Development of nanoporous aerogel-based thermal insulation products: 'Make in India' initiative

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The technology of manufacturing a silica aerogel thermal insulation product has been developed with the objective of indigenization under the 'Make in India' initiative. This world class product is now ready for commercial production. It possesses all the features and properties required for any ideal industrial thermal insulation material such as low thermal conductivity, light weight, good compressive strength, moisture, fire, corrosion and chemical resistance, antifungal, low shrinkage, sound-proof, non-toxic and eco-friendly. The increasingly gaining attention towards this highly efficient thermal insulation material is a hope to significantly contribute in achieving targets of energy conservation and saving.

Keywords: Aerogel, energy conservation, industrial applications, silica, thermal insulation.

Introduction

AEROGELS possess unique set of extraordinary properties in single material. These are ultra-low density man-made materials. The lowest density that has been achieved is only three times more than air. This light weight arises due to the open, interconnected porosity in the size range of a few tens of nanometres. Aerogels are formed when liquid present in a gel is replaced by air, retaining the solid network intact and unaltered. The technique to achieve this is known as supercritical drying (SCD), which was invented by Samuel Kistler in late 1920s. He published the first paper[1] on aerogels in 1931. Aerogel is technically defined as 'an open-celled, mesoporous, solid foam that is composed of a network of interconnected nanostructures and that exhibits a porosity of not less than 50%'. Other than the most popular silica aerogels, these can be made from various chemical compounds like organic polymers[2], biological polymers[3], most of the transition metal oxides[4–8], semiconductor nanostructures[9,10], carbon[11], carbon nanotubes[12], graphene[13,14], gold[15], etc. Silica aerogels are the most studied, explored in several applications and successfully commercialized. The silica aerogels are usually transparent with a blue tinge, as their primary building blocks of the network scatter shorter wavelength in the visible light. Figure 1 shows a photograph of a typical silica aerogel, produced in the present author's laboratory.

The silica aerogel has a combination of tunable properties such as highest specific surface area, lowest dielectric constant among solids, excellent insulator of heat, electricity and sound, and wide range, cryo to high temperature stability. Figure 2 provides the general properties and applications of silica aerogel.

General preparation method for aerogels

Aerogels are derived by a well-known sol–gel method, followed by SCD of the gel. There are some excellent review articles on the preparation, properties and applications of aerogels[16–19] and books on all aspects of aerogel synthesis, properties and applications[20,21]. The process is briefly described below.

Preparation of gel: The sol–gel method involves hydrolysis and condensation of the precursor in the presence of

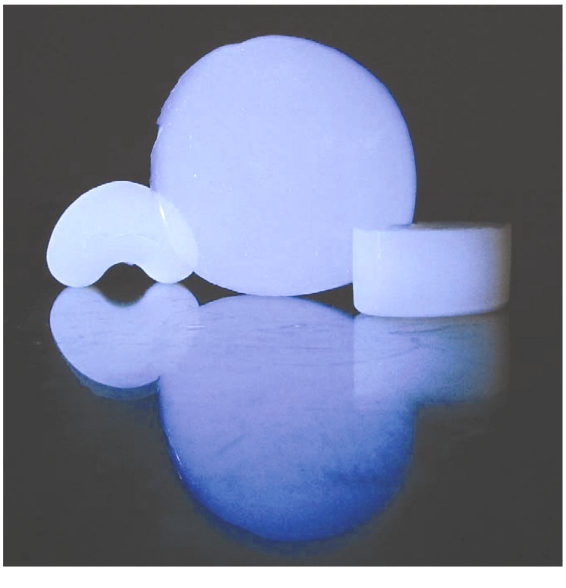

Figure 1. Photograph of silica aerogel monolith.

