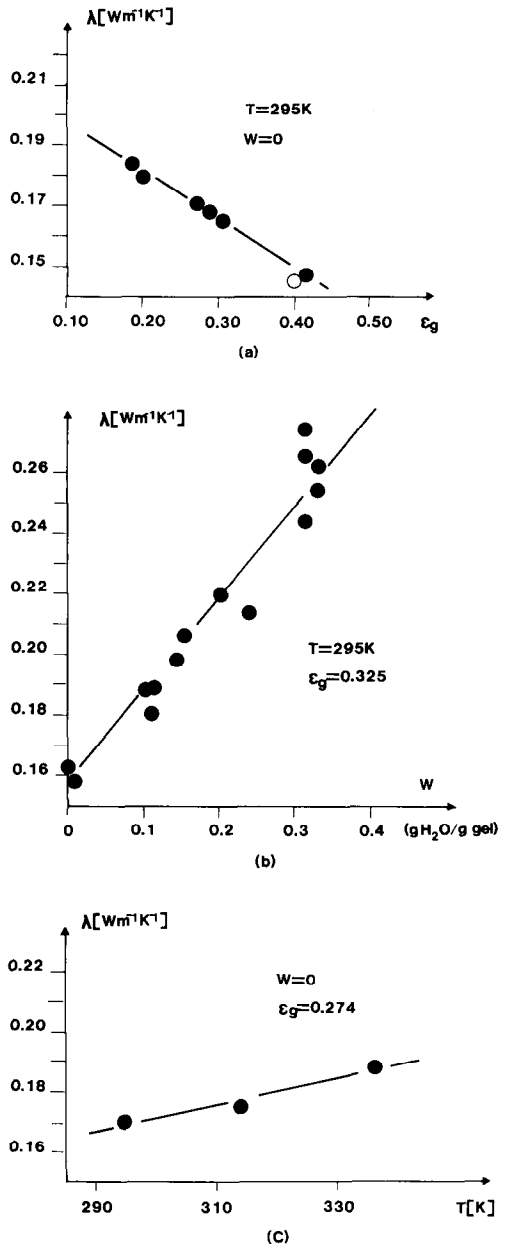

FIG. 3. The thermal conductivity values λ obtained for the gel type 125 with the THS technique as a function of (a) porosity ε_g, (b) water content and (c) temperature.

where ρ is the bed density and $\rho_{p,0}$ is the density of a particle of dry silica gel. The thermal conductivity values at $\varepsilon_g = 0.325$ in Fig. 3(b) are calculated from the experimental values for various water contents by assuming that the dependency on macroporosity is the same as that for the dry gel in the pertinent interval.

The close agreement between the heat capacity values from the THS measurements and those obtained through DSC is demonstrated in Fig. 4.

The thermal conductivities obtained in the cylindrical reactor at varying total air pressures are illustrated for the dry gels 125 and 119 in Fig. 5. At atmospheric pressure these results match well with those obtained in the THS measurements indicating that the particle size is of minor importance. The results agree well with the value reported by Mantell for the Davison gel, see Fig. 3(a). The skin effect observed at low total pressures, below 10^2 Pa, is not apparent at higher total pressures. Its occurrence is accompanied by a drastic reduction in thermal conductivity for the bed of particles. This is due to the increase of the mean free path of the gas with decreasing pressure beyond the characteristic length of the interstices between the particles. The data points obtained in pressure lowering series and those obtained in pressure increasing series do not exhibit any significant differences.

4. ANALYSIS

4.1. *Models for predicting the thermal conductivity of heterogeneous mixtures*

Formulas stemming from four models are used for the computation of the thermal conductivity of the silica gel beds.

We have chosen these four models because of the simplicity of the geometrical structures assumed in each of them. They also cover different representations of the contact between particles.

(a) *The unit cell model as proposed by Dulnev and extended by Luikov.* The unit cell model [18] represents the structure of the mixture as two intertwined three-dimensional networks composed of repeated units. The calculation of the thermal resistance of the system is reduced to that of a quarter of a unit cell, see Fig. 6(a). Luikov [15] extended the model to account for the contact resistances between particles. The effective thermal conductivity is calculated from the following equation

$$\frac{\lambda_{\text{eff}}}{\lambda_s} = \left(\frac{1}{(h/L)^2} + A\right)^{-1} + \frac{\lambda_g}{\lambda_s}\left(1 - \frac{h}{L}\right)^2 + 2\left(1 + \frac{h}{l} + \frac{\lambda_s L}{\lambda_g h}\right)^{-1}. \quad (3)$$

The parameter A which was introduced by Luikov is the sum of two parallel resistances in the contact between two particles: conduction through the solid contact and conduction in the gas in the gap around the contact spot (see Appendix A).

