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OPACIFIED SILICA AEROGEL POWDER INSULATION

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ABSTRACT

We have investigated the thermal conductivity of powder and granular SiO_2-aerogels with a density in the 80 to 150 kg/m^3 range; the specimens were opacified with carbon soot. The caloric measurements were performed as a function of temperature, gas pressure and mechanical load. The smallest total conductivities for non-evacuated specimens are around 0.017 W/(m·K) at 300 K. The extracted solid conductivities are in the range 0.002 to 0.004 W/(m·K), depending on density, mechanical load and grain size; the radiative conductivity at 300 K is about 0.001 W/(m·K) for a fine powder; this corresponds to an extinction $E \approx 6000$ m^{-1} or a specific extinction $e = 60$ m^2/kg. For a coarse granular fill a considerably smaller specific extinction of $e \approx 20$ m^2/kg is found. The gaseous conductivity is about 0.013 to 0.017 W/(m·K), depending on the inter-grain pore space fraction. The investigated aerogel powders can be easily filled into hollow spacings and used as an effective non-evacuated insulation or, if evacuated, as a thermal superinsulation.

INTRODUCTION

Today thermal insulation is generally provided by polystyrene (ps) or polyurethane (pu) foams or by fiber mats. Such insulations are cheap, however,

- are combustible (ps, pu),
- give off poisonous gas on smoldering (pu),
- are dangerous to the environment, if CFC's are used as blowing agent,
- may pose a health hazard (most of the fiber insulations contain non-negligible fractions of fibers with diameters below 2 μm).

On the other hand, up to now, powders (e.g. fumed silica) have only been used for the production of prepressed insulation boards with densities as large as 300 to 350 kg/m^3. Such boards (WDS™ [Wacker], Microtherm™ [Micropore]) have rather low thermal conductivities of about 0.025 W/(m·K) in air; however, they also contain a considerable amount of fibers with small diameters, which are admixed for better mechanical stability. The thermal resistance of traditional powder insulants, like perlite or diatomite, is rather limited: in air their thermal conductivities are between 0.045 to 0.070 W/(m·K) for 300 K [Fricke 1990].

Recently SiO_2-aerogel powders were discussed as possible non-hazardous substitutes for CFC-blown insulating foams [Fricke 1990]. Aerogels are made in a sol-gel process with subsequent supercritical drying in an autoclave [Fricke 1986]. The structures of aerogel monoliths extend from the 1 nm to the 100 nm range ("nanoporosity") and thus are much smaller than those in perlite or diatomite with "microporosity". Typical densities for aerogels are 100 kg/m^3. Due to the low density and the nanostructural porosity the solid and the gaseous conductivity in aerogels are small. A reduction of the infrared (IR) radiative heat transfer can be achieved, if IR opacifiers like TiO_2, Fe_3O_4 or carbon soot are integrated into the tenuous SiO_2 skeleton.

THERMAL TRANSPORT IN OPACIFIED AEROGEL MONOLITHS

The thermal transport in monolithic aerogels has been described elsewhere [Fricke 1991]. Here we only want to summarize the most important facts:

- The thermal conductivity can be interpreted to consist of three contributions, solid, gaseous and radiative conductivity, all three of which are additively superimposed.

- The solid conductivity λ_S strongly depends on the density ρ; for $\rho \approx 70$ kg/m^3 we derive $\lambda_S \approx 0.002$ W/(m·K). In the density range $\rho = 70$ to 230 kg/m^3 the dependence on ρ can be approximated by the expression $\lambda_S \propto \rho^{\alpha}$, with $\alpha = 1.5$ [Fricke 1991]. The temperature dependence of λ_S is comparable to the one of vitreous silica [Scheuerpflug 1991].

