Thermal Superinsulation for Building Applications - From Concepts to Experimental Investigations

Bjørn Petter Jelle, Tao Gao, Linn Ingunn Christie Sandberg, Bente Gilbu Tilset, Mathieu Grandcolas and Arild Gustavsen

Abstract—**The application of traditional thermal insulation materials requires thicker building envelopes in order to satisfy the requirements of the emerging zero energy and zero emission buildings. This work summarizes the steps from the state-of-the-art thermal insulation materials and solutions, like vacuum insulation panels (VIP), gas-filled panels (GFP) and aerogels which all have various drawbacks, to our concepts and experimental investigations for making superinsulation materials (SIM) like e.g. nano insulation materials (NIM).**

Keywords—**superinsulation, SIM, nano insulation material, NIM, thermal conductivity, building, concept, experimental**

I. Introduction

A major mean on the path towards a more sustainable world is energy-efficiency and zero emissions in the building sector, where thermal insulation both for new and existing buildings plays an important role [1, 2]. As very thick building envelopes are not desirable due to several reasons, e.g. considering space issues with respect to both economy, floor area, transport volumes, architectural restrictions and other limitations, material usage and existing building techniques, there is a demand for developing high performance thermal insulation, also denoted as advanced insulation materials (AIM) and superinsulation (SIM). The objective of this work is to summarize the path from the state-of-the-art thermal insulation materials and solutions, like vacuum insulation panels (VIP), gas-filled panels (GFP) and aerogels which all have various drawbacks, to our concepts and experimental investigations for making superinsulation materials like e.g. nano insulation materials (NIM). A focus will be given on our current attempts to make NIM based on hollow silica nanospheres (HSNS).

Bjørn Petter Jelle

SINTEF Building and Infrastructure, Department of Materials and Structures, NO-7465 Trondheim, Norway, and,
Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, NO-7491 Trondheim, Norway.

Tao Gao and Arild Gustavsen

Norwegian University of Science and Technology (NTNU), Department of Architectural Design, History and Technology, NO-7491 Trondheim, Norway.

Linn Ingunn Christie Sandberg

Norwegian University of Science and Technology (NTNU), Department of Civil and Transport Engineering, NO-7491 Trondheim, Norway.

Bente Gilbu Tilset and Mathieu Grandcolas

SINTEF Materials and Chemistry, Materials and Nanotechnology Sector, NO-0314 Oslo, Norway.

II. Thermal Conductivity

In the development of thermal superinsulation a very low thermal conductivity is targeted. That is, all the contributions to the conductivity have to be minimized. The total overall thermal conductivity λ_{tot}, i.e. the thickness of a material divided by its thermal resistance, is in principle made up from the following parts:

$$\lambda_{tot} = \lambda_{solid} + \lambda_{gas} + \lambda_{rad} + \lambda_{conv} + \lambda_{coupling} + \lambda_{leak}. \qquad (1)$$

where λ_{tot} is the total overall thermal conductivity, λ_{solid} is the solid state thermal conductivity, λ_{gas} is the gas thermal conductivity, λ_{rad} is the radiation thermal conductivity, λ_{conv} is the convection thermal conductivity, $\lambda_{coupling}$ is the thermal conductivity term accounting for second order effects between the various thermal conductivities in (1), and λ_{leak} is the leakage thermal conductivity. The leakage thermal conductivity λ_{leak}, representing an air and moisture leakage driven by a pressure difference, is normally not considered as insulation materials and solutions are supposed to be without any holes enabling such a thermal leakage transport. The coupling term $\lambda_{coupling}$ may be included to account for second order effects between the various thermal conductivities in (1), however, this coupling effect can be quite complex and will be neglected in the following. Besides, theoretical approaches to thermal performance of vacuum insulation panels (VIP) usually assume this coupling effect to be negligible [3]. Note that in general another coupling term may also be included in (1), i.e. the interaction between the gas molecules and the solid state pore walls. However, as we will see later this last coupling term is included through a factor in the expression for the gas conductivity as given in (2) for the Knudsen effect. For further information on thermal conductivity aspects it is referred to the studies by Jelle et al. [2] and Jelle [4].

III. State-of-the-Art Thermal Insulation

The state-of-the-art thermal building insulation materials and solutions of today are summarized briefly in the following, where these represent a starting point or basis for the idea generation and subsequent experimental attempts to develop the high performance thermal insulation materials of tomorrow.

