Vacuum insulation panel core materials and modelling the thermal conductivity of granular materials

by

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CHAPTER 1
GENERAL INTRODUCTION

1.1 Heating, Cooling and the Importance of Insulation

The US Energy Information Administration (EIA) reported that in 2010, a total of $203 billion was spent on the heating and cooling of residential and commercial buildings. This accounted for 47.1% of the total dollars spent in the building sector. These factors including the projection that energy prices will increase at a steady rate in the coming decades have escalated the demand for high performance insulation [1].

Fiberglass and polymer foams are presently the most common insulation materials used for building applications in the US. [1] These materials have thermal conductivities ranging from 30 – 40 mW/m.K. The R-value (US) of these materials is equivalent to 3.5 – 5 (see Appendix for conversion). However, more stringent insulation requirements are pushing the limits of these materials, forcing developers to allocate more space for insulation, which tapers with the versatility of the building design. Under these circumstances, a new form of thermal insulation known as vacuum insulation panels (VIP) have gained notable attention [2].

1.2 Vacuum Insulation Panel (VIP)

VIPs possesses an extremely low thermal conductivity (3 – 4 mW/m.K), typically 10 times lower compared to traditional insulation materials mentioned previously [3]. This property makes it a highly desirable product not just for building applications but also for appliances such as refrigerators, as well as commercial cold rooms, refrigerated transportation systems among others. VIPs consist of a core material and a barrier laminate, which seals the vacuum. The core material is made of a highly porous solid, which can be particulate or fibers while the barrier laminate consist of layers of aluminum and polymer films [4].
Vacuum insulation has been invented more than a century ago by James Dewar. Vacuum flasks were made using glass and metal, which could support the compression force generated from the pressure difference between the vacuum layer between the walls of the flask and atmospheric pressure outside [4]. Heat transmission across the vacuum insulating layer is only possible via radiation, which is negligible at ambient temperatures. Thus, an exceptional insulator is produced between the walls of the flask.

Figure 1: Schematic of a vacuum flask [5].

In order to extend the applications of vacuum insulation, VIPs were produced whereby a highly porous core material is used instead of a hollow layer. The core material is sealed from the environment by a thin metallized polymer film. In this case, the core material acts as the compressive load bearer.
Nevertheless, VIPs have a limited service life because the barrier laminates do not provide a perfect vacuum seal. As vacuum in the panel degrades, the insulation performance also deteriorates. Solutions to this problem include using a thicker layer of aluminum as the barrier but this would result in significant thermal bridging at the edges of the panel. Another solution would be to add getters within the panel that absorb the gases that diffuse through the barrier laminate [6].

![Barrier laminate diagram](image)

**Figure 3: Various types of barrier laminate configurations [7].**
Furthermore, VIPs are considerably more expensive compared to traditional insulation materials due to processing requirements and material cost. The most common material used in VIPs is fumed silica. This is because it consists of only nano-pores, which strongly influences gaseous thermal conductivity (further discussed in section 1.5) [4]. Fumed silica is synthesized by pyrolysis of silicon tetrachloride at extremely high temperatures (1500°C) in a water cooled aluminum and steel chamber [8], making it a lot more costly than its traditional counterparts. Low cost alternatives such as glass fibers and expanded polymer foams exist for VIPs but the service life of these alternatives are considerably shorter [9–11].

In pursuit of an improved core material, research groups have focused on naturally occurring materials to reduce cost. Perlite [12] and pumice [13] are two types of volcanic rocks that were studied for their potential as low cost alternatives. In both cases, the natural powders were mixed with other constituents to form composites.

1.3 Thermal conductivity measurement

The transient plane source (TPS) technique was used for measuring thermal conductivity for all the experiments in this work. Unlike standard methods, TPS involves taking measurements as function of time. A thin film nickel sensor is used as a resistance thermometer and heat source during experiments. The sample of interest must completely envelope the sensor because the technique assumes an infinite heat sink. By analyzing the temperature change as a function of time, the thermal conductivity can be calculated from Equation 1. [14]

\[
\Delta T(\tau) = P_0 (\pi^{3/2} \alpha \Lambda)^{-1} D_1(\tau) \quad (1)
\]
$\Delta T$ is the change in temperature, $D_s (\tau)$ is the time dependent function, $P_0$ is the power, $a$ represents sensor radius, $\Lambda$ is thermal conductivity and $\tau$ is a dimensionless time variable. It has been shown that this technique produces higher thermal conductivity values compared to standard methods but the measured trends are identical. [15, 16].

Standard methods of measuring thermal conductivity for VIPs include the guarded hot plate and heat flow meter [17]. Both of these techniques require heating the sample on one side and cooling on the other. Measurements can only be taken once steady state is reached. Hence, TPS has an advantage in terms short measurement time.

### 1.4 Heat transfer mechanisms

#### 1.4.1 Conduction

Heat transferred by conduction is associated with energy transfer between atoms or molecules from a hot to cold region. For non-metallic solids, it is typically assumed that heat is primarily carried by phonons, a particle representation of the vibrations between atoms. Hence, heat conduction in such solids is treated as a phonon gas, whereby scattering occurs between particles and at the boundaries [18].

$$q = -k \frac{dT}{dx}$$

$q \ (W/m^2)$ is the heat flux through the medium, $T \ (K)$ is the temperature while $x \ (m)$ is the thickness of the medium parallel to the direction of heat flow. $k \ (W/m.K)$ is the thermal conductivity of the medium.
1.4.2 Convection

Convective heat transfer occurs in fluids whereby heat is transported via bulk motion and diffusion of the fluid. Heat is essentially transported by the flow of the fluid rather than vibrations between atoms [19].

\[ q = h(T_s - T_\infty) \]  
\( q \) (W/m\(^2\)) is the heat flux, \( T_s \) (K) is the temperature of the surface while \( T_\infty \) (K) is the temperature of the fluid. \( h \) (W/m\(^2\).K) is the convective heat transfer coefficient.