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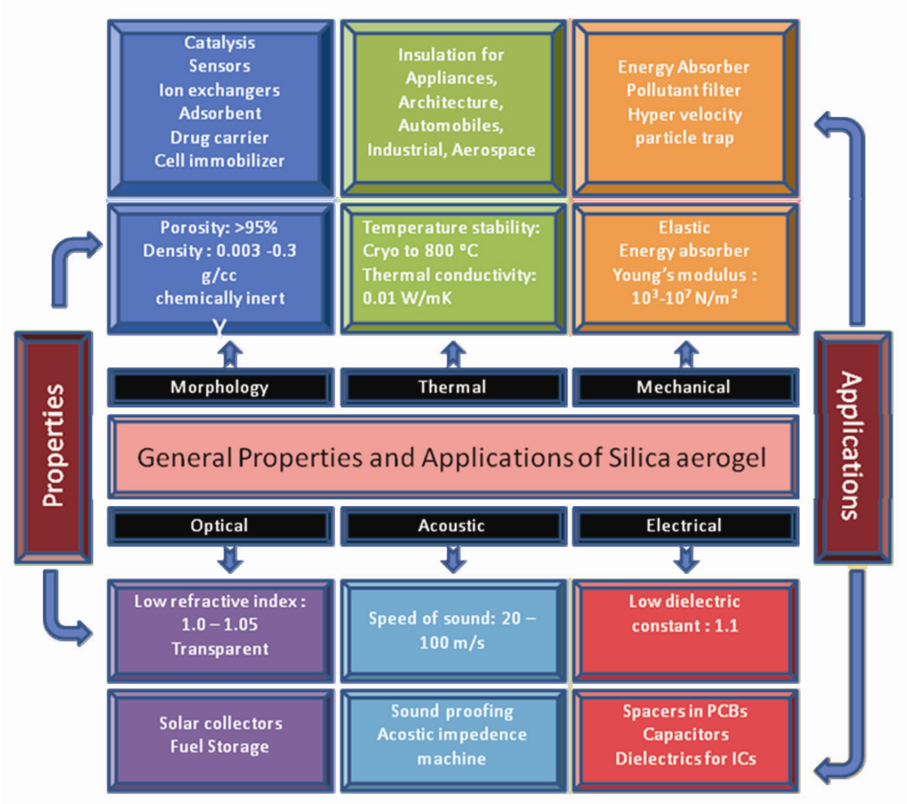


Figure 2. General properties and applications of silica aerogel.

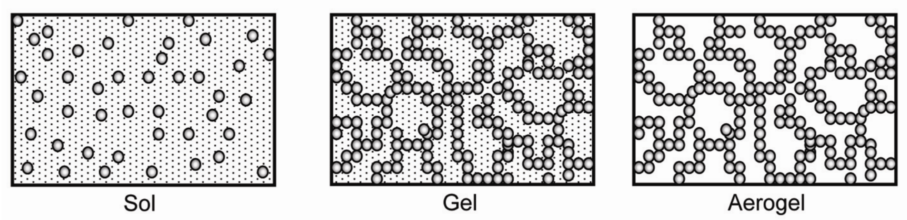


Figure 3. Schematic representation of sol–gel aerogel.

a catalyst to first prepare a suspension of monomer particles called 'sol' and further cross-linking of monomer particles into three-dimensional polymeric network to form a 'gel'. The gel is 'washed' several times to exchange the pore liquid with a pure solvent and then dried to get a nanoporous solid, where liquid in the gel is replaced by air, as schematically shown in Figure 3. Silica aerogels are prepared typically using a precursor, tetraethyl ortho silicate (TEOS). The reaction of hydrolysis and condensation of TEOS is as follows

$$\text{Si-OC}_2\text{H}_5 \text{ (TEOS)} + 4\text{H}_2\text{O} \rightarrow \text{SiO}_2 \text{ (Silica)} + 4\text{C}_2\text{H}_5\text{OH (ethanol)} + 2\text{H}_2\text{O}.$$

Drying of gel: In SCD, the gel is placed in a pressure vessel (autoclave) and taken to the supercritical condition of the solvent present in the pore. The vapours are then vented slowly to extract solvent from the gel to form the aerogel. The most common liquids used as solvents for SCD are ethyl alcohol and liquid carbon dioxide. The critical temperature and pressure of ethyl alcohol and liquid carbon dioxide are 243°C, 63 bar, and 31°C, 73 bar respectively.