- The gaseous conductivity λ_G is much smaller than the conductivity of non-convecting air (0.026 W/(m·K) at 300 K); this is understandable, as the mean free path of air molecules at 1 bar is around 70 nm, which is comparable to the size of the largest pores of the aerogel skeleton. As the pore sizes vary with the aerogel density ρ, also a correlation between the gaseous conductivity λ_G and ρ is expected: experimentally derived values are $\lambda_G \approx 0.010$ and 0.005 W/(m·K) for $\rho = 70$ and 230 kg/m^3, respectively. The variation can be approximated by the relation $\lambda_G \propto \rho^{-\beta}$, with $\beta \approx 0.6$ [Fricke 1991].

- The radiative conductivity λ_R in opacified aerogel monoliths can be described by the expression

$$\lambda_R = \frac{16n^2 \cdot \sigma T^3}{3E} \tag{1}$$

where n is the index of refraction, σ the Stefan-Boltzmann constant, T the temperature and $E = e \cdot \rho$ the extinction coefficient; the specific extinction e can be determined calorimetrically or via IR-optical measurements. Typical values for opacified aerogels are $e \approx 30$ to 60 m^2/kg, providing $E \approx 3000 \ldots 6000$ m^{-1}, for $\rho \approx 100$ kg/m^3. For $T \approx 300$ K this corresponds to radiative conductivities $\lambda_R = 0.003$ to 0.0015 W/(m·K).

• At 300 K the total conductivity shows a minimum around ρ = 120 kg/m³, which measures $\lambda \approx 0.013$ W/(m·K) [Fricke 1991]. To our knowledge this is the lowest conductivity ever determined for a solid body in air. For other temperatures the conductivity λ can be calculated from the general expression

$$\lambda(\rho) = \lambda_1\left(\frac{\rho}{\rho_1}\right)^{1.5} + \lambda_2\left(\frac{\rho}{\rho_1}\right)^{-0.6} + \lambda_3\left(\frac{\rho}{\rho_1}\right)^{-1}\left(\frac{T}{T_1}\right)^{3} \qquad (2)$$

with λ_1 = 0.002 W/(m·K), λ_2 = 0.010 W/(m·K), λ_3 = 0.004 W/(m·K), ρ_1 = 70 kg/m³ and T_1 = 300 K. This dependence is shown in Fig. 1.

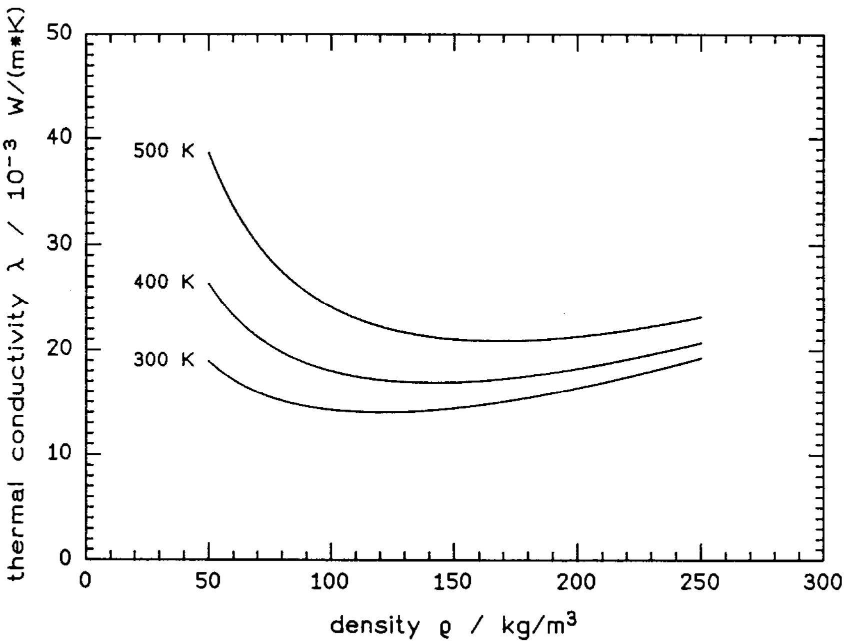

Fig. 1.: Calculated variation of total conductivity λ according to equ. (2) for opacified monolithic aerogels as a function of density ρ for various temperatures (T = 300, 400 and 500 K), using the parameters given in the text, with n ≈ 1 and e = 30 m²/kg.

