

Production of Silica Aerogel

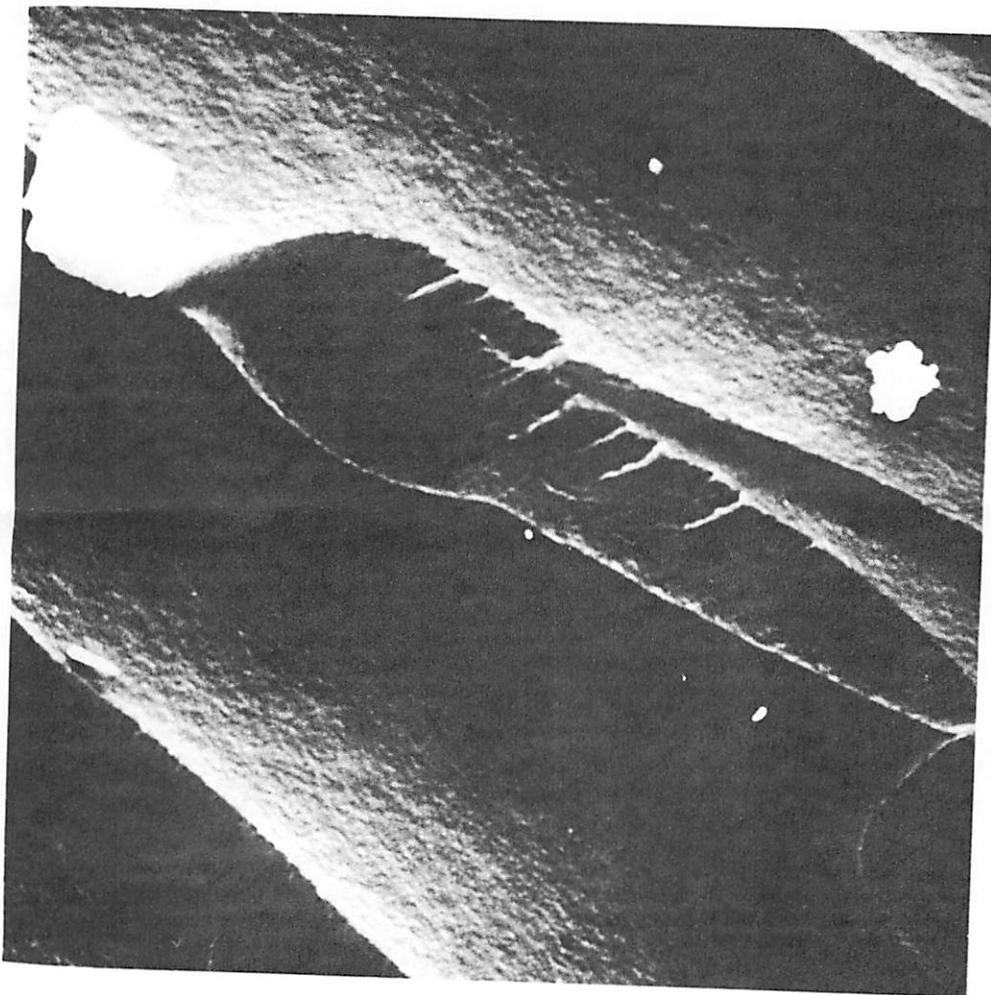
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Abstract

A production facility for silica aerogel has been set up in Lund. Aerogel is now produced in large quantities with the refractive indices of 1.03 to 1.05. The standard block size is $18 \times 18 \times 3$ cm³.



1. Introduction

In the search for a Čerenkov radiator with a refractive index between 1.01 and 1.30, free from the problems that pressurized or cryogenic systems pose, Linnay and Peters made blocks of compressed powder of quartz glass with refractive indices of 1.05 to 1.20 [1]. The radiator was, however, very fragile and had bad transparency due to the weak bonding between the SiO₂ particles, and inhomogeneities in the material.

Cantin et al. [2] developed a method in which the space net of silicon dioxide particles is achieved through chemical bonds. In this way it is possible to have a more homogeneous quartz material, called silica aerogel, with a refractive index between 1.01 and 1.06 with much better mechanical and optical properties than the compressed radiator.