A. *Vacuum Insulation Panels*

Vacuum insulation panels (VIP) consist typically of an open porous core of fumed silica enveloped of several metallized polymer laminate layers, and represent today's state-of-the-art thermal insulation with thermal conductivities ranging from between 3 to 4 mW/(mK) in pristine (non-aged) condition to typically 8 mW/(mK) after 25 years ageing due to water vapour and air diffusion through the VIP envelope and into the VIP core material which has an open pore structure. Depending on the type of VIP envelope, the aged thermal conductivity after 50 and 100 years will be somewhat or substantially higher than this value. Originating from the challenge of maintaining a vacuum inside a core material with a protective foil around the core, where a total loss of vacuum leads to an increase in thermal conductivity from typically around 4 mW/(mK) up to about 20 mW/(mK), the VIP thermal solution has several drawbacks, which may be summarized into the following four cardinal weaknesses of VIPs: (a) fragility, (b) perforation vulnerability, (c) increasing thermal conductivity during time (Fig. 1), and (d) lack of building site adaption cutting.
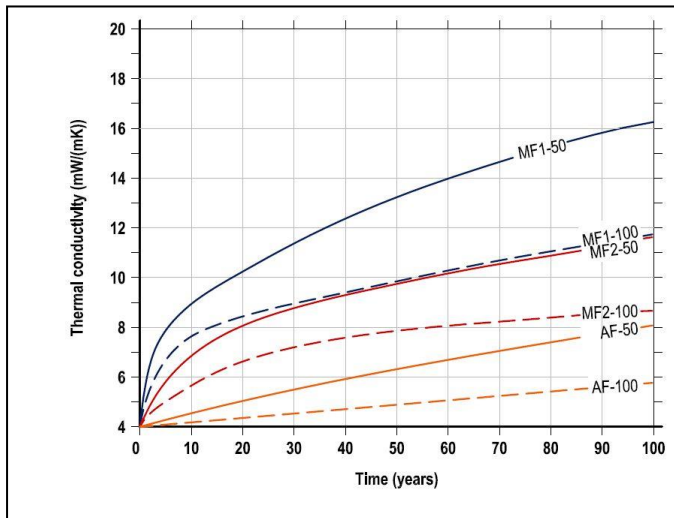

Figure 1. Centre-of-panel thermal conductivity for VIPs with a fumed silica core as function of elapsed time. For two different panel sizes of 50 cm x 50 cm x 1 cm and 100 cm x 100 cm x 2 cm, and for three different foil types AF, MF1 and MF2 [5].

The difference between 4 mW/(mK) (pristine condition) and 20 mW/(mK) (punctured) of 16 mW/(mK) is due entirely to gas thermal conductivity (not taking into account any changes to the solid core due to the loss of vacuum). That is, the combined solid state and radiation thermal conductivity of fumed silica is as low as 4 mW/(mK) or in principle somewhat lower (as there is still a very small air residue inside a VIP a small part of the 4 mW/(mK) value is due to gas conduction), Thus, as it is possible to make materials with such a very low solid state and radiation conductivity, there are rather good opportunities to make a superinsulation material functioning at atmospheric pressure by lowering the gas thermal conductivity. For further information of VIP it is referred to the available literature [2, 4-9].

B. *Gas-Filled Panels*

Gas-filled panels (GFP) apply a gas less thermal conductive than air, e.g. argon (Ar), krypton (Kr) or xenon (Xe), instead of vacuum as in VIP. To maintain the low-conductive gas concentration inside GFP and avoid air and moisture penetration into GFP are crucial to the thermal performance of these panels. Vacuum is a better thermal insulator than the various gases employed in GFP. On the other hand, the GFP grid structure does not have to withstand an inner vacuum as in VIP. Furthermore, low emissivity surfaces inside GFP decreases the radiative heat transfer. However, thermal conductivities for prototype GFPs are rather high, e.g. 40 mW/(mK), although much lower theoretical values have been calculated.

Hence, GFP hold many of the advantages and disadvantages of VIP. Nevertheless, the future of GFPs as thermal building insulation may be questioned as compared to them VIP seem to be a better choice both for today and the near future. For further information of GFP it is referred to the available literature [2, 4, 10-12].

C. *Aerogels*

Another state-of-the-art thermal insulation material, and maybe the most promising with the highest potential of them all at the moment, is represented by the aerogels. Carbon black may be used to suppress the radiative transfer, thereby thermal conductivities as low as 4 mW/(mK) may be reached at a pressure of 50 mbar. At ambient pressure though, commercially available state-of-the-art aerogels have been reported to have thermal conductivities between 13 to 14 mW/(mK). The production costs of aerogels are still very high, and although aerogels have a relatively high compression strength, they are very fragile due to their very low tensile strength, which again may be increased by incorporation of a carbon fibre matrix.

Aerogels can be produced as either opaque, translucent or transparent materials, hence enabling a wide range of possible building applications. However, for aerogels to become a widespread thermal insulation material for opaque applications, the costs have to be considerably lowered. For further information of aerogels it is referred to the available literature [2, 4, 13-16].