THERMAL TRANSPORT IN OPACIFIED AEROGEL POWDERS

How does the thermal transport change, if instead of monolithic aerogel a powder (ø < 1 mm) or granular form (ø > 1 mm) is considered?

The additive superposition of the thermal conductivities described above requires that none of the three heat transfer modes is hindered or interrupted on a local basis. Such interruptions, however, occur for powders and granules.

Here the solid heat transfer is reduced by the contact resistances between adjacent grains. The resistances strongly depend on the ratio of the external mechanical load and the Young's modulus as well as the conductivity of the grains.

• At full atmospheric pressure for powders and granular fills the gaseous conductivity is expected to be larger than in aerogel tiles. This is plausible, as in the former gaseous conduction occurs not only within the bulk material, but also between the powder grains. Thus an important goal for the minimization of the gaseous conductivity is to reduce the pore space between the grains as much as possible. For an aerogel fill (powder or granular) typical inter-grain pore space fractions are of the order of 40 %. With bi- or polymodal size distributions values of about 20 % should be achievable, in this case the small grains can fill the voids between the larger ones effectively. Another possibility to reduce the gaseous conduction is evacuation. Upon decrease of pressure first the gaseous conduction within the aerogel grains, then the conduction between the grains ceases.

• For the infrared radiative transport two cases have to be considered: Within optically thick grains the radiative transfer is the same as in monolithic aerogel; between adjacent grain surfaces practically unrestrained radiative exchange occurs. For optically thin grains the fill can be considered a homogeneous medium; the mass specific extinction coefficient e of the fill then is the same as the one of the grain material; (this leads to a reduced extinction coefficient $E = e \cdot \rho$ for the fill compared to a monolith, however). The radiative exchange in a coarse fill can be reduced if the open space is filled with smaller sized grains, as was discussed above.

MEASUREMENTS

Various powder and granular aerogels were measureded in our evacuable, load bearing guarded hot plate devices [Büttner 1986]. For comparison also a hot wire probe was used [Nilsson 1989]. The measurements provided conductivity data for aerogel fills under the variation of temperature, gas pressure and external load onto the specimens.

Fig. 2 shows the variation of thermal conductivity with air pressure for an opacified monolith, a coarse granular fill, a powder fill as well as two examples of optimized fills. As expected, the monolith shows the smallest conductivity in air. The suppression of gaseous thermal conduction occurs at pressures of about 50 mbar.

For the coarse granular fill the conductivity in air is considerably above the value for the monolith, which is mostly due to the relatively large gaseous conduction and unhindered radiative transport between the grains. The increase in the total conductivity at pressures above 50 mbar is caused by the onset of gaseous conduction within the nm-sized pores of the grains; the rise of λ at pressures of 0.1 to 1 mbar results from gaseous conduction in the mm-sized pores between the grains.