(b) *Russell's model.* In the well-known model proposed by Russell [19] the structure of the heterogeneous system is also assumed regular. However, no contact exists between the elements of the discontinuous phase and the effective thermal conductivity is calculated as

$$\frac{\lambda_{\text{eff}}}{\lambda_{\text{con}}} = \frac{\varepsilon_{\text{dis}}^{2/3} + \frac{\lambda_{\text{con}}}{\lambda_{\text{dis}}}(1 - \varepsilon_{\text{dis}}^{2/3})}{\varepsilon_{\text{dis}}^{2/3} - \varepsilon_{\text{dis}} + \frac{\lambda_{\text{con}}}{\lambda_{\text{dis}}}(1 - \varepsilon_{\text{dis}}^{2/3} + \varepsilon_{\text{dis}})}. \quad (4)$$

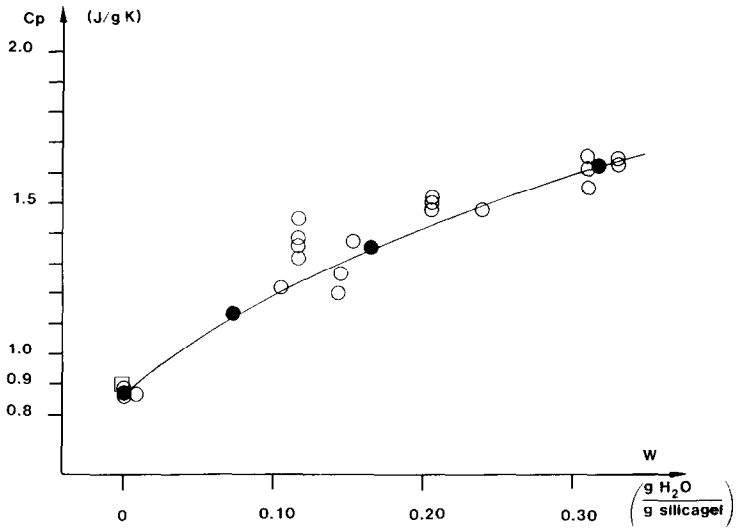

FIG. 4. A comparison between heat capacity values for moist silica gel of type 125 at 22°C as obtained through DSC (●) and with the THS technique (○). Literature value [3]: □. The DSC data are correlated with equation [2]: $c_p = 0.402 + 2.483w + (1.578 + 5.526w - 29.10w^2 + 33.03w^3) \times 10^{-3} T$.

(c) *The stochastic model of Zarichniak and Novikov.* A simple model which accounts for the disordered distribution of the elements of both discontinuous and continuous phases is that of Zarichniak and Novikov [20]. The bed is schematized as an assembly of cubes with the same dimensions, representing one or the other phase in a random manner, stacked upon each other, see Fig. 6(b). Using a layer depth of two small cubes, they obtain

$$\lambda_{\text{eff}} = \lambda'_s \varepsilon_s^2 + \lambda_g \varepsilon_g^2 + 4 \frac{\lambda'_s \lambda_g}{\lambda'_s + \lambda_g} \varepsilon_g \varepsilon_s \qquad (5)$$

where λ'_s stands for a conductivity in the solid phase corrected for the contact resistances, as shown in Appendix A. The same approach is used by Prakouras *et al.* [21]. The heat conductivity problem is solved for a control volume of 12 × 12 × 12 cubes. This should yield more accurate results but at the price of a lengthy computer calculation.

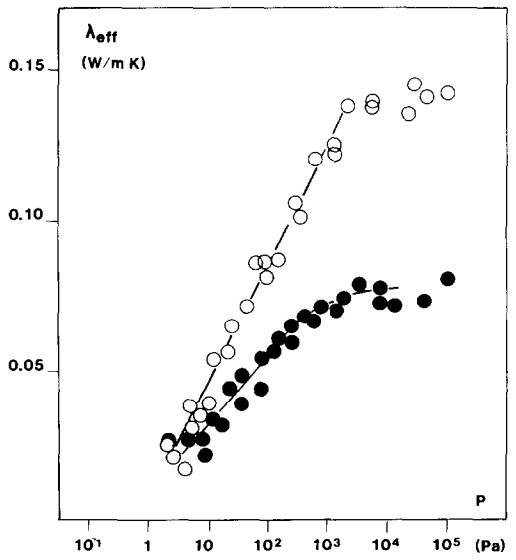

FIG. 5. The thermal conductivity of dry silica gels as a function of pressure. ○, type 125; ●, type 119.

(d) *The geometric mean model as proposed by Woodside and Messmer.* The lower bound to the effective thermal conductivity of an heterogeneous mixture is obtained by assuming a series distribution of the phases and their resistance to heat flow. An upper bound is obtained by assuming a parallel distribution [22, 23].

The weighed geometric mean of the constituents thermal conductivity

$$\lambda_{\text{eff}} = \lambda_g^{\varepsilon_g} \lambda_s^{\varepsilon_s} \qquad (6)$$

has been proposed by Woodside and Messmer [22] as a suitable intermediate between these two extrema.