1.4.3 Radiation

Radiation heat transfer is the only mode that does not require a medium for propagation. This is because it travels in the form of electromagnetic waves [19]. However, heat transport by radiation is only significant at higher temperatures because the generation of photons require high energy input. As the following equation indicates, it becomes dominant heat transfer mechanism when the temperature difference between the surface and surrounding becomes large.

\[ q = \varepsilon\sigma(T_s^4 - T_{sur}^4) \]  
\( q \) (W/m\(^2\)) is the heat flux, \( T_s \) (K) is the temperature of the surface and \( T_{sur} \) (K) is the temperature of the surroundings. \( \varepsilon \) is the emissivity of the surface and \( \sigma \) is the Stefan-Boltzmann constant, which is equal to 5.67 x 10\(^{-8}\) W/m\(^2\).K\(^4\).
1.5 Heat conduction in granular solids

Granular solids are very suitable for insulation due to their highly porous structure and high interfacial area formed between particles increasing thermal resistance.

![Figure 4: Schematic of heat conduction mechanisms in a granular solid.](image)

Figure 4 shows three mechanism of heat conduction in a granular solid. Assuming that all three terms are independent of each other, the effective thermal conductivity can be written as

\[ k_{\text{eff}} = k_s + k_c + k_f \quad (5) \] [20]

\( k_{\text{eff}} \) is the effective thermal conductivity, \( k_s \) is the conduction at the solid contacts, \( k_c \) is the coupling conduction and \( k_f \) is the fluid thermal conductivity. Radiation contribution is not included in equation 5 because it is only significant at elevated temperatures as mentioned previously. Thermal conductivity becomes exceptionally low at high vacuum (assuming no fluid is present) because heat conduction occurs only at the solid contacts according to equation 5.
1.5.1 Gaseous thermal conductivity

The thermal conductivity of air as a function of pressure is commonly described using the Kaganer relation [21], which utilizes the Knudsen number to account for the size effects on the thermal conductivity of gases [18].

\[
k = \frac{k_0}{1 + 2\beta \left( \frac{P_0}{P} \frac{l_p}{D} \right)}
\]  

(6)

\(k\) is the effective thermal conductivity of the gas, \(k_0\) is the thermal conductivity of the gas at ambient pressure, \(P_0\) represents atmospheric pressure and \(P\) is pressure. \(l_p\) is the mean free path of the gas while \(D\) is the effective pore size of the porous solid. \(\beta\) is the energy transfer efficiency constant that depends on the solid surface and the gas molecules.

![Figure 5: Thermal conductivity of air as a function of pressure.](image)

Figure 5: Thermal conductivity of air as a function of pressure.
From Figure 5, the thermal conductivity of air decreases as pressure is reduced. Furthermore, the effective pore size affects the level of pressure at which thermal conductivity of air experiences a sharp decline. This occurs because the mean free path of the gas increases as pressure is reduced. The mean free path is the average distance travelled by a gas molecule before scattered by another gas molecule. When the mean free path is increased to the point where it is comparable to the pore size or boundary size, gas molecules will start scattering significantly at the walls of the solid, which greatly disrupts the gas conduction. The heat transport is said to transition from diffusive (limited by scattering between energy carriers) to ballistic (scattering between energy carriers is negligible). [22]

1.5.2 Coupling effect on thermal conductivity

The coupling effect is defined here as the interaction between solid and fluid phase, producing an intermediate thermal conductivity. It is frequently modelled by assuming a series resistance circuit connection between the solid and fluid [23–30]. It is also related to porosity. Thermal resistance circuits are analogous to electrical circuits whereby a series connection involves heat flow through the contact surface between two components.

\[ R_t = R_1 + R_2 \]  \hspace{1cm} (7)

\[ \frac{l_t}{k_t} = \frac{l_1}{k_1} + \frac{l_2}{k_2} \]  \hspace{1cm} (8)

Parallel connection involves heat flow along the contact surface.

\[ \frac{1}{R_t} = \frac{1}{R_1} + \frac{1}{R_2} \]  \hspace{1cm} (9)

\[ k_t = k_1 + k_2 \]  \hspace{1cm} (10)

\( R \) is thermal resistance and \( k \) is thermal conductivity.
1.6 Alternative core materials

1.6.1 Diatomaceous Earth

Diatomaceous earth (DE) or Diatomite consists of skeletal remains (frustules) of diatoms, unicellular algae that populate both salt and fresh waters. DE is mainly comprised of amorphous silica (~80%) [31], which has a relatively low thermal conductivity of 1.3 W/m.K [32]. More importantly, the structure of DE highly porous as shown in Figure 6, which includes nanopores within the frustules.

![Figure 6: SEM image of DE frustules showing a hollow cylinder with periodic cavities along its walls. Particle size typically range from 2 – 200 µm.](image)

Intuitively, the porous nature of these powders makes it a good insulator. The porosity and chemical inertness also makes DE a suitable filtering medium [33]. However, limited information is available in literature regarding the vacuum insulation performance of this material. DE is also a highly abundant material and therefore very cheap [34]. Provided that a favorable composite can be produced with DE, it will prove to be a low cost alternative for VIP core materials.
1.6.2 Glass bubbles

Glass bubbles (GB) are a product of 3M™ whereby soda borosilicate glass is processed into hollow microspheres. This results in a highly porous structure with a particle density as low as 0.15 g/cm\(^3\) [35]. The particle size of the GB particles range from 20 to over 100 \(\mu\)m and the wall thickness depends on the grade of the GB used (0.7 \(\mu\)m – 1.2 \(\mu\)m).

![SEM image of K20 GB](image)

Figure 7: SEM image of K20 GB. Large particle size distribution can be observed.

Interestingly, the air inside the GB is completely enclosed by the solid. By analogy of Figure 4, the trapped air is effectively part of the solid particle. In other words, GB can be treated as solid particles that have very low thermal conductivity. Thus, it could potentially function as an ideal filler material for VIP core materials, provided that the large interparticle pores can be completely eliminated.
1.7 Modelling effective thermal conductivity

Modelling of the effective thermal conductivity of a porous solid have traditionally considers a two phase mixture, which includes a solid phase and a fluid phase [36]. Mixture equations typically assume an ideal structure that does not necessarily represent a random granular solid assemblies [37, 38].