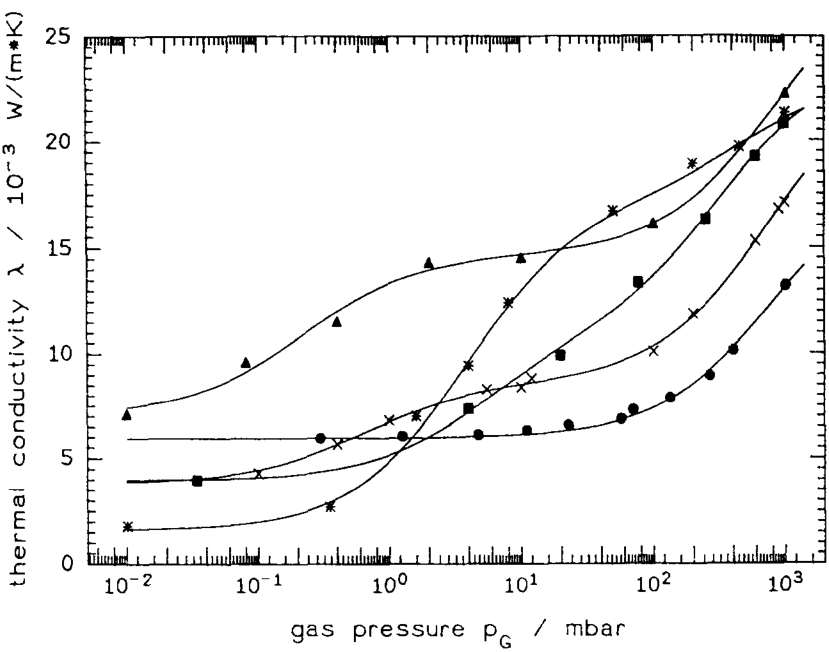

Fig. 2.: Variation of total conductivity λ with air pressure p_G at 300 K for various aerogel insulants; ● = monolithic aerogel with density ρ_0 = 120 kg/m³ [Fricke 1991]; ▲ = coarse granular aerogel fill with grain density ρ_0 = 230 kg/m³ and an apparent density ρ_{APP} = 135 kg/m³; ■ = powder aerogel fill with the same ρ_0 and ρ_{APP}; all three specimens contain about 5 % carbon soot. In addition data for an optimized fill (x) with a broad grain size distribution, a smaller grain density ($\rho_0 \approx$ 160 kg/m³, $\rho_{APP} \approx$ 90 kg/m³) and a soot content of about 10 % are shown. Optimized with respect to the evacuated state is an aerogel powder fill with 10% soot, ρ_0 = 210 kg/m³ and ρ_{APP} = 160 kg/m³ (✱). The external mechanical load onto the three fills was about 0.1 bar; at 1 bar the solid conductivity increases by 0.001 W/(m·K) at most.

The third curve in Fig. 2 for a powder aerogel fill displays a more or less continuous increase of λ with p_G. This can be understood from the fact that due to the small particle size (ø ≈ 50 µm) the low-pressure "step" in λ is shifted towards higher pressures and merges with the increase of λ for p_G > 50 mbar.

The fourth curve is for an optimized fill with a broad grain size distribution thus with an especially small inter-grain pore space fraction. In addition the grain density is lower than for the other fills and the carbon content is higher. Over-all, this leads to the smallest total conductivity among the four fills at atmospheric pressure.

The fifth curve is for a fill optimized with respect to an extremely low conductivity in the evacuated state (λ = 0.0018 W/(m·K)).