4.2. *A model for a moist gel particle*

The unit-cell model, see Fig. 6(a), can easily be extended to account for the transmission of heat through the water sorbed in the micropores. Let us assume, albeit unrealistically at very low water contents, that the water adsorbed is distributed as a film with thickness m around the solid skeleton of the gel, as shown in Fig. 6(c). If the gel is assumed not to swell upon adsorbing water, the volume of water in the pores can be found by geometric calculations. The volume of water V_w relative to that of the pore V_p can be expressed as

$$\frac{V_w}{V_p} = \frac{m(3hl - 3hm - 3ml - 4m^2)}{l^2(L/4 + h/2)} \qquad (7)$$

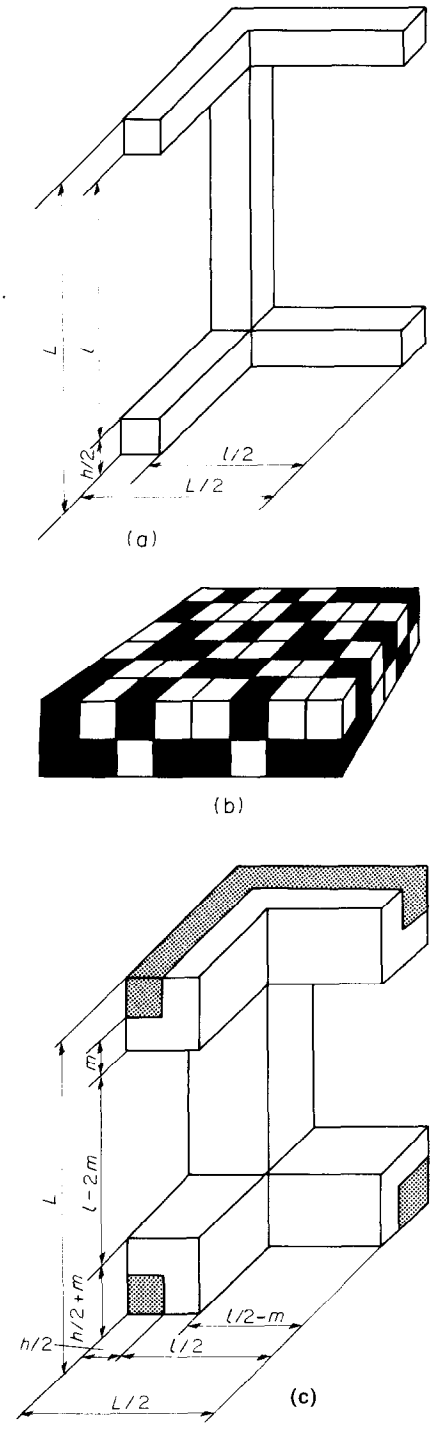

FIG. 6. Illustration of model structures: (a) the unit-cell model [15, 18], here a quarter of the unit cell; (b) the stochastic model [20]; (c) the modification of the unit-cell model proposed here, the dotted parts are the solid skeleton.

but also as

$$\frac{V_w}{V_p} = \frac{w}{w_{max}} \tag{8}$$

where w_{max} is the maximum amount of water that can be sorbed by the microporous sorbent. The parameter m is solved from the following equation

$$4\left(\frac{m}{l}\right)^3 - 3\left(1-\frac{h}{l}\right)\left(\frac{m}{l}\right)^2 - 3\frac{h}{l}\frac{m}{l} + \frac{w}{w_{max}} \times \frac{1+3(h/l)}{4} = 0. \tag{9}$$

Using the same electrical analogy as Dulnev and Luikov, one obtains the following expression for the thermal conductivity of the particles, see Appendix B for its derivation

$$\frac{\lambda_p}{\lambda_s} = \left(\frac{h}{L}\right)^2 + 4\left(\frac{L}{m} + \frac{\lambda_s}{\lambda_w}\frac{L}{h}\frac{l}{m}\right)^{-1} + 4\frac{\lambda_w}{\lambda_s}\left(\frac{m}{L}\right)^2 + 2\left(\frac{L}{l-2m} + 2\frac{\lambda_s}{\lambda_w}\frac{Lm}{h(l-2m)} + \frac{\lambda_s}{\lambda_g}\frac{L}{h}\right)^{-1} + 4\left(\frac{\lambda_s}{\lambda_w}\frac{L}{m}\frac{h+2m}{l-2m} + \frac{\lambda_s}{\lambda_g}\frac{L}{m}\right)^{-1} + \frac{\lambda_g}{\lambda_s}\left(\frac{l-2m}{L}\right)^2. \tag{10}$$

4.3. *Results of the calculations*

The thermal conductivity of a particle is calculated first and this value is used for calculating that of a bed of particles. The thermal conductivity for vitreous silica, water, air and water vapour are taken from ref. [24].