Kunii et al. pioneered the use of a unit cell, which includes touching spheres to represent a granular solid [23]. Thermal resistance circuits were used to calculate the effective thermal conductivity from each mechanism in the unit cell. Zehner et al. followed with a cylindrical unit cell and a semi-empirical relationship that partitions the contributions of each conduction mechanism [25]. The aerogels community adopted the same approach to model effective thermal conductivity [24, 28, 29].

Horai et al. [39] applied the Hashin and Shrikmann (HS) bounds [38] to back calculate solid thermal conductivity from measured effective thermal conductivity of rocks with complex compositions. The HS bounds provide the upper and lower limit of the effective thermal conductivity. Horai et al. assumed the effective thermal conductivity to be the average between the upper and lower bounds. However, this assumption is only valid when the difference between the HS bounds is small because error associated with the effective thermal conductivity remains low. Since the difference between the HS bounds scale with the difference between the thermal conductivity of the solid and fluid phase, this method is restricted to solids with low thermal conductivity. Realizing that models mentioned above are applicable to the systems employed in this research, an improved model that is capable of predicting thermal conductivity of highly conductive solids was developed as part of this research work.
CHAPTER 2
ALTERNATIVE CORE MATERIALS FOR VACUUM INSULATION PANELS

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Abstract

Two potential alternative core materials, diatomaceous earth (DE) and glass bubbles (GB), were considered for cost effective and long life-time vacuum insulation panels (VIP). The pore size distribution of the DE was determined quantitatively by mercury porosimetry and nitrogen sorption. The majority of pores in DE centered around 1 µm. The average pore size of GB was estimated to be 50 µm via scanning electron microscopy. Subsequently, the relationship between pore size and gaseous thermal conductivity was established using the Kaganer relation. Composites of DE and fumed silica (FS) showed remarkable insulating performance whereby thermal conductivity only rose by 11 mW/m.K as pressure increased to 10,000 Pa. A similar analysis on composites of GB and fume silica showed an increment of 16 mW/m.K. It was estimated that the duration for a typical VIP to reach 10,000 Pa is approximately 50 - 100 years depending on the type of barrier used. [30] Hence, both composites are capable of providing long vacuum insulating service life. Furthermore, DE/FS composites would greatly reduce the cost of VIPs because of the inexpensive nature of DE. Both composites show superior life-time when compared to glass fibers, which are already commercially used in VIPs.
2.1 Introduction

Vacuum insulation panels (VIPs) have been an active area of research due to its ability to provide high performance insulation for a variety of applications including building, transportation and appliances. The thermal conductivity as low as 4 mW/m.K at the center of the panel have been reported, approximately 10 times lower compared to traditional insulation materials such as expanded polystyrene, which have thermal conductivity values ranging from 30 - 40 mW/m.K. [1, 2] VIPs consist of a core material that withstands compression due to pressure difference and a barrier laminate, which provides the vacuum seal for the underlying core material. Although the advent of vacuum insulation occurred more than a 100 years ago, it was mainly used for cryogenic containers known as Dewars, named after the founder of this technology. [3] Dewars utilized steel and glass barriers to enclose a hollow evacuated region because of the structural strength required to withstand pressure difference. The introduction of a core material permits the application of thin metallized polymer foils for barrier laminate. However, the Achilles heel of VIPs is its service life because the vacuum is lost over a period of time as air permeates through the thin metallized polymer foil. The rate of vacuum degradation in the panel dictates its lifetime and this is especially critical for building applications, which typically require efficient insulation for an extended period of time (30 - 50 years).

Silica aerogels are by far the best materials for vacuum insulation. [4] However the cost of production of aerogels are far too high and it lacks the mechanical strength for VIPs applications. [5] Fumed silica (FS) instead became a popular core material used for VIPs because it is similar to silica aerogel in terms of insulating ability. Although less expensive than silica aerogel, fumed silica is still a costly material (at \( \approx \$4/\text{kg} \)). [6] This creates a challenge for the widespread
application of VIPs in appliance and large scale structures due to its cost relative to traditional insulation materials. Thus, alternative core materials were introduced into the market. Glass fiber, for example, are now commonly used for VIPs because of its lower cost compared to fumed silica. [7] Glass fibers have low thermal conductivity (~30 mW/m.K) even at atmospheric pressure and have been reported to show slight improvement in terms of insulating ability compared to fumed silica at very low gas pressures (< 10 Pa). [3] However, its effectiveness quickly deteriorates when gas pressure in the panel increases above 100 Pa. [3] This behavior is highly unfavorable for VIP applications that require long service life e.g. building insulation. Polyurethane and polystyrene foams have similar shortcoming at gas pressures above 100 Pa. [8, 9] To the best of our knowledge, there are two other naturally occurring materials that have been studied as potential VIP core material. Pumice is a highly porous volcanic rock that contain pores averaging at 3.4 – 40 μm. [7, 10] Similarly, perlite is also a type of highly porous volcanic rock but it has a wider range of pores from 0.01 - 100 μm. [6, 11] Both powders were mixed with other constituents to form composites and tested for their thermal conduction properties under varying gas pressures. Since these powders are both naturally occurring and require very little processing, they serve to be low cost alternatives. In the present study, two potential composites are considered as VIP core materials. The first composite is mainly comprised of diatomaceous earth (DE), skeletal remains (frustules) of microscopic plants that are closely related to the brown algae. [12] The second material is glass bubbles (GB) produced by 3M. GBs are soda—lime—borosilicate glass that is processed into hollow spheres. [13]

The aim of the present work is to introduce DE and GB for VIP applications in comparison with glass fibers and fumed silica. Although both DE and GB had been studied for their vacuum insulating performance but composites of these materials have not been investigated. [3, 14] Thus,
composites with these materials will be characterized for their vacuum insulating performance in relation to pore structure. Specific processing requirements, addition of opacifying agents and getters for these composites are important considerations for large scale VIP manufacturing. However, these subjects are beyond the scope of this paper. The present study focuses on the potential of these composites as long life-time VIP core materials relative to fumed silica and glass fiber.