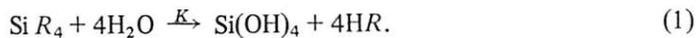
The production process as outlined by Cantin et al. proceeds in mainly two steps. First an alcogel is formed by the hydrolysis of a silane in a solvent. The quantity of solvent will govern the density of the subsequent aerogel, ie. its refractive index. Then the solvent is removed from the alcogel. This is done in the following way. The alcogel is placed in an autoclave containing additional solvent. It is heated and pressurized to get around the critical point of the solvent, and then gaseous solvent is let out.

1.1. The alcogel

For the production of a silicon based gel, silicic acid in liquid form, Si(OH)₄, is well suited. But due to its unstable nature it polymerizes very easily and condensates to silicon dioxide in the shape of colloidal particles, or to a gel. More suitable carriers of

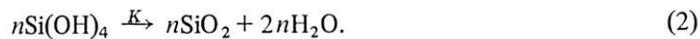
silicon are different esters of silicid acid due to their chemical stability that makes them easy to handle, and due to the ease of hydrolysing the esters.

To produce the alcogel an ester of silicid acid is mixed with a solvent and water. The water content has to be sufficient for the hydrolysis to be fully accomplished, i.e. the ester is converted to silicid acid. Silicon may have a higher valence than 4 (5 or 6) for small radicals. This makes it possible for the hydroxyl group to be attached in an extended covalent bond. The hydrolysis proceeds under the influence of a catalyst and is exothermic by the interchange of the radical, R , and the hydroxide ion, OH^- . The reaction is



In our case R is the alcoxy group, OCH_3 , the catalyst K is ammoniumhydroxide, NH_4OH , and the solvent is methanol, CH_3OH .

The silicid acid formed by the hydrolysis is immediately dehydrated and polymerized through siloxan links (Si-O-Si). In this reaction water is given off. The hydroxide ion functions as the catalyst.



In this way many kernels are produced throughout the whole volume.

Each kernel starts to grow uniformly and consists of amorphous silicon dioxide (SiO_2) in the inner region and silanol (SiHO) groups at the boundary, see Fig. 1. When the size and concentration of kernels increase in the mixture they are coupled by siloxan links. The formation rate of the space net depends, besides on the concentration of silicon and OH^- , on the presence of negatively charged ions. Further, the primary quartz kernel is screened by the solvent (methanol). The polymerisation time depends on the dielectric constant of the solvent.

After the formation of the alcogel there may still be silicon dioxide grains that are not linked. Another disturbance is the water left after the dehydration which together with the silanol groups might form "water bridges" and thereby disturb the links between the quartz grains. It is also possible that methanol molecules are linked to the silanol groups.

1.2. The aerogel

To obtain aerogel one must remove the solvent from the alcogel.

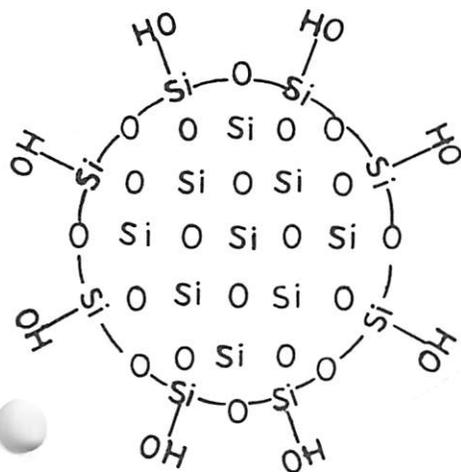


Fig. 1. The structure of a kernel.

This is done by bringing the solvent around its critical point and thereafter taking out the vapour by isothermic expansion.

The refractive index of the final product, silica aerogel, depends on the volume occupied by the two components, air and the amorphous silicon dioxide. We have

$$n(\text{aerogel}) V(\text{tot}) = n(\text{SiO}_2) \cdot V(\text{SiO}_2) + n(\text{air}) \cdot [V(\text{tot}) - V(\text{SiO}_2)] \quad (3)$$

where V is the volume and n is the refractive index. Thus, assuming $n(\text{air}) = 1$

$$n(\text{aerogel}) = 1 + [V(\text{SiO}_2) \cdot (n(\text{SiO}_2) - 1)] / V(\text{tot}) \quad (4)$$

The density, ρ , for the aerogel is

$$\rho(\text{aerogel}) = [\rho(\text{SiO}_2) \cdot V(\text{SiO}_2) + \rho(\text{air}) \cdot V(\text{air})] / V(\text{tot}) \quad (5)$$

Assuming that the density of air can be neglected we obtain the following relation between the refractive index and the density for the aerogel

$$n(\text{aerogel}) = 1 + [(n(\text{SiO}_2) - 1) / \rho(\text{SiO}_2)] \rho(\text{aerogel}) \quad (6)$$

The values of the constants are $n(\text{SiO}_2) = 1.45$ and $\rho(\text{SiO}_2) = 2.19 \text{ g/cm}^3$ (amorphous structure!), i.e.

$$n(\text{aerogel}) = 1 + 0.21 \rho(\text{aerogel}) \quad (7)$$

This relation has been tested experimentally and the factor 0.21 is verified, confirming the amorphous structure of the SiO_2 grains rather than the crystalline structure suggested in [2], see Fig. 2.