D. *Phase Change Materials*

Although phase change materials (PCM) are not really thermal insulation materials, they are still mentioned briefly within this context as they are interesting for thermal building applications. PCM change phase from solid state to liquid when heated, thus absorbing energy in an endothermic process, whereas when the ambient temperature drops again, the liquid PCM will turn into solid state materials again while giving off the earlier absorbed heat in an exothermic process. Thereby, the phase change cycle stabilizes the indoor building temperature and decreases the heating and cooling loads. For further information of PCM it is referred to the available literature [2, 4, 17-21].

IV.   Concepts of New Superinsulation Materials

The following presents some possible concepts for the new superinsulation materials of the future, among them nano insulation materials (NIM).

A.   *Vacuum Insulation Materials*

Basically, a vacuum insulation material (VIM) is defined as a homogeneous material with a closed small pore structure filled with vacuum with an overall thermal conductivity of less than 4 mW/(mK) in pristine condition (Fig. 2) [2]. Thus, the VIM can be cut and adapted at the building site with no loss of low thermal conductivity, as perforating the VIM with a nail or similar would only result in a local heat bridge, i.e. no loss of low thermal conductivity. One possible way to produce a VIM may be to envision a solid state material blowing itself up from within during the formation and subsequent expansion of an inner pore structure (Fig. 3). For further details on VIM it is referred to the work by Jelle et al. [2].
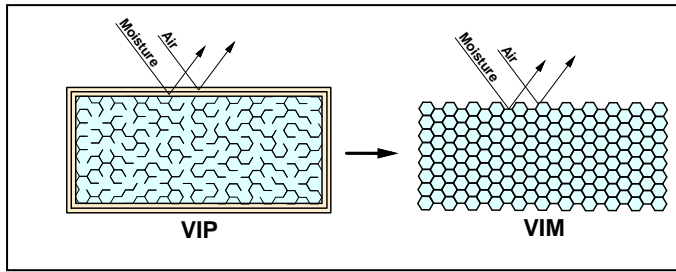

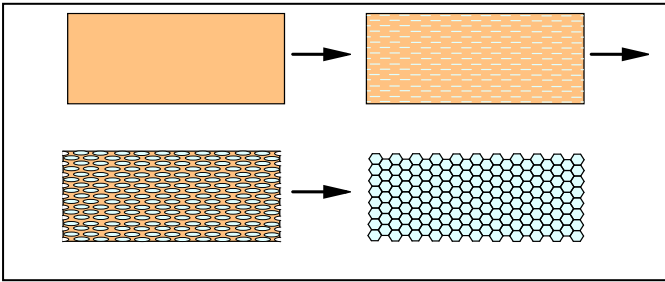Figure 2.   The development from VIP to VIM [2].

Figure 3.   Envisioned creation of VIM as a solid state material blowing itself up from within during the formation and subsequent expansion of an inner pore structure [2].

B.   *Gas Insulation Materials*

Analogously, a gas insulation material (GIM) is basically defined as a homogeneous material with a closed small pore structure filled with a low-conductance gas, e.g. argon (Ar), krypton (Kr) or xenon (Xe), with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition (Fig. 4) [2]. That is, a GIM is basically the same as a VIM, except that the vacuum inside the closed pore structure is substituted with a low-conductance gas. For further details on GIM it is referred to the study by Jelle et al. [2].
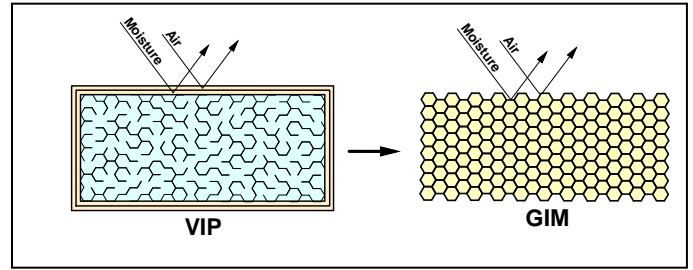

Figure 4.   The development from VIP to GIM [2].

C.   *Nano Insulation Materials*

Of great interest is the development from VIP to nano insulation materials (NIM) as depicted in Fig. 5. In the NIM the pore size within the material is decreased below a certain level, i.e. 40 nm or below for air, in order to achieve an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition. That is, a NIM is defined as basically a homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition [2].
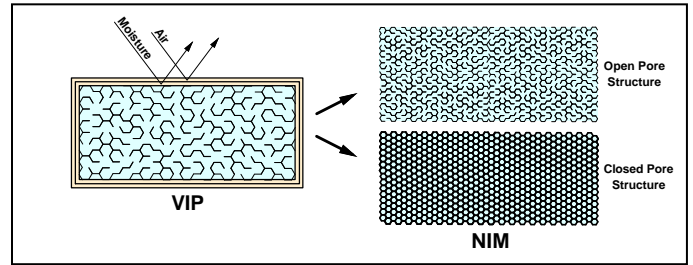

Figure 5.   The development from VIP to NIM [2].