2.2 Experimental

Thermal conductivity measurements were made using a Thermal Constants Analyzer (Hot Disk TPS 1500) coupled with a 6.4 mm Kapton sensor (C5501). This instrument employs the transient plane source (TPS) technique, which as its name implies measure temperature as a function of time. By contrast, standard methods such as the guarded hot plate typically require steady state conditions whereby temperature distribution in the sample is independent of time. The relationship between temperature change ($\Delta T$), time, and thermal conductivity ($\Lambda$) for the transient plane source technique is given by Equation 1. [15]

$$\Delta T(\tau) = P_0 (\pi^{3/2} \alpha \Lambda)^{-1} D_s(\tau)$$

(1)

$P_0$ represents the heating power supplied into the sensor, $\alpha$ is the sensor radius, $\tau$ is a dimensionless time variable and $D_s(\tau)$ is a time dependent function. Thermal conductivity is extrapolated from the slope when $\Delta T$ is plotted with $D_s(\tau)$. The sample compartment of the instrument was incorporated with a bell jar vacuum chamber, which enabled measurements in controlled atmospheres and gas pressures. A schematic of the setup is shown in Figure 1.
Micromeritics ASAP 2010 was used for nitrogen gas adsorption measurements. Specific surface area was calculated using the BET method while pore size distributions were calculated using the BJH and t-plot methods. However, the BJH and t-plot methods are limited to meso- and micro- pores. Therefore, larger pores were evaluated quantitatively by mercury porosimetry (Poremaster-60). In addition, pore size was also assessed qualitatively using transmission electron microscopy (FEI Technai G2 F20) and scanning electron microscopy (JEOL JSM-6060LV). Perkin Elmer Frontier FT-MIR spectrometer was used to determine the IR transparency of the samples in the attenuated total reflectance (ATR) mode.
2.3 Materials

Diatomaceous earth (DE), also known as Diatomite, is sediments of skeletal remains (frustules) of diatoms, a common algae that is found in both salt and fresh water. The frustules are mainly comprised of amorphous silica and typically contain small amounts of lime, alumina, iron and structural water. [16] The exact composition of the frustules vary depending on the source. However, amorphous silica is always the main constituent in all cases. The range of values for the composition of DE is given in Table 1. The DE used in this study is supplied by Perma-Guard™ (PG) and Ames flower shop (EMO).

Table 1: Range of compositions of DE. [16]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>77 – 88</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1 – 8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0 – 3</td>
</tr>
<tr>
<td>CaO</td>
<td>0 – 2</td>
</tr>
<tr>
<td>MgO</td>
<td>0 – 2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0 – 3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0 – 2</td>
</tr>
<tr>
<td>H₂O &amp; organics</td>
<td>5 – 15</td>
</tr>
</tbody>
</table>
Figure 2: Electron micrographs of DE. a) SEM micrograph of DE frustules from 2 different sources. The frustule diameter and length are in the range of 5-10 μm and 10-15 μm respectively, b) TEM micrograph of DE (PG). c) Higher magnification of diatom feature showing nanostructure of the silica grains.

The structure of DE as shown in Figure 2 (a-c) is evidently very porous, which explains its low bulk density of 0.38 g/cm³. The light spots present around the cross-section of the frustules seen in Figure 2 (c) depicts the nanostructure of diatom frustule. This observation is also supported by nitrogen sorption data (see Table 2).
Glass bubbles (GB) are hollow spheres that are made of soda-lime-borosilicate glass, procured from 3M™ (Glass bubbles K15). GB have a large distribution of sizes as shown in Figure 3 (a) and it is specified by the supplier that 80% of the spheres are within 30 – 105 μm. The wall thickness of these spheres is approximately 1 μm as shown in Figure 3 (b).

Figure 3: SEM micrographs of GB. a) GB particles ranging from approximately 10 – 100 μm in diameter, b) broken GB particles with wall thickness of approximately 1 μm.

GB has a lower bulk density (0.13 - 0.17 g/cm³) compared to DE, translating to a porosity of approximately 96%. It should be noted that the gas trapped within the GB will not be evacuated as it is completely encapsulated. The composition of GB is mainly comprised of SiO₂ (60-80%), but it also contains considerable amounts of Na₂O (5-16%), B₂O₃ (0-20%), CaO (5-25%), K₂O and Li₂O (0-10%). [14]

The surface area of GB was not measured by nitrogen sorption because of its low surface area. Since GBs are known to have smooth, nonporous surface, their surface area is estimated using the following equation: [17]

$$A = \frac{3}{\rho r}$$

(2)
Whereby $A$ is the specific area, $\rho$ is bulk density and $r$ is the average particle radius. By assuming the bulk density to be 0.15 g/cm$^3$ and the average particle radius to be 30 μm, the estimated surface area was calculated to be 0.6 m$^2$/g.

Fumed silica (FS) is widely used in VIPs because of its superior insulating ability even at elevated gas pressures. FS is also known as pyrogenic silica because it is typically synthesized by pyrolysis of silicon tetrachloride. [18] As a result, the product is usually slightly contaminated with hydrochloric acid. The FS used in this study was sourced from Sigma-Aldrich (S5505). The density in powder form was specified by the vendor to be 0.037 g/cm$^3$.

![Figure 4: Electron micrographs of fumed silica. (a) SEM image of FS agglomerate. (b) TEM image of FS showing 5 –10 nm primary particles that form a network of pores ranging from 10 – 50 nm in size.](image)

From Figure 4 (a), FS exhibits submicron features indicating that it is highly porous and contain mostly meso- and micro-pores. In fact, from Figure 4 (b) the pores are estimated to be in the range of 10 – 50 nm whereas the primary particles that make up the network are 10 – 20 nm in size.
DE and FS samples were analyzed for pore size distribution by mercury porosimetry (Material Characterization Lab, Quantachrome). GB was not analyzed here because they would crush under pressure. The pore size distribution for DE and FS are presented in Figure 5.

Figure 5: Normalized pore size distribution from 0.004 -1000 μm. dV/d(log D) represents pore volume for a given pore diameter.