The values obtained for the thermal conductivity of a silica gel particle of Grace 125 type at 25°C are listed in Table 4 both for a dry and for a fully hydrated gel. When using the unit cell (a) and the stochastic model (c) the contact resistance between the grains in the particle is neglected, i.e. $A = 0$ in equation (3) and $\lambda_s' = \lambda_s$ in equation (5). These models give values that are close to each other. When taking the gas phase as the continuous phase in Russell's model (b), one obtains a thermal conductivity value that is obviously too low: 1.2 mW m^{-1} K^{-1}. The higher value in the table, obtained when taking the silica skeleton as the continuous phase is then in some doubt, as the picture underlying the model does not seem reasonable. The geometric mean model (d) gives too low a value for the dry particle. Moreover, this value is sensitive to pressure which should not be the situation as the micropore size is much smaller than the mean free path of air at atmospheric pressure. The disagreement between the different models is minor, however, when the conductivities of the constituents are close to each other, as the right-hand column in Table 4 shows for the fully hydrated gel.

Table 4. Thermal conductivities calculated for the silica gel particles with $\rho_{p,o} = 1201$ kg m^{-3}

Model	Dry gel	Wet gel
Unit-cell	0.380	0.938
Stochastic	0.406	0.941
Russell	0.641	0.983
Geometric mean	0.027	0.938

Table 5. Comparison between experimental and calculated thermal conductivities

Sample	ε_g	λ_{exp} (W m^{-1}K^{-1})	λ_{calc} (W m^{-1}K^{-1}) (a)	(b)	(c)	(d)
Type 119						
ρ_p = 689 [4]	0.435	0.078	0.076	0.078	0.076	0.079
λ_p = 0.187*						
(22°C)						
Ref. [11]						
ρ_p = 870 [12]	0.300	0.132†	0.143	0.146	0.147	0.158
λ_p = 0.30*	0.400	0.115	0.121	0.121	0.122	0.127
140°C	0.470	0.107	0.108	0.108	0.106	0.110
Ref. [10]						
ρ_p = 891* [9]	0.225	0.147	0.127	0.133	0.130	0.153
λ_p = 0.268*	0.300	0.140	0.112	0.116	0.110	0.127
48.7°C	0.395	0.128	0.096	0.096	0.096	0.101
Type 125						
ρ_p = 1200 [4]	0.197	0.179	0.176	0.180	0.185	0.222
λ_p = 0.378*	0.304	0.165	0.144	0.136	0.150	0.167
22°C	0.417	0.147	0.118	0.106	0.118	0.124

* Calculated value.
† Average value.

The results of the calculation of the thermal conductivity of a bed are compared in Table 5 with our experimental results and with data available in the literature. The thermal conductivity of a particle was computed with the unit-cell model. All models give predictions of the thermal conductivity within 25% of the experimental values for bed porosities between 0.2 and 0.4. However, none of the models predict very accurately the general trend of variation of the conductivity with bed voidage: all predict a larger dependency of porosity than the actual one, especially for larger particle densities, see Fig. 7.

It should be noted that the thermal conductivity of a particle calculated with the unit-cell model for the gel investigated by Blasinski and Heim is different from the 0.23 W m^{-1} K^{-1} reported by these authors. On the other hand, the use of 0.23 W m^{-1} K^{-1} in the calculations gives effective conductivities 30% below the experimental values.

The occurrence of a large drop in thermal conductivity under a certain threshold pressure, the value of which is determined by the size of the particles can be reproduced with a tolerable accuracy by all models, see Fig. 8, where experimental data for the 125 type gel are compared with the predictions of the different models. The same good agreement is also found for the 119 type gel.

In Fig. 9(b) experimentally determined thermal conductivity data for the Grace 125 gel at various water contents and at a porosity of 0.325 are reproduced from Fig. 3(b) and compared with the results of calculations. Equation (10) is used to compute the thermal conductivity of the particle, shown in Fig. 9(a). The model underlying equation (10) predicts a non-linear dependency of the thermal conductivity on water content. This is particularly pronounced with water contents corresponding to an almost fully hydrated gel, see Fig. 9(a). The experimental values for the thermal conductivity of a bed also show a steep increase at water contents close to saturation.