As a NIM achieves its low thermal conductivity, without applying a vacuum in the pores, by utilizing the Knudsen effect, the grid structure in a NIM does not, unlike VIM and GIM, need to prevent air and moisture penetration into their pore structure during their service life for at least 100 years. The gas thermal conductivity λ_{gas} taking into account the Knudsen effect may be written in a simplified way as [2, 4, 5]:

$$\lambda_{gas} = \frac{\lambda_{gas,0}}{1+2\beta Kn} = \frac{\lambda_{gas,0}}{1+\dfrac{\sqrt{2}\beta k_B T}{\pi d^2 p \delta}} \qquad (2)$$

where

$$Kn = \frac{\sigma_{mean}}{\delta} = \frac{k_B T}{\sqrt{2}\pi d^2 p \delta} \qquad (3)$$

where λ_{gas} is the gas thermal conductivity in the pores (W/(mK)), $\lambda_{gas,0}$ is the gas thermal conductivity in the pores at STP (standard temperature and pressure) (W/(mK)), β is a coefficient characterizing the molecule-wall collision energy transfer (in)efficiency (between $1.5 - 2.0$), k_B is Boltzmann's constant $\approx 1.38 \cdot 10\text{-}23$ J/K, T is the temperature (K), d is the gas molecule collision diameter (m), p is the gas pressure in pores (Pa), δ is the characteristic pore diameter (m), and σ_{mean} is the mean free path of gas molecules (m).

When the pore size within a material is decreased below a certain level, i.e. a pore diameter of the order of 40 nm or below for air, the gas thermal conductivity, and thereby also the overall thermal conductivity, becomes very low (< 4 mW/(mK) with an adequate low-conductivity grid structure) even with air-filled pores. This is explained by the Knudsen effect where the mean free path of the gas molecules is larger than the pore diameter. That is, a gas molecule located inside a pore will hit the pore wall and not another gas molecule, and where the solid state and gas interaction is taken care of by the β coefficient in (2). Hence, the resulting gas thermal conductivity λ_{gas}, also including the gas and pore wall interaction, versus pore diameter and pore gas pressure, may be calculated in this simplified model and depicted as in Fig. 6. For further details on NIM and the Knudsen effect, also including thermal radiation aspects, it is referred to the work by Jelle et al. [2].
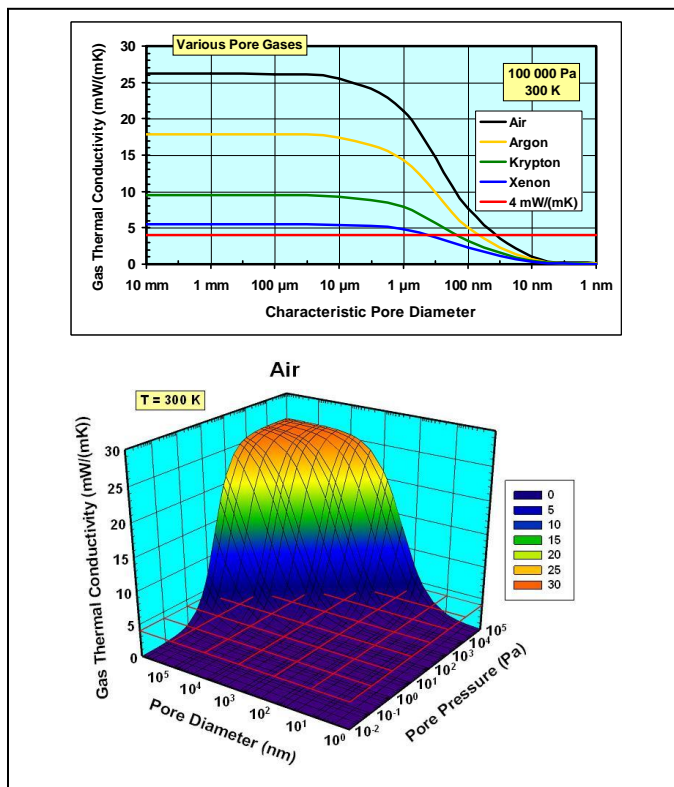

Figure 6.   Graphical illustrations of gas thermal conductivity with a (top) 2D-plot depicting the effect of pore diameter for air, argon, krypton and xenon and a (bottom) 3D-plot depicting the effect of pore diameter and gas pressure in pores for air [2].