Figure 5 suggests that most of the pores in DE are located in the 0.1-5 μm range with a smaller portion in the 5-200 μm range. Note that below 0.01 μm (10 nm), a short peak representing nano—pores supports the TEM observation in Figure 2 (c). The highest peak found in FS ranges from 0.01-0.03 μm (10-30 nm) corresponds to pores formed by the network of primary particles viewed in Figure 4 (b). However, Figure 5 also show that pores exist between 0.1-50 μm and 90-800 μm in FS. The pores corresponding to 0.1 to 50 μm are thought to be inter-agglomerate pores while the largest pores are aberrations that stem from sample preparation and are misinterpreted to be large pores.
Table 2: Nitrogen sorption summary. A significant fraction of pores in FS are within the meso- and micro-pore range in agreement with the TEM observations in Figure 4.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)</th>
<th>Mesopore volume (cm³/g)*</th>
<th>Micropore volume (cm³/g)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE - PG</td>
<td>39</td>
<td>0.098</td>
<td>0.004</td>
</tr>
<tr>
<td>FS</td>
<td>165</td>
<td>0.54</td>
<td>0.013</td>
</tr>
</tbody>
</table>

* 2-50 nm by BJH  
** <2 nm by t-plot

Previous studies have shown that moisture adsorption plays a notable role in increasing the thermal conductivity of the core material in VIPs. [19] Thus, the effect of humidity on the thermal conductivity of DE and GB was compared to FS. Thermal conductivity measurements for each material were made under dry (<1% RH, synthetic dry air) and humid (60% RH, standard laboratory atmosphere) conditions. The increase in thermal conductivity in humid air was insignificant for GB (3.1%) whereas DE and FS corresponded to 21, and 24 %.

These measurements also indicate that both DE and FS exhibit similar percentage increase while GB showed negligible change. Relative increase in TC with humidity correlates with the specific surface area as given in Table 2. Larger surface area corresponds to a greater capacity for moisture adsorption, which acts as a thermal bridge between particles.

Radiation contributes to a fraction of the total heat transfer across a porous material. The radiative heat transfer becomes more pronounced under vacuum as gaseous conduction diminishes. Nevertheless, the contribution of IR radiation to heat transfer is minimal and thus will not be studied in detail. [6] We qualitatively assessed the IR transmission of the materials by FTIR spectroscopy.
Figure 6: FTIR spectra of DE, GB and FS. All three types of materials displayed similar peak positions due to their similarity in composition as indicated before.

The IR transmission spectra was obtained between 650 and 4000 cm$^{-1}$ but plotted only up to 2650 cm$^{-1}$. All three materials used mainly consist silica, and as a result, Si-O stretching peaks are prevalent around 1050 cm$^{-1}$. [17] The smaller peak around 800 cm$^{-1}$ corresponds to Si-O-Si symmetrical bond stretching. [20] GB produced a broader peak compared to the rest. This is attributed to variation in the environment of Si-O bonds due to the larger amounts of alkaline and alkaline earth metals in the material. DE and FS have very similar transmission spectra. All three materials have high IR transmission above 1150 cm$^{-1}$. Thus, an opacifier with high absorption above 1150 cm$^{-1}$ is generally added to reduce radiative heat transfer.
2.4 Sample Preparation

Composites of DE and GB with FS were produced at varying fractions (by weight). Samples of DE/FS mixtures were prepared by pressing the powder mixtures into cylindrical compacts. The density of the compact is dependent on the applied force. All GB/FS mixtures were only lightly compressed by placing a known weight on powder pack resulting only 0.03 psi pressure. Larger loads lead to the fracture of glass bubbles. Table 3 shows the sample compact density and estimated porosity for DE/FS mixtures according to:

\[ v_p = 1 - \frac{\rho}{\rho_0} \]  

\( v_p \) represents porosity, \( \rho \) is the compact density and \( \rho_0 \) is the true density of the material. \( \rho_0 \) was assumed to be the same for both DE and FS at 2.2 g/cm\(^3\), which is the density of silica [21]. The assumption is validated from the composition data in Table 1.

For DE/FS composites, two sets of samples were prepared, the first set was made for measurements at atmospheric pressure while the second set was involved in measurements at varying gas pressures. The applied force was varied to assess the effect of density on thermal conductivity at atmospheric pressure.
Table 3: Compact density and porosity of DE/FS composite compacts for atmospheric pressure measurements.

<table>
<thead>
<tr>
<th>DE (PG)</th>
<th>FS</th>
<th>Applied load, psi</th>
<th>Density, $\rho$ (g/cm$^3$)</th>
<th>Porosity, $v_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>796</td>
<td>0.61</td>
<td>0.72</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>764</td>
<td>0.54</td>
<td>0.75</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>732</td>
<td>0.51</td>
<td>0.77</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>700</td>
<td>0.49</td>
<td>0.78</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>668</td>
<td>0.45</td>
<td>0.8</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>477</td>
<td>0.43</td>
<td>0.81</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>255</td>
<td>0.3</td>
<td>0.86</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>191</td>
<td>0.26</td>
<td>0.88</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>477</td>
<td>0.34</td>
<td>0.85</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>477</td>
<td>0.3</td>
<td>0.87</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>446</td>
<td>0.27</td>
<td>0.88</td>
</tr>
</tbody>
</table>

For the second set of DE/FS composites, a constant applied load of 255 psi was used. This resulted in a lower density compared to the first set. The properties this set of samples are given in Table 5.

Table 4: DE/FS samples for thermal conductivity measurements under varying gas pressure.

<table>
<thead>
<tr>
<th>DE (PG)</th>
<th>FS</th>
<th>Density, $\rho$ (g/cm$^3$)</th>
<th>Porosity, $v_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>30</td>
<td>0.29</td>
<td>0.87</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.23</td>
<td>0.89</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.26</td>
<td>0.88</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0.12</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Comparing the level of applied loads, it can be inferred that DE is capable of resisting mechanical constraints incurred during fabrication similar to FS. GB on the other hand will require more attention during manufacturing if it is to be implemented as a VIP core material. However, higher strength glass bubbles are available from the manufacturer.
2.5 Thermal conductivity of porous materials

The mixtures presented in this work are assumed to be homogeneous. Furthermore, the characterization data confirms that amorphous silica is the main constituent for DE, GB and FS. Thus, the composites of these materials were assumed to be a binary mixture consisting of amorphous silica and air. This simplification permits the application of the Landauer relation to model effective thermal conductivity of the composites. [22] Although it was originally developed to model electrical conductivity of a homogeneous binary phase, it was shown to be applicable for modeling thermal conductivity as well [23]. The Landauer relation for thermal conductivity and porosity is given in Equation 4.