The unit-cell model and the stochastic model predict thermal conductivities within 25% of the experimental values. Their sensitivity can be expressed as follows: the

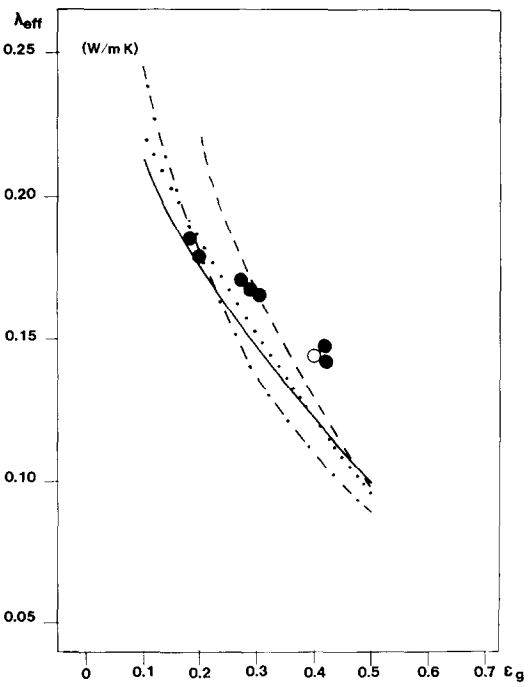

FIG. 7. A comparison between experimental results and predicted values. The effective thermal conductivity as a function of porosity. Unit-cell model, ——; stochastic model, ·····; Russell's model, – · – · –; geometric mean, ———. THS and bench-scale reactor experimental data, ●; literature value, ○ [3, 4].

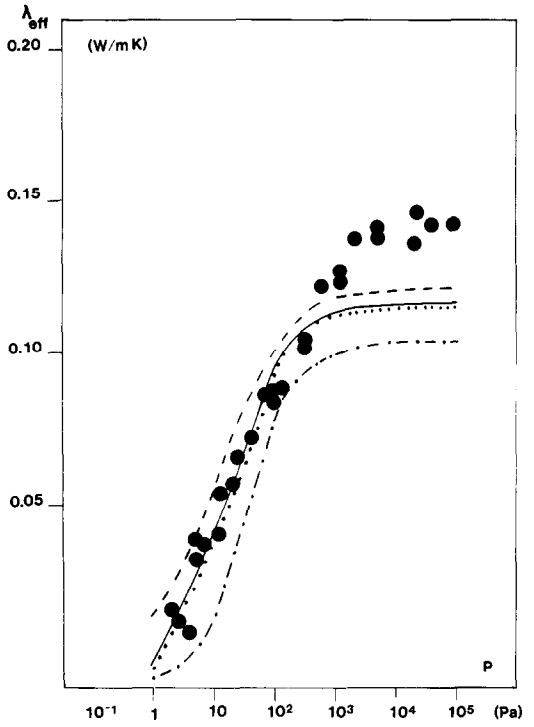

FIG. 8. A comparison between experimental results and predicted values. The effective thermal conductivity as a function of pressure. Models, see Fig. 7. Bench-scale reactor experimental data, ●.

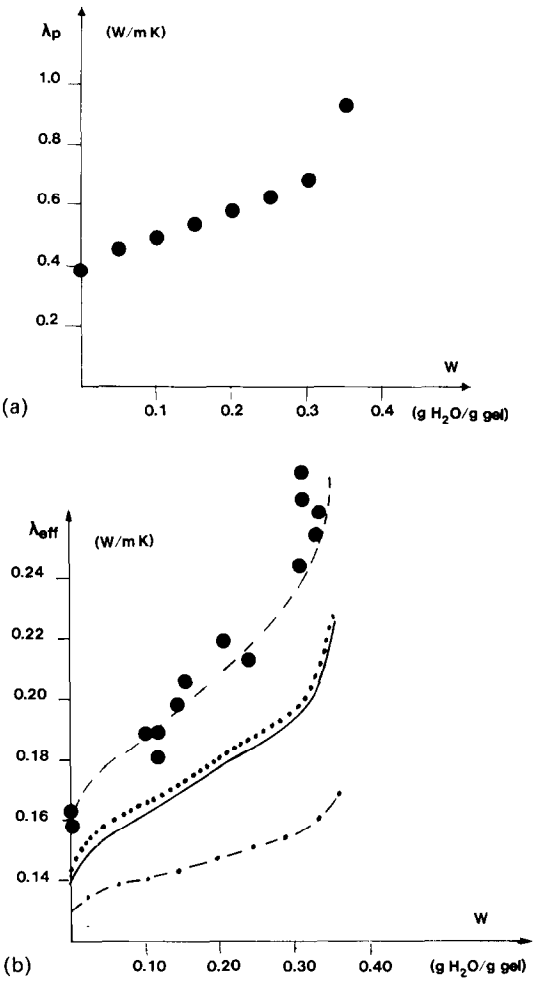

FIG. 9. The thermal conductivity of moist silica gel of type 125 at 22°C: (a) computed conductivities of particles as a function of water content; (b) a comparison between experimental results and predicted values for a bed. Models, see Fig. 7. THS experimental data, ●.

computed conductivity increases *ca* 25% between $w = 0$ and 0.20 as compared to the experimental increase of 31%. Model (d) is even more sensitive: with a 33% computed increase. The increase predicted by Russell's model is only 15%.