D. *Dynamic Insulation Materials*

Conceptually, a dynamic insulation material (DIM) is a material where the thermal conductivity can be controlled within a desirable range [2]. The thermal conductivity control may be achieved by being able to change in a controlled manner e.g. (a) the inner pore gas content or concentration including the mean free path of the gas molecules and the gas-surface interaction, (b) the emissivity of the inner surfaces of the pores, and (c) the solid state thermal conductivity of the

lattice. Furthermore, two models or transfer mechanisms exist for describing solid state thermal conductivity. That is, the phonon thermal conductivity, i.e. atom lattice vibrations, and the free electron thermal conductivity. Thus, one may ask if it could be possible to dynamically change the thermal conductivity from very low to very high, i.e. making a DIM? Other fields of science and technology could inspire and give ideas about how to be able to make a DIM, e.g. the fields electrochromic materials, quantum mechanics, electrical superconductivity, and possible others. The thermal insulation regulating abilities of DIM give these conceptual materials a great potential. Noteworthy, it remains to be demonstrated that such a robust and practical DIM can be manufactured. It is referred to the study by Jelle et al. [2] for further details and elaborations concerning DIM.

E. *NanoCon*

On a conceptual basis, NanoCon is introduced and defined as basically a homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 4 mW/(mK) (or another low value to be determined) and exhibiting the crucial construction properties that are as good as or better than concrete (Fig. 7) [4, 22]. If such a material like NanoCon could be realized, the potential impact is tremendously huge. For further information and discussion concerning NanoCon it is referred to the study by Jelle et al. [4, 22].
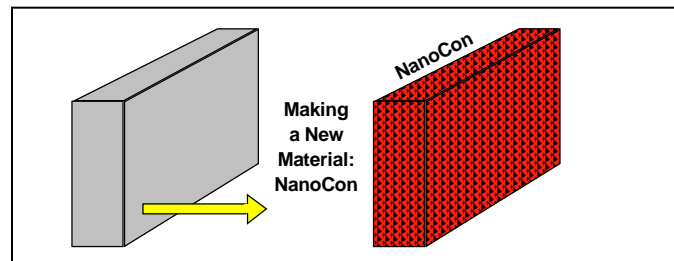

Figure 7.   NanoCon is essentially a NIM with construction properties matching or surpassing those of concrete [4, 22].

V. Experimental Pathways for Making Superinsulation Materials

A. *From Concepts to Experiments*

With the basis in our conceptual studies [2, 4, 5, 22-24], various experimental pathways have been attempted in the quest of making thermal superinsulation materials [25], where at the moment most of these are based on fabricating hollow silica nanospheres (HSNS) by the sacrificial template method [25-30]. However, it should be noted that manufacturing a bulk material with nanopores directly, may be regarded as a more ideal and efficient way of producing a superinsulation material, i.e. and not first making hollow nanospheres which then need to be pieced together and assembled into a bulk material. Nevertheless, currently the HSNS represent an experimental feasible method of actually obtaining a thermal superinsulation material.

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B. *Membrane Foaming Method*

The principle of membrane foaming is to make foams with nanoscale bubbles, followed by condensation and hydrolysis within the bubble walls to obtain a silica nanofoam. In the process, gas is pressed through a membrane to obtain bubbles with controlled size as depicted in Fig. 8. Hydrolysis and condensation of precursors at the bubble-liquid interface should result in formation of gas capsules. This method was previously used to obtain nitrogen-containing capsules with titania-polypyrrole composite shells. Initial experiments indicated that preparation of silica nanofoams may be difficult to accomplish, which was supported by theoretical considerations. The gas pressure must be very accurately adjusted, i.e. if the pressure is too low, no bubbles will be formed and if it is too high, a continuous gas stream will be the result. The size of the bubbles may be decreased by decreasing the pore size of the membrane and adjusting its surface properties to obtain a high contact angle with the solvent, i.e. the solvent should be repelled from its surface. Furthermore, the solvent density should be rather high and its surface tension low. In principle, it should be possible to design a reaction system that fulfills these requirements, so that production of nanosized bubbles is viable [25].
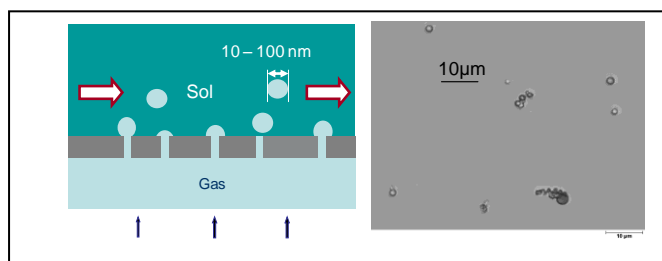

Figure 8. Preparation of gas capsules by membrane emulsification. Left: Principle of experimental method. Right: Micron-sized capsules obtained by Yang et al. [31].