\[ k_{\text{eff}} = \frac{1}{4} \left[ k_{p}(3v_{p} - 1) + k_{s}(2 - 3v_{p}) + \left\{ [k_{p}(3v_{p} - 1) + k_{s}(2 - 3v_{p})]^{2} + 8k_{s}k_{p} \right\}^{0.5} \right] \]  

(4)

Whereby \( k_{\text{eff}} \) is the effective thermal conductivity of the composite, \( k_{p} \) is the thermal conductivity of the air, \( k_{s} \) is the thermal conductivity of the solid phase and \( v_{p} \) is the volume fraction of pores. Gas conduction plays a dominant role in the effective thermal conductivity of porous solids. The effective thermal conductivity falls sharply as gas pressure is reduced. The gaseous thermal conductivity as a function of gas pressure is modelled by the Kaganer relation as shown in Equation 5. [24]

\[ k = \frac{k_{0}}{1 + 2\beta \left( \frac{P_{0}}{P} \right)} \]  

(5)

\( k \) is the effective gaseous thermal conductivity, \( k_{0} \) is the gaseous thermal conductivity at standard pressure and \( \beta \) is a constant that is approximately 1.5-2. This constant represents the efficiency of energy transfer from gas molecules to solid surface. [25] \( l_{p} \) is the mean free path of gas particles at standard pressure, \( P \) represents actual pressure, \( P_{0} \) represents standard pressure (1
atm) and $D$ is the effective pore diameter. Figure 7 illustrates the Kaganer relation plotted using several pore diameters. According to Equation 5 and data in Figure 7, materials with smaller pore size will retain thermal resistance (lower thermal conductivity) to higher gas pressures, a preferred morphology for design of robust VIP.

Figure 7: Plots of the Kaganer relation at several pore diameter values, $D$. 
2.6 Results and discussion

The thermal conductivity as a function of pressure of FS, GB, DE and glass fiber (GF) is plotted in Figure 8, to compare current VIP core materials, such as GF and FS with DE and GB.

![Graph showing thermal conductivity vs pressure for DE-PG, GF, GB, and FS](image)

Figure 8: Thermal conductivity of several materials as a function of gas pressure. The numbers on the right side of each plot represent the relative volume fraction of the porosity. Also, note that the thermal conductivity approaches to a common value as pressure is lowered.

DE and GB were measured as loose powder while FS was measured in compacted form. Figure 8 clearly shows that at pressures below 200 Pa, the thermal conductivity values converge to approximately 10 mW/m.K independent of composition. This finding is consistent with literature although the values reported here are higher in comparison. [3, 7, 26, 27] The TPS technique has been reported to measure values that are higher by up to 20% for polymer foams when compared to the heat-flow method. However, that study also showed that the both techniques are capable of producing identical trends. [28] Karami et al. also reached the same conclusion in a study involving both TPS and hot plate method. [29] Thus, although the absolute accuracy of the
conductivity values maybe questioned, relative values and trends are perfectly valid and appropriate. The dependence of thermal conductivity to gas pressure for the samples in Figure 8 obeys the Kaganer relation, whereby the pore size of the samples dictate the level of pressure at which gaseous thermal conductivity is suppressed. The potential of DE and GB for vacuum insulation is clearly shown in Figure 8 but they still show higher susceptibility to thermal conductivity increase at moderate pressures. To accomplish cost effective VIPs without compromising service life, a strategy that was employed by several other groups was to mix FS with other low cost material. [6, 7] In this case, FS was mixed with DE and GB.

The thermal conductivity measurements at atmospheric pressure presented in Figure 9 were made using a separate Kapton sensor compared to vacuum measurements. This resulted in a slightly different values. However, the difference is negligible (0.002 W/m.K) which is beyond the accuracy of the instrument and the only sample that was measured using both sensors was 100% GB. Hot Disk specifies that the TPS 1500 is capable of measuring thermal conductivity from 0.01-400 W/m.K with 5% accuracy.
Composites made using different sources of DE showed similar results as expected due to their similarity in composition and morphology. Hence, it can be deduced that regardless of the source, DE would show consistent insulating properties. Although it can be inferred that larger amounts of FS results in lower thermal conductivity, the relationship between composition and thermal conductivity does not fully explain the step-like behavior in Figure 9. Instead, a more explicit trend was obtained when thermal conductivity was plotted against compact density (Figure 10). Compact density can be converted into porosity by applying Equation 3 and this allows the usage of thermal conductivity mixture models such as the Landauer relation. There was no appreciable difference between the thermal conductivity of GB/FS composites at atmospheric pressure and therefore the data was not plotted. (Thermal conductivity fluctuated around 0.039 W/m.K)

Figure 9: Thermal conductivity of DE/FS composites at atmospheric pressure. The thermal conductivities are significantly lowered with additions of FS.
Figure 10: Thermal conductivity as a function of compact density of the DE/FS composites at atmospheric pressure. (Numbers next to each data point represents the composition of the sample as mass % FS)
Figure 11: Thermal conductivity versus porosity of DE/FS composites at atmospheric pressure. Note the experimental data compares quite well to the prediction of Landauer’s relation independent of the composition. (Numbers next to each data point represents the composition of the sample as mass % FS)

The Landauer relation correlated very well with the data in Figure 11. The result suggest that regardless of composition, as long as the porosity of the material is high we will achieve lower thermal conductivity at atmospheric pressure.
Figure 12: Thermal conductivity of GB/FS composites as a function of gas pressure. Numbers in the legends represent mass % of GB in the composite mixture.