5. CONCLUSIONS

It has been shown that the advantages offered by the THS method for measurements on particulate and moist materials are its speed and accuracy. The perturbation introduced into the material investigated is very small, which allows measurements on samples that can undergo chemical changes upon a temperature increase, here the redistribution of moisture. However, as in all methods utilizing the conditions close to the heat source, problems arise when a close contact between sample and heat source cannot be achieved. Complementary measurements have therefore been performed in a bench-scale reactor under static conditions.

The thermal conductivity of a bed of silica gel has been determined as a function of porosity, water content, total gas pressure and temperature. Such a systematic study was found necessary, as the silica gels for which thermal conductivity data are reported in the literature are not defined well enough. It turns out that the experimental results at bed voidages between 0.2 and 0.4 can be predicted within 25% with any of the four models used here.

The unit-cell model has been extended in order to calculate the thermal conductivity of a moist silica gel particle. The model gives thermal conductivities of the bed that are in good qualitative agreement with the experimental observations. The general sensitivity of the conductivity seems to be described accurately. In a previous study [2] the thermal conductivity of moist silica gel during sorption and desorption was calculated from experiments at 11.3 kPa (8.7 Torr) water vapour and total pressure. These values are shown in Fig. 10 together with the predictions of the model equations. The agreement is quite satisfactory with an error below 20%, except for Russell's equations. It should be noted that the temperature is not the same for all the experimental points, each water content being determined, assuming local thermochemical equilibrium, by the values of both temperature and water vapour pressure. A decrease in water content, which decreases the thermal conductivity, is offset by an increase in temperature that follows from the condition

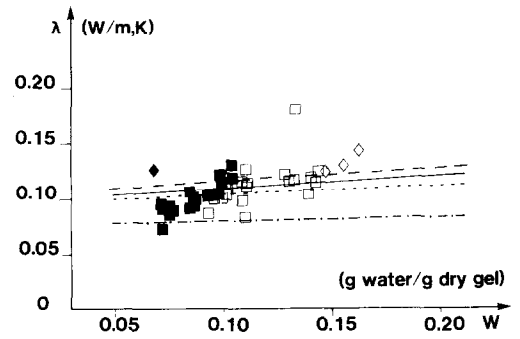

FIG. 10. A comparison between thermal conductivity values computed from experiments in ref. [2] and values predicted by models for a water vapour and total pressure of 11.3 kPa. ◇ Steady-state and □ transient conditions in sorption experiments. ◆, steady-state and ■ transient conditions in desorption experiments.

of equilibrium, having the opposite effect on thermal conductivity, compare Figs. 3(b) and 3(c) with Fig. 10.

The experimentally observed dependency of the effective thermal conductivity on bed voidage is not as strong as the one predicted by the models, and experimental data suggest a much simpler function of porosity, which is in agreement with the conclusions of Sharma *et al.* [8]. The differences between the thermal conductivities of the components are, however, not very large and in this case errors in predictions will perhaps not clearly enough show whether a specific model is inappropriate.

An important uncertainty is the estimation of contact resistance between particles. Without any correction the unit-cell model gives values 25–30% above the values with correction as in Appendix A. Analogously, the corrections for the stochastic model are 5–10%. Approximating irregular particles with stiff spheres for calculating the surface of the contact spot is perhaps not very realistic. The unit-cell model and the stochastic model, including the contact resistance, Russell's model and the geometric mean model all reproduce the drastic decrease of the effective thermal conductivity of the bed with decreasing total gas pressure.

For materials having a dense skeleton we can suggest the following procedure for calculating speedily the effective thermal conductivity of a bed. The unit-cell model without the Luikov extension is used in the calculation of that of the particles. The geometric mean model is used for calculating the conductivity of the bed, as it is much simpler than the Luikov unit-cell model.

Acknowledgements—This work has been financed by grants from the Swedish Council for Building Research. The continuing support of Professor A. Lundén is gratefully acknowledged. Thanks are due to the people of Televerket (National Telephone Company) at Farsta for graciously letting us use their DSC instrument. The experimental assistance of Dr S. Lourdudoss in this connection is gratefully acknowledged. Thanks are due to W. R. Grace AB for supplying us with a sample of the 119 type gel.

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APPENDIX A

CALCULATION OF THE CONTACT RESISTANCE

The contact between two particles presents a resistance to heat flow between particles to be added to the resistance of the solid phase itself. The contact resistance consists of two parallel resistances: conduction through the solid contact and conduction through the gas in the gap around the contact spot. The total resistance R_p to heat flow between particles is then written as

$$R_p = R_s + \left(\frac{1}{R_c} + \frac{1}{R_g}\right)^{-1} \tag{A1}$$

with R_s, the resistance to heat flow in the solid phase, R_c the resistance in the contact spot and R_g the resistance of the gas in the gap.