For the production of a solid nanofoam, the liquid foam must be stable long enough for the reactions to proceed, e.g. hydrolysis and condensation of silane precursors to form the solid network. Furthermore, if the foam is to be of interest as a thermal insulator, the foam walls must be thin in order to keep the solid contribution to the overall thermal conductivity low. Wall thicknesses of about 20 nm may be achieved if surfactant bilayers are used to stabilize the walls and the applied solvent has low viscosity and is rapidly drained from the wall interior which is possible to achieve in water-based systems. However, the reactions are generally performed in alcohol solutions like ethanol or isopropanol. No surfactant was found that could stabilize nanofoams long enough, thus work along this line has so far been abandoned [25].

C. *Gas Release Method*

Applying the gas release method would require simultaneous formation of nanosized gas bubbles throughout the reaction system, followed by hydrolysis and condensation to form a solid at the bubble perimeter. Bubble formation could be achieved by either evaporation or decomposition of a component in the system. This method is similar to the process described by Grader et al. [32], where crystals of $AlCl_3(Pr^i_2O)$ were heated to produce foams with closed cell structures. In this case, the crystals themselves decomposed. Upon further heating, the remaining solid dissolved in the generated solvent, whereupon a polymerization reaction occurred at the temperature of solvent evaporation. The solvent bubbles were trapped within the polymerizing gel, thus forming a stable foam with pore sizes 50-300 μm after completion of the reaction.

However, the gas release process entails several challenges. To obtain nanosized bubbles with a sufficiently narrow size distribution, the temperature must be the same throughout the liquid phase, which would be difficult to achieve at ordinary reaction conditions. Furthermore, the reaction to form the solid shell must proceed very rapidly if the shell is to be formed before the bubbles grow too large, which would require very reactive chemicals where their application would require strict control of humidity both in the working environment and in the solvents used. Due to these practical difficulties, work in this direction has at the moment been terminated [25].

D. *Template Method*

Utilizing the template method, a nanoscale structure in the form of a nanoemulsion or polymer gel is prepared, followed by hydrolysis and condensation to form a solid. This procedure is applied for preparing e.g. catalysts and membrane materials. Our current approach is to prepare hollow silica nanospheres, followed by condensation and sintering to form macroscale particles or objects. For thermal insulation applications, small pore sizes combined with small wall thicknesses are desired and required [25]. Several methods for nanosphere fabrication are reported in the literature. Our starting point was based on the studies by Du et al. [33] and Wan and Yu [34], where the former ones used the template method to prepare antireflection coatings, and the latter ones described the method more in detail where their schematic depiction of the synthesis process is shown in Fig. 9.
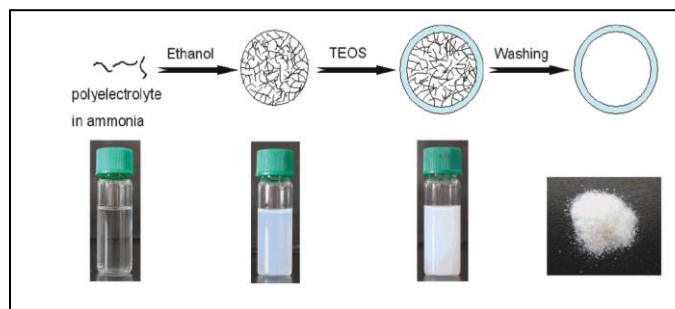

Figure 9. Schematic diagram showing the formation mechanism of hollow silica spheres, with corresponding real samples [34].

Currently, our experimental work has been concentrated on making hollow silica nanospheres by applying polyacrylic acid (PAA) and polystyrene (PS) sacrificial templates, where the templates PAA and PS have been removed by a washing and a heating process, respectively (the template materials diffusing and evaporating through the silica shell), where

Fig. 10 shows scanning electron microscope (SEM) images of the first HSNS we produced.
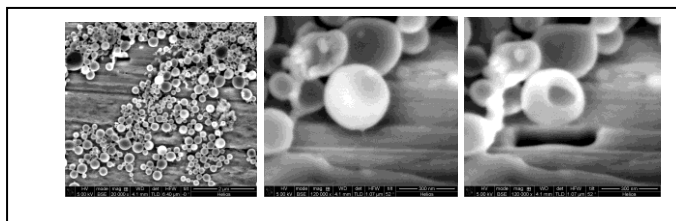

Figure 10. SEM images showing an overview of the HSNS sample (left, scale bar 2 μm) and an unetched sphere (middle, scale bar 300 nm), as well as the same sphere after extensive etching with a focused ion beam (right, scale bar 300 nm) [25].