Figure 12 shows the variation of thermal conductivity as a function of gas pressure for GB/FS composites. The plots show that GB/FS composites are less sensitive to compositional variation within the range investigated. Furthermore, it seems the thermal conductivity is less susceptible to gas pressure. This is not surprising as the significant volume fraction of the composite is “encapsulated” within the glass bubbles and independent of the gas pressure. It should be noted that the 0 GB (100% FS) sample in this plot was prepared the same manner as the other GB/FS composites (refer to Sample Preparation) in order to appropriately compare the results. In agreement with the Kaganer relation, larger fractions of GB, which lead to a larger average pore size results in higher vacuum required for the suppression of gaseous thermal transport. 50% GB proves to be a potential composite given that it has a 16 mW/m.K increment in thermal conductivity as gas pressure increased to 10,000 Pa.
DE/FS composites exhibit remarkable insulating performance, which closely resemble FS as shown in Figure 13. The numbers in the legend represent the mass percent of DE mixed with FS while the porosity of the samples are labeled next of each curve. Below 200 Pa all the samples converge at approximately 10 mW/m.K. Samples containing 50% and 60% DE are very promising composites for VIP applications because they remain at 21 mW/m.K even after the gas pressure has reached 10,000 Pa. Assuming a multilayer metallized polymer is used as the barrier laminate, the pressure intake per year is approximately 100 Pa, [30] a duration of 100 years is required to reach 10,000 Pa. Thus, the results indicate that in a span of 100 years the thermal conductivity of these composites will only increase by 11 mW/m.K, making it highly suitable for long term VIP applications. In comparison to glass fiber (Figure 8), DE/FS composites evidently have
substantially longer lifetime. Furthermore, these composites serve as low cost alternatives because the commodity price of DE is approximately 10 times lower than FS. [31] The application of DE/FS composites as core materials will significantly reduce the cost of VIPs while providing insulating performance comparable to that of FS.

2.7 Conclusion

The thermal conductivity of diatomaceous earth (DE) and glass bubbles (GB) composites were studied at varying gas pressures and compositions. Both materials have unique morphology and their composites with fumed silica (FS) showed great potential for long life-time VIP applications. The relationship between thermal conductivity and porosity of DE composites was also successfully modeled using the Landauer relation. The model suggests that the thermal conductivity in DE composites at atmospheric pressure is dictated by the porosity rather than composition. The thermal conductivity of DE/FS composites containing 60% DE increased by only 11 mW/m.K when pressure increased to ambient pressure. DE costs 10 times less compared to FS, which makes it possible for widespread implementation in appliances or other high value applications and can potentially be feasible in building insulation with an appropriate barrier film. Similarly, thermal conductivity of 50% GB with FS showed an increase in thermal conductivity of 16 mW/m.K when pressure reached ambient. The cost of GB is currently higher than DE but this is largely due to its limited applications. Thus, with increased demands the price of GB is expected to be much lower. Finally, both composites have proven to be cost effective core materials that are clearly superior in terms of life-time compared to glass fibers, which are commonly used in VIPs.
2.8 Acknowledgements

We would like to thank H. Zhang & S. Oyola-Reynoso for their help in taking the TEM images and some of the SEM images used in this paper. We would also like to acknowledge B. Erickson and B. Halterman for their services in modifying the Thermal Constants Analyzer. This project was supported by Iowa Energy Center, Grant #13-04.

2.9 References


CHAPTER 3
APPLICATION OF GLASS BUBBLES IN VACUUM INSULATION PANELS

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Abstract
The adoption of glass bubbles (GB) in core materials for vacuum insulation panels (VIP) will be demonstrated in this article. GB was mixed into fumed silica (FS) and then pressed into compacts. The thermal conductivity of these compacts was compared with pure FS. Experimental results show that up to 20% (by volume) GB can be added to FS in order to produce a composite that is identical to pure FS in terms of thermal conductivity at various pressures. This result was associated with the ability of FS to form a matrix that completely envelops the GB particles, which eliminates the large interparticle pores that are responsible for gaseous conduction at low vacuum (>1000 Pa). Three-component composites were also considered whereby GB was added into diatomaceous earth (DE) and FS mixtures. It was found that DE/FS mixtures also form a matrix that completely surrounds GB particles when 10% (volume) GB is added, which resulted in a thermal conductivity that closely resembled the matrix.
3.1 Introduction

Approximately half the total energy consumed by the average household in the US is used for heating and cooling [1]. The rising cost of energy and strict government policies for greener technology boosted the popularity of vacuum insulation panels (VIP), which have 10 times lower thermal conductivity than traditional insulation materials [2]. This can be achieved because heat transfer in a vacuum is limited conduction at the particle or fiber contact points. However, there is a major disparity between the price of VIPs and traditional insulating materials. The cost of VIPs are much higher due to the core material, which is fumed silica. Low cost alternatives such as glass fibers and expanded polystyrene exist but these materials are not suitable for long term applications because of their large pore size distribution [3, 4]. Such materials rely on complex barrier laminates and getters to improve service life [5].

Traditionally, porosity is the main parameter that dictates thermal conductivity for a given material, owing to the fact that air has a very low thermal conductivity (0.0263 W/m.K). It is known that in highly porous materials, heat is primarily transmitted by gas conduction [6]. However, for vacuum insulation panels the pore size distribution also significantly affects thermal conductivity. Materials with smaller pore size are desired because they are capable of maintaining low thermal conductivity as vacuum in the panel degrades. A relationship between pore size, gas pressure and thermal conductivity developed by Kaganer was widely used to model gaseous thermal conductivity for a single pore size [7]. Reichenauer et al. modified this model to account for multiple pore sizes [8]. Their model for gaseous thermal conductivity agreed with experimental results for samples with high porosity. However, thermal conductivity of solid glass spheres were significantly higher than predicted, and they postulated that this phenomenon occurs due to the
coupling effect. The solid phase couples with the gas phase resulting in an intermediate thermal conductivity that is much higher than gaseous thermal conductivity. This effect was also observed in naturally occurring materials such as diatomaceous earth, perlite and pumice [9, 10, 11]. Swimm et al. modelled the coupling effect of aerogels using the Zehner unit cell [12, 13]. According to the model, the coupling effect is a function of porosity and intrinsic thermal conductivity of the solid. Similar methods were later adopted by other groups to model the coupling effect [14, 15]. Thus, the selection of alternative core materials for VIPs require careful considerations of both total porosity and pore size distribution.