In the unit-cell model modified by Luikov these two last resistances are accounted for with the parameter A in equation (3). Luikov *et al.* [15] wrote A as

$$A^{-1} = \frac{\lambda_c}{\lambda_s} + \frac{\lambda_g}{\lambda_s}\frac{h^2}{4h_r k_k}. \tag{A2}$$

where λ_c is the conductivity of the solid contact defined on the particle size L as action distance, and $h_r k_k$ is the action distance for conduction through the gas in the gap. h_r is the height of particle microroughness and k_k a coefficient of particle adhesion. Following Luikov *et al.* [15] the product $h_r k_k$ is here taken as 6×10^{-3} L. λ_c is calculated as

$$\lambda_c = \lambda_s\left(\frac{1.0-\varepsilon_g}{0.75}\right)^{1/3}\left(\frac{2.82\,s}{Lh_r k_k} + \frac{P^{2/3}k_c}{75}\right) \tag{A3}$$

with S the area of the contact spot, P the mechanical pressure on the bed and k_c an empirical coefficient, here 0.35 as the pressure is low. The contact spot is assumed to have a circular surface, the radius being given by [21]

$$r = 0.465L\left(\frac{(1-\nu^2)}{E}\frac{\rho_p H}{(1-\varepsilon_g)}\right)^{1/3} \tag{A4}$$

with ν the Poisson ratio, E Young's modulus, H the height of the bed considered. For this study we have taken ν and E to be 0.25 and 5.5×10^{10} $N\,m^{-2}$, respectively, the values for perlite used by Luikov *et al.* [15].

In the calculations with the stochastic model of Zarichniak and Novikov the solid contact conductivity is computed with equation (A3). The action distance for the gas gap resistance is taken as $0.03L$, following Woodside and Messmer [22]. The corrected thermal conductivity λ_s' of the solid phase is then

$$\frac{1}{\lambda_s'} = \frac{1}{\lambda_s} + \frac{1}{\lambda_c + \lambda_g/0.03}. \tag{A5}$$

APPENDIX B

DERIVATION OF EQUATION (10)

The heat flow pattern in the quarter of the unit cell shown in Fig. 6(a) can be represented by the resistance diagram in Fig. B1. The first index of the resistances stands for the medium

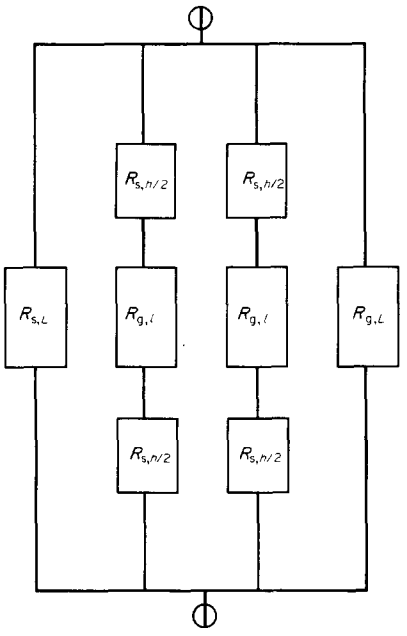

FIG. B1. The resistance diagram corresponding to the unit-cell model of Fig. 6(a).

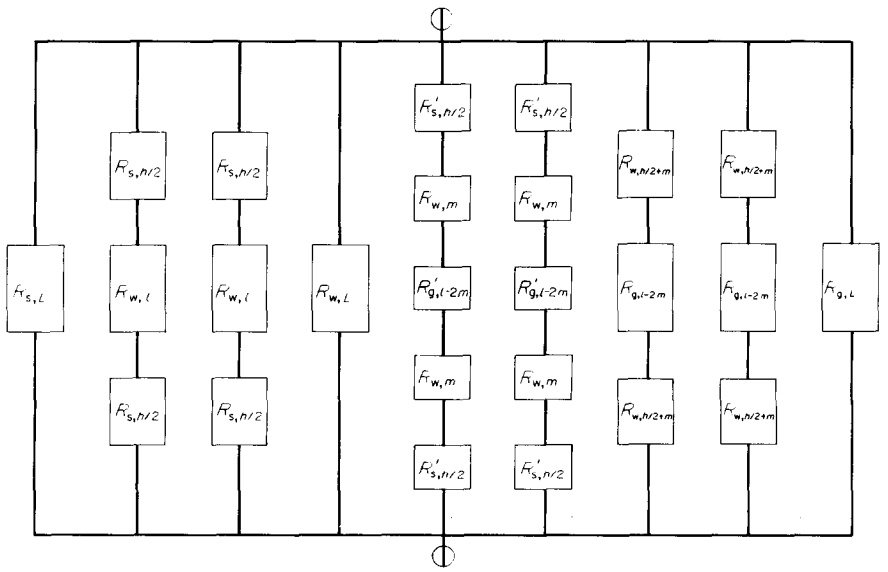

FIG. B2. The resistance diagram corresponding to the modified unit-cell model of Fig. 6(c).