2. Production of aerogel

A production facility consisting of equipment for the preparation of alcogel, an autoclave and an oven, has been set up in Lund. The autoclave with its control system is shown in Fig. 3. The mechanical specifications of the autoclave are:

volume	98 litres
inner diameter	340 mm
working pressure	90 bar
test pressure	117 bar

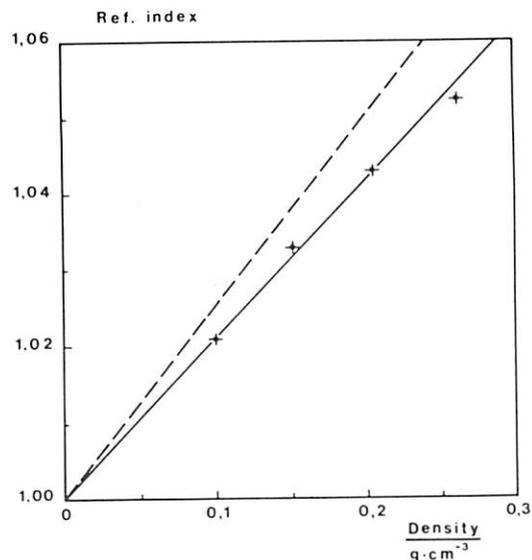


Fig. 2. The refractive index as function of aerogel density. The solid line assumes amorph structure (proportionality constant 0.21) while the dashed line assumes crystalline structure (0.25, [2]).