VI. Hollow Silica Nanosphere Results

A. *Experimental Details*

Detailed experimental information and procedures concerning the various fabrications of hollow silica nanospheres (HSNS) are found in our earlier studies [25-28]. Basically, the HSNS manufacturing applies the template method as described earlier, with either polyacrylic acid (PAA) or polystyrene (PS) as sacrificial templates. The principle of the sacrificial template method for HSNS fabrication is illustrated in Fig. 11, where Fig. 12 depicts the laboratory scale production of the PS templates including a SEM image of the resulting PS template spheres.
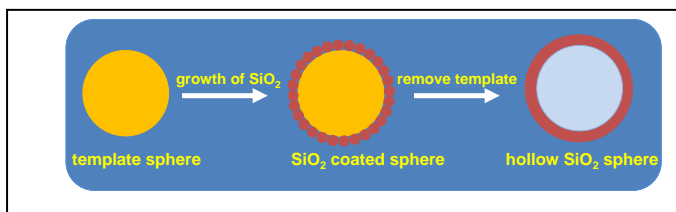

Figure 11. Illustration of the sacrificial template method for HSNS fabrication.
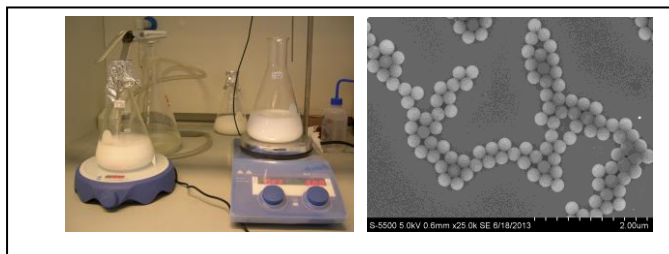

Figure 12. Photo from laboratory scale production (left) of PS templates, and SEM image of resulting PS template spheres.

B. *Various Hollow Silica Nanospheres*

Nano insulation materials (NIM) have been attempted made in the laboratory as various hollow silica nanospheres (HSNS). In Fig.13 there is shown a principle drawing of a NIM alongside a transmission electron microscope (TEM) image of actual manufactured HSNS, depicting the close resemblance from theoretical concepts to experimental fabrication attempts.
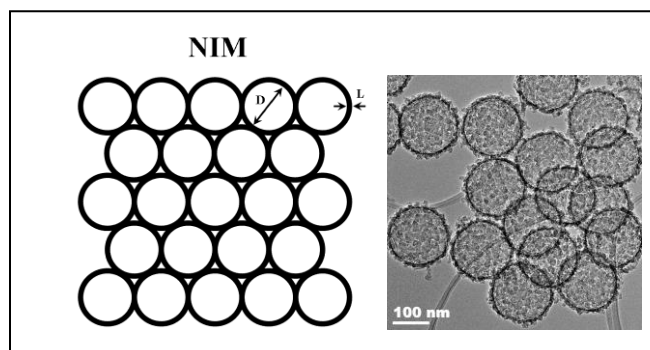

Figure 13. Principle drawing of a NIM (left) alongside a TEM image of actual manufactured HSNS (right).

A SEM image of manufactured spherical PS templates are shown in Fig. 14 (left). The PS templates were hence coated with small silica particles, where an example is depicted in Fig. 14 (right). By removal of the templates, HSNS are formed, where one example is depicted in Fig. 15. Another example of HSNS with PS templates underneath is depicted in Fig. 16.
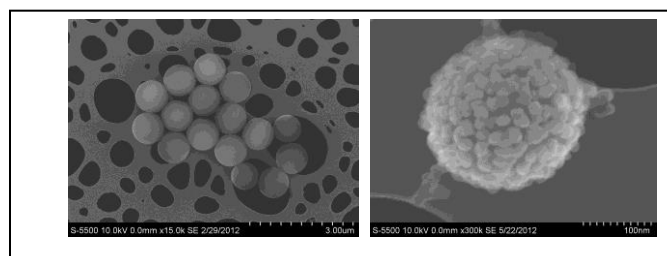

Figure 14. SEM images of spherical PS templates (left) and small silica particles coated around a spherical PS template (right).
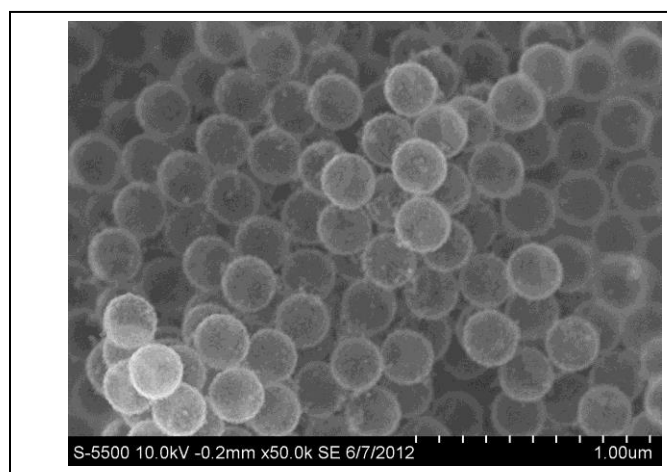