Thermal insulation property of aerogels

Aerogels are known as the best thermal insulator materials in the world. Table 1 lists the thermal conductivity of conventional insulation materials. Silica aerogel not only takes a top position, but also shows a wide temperature range.

Interestingly, the apparent thermal conductivity of aerogels is smaller than air, though aerogels have more than 95% air filled in them. Lu *et al.*[22] have explained the correlation between structure and thermal conductivity in aerogels. The air present in aerogels is confined in the nanometre-sized pores. Typically at ambient temperature and pressure, the mean free path of air molecules is ~70 nm. The average pore size in aerogels is equivalent or less than this mean free path, which restricts air molecule collisions and so the convective heat transfer. The small fraction of solid present in the aerogels is in the form of a thin-walled, random network with many dead-ends. Hence heat conduction through it is minimal. The radiative heat transfer through silica aerogels is not-negligible, as it is transparent to some wavelengths in the infrared region[17]. Hence achieving the lowest density, optimum required size of the porosity and inclusion of infrared radiation opacifier are the key parameters to obtain the superior thermal insulation property in aerogels. It can be further improved to almost double by evacuating the aerogel pores, which elongates the air mean free path to reduce the gaseous heat transfer[23].

Aerogels in various forms

Commercial production and industrial applications of silica aerogel were limited due to its high production cost and, importantly, its fragile nature in pure monolithic form. The latter limitation was overcome by developing new varieties of aerogels in the form of granules and flexible sheets. The aerogel granules are a convenient form in certain applications, where these can be filled in a proper way around the object to be insulated, or can be sandwiched between layers of wood, plastic, fabric, glass, etc. to make the panels ready for use. The flexible sheets are made by in-filtering aerogels in the fibre blankets, where the fibres in the blanket may be of many types such as polymeric, organic, inorganic, woven, non-woven, etc. The flexible sheets are easy to wrap around the object and can be precisely cut into the required shape. The thermal insulation performance of granules or sheet forms of aerogel is slightly minimized compared to its pure monolithic form due to air in the inter-granular pockets or fibres respectively. Few aerogel products are commercially available in the market.

Table 1. Thermal conductivity of thermal insulation materials

Insulation material	Thermal conductivity at 25°C (W/mK)	Temperature range (°C)
Vacuum insulation panels	0.003	
Silica aerogel	0.01	–200 to 800
Aerogel sheets	0.013	Up to 600
Air	0.025	–
Glass fibre mat	0.035	–200 to 500
Cellulose	0.035	Up to 50
Polyurethane	0.036	–40 to 105
Mineral fibre	0.037	Up to 650
Polystyrene	0.037	–40 to 80
Cellular glass	0.048	–200 to 400
Calcium silicate	0.065	Up to 650
Expanded perlite	0.076	Up to 650
Ceramic fibre	0.08	Up to 1260
Gas-filled panels	0.03–0.09	
Phase change materials		50–150
Water	1.6	
Sodium silicate	0.103	
Paraffin	0.25	

National and international status of commercial aerogel products

To the best of our knowledge, no aerogel product has been commercially manufactured in India till date. However, there are more than a dozen companies which manufacture and market aerogel products in the global market.

Product development at author's lab

Technology development of various aerogel products is in progress in the present author's laboratory. These include aerogels of organic, carbon, silica, titania, alumina and their composites. Among these, silica aerogel granules and sheets which are at the advanced level of development are described here.

Silica aerogel granules

Silica aerogel granules or beads were mainly synthesized by breaking down the wet gel[24] or by emulsion technique[25,26]. We have developed a simple one-step method to produce nearly spherical and highly porous silica aerogel granules and applied for a patent. Here, the granules can be tailored by *in situ* generation of carbon nanoparticles which act as an infrared opacifier and minimize radiative heat transfer at higher temperatures.