Naturally occurring materials such as diatomaceous earth and perlite were studied for their potential as low cost core materials for VIPs [9, 10]. Composites of these materials were made with fumed silica in order to reduce pore size distribution. However, experimental results show that coupling effect still occurs in the composites, presumably due to lower porosity. If a highly porous composite can be produced while maintaining a small pore size distribution, a reduction in thermal conductivity should be realized. A possible solution is to introduce glass bubbles into the composites. Glass bubbles consist of hollow borosilicate microspheres, which result in a highly porous material [16]. Experiments have shown that coupling effect is almost unnoticeable in glass bubbles [9, 17]. In theory, air trapped within the sphere should not contribute to gaseous thermal conductivity because it is limited to heat transfer between the walls of the sphere.

In this article, it will be experimentally shown that air trapped inside of the glass bubbles do not significantly contribute to gaseous thermal conductivity. The applicability of glass bubbles in reducing the use of fumed silica in VIP core composites will also be demonstrated. Finally, the thermal conductivity of the resulting composites were related to the morphology of the composites.
3.2 Experimental

The transient plane source technique was used for thermal conductivity measurements. In this technique, a disk-shaped nickel thin film sensor is sandwiched between two samples and acts as both a resistance thermometer and heat source. Power supply into the sensor is set and the change in temperature is recorded as a function of time. Thermal conductivity is then obtained from Equation 1[18].

\[
\Delta T(\tau) = P_0 (\pi^{3/2} \alpha \Lambda)^{-1} D_s(\tau) \quad (1)
\]

\( P_0 \) is the heating power supplied into the sensor, \( \Lambda \) is thermal conductivity, \( \alpha \) represents sensor radius, \( \tau \) is a dimensionless time variable and \( D_s(\tau) \) is a complex time dependent function. Thermal conductivity is calculated from the slope when \( \Delta T \) is plotted with \( D_s(\tau) \). This technique is known to produce higher thermal conductivity values compared to steady-state methods such as the guarded hot plate and heat flow methods [19, 20]. However, the trends in thermal conductivity measured are equivalent to steady-state measurements. A bell jar vacuum chamber was used to make measurements under variable pressure, schematic of the setup was given previously [9]. The morphology of the selected samples was analyzed using scanning electron microscopy (JEOL JSM-6060LV).
3.3 Sample Preparation

The three types of powders used in this study are glass bubbles (GB), fumed silica (FS) and diatomaceous earth (DE). Powder characteristics of the samples used in this study were reported in an earlier manuscript [9]. The powders were mixed using a vibratory mill (Sweco GM18L) and then dry pressed into compacts at 255 psi. Table 1 and 2 shows the lists of all the samples prepared. In addition to the three powders mentioned, fly ash was also measured for the change in its thermal conductivity with respect to gas pressure. The fly ash data is presented in the Theory section to illustrate the coupling effect.

Table 1: Composition, density and porosity of GB/FS composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Composition by volume %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Porosity&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB (K20)</td>
<td>47 GB, 53 FS</td>
<td>0.133</td>
<td>0.94</td>
</tr>
<tr>
<td>43% GB</td>
<td>43 GB, 57 FS</td>
<td>0.142</td>
<td>0.94</td>
</tr>
<tr>
<td>40% GB</td>
<td>40 GB, 60 FS</td>
<td>0.144</td>
<td>0.93</td>
</tr>
<tr>
<td>37% GB</td>
<td>37 GB, 63 FS</td>
<td>0.136</td>
<td>0.94</td>
</tr>
<tr>
<td>34% GB</td>
<td>34 GB, 66 FS</td>
<td>0.140</td>
<td>0.94</td>
</tr>
<tr>
<td>30% GB</td>
<td>30 GB, 70 FS</td>
<td>0.154</td>
<td>0.93</td>
</tr>
<tr>
<td>20% GB</td>
<td>20 GB, 80 FS</td>
<td>0.137</td>
<td>0.94</td>
</tr>
<tr>
<td>10% GB</td>
<td>10 GB, 90 FS</td>
<td>0.145</td>
<td>0.93</td>
</tr>
<tr>
<td>FS</td>
<td>0 GB, 100 FS</td>
<td>0.130</td>
<td>0.94</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from Equation 2. <sup>b</sup>Calculated from Equation 3.

\[
\frac{1}{\rho_{GB}} (m_{GB}) + \frac{1}{\rho_{FS}} (m_{FS}) = V \quad (2)
\]

\(\rho_{GB}\) is the average particle density of K20 GB (0.2 g/cm<sup>3</sup>), \(\rho_{FS}\) is the density of FS compacted at 255 psi, \(m_{GB}\) and \(m_{FS}\) are the masses of GB and FS added in the mixture. \(V\) is the measured volume of the pressed composite.

\[
\varphi = 1 - \frac{\rho_{\text{compact}}}{\rho_{\text{SiO}_2}} \quad (3)
\]
φ is the porosity of the composite, ρ_{compact} is the density of the composite and ρ_{SiO2} is the density of amorphous silica (2.2 g/cm³).

Table 2: Composition, density and porosity of GB/60DE composites.

| Composite     | Composition (volume %)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GB (K20)</td>
</tr>
<tr>
<td>20% GB (60 DE)</td>
<td>20</td>
</tr>
<tr>
<td>10% GB (60 DE)</td>
<td>10</td>
</tr>
<tr>
<td>60 DE</td>
<td>0</td>
</tr>
</tbody>
</table>

\(\text{a}^{a}\) Calculated from Equation 2 by replacing FS with 60 DE. \(\text{b}^{b}\) Calculated from Equation 3.

60 DE is a DE/FS composite made with 60% DE and 40% FS in mass percentage, which was studied in a previous work [9]. The composite was very similar to pure FS in terms of thermal conductivity but only cost a fraction of pure FS.

3.4 Theory

Thermal conductivity of the gas phase is typically described using the Kaganer relation, which relates effective pore size, gas pressure and gaseous thermal conductivity [7].

\[
\begin{align*}
    k_{gas} &= \frac{k_0}{1 + 2\beta \left(\frac{P_0P}{P_D}\right)} \\
    (4)
\end{align*}
\]

\(k_{gas}\) is the effective gaseous thermal conductivity and it is written as a function of \(k_0\), the gaseous thermal conductivity at ambient pressure