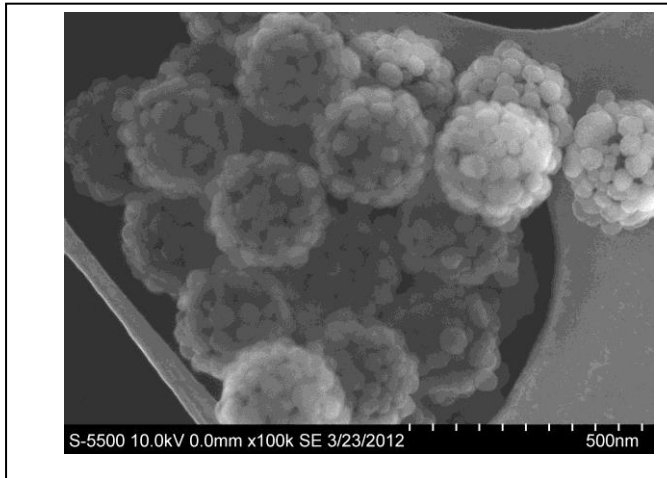Figure 15. SEM image of HSNS after removal of PS.

Figure 16. SEM image of small silica particles coated around spherical PS templates, i.e. HSNS before removal of PS.

When attempting to make monodisperse PS nanospheres, the results are not always as planned or hoped for, although some rather intriguing patterns may be revealed in the SEM images, where an example is shown in Fig. 17.
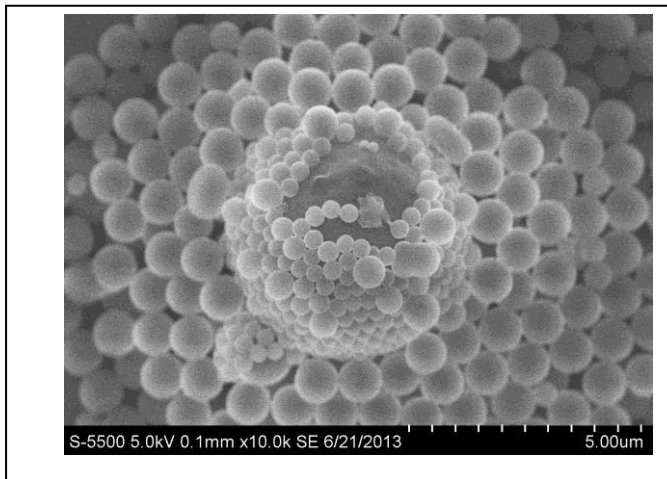

Figure 17. The results are not always as planned when attempting to make monodisperse PS nanospheres, although some rather intriguing patterns may be revealed in the SEM images.

Thermal conductivity has been measured for various powder samples of HSNS, where the conductivity values are typically in the range 20 to 90 mW/(mK), though some uncertainties in the Hot Disk apparatus measurement method have to be further clarified [29, 30]. In this respect, the specific powder packing of the HSNS in the bulk condition is also an issue to be addressed.

The thermal conductivity is currently being attempted lowered by a parameter variation and optimization of the hollow silica sphere inner diameter and wall thickness. Furthermore, aspects like e.g. thermal radiation, mesoporosity, powder packing at bulk scale and nanosphere packing at nano scale should be addressed.

Life cycle analysis (LCA) of NIM as HSNS has been carried out in the study by Gao et al. [27], and follow-up investigations are currently being conducted.

Initial experiments attempting to improve the thermal resistance of concrete by incorporation of aerogel have also been performed [35], where naturally any new development of NIM will be interesting for further work.

For additional information on fabrication of monodisperse PS nanospheres it is referred to the work by Du and He [36]. More information on hollow silica nanospheres may be found in the studies by e.g. Liao et al. [37], Wang et al. [38], Han et al. [39] and Yuan et al. [40].

VII. Further Work

Currently, our SIM and NIM research is mainly focused on various attempts to tailor-make HSNS by manufacturing and applying different sacrificial templates, synthesis procedures, parameter variations, and inner diameters and shell thicknesses of the nanospheres. A crucial issue will be how to assemble the HSNS together into a practical bulk material.

It should be noted that the future NIM may not necessarily be based on HSNS, nevertheless the investigations on the HSNS represent a possible stepping-stone towards the ultimate goal of achieving thermal superinsulation materials.

Although we at the moment are not pursuing fabricating NIM according to the membrane foaming and gas release methods, these methods should definitely not be forgotten as they may still represent a possible way of achieving SIM and NIM.

Finally, it should be emphasized that also methods and materials not included within this summary, even hitherto unknown methods and materials, may hold the solution for the future SIM and NIM.

VIII. Conclusions

The theoretical concepts and experimental investigations for making thermal superinsulation materials (SIM) for building applications have been summarized. A special focus has been given on nano insulation materials (NIM), where hollow silica nanospheres (HSNS) have been manufactured, which thus represent a possible foundation or stepping-stone for the development of the NIM of tomorrow.

Acknowledgements

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