An organic sponge is used as a template where silica precursor solution, i.e. 'sol' is soaked in it. The sol converts into 'gel' within the pores of the sponge to form sponge–gel composite. During SCD in ethanol solvent, the sponge degrades completely releasing the silica aerogel granules from its pores. SCD is done such that the degraded organic sponge molecules are trapped in the silica porous structure in a controlled manner by varying the organic content in the silica aerogel granules formed. Such granules are heated either in air to get completely pure silica aerogel granules or in inert atmosphere to obtain carbon containing granules. Thus the SCD conditions and nature of heat treatment decide the composition of the granules. Figure 4 is schematic representation of the process. Table 2 lists the important features of silica aerogel granules. The scanning electron microscopy

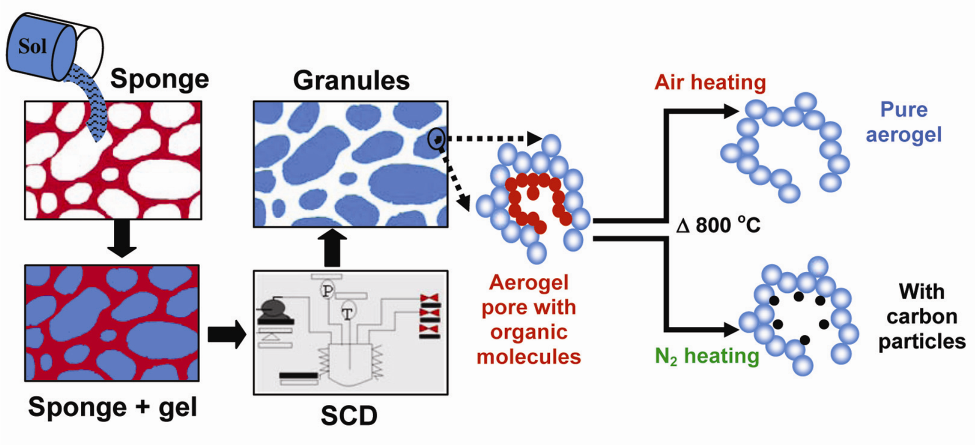


Figure 4. Schematic representation of the process of producing pure and carbon-containing silica aerogel granules.

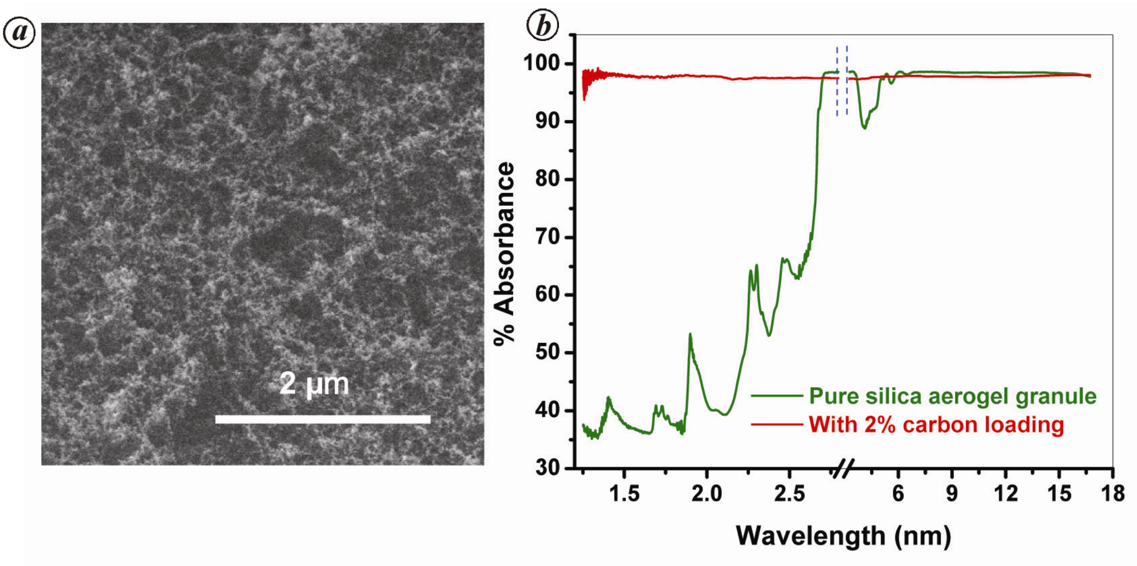


Figure 5. ***a***, Porosity in silica aerogel granules as seen in SEM image. ***b***, Infrared absorption of carbon containing silica aerogel granules.