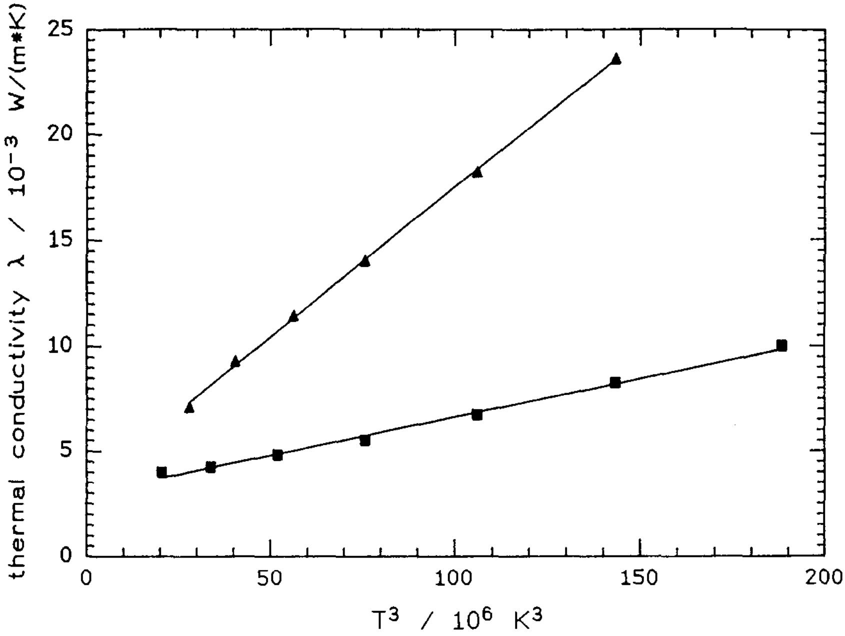

Fig. 3.: Variation of thermal conductivity λ_{EVAC} of a granular (▲) and a powder (■) aerogel fill with the third power of temperature; clearly visible is the much stronger increase of λ_{EVAC} for the granular specimen.

In Fig. 3 the variation of the conductivity with temperature for the coarse granular and the powder specimen is shown. The lower curve represents the data for the aerogel powder; from the straight-line behavior in the $\lambda(T^3)$-plot a value for the specific extinction $e \approx 60$ m²/kg can be derived. For the granular fill a larger slope and thus a smaller specific extinction $e \approx 20$ m²/kg results. As the grains consist of the same aerogel in both cases, this effect obviously is a consequence of the different grain sizes, as was already addressed in the chapter before.

COMPARISON WITH OTHER NON-EVACUATED INSULANTS

For technical applications the variation $\lambda(T)$ for non-evacuated specimens is most important (Fig. 4). As can be seen an optimized aerogel fill has a smaller thermal conductivity than Microsilica™, CFC-blown polyurethane foam and fiber insulation; the aerogel fill is even superior to high density WDS™ insulation.

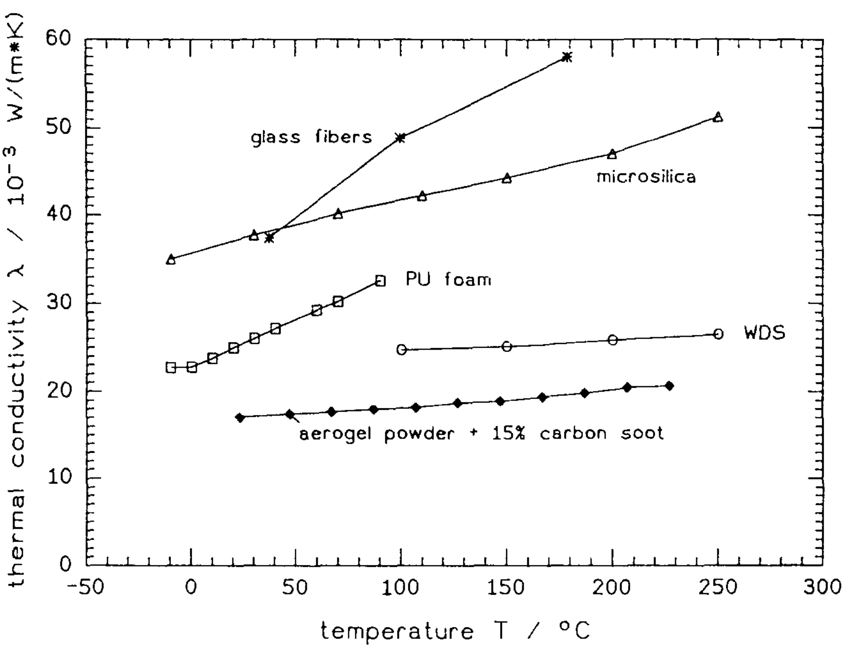

Fig. 4.: Variation of thermal conductivity λ with temperature T for non-evacuated insulants: ◆ = optimized aerogel fill, o = WDS™ insulation board [Fricke 1990] (density 300 kg/m³), □ = aged CFC-blown polyurethane foam [Hetfleisch 1988], ✱ = fiber mat [Kuhn 1990] (160 kg/m³) and Δ = Microsilica™ (300 kg/m³).

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