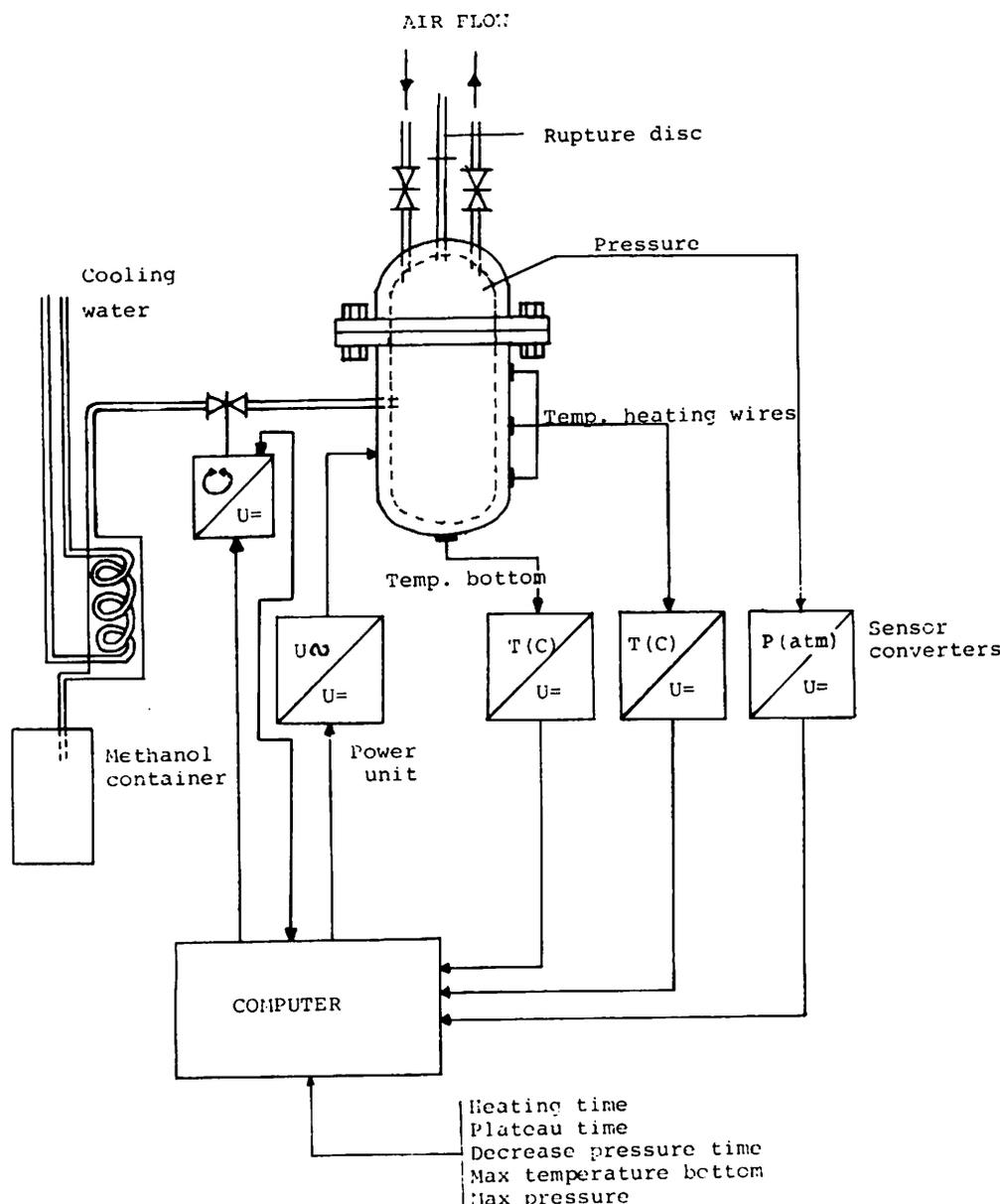


Fig. 3. Schematic layout of the autoclave and its control system.

working temperature	260°C
rupture disc	115 ± 2 bar

A heating mantle is placed around the autoclave. This mantle can develop an electric power of 5 kW. This is sufficient to have a linear increase in temperature to 260°C in 13 hr. For the sake of regulation there is a temperature sensor and a pressure sensor. With a remotely controlled valve it is possible to regulate the outlet vapour flow at the isothermic expansion. At the top of the autoclave there is an outlet for the final evacuation of the remaining methanol vapour.

2.1. Raw materials

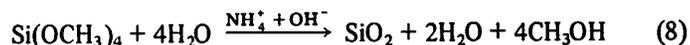
Both the technical [3] and the purum quality of tetramethoxysilane have been tested. We do not find any significant difference of the aerogel quality. Methanol of different qualities has been used, and the purum quality is good. The water used is distilled water.

2.2. Preparation of alcogel

Two solutions are prepared. One contains the tetramethoxysilane at about room temperature, and the other contains the

methanol and water mixture at about -10°C. The catalyst is added to the second solution just before the mixing. The mixture of the two solutions is stirred thoroughly. Firstly an emulsion is formed, because tetramethoxysilane is not soluble in water. After about 10 min one gets a transparent colloidal dispersion. The stirring is continued for a few more minutes and the mixture is then poured into the molds. The molds for our autoclave are made of stainless steel coated with teflon on the inside and have the dimensions 19.9 × 19.5 × 4.5 cm³.

The alcogel formation time is determined by the amount of ammonium added, as shown in Fig. 4. Normally a setting time of 20–30 min is used. While the alcogel is formed the transparency deteriorates slightly, as shown in Fig. 5. The process of alcogel formation is



The relative quantities used are (by volume) 6 parts of dynasil, 3 parts of water, and X parts of methanol, where e.g. $X = 2$ gives $n = 1.05$. Figure 6 shows how the refractive index varies with X . The detailed shape of this curve depends on the autoclave cycle.