Table 2. Important features of granular and flexible sheet aerogels developed at author's lab, Hyderabad

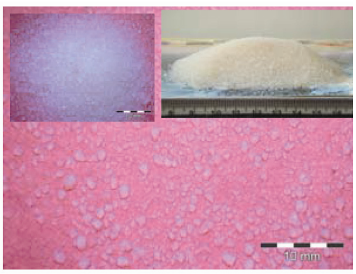
	Granule size: ~1 mm (tunable)
	Packing density: 0.07 g/cm^3
	Thermal stability: –200°C to 800°C
	Surface area: ~ 800 m^2/g
	Thermal conductivity: 0.03 W/mK at room temperature (transient plane method)
	Colour: Translucent or opaque or black (depending on functionality)
	Hydrophobic or hydrophilic

image shown in Figure 5 *a* is evidence of the highly porous nature in the granules. Figure 5 *b* shows the excellent infrared opacification by absorption by granules containing just 2% carbon, which covers wavelength range from 1 to 18 µm.

Silica aerogel flexible sheets

Silica aerogel flexible sheet is the most convenient form of aerogel suitable for many industrial applications. The product developed in the present author's laboratory has been envisioned to compete globally in the international market with superior thermal insulation performance. Presently, the technology of manufacturing this product is ready for commercialization with industry partner in India.

The basic product is made up of a silica aerogel in-filtered into the fibre mat. In-filtration of aerogel is done by soaking the 'sol' into the fiber mat, followed by 'sol' to 'gel' conversion to get fibre mat–gel sheet. This gel sheet is then dried supercritically to get the aerogel sheet.

The silica aerogel present in the sheet has best quality with >95% porosity and pores in the size range 2–120 nm. These aspects take care to minimize heat transport through conduction and convection. The special property of reflecting infrared radiation was achieved by a novel and efficient method. It was done by uniformly dispersing extremely fine metal-oxide particles in small concentration, by an *in situ* process during the production of silica aerogel. The fibre mat used for in-filtration was selected based on the application temperature range, and desired thermal and mechanical properties. It covers a large variety of compositions such as glass/silica, alumina, zirconia with many commercial names such as silica, high silica, e-glass, refractory, ceramic fibres, etc. For low-temperature applications, fibres can be chosen from polymeric types which can withstand the ethanol SCD temperature (260°C) and pressure. Morphologically, the fibre mat can be of woven or non-woven fibres. The density and in turn the porosity of the fibre mat determine the maximum space available for the aerogel. Hence the aerogel content in the mat can be tailored. The fibre mat with good mechanical strength can take up about 50 wt% of aerogel content in the sheets. To increase this further, another novel product has been developed which can possess up to 90% aerogel, where extra aerogel is in the form of granules sandwiched between the layers for aerogel in-filtered fibre mats. There is no restriction on the number of layers and thickness of each layer. We have applied for a patent on the process of making such sheets having all these features. Table 3 lists properties and features of the aerogel flexible sheet product developed in the present author's laboratory.

Up-scaling

The aerogel technology development has a strong foundation due to the basic research carried out during the present author's doctoral research carried out in the Department of Physics, University of Pune. Silica and organic aerogels were developed for thermal insulation application. Carbon aerogels developed showed promising results for their supercapacitor applications[27]. During initial stage of research the autoclave used for SCD was of 300 ml capacity. The possible dimensions of the sample to be produced were 1–2 inch. In the next level, the autoclave capacity was doubled during the initial stages of research and development work at present author's current workplace. Further up-scaling was necessary to develop a prototype of reasonably larger size to attract attention of industry. A facility of custom-designed 20 litre capacity pressure vessel was established which could produce about half a kilogram of silica aerogel granules and a roll of 3000 × 30 × 10 mm flexible sheet in one batch. Figure 6 shows the level of up-scaling done and the products prepared. Considering the risk factor involved in the SCD process, all possible safety precautions were taken care of and since 2012, this 20 litre capacity autoclave has served without any casualties.