through which heat is flowing, and the second index for the length of the path of heat through this medium. The total resistance of the network, i.e. that of the resistance of the quarter of the unit cell, is then

$$R_p^{-1} = R_{s,L}^{-1} + 2(2R_{s,h/2} + R_{g,l})^{-1} + R_{g,L}^{-1}. \quad \text{(B1)}$$

The modifications in the resistance diagram brought about by the addition of a water film is illustrated in Fig. B2, see also Fig. 6(c). The resistance of the quarter of the unit cell is then written as

$$\begin{aligned} R_p^{-1} = {} & R_{s,L}^{-1} + 2(2R_{s,h/2} + R_{w,l})^{-1} + R_{w,L}^{-1} \\ & + 2(2R'_{s,h/2} + 2R_{w,m} + R'_{g,l-2m})^{-1} \\ & + 2(2R_{w,h/2+m} + R_{g,l-2m})^{-1} + R_{g,L}^{-1}. \end{aligned} \quad \text{(B2)}$$

Inserting explicit expressions for the thermal resistances, one obtains

$$\begin{aligned} \frac{\lambda_p L}{4} = {} & \frac{\lambda_s h^2}{4L} + 2\left(\frac{4}{\lambda_s l} + \frac{2l}{\lambda_w hm}\right)^{-1} + \frac{\lambda_w m^2}{L} \\ & + 2\left\{\frac{4}{\lambda_s(l-2m)} + \frac{8m}{\lambda_w h(l-2m)} + \frac{4}{\lambda_s h}\right\}^{-1} \\ & + 2\left(\left(\frac{2(h+2m)}{\lambda_w m(l-2m)}\right) + \frac{2}{\lambda_g m}\right)^{-1} + \frac{\lambda_g(l-2m)^2}{4L}. \end{aligned} \quad \text{(B3)}$$

Dividing both sides by $\lambda_s L/4$ and simplifying the resulting expression gives equation (10).

CONDUCTIVITE THERMIQUE D'UN MILIEU PARTICULAIRE ET MICROPOREUX: SILICAGEL HUMIDE

Résumé—On présente une étude systématique de la conductivité thermique des lits de silicagel humide. L'influence de la porosité, du contenu d'eau, de la pression totale du gaz, de la température, est déterminée à partir de mesures dans des conditions transitoires, par la méthode du ruban chaud et dans des conditions statiques dans un réacteur. Ces prévisions de la conductivité thermique effective des lits, à partir de quatre modèles simples (Russell, valeur moyenne géométrique, modèle à cellule unitaire et modèle stochastique) s'accordent assez bien avec les résultats expérimentaux. Le modèle à cellule unitaire est élargi de façon à prendre en compte l'eau fixée dans les micropores et il décrit convenablement la dépendance de la conductivité thermique effective vis-à-vis de l'eau contenue.

WÄRMELEITFÄHIGKEIT EINES ZUSAMMENGESETZTEN MIKROPORÖSEN MEDIUMS: FEUCHTES SILIKAGEL

Zusammenfassung—Eine systematische Untersuchung der Wärmeleitfähigkeit von Betten aus feuchtem Silikagel wird dargestellt. Der Einfluß von Porosität, Wassergehalt, Gesamtgasdruck und Temperatur wird durch Messungen unter instationären Bedingungen mit Hilfe der Hot-Strip-Methode und unter stationären Bedingungen in einem Labor-Reaktor ermittelt. Die Voraussagen hinsichtlich der effektiven Wärmeleitfähigkeit des Bettes nach vier verschiedenen einfachen Modellen (Russel, geometrischer Mittelwert, Einheitszellenmodell und stochastisches Modell) stimmen ziemlich gut mit den Versuchswerten überein. Das Einheitszellenmodell wird erweitert, um das in den Mikroporen aufgenommene Wasser zu berücksichtigen, wobei die Abhängigkeit der effektiven Wärmeleitfähigkeit vom Wassergehalt befriedigend beschrieben werden kann.

ТЕПЛОПРОВОДНОСТЬ ПОРИСТОЙ СРЕДЫ, СОСТОЯЩЕЙ ИЗ МИКРОЧАСТИЦ ВЛАЖНОГО СИЛИКАГЕЛЯ

Аннотация—Проведено исследование теплопроводности слоев, состоящих из влажного силикагеля. Влияние на теплопроводность пористости слоя, содержания воды, полного давления газа и температуры определялось путем измерения этих величин в неустановившемся режиме нестационарным методом нагретой пластинки и в стационарных условиях в экспериментальном реакторе. Результаты расчетов эффективной теплопроводности слоев по четырем различным упрощенным моделям (Расселя, геометрической средней величины, одноячеистой и стохастической) довольно хорошо согласуются с экспериментальными данными. Одноячеистая модель видоизменена, с тем чтобы можно было учитывать количество воды, поглощаемой микропорами. Показано, что модель удовлетворительно описывает зависимость эффективной теплопроводности от содержания воды.