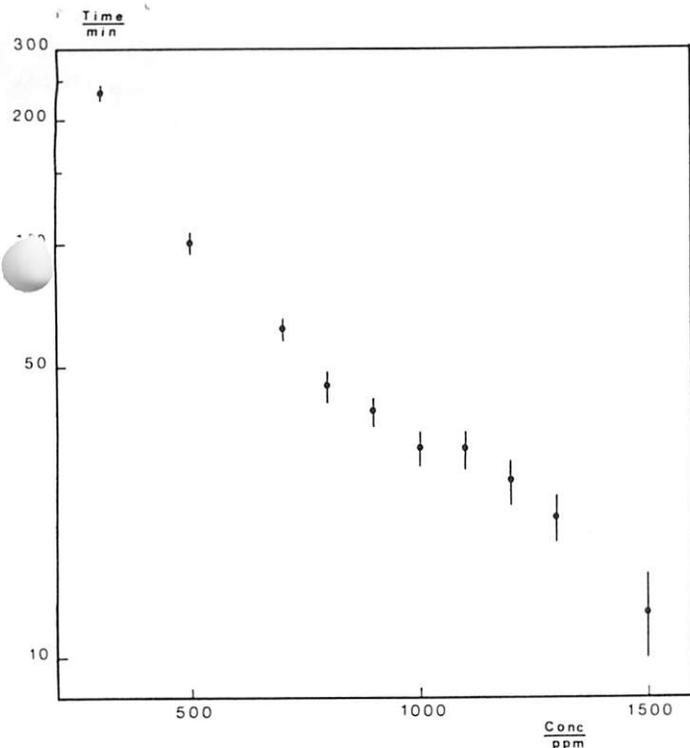


Fig. 4. The algogel formation time as function of catalyst (ammonium-hydroxide) concentration.

To avoid evaporation, which would cause surface tension that build up stresses in the algogel, it has to be covered with a layer of methanol. If the water content in the algogel is high relative to the contents of methanol, i.e. n larger than 1.04, it must be washed out by placing the algogel in successive baths of methanol of increasing configuration. Figure 7 illustrates how the transparency of the final product changes as a function of remaining water contents (which is a function of time) for algogel with $n = 1.05$. As mentioned above the washing pro-

cedure is unnecessary for the lower refractive indices and the autoclave process may proceed immediately.

2.3. The autoclave process

The algogel is placed in the autoclave and enough methanol is added to give the required pressure to reach the critical point. The temperature and pressure cycles are shown in Figs. 8 and 9. The process proceeds in four phases: heating, equilibrium, vapour outlet, and cooling.

In phase 1 there is a linear increase in temperature to avoid high gradients during the heating. For $n = 1.05$ the suitable time for giving crack free aerogel is 24 hr. This corresponds to a temperature rise of 11°C per hour. The pressure follows the phase diagram of Fig. 9.

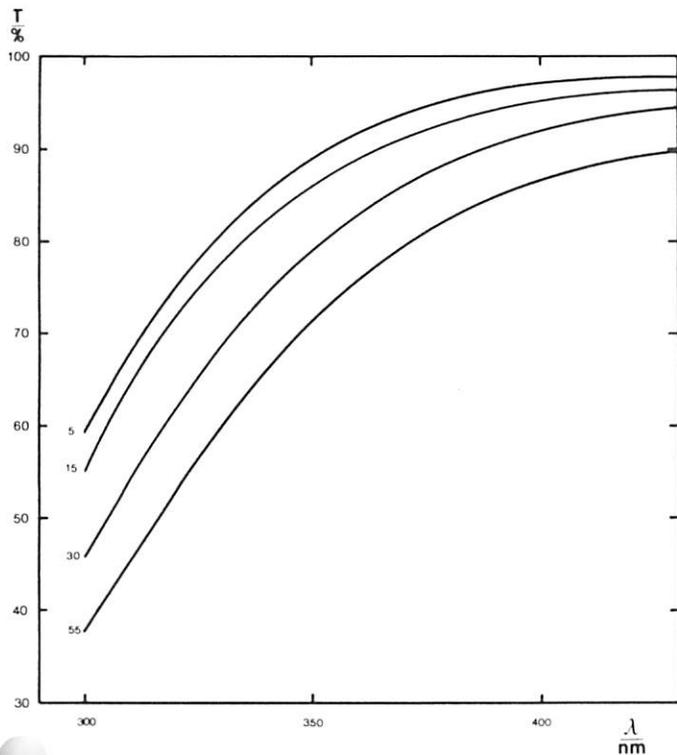


Fig. 5. Transparency, T , of the mixture as function of wavelength, λ , at different times after mixing: 5, 15, 30 and 55 min. The algogel was formed after 30 min.