Making cost-effective products

The saleability of any product depends upon the best efficiency of the desired application and more importantly, on cost-effectiveness. A product with only one aspect of efficiency limits it use only for special or strategic applications. The approach followed for making our product cost-effective was using indigenously produced (Indian-make) raw materials. Secondly, the effluents generated during processing are recycled for solvent recovery and its reuse. With these efforts, now it is predicted that the product can be manufactured at the affordable cost.

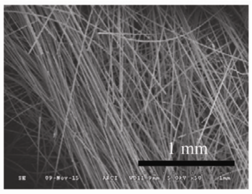
Potential industrial applications

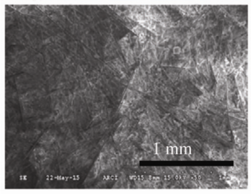
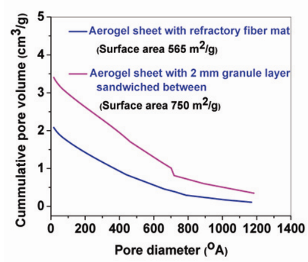
Major industries attracted towards aerogel insulation are oil and gas refineries, power-generation plants and those where high or cryo temperature processes or fluids are in use. The volume of insulation material required for these industries is huge. Hence every step taken to reduce heat losses contributes to the energy-saving, and aerogel insulation plays an important role to achieve this. The fuel consumption to maintain high or low temperature, reduces to a large extent and helps in lowering the CO_2 footprint. Additionally, the lightweight and yet superior insulation performance leads to cost saving due to reduced volume, space and weight of the material, which requires less transportation cost, and storage and labour charges. Other major sectors are architectural[28–32], automobiles[33–35], cryogenics[36–38], aerospace[39,40] and textiles[41].

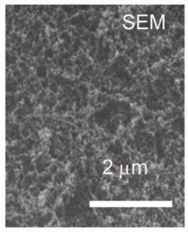
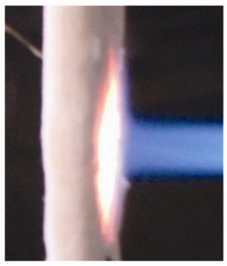
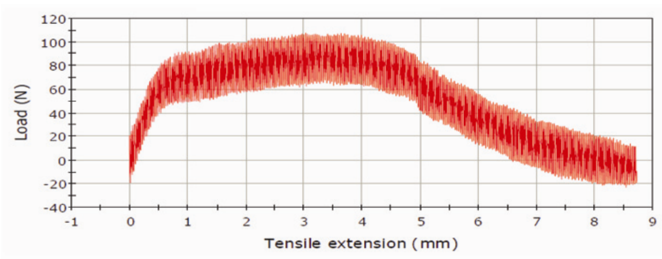
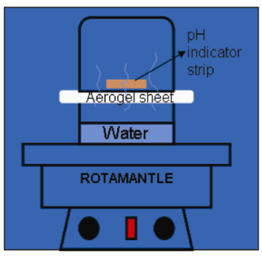
Energy conservation

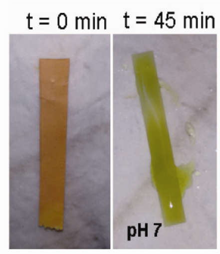
Energy saved is energy produced. New superior insulation materials can substantially reduces the heat losses and save energy. According to the experts from the insulation industry, huge energy and cost saving is possible if aerogel insulation is used in place of conventional mineral wool. For example, in a boiler, if 2500 m^3 mineral wool is required, the quantity of aerogel sheet insulation

Table 3. Properties of silica aerogel flexible sheets developed at ARCI

<table>
<tr><th>Property/feature</th><th>Results</th></tr>
<tr><td>Morphology
Fibre mat with fully packed silica aerogel</td><td>Bare fibre mat


Aerogel–fibre mat composite

</td></tr>
<tr><td>High porosity
Surface area: 300–800 m^2/g
Pore volume: 2–3.5 cm^3/g</td><td>