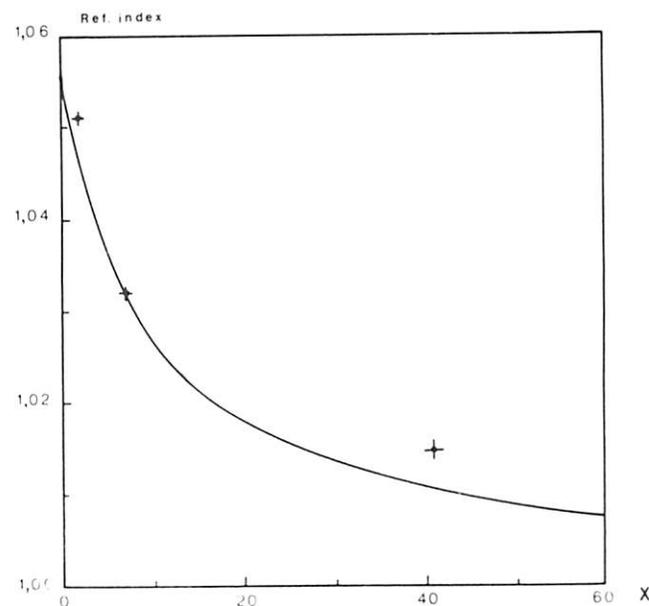


Fig. 6. The refractive index as function of the methanol content X . X parts of methanol, 6 parts of tetramethoxysilane and 3 parts of water are mixed.

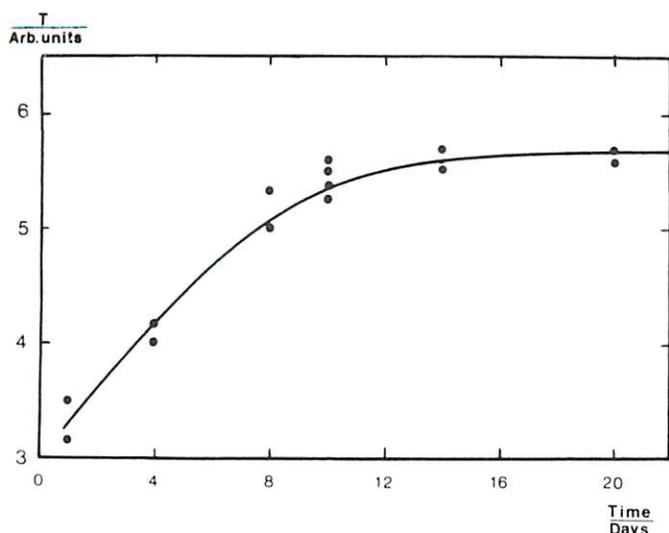


Fig. 7. Transparency, T , as function of the time in methanol baths ($n = 1.05$).

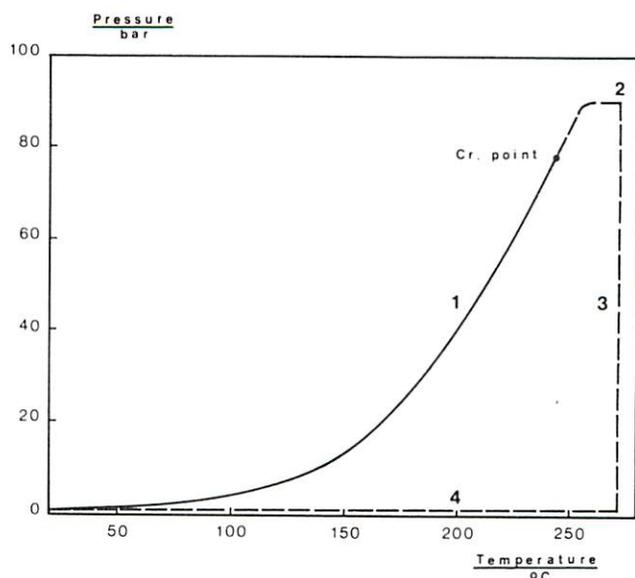


Fig. 9. Phase diagram for methanol. The dashed line completes the autoclave cycle.

In the short equilibrium phase the temperature and pressure stabilize. All the methanol is now in a gaseous state.

In phase 3 the methanol vapour is let out, keeping the temperature constant. The pressure gradient is kept constant to avoid stresses in the aerogel. For $n = 1.05$, 16 hr is the optimum interval, also considering the overall weekly time scale, i.e. a gradient of 5.6 bar per hour.

Before cooling down the autoclave, it is evacuated to remove the remaining methanol vapour. During the cooling phase an air flow is flushed through the autoclave.

2.4. Heat treatment

A chemical analysis of the aerogel after the autoclave process shows that 3.4% carbon and 0.9% hydrogen (by weight) are left in the aerogel. To get rid of these pollutants the aerogel is heated to 500°C and kept at this temperature for a few hours. The heating and cooling cycle is linear with a gradient of only 35°C per hour to avoid cracks in the aerogel. The purpose of this heating is to oxidize the pollutants. The heat treatment gives at 10 to 15% better transparency for all refractive indices.

A new chemical analysis after the heat treatment shows that 0.3% carbon and 0.7% hydrogen remain. This chemical test was done in an oxygen flow at 500°C.

Heating to a higher temperature, 750°C, does not improve the transparency. Sintering occurs when the temperature is further increased. In this process the aerogel shrinks giving a higher density and also a higher refractive index.

3. Measurements on aerogel

With the help of a laser beam it is possible to measure the refractive index of the aerogel. We determine the angle of minimum deviation, δ_{\min} , using a Ne-He laser. The experimental arrangement is shown in Fig. 10. The simple relation between the angle of minimum deviation and the refractive index is

$$n = \sin [(\delta_{\min} + \alpha)/2] / \sin(\alpha/2) \tag{9}$$

With $\alpha = 90^\circ$

$$n = \sqrt{2} \sin (\delta_{\min}/2 + 45^\circ) \tag{10}$$

The error in this determination is about 0.001, when the mean value of the four corners is measured.

A simple apparatus has been constructed to make measurements of the transparency under constant conditions. The coefficient, μ , describing the scattering and absorption is given by

$$\mu = \ln (l_0/l)/x, \tag{11}$$

where l_0 and l are the incoming resp. transmitted light, and x is the thickness of the aerogel sample. Figure 11 shows the results

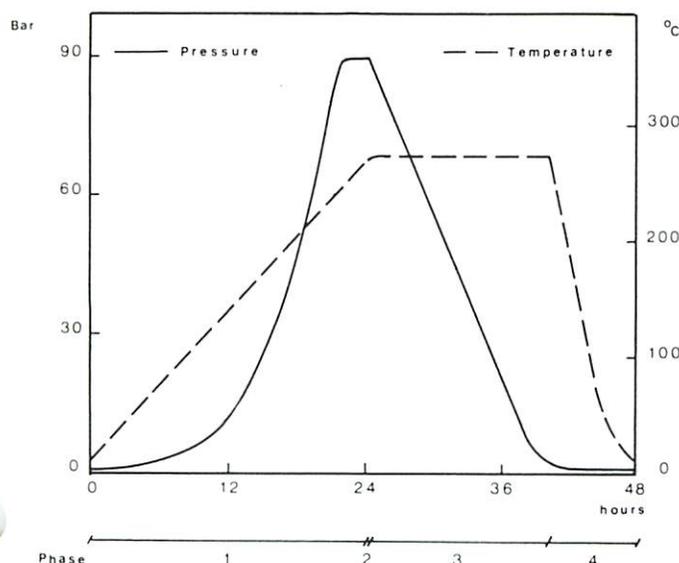


Fig. 8. The autoclave cycle with its four phases: 1, heating; 2, equilibrium; 3, vapour outlet; and 4, cooling.

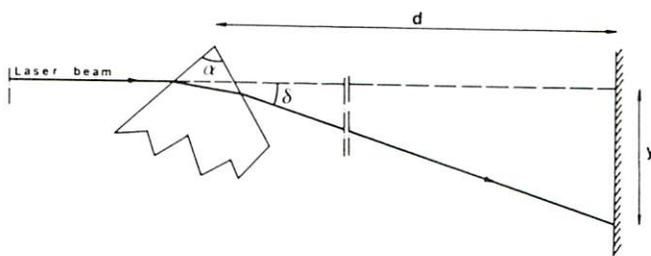


Fig. 10. Determination of refractive index.

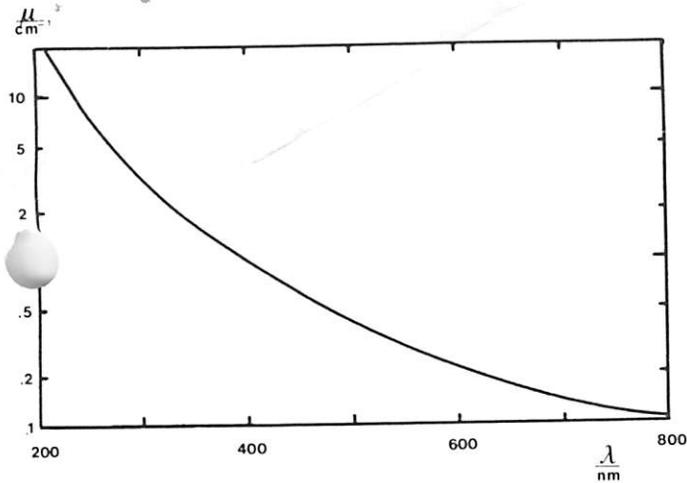


Fig. 11. The coefficient μ , describing the scattering and absorption, as function of wavelength, λ . μ is given by $I = I_0 e^{-\mu x}$, where I_0 and I are the intensities before and after x cm of aerogel ($n = 1.05$).

of measuring the transmission of light of different wavelengths in a spectrograph. The absorption coefficient measured this way includes both the genuinely absorbed light and the scattered light. In our transmission tests we usually quote the sample thickness where the intensity has been reduced to 50%. This is a relative measure that depends on the light source, the light filter and photon detector.

An aerogel sample has been analyzed with a scanning elec-

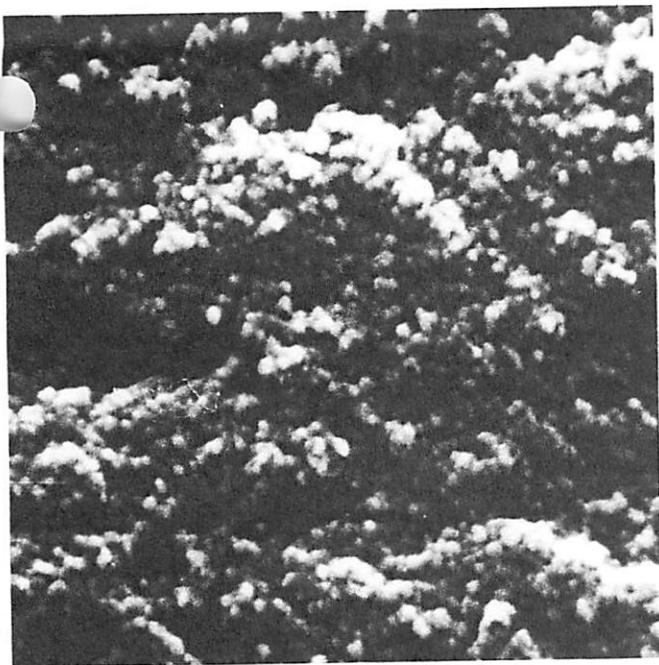


Fig. 12. Picture of aerogel taken with a scanning electron microscope, enlarged 19400 diameters. Compare with the picture on the front page where the enlargement is 1200.

tron microscope. To do this a thin metal layer is evaporated onto the sample. In Fig. 12 a crack surface is shown, enlarged by a factor of 19400. The size of the grains vary from 40 to 120 nm. The silicon kernels are actually smaller, because the metal layer has a mean thickness of about 20 nm and several small grains may be covered by the layer so that they look like a bigger grain. An independent value has been obtained through the measurement of the total internal area using a gas flow method. For $n = 1.03$ the result was $402 \text{ m}^2 \text{ g}^{-1}$. Assuming that the grains are spherical and uniform in size, we can calculate the diameter of the grains which comes out as 7 nm.

The cover photograph is also a crack surface of the same sample of aerogel enlarged 1200 diameters.

Finally, to complete this investigation of the microstructure we made an X-ray diffraction study. This gave no indication of any scattering in the aerogel except background, in agreement with the assumption of an amorphous structure.

4. Results of the production

So far about 800 litres of aerogel with $n = 1.050$ and about 400 litres with $n = 1.030$ have been produced. For the moment our production is about 50 litres per week. Other refractive indices have been produced but only in small quantities.

Several experimental groups are now using aerogel produced in Lund. The EHS group [4] and the European Muon Collaboration [5] use aerogel with $n = 1.030$. Both groups have built and tested detectors [4, 5]. In a separate report submitted to this conference the aerogel detector of the AFS group is described where aerogel with $n = 1.050$ is used in an unusual configuration [6].

Finally, for those who are planning to make aerogel it should be stressed that the vapours from tetramethoxysilane can cause damages to eyes and skin. Therefore, read the suppliers instructions carefully. The silica aerogel, however, does not give off any vapours.

Acknowledgements

We wish to thank Prof. G. von Dardel who introduced us to the subject and has contributed with fruitful suggestions throughout the project. The production facility has been set up with the help of Messrs. L. Hansson, T. Nilsson, R. Petersen and W. Key. Finally, we acknowledge useful discussions with Dr. G. Jarlskog.

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