</td></tr>
<tr><td>Fire-proof and thermal insulator
Thermal conductivity: 0.016 W/mK at room temperature (guarded hot plate method)</td><td>
</td></tr>
<tr><td>Hydrophobic
Contact angle: 140–150°
Retains 1% water when immersed in it for 5 h
Breathable</td><td></td></tr>
<tr><td>Tensile strength
Can take ~80 N force and elongation of 5 mm (when prepared with e-glass fibre mat)</td><td>
</td></tr>
<tr><td>Non-corrosive
Water vapour passing through the sheet is neutral in pH</td><td>



pH indicator strip</td></tr>
</table>

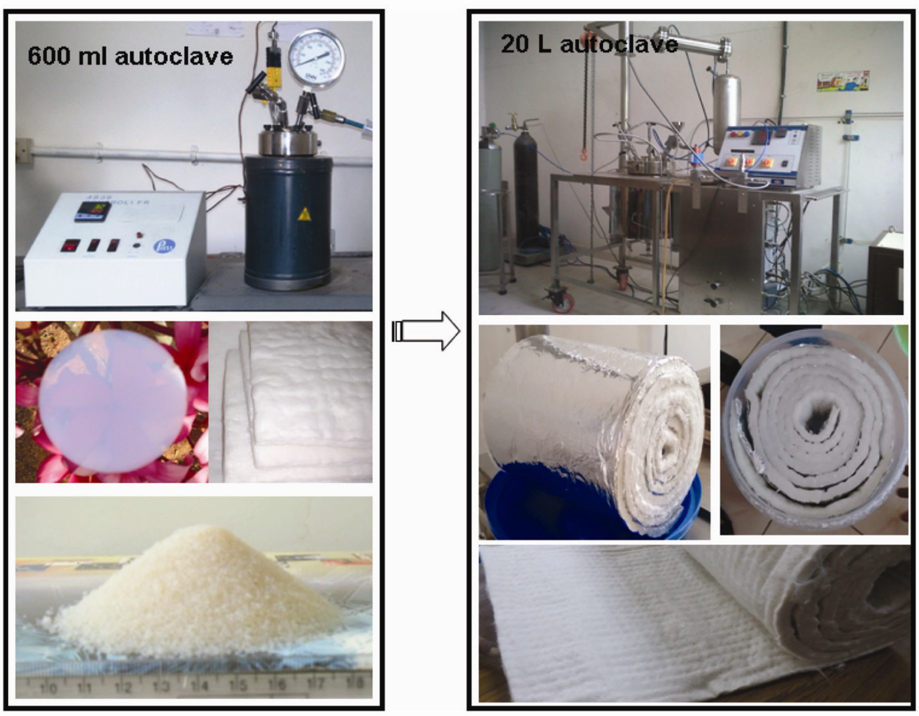


Figure 6. Up-scaling of silica aerogel product development from a small 600 ml autoclave to a 20 l autoclave and photographs of the products at the respective scales.

is expected to reduce by 2.7 times. The higher cost of aerogel insulation compared to conventional materials may be compensated as about 300% savings due to reduced heat loss is predicted.

Safety and hazard

Chemically the silica in aerogel resembles sand. However, the primary building blocks are amorphous silica particles in nanometre size. The aerogel powder may fly while handling, cutting or crushing. This may cause damage to the respiratory system if inhaled, and also cause dryness in skin and eyes. There are no standards from OSHA (Occupational Safety and Health Administration, USA) for silica aerogel. According to the standards for amorphous silica, the permeable exposure limit is 5 mg/m^3 as respirable fraction. It is recommended to follow all the standard industrial hygiene practices during production, handling, transport and storage.

Summary

The present author's laboratory has embarked on world-class product development for thermal insulation with the objectives of indigenization under the 'Make in India' initiative. Silica aerogel flexible sheets and silica aerogel granules have been developed. Recently, the technology of manufacturing aerogel sheets has been transferred to an Indian industry for commercialization. Being a light-weight and superior thermal insulator, the aerogel product shows energy efficiency by minimizing heat loss to a large extent.

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ACKNOWLEDGEMENTS. I thank ARCI, Hyderabad for encouragement and support, and Prof. Sulabha Kulkarni who inspired me to work on aerogel materials for my doctoral research. I also thank my students and other team members for their contribution in the technology development, demonstration and transfer work.

doi: 10.18520/cs/v112/i07/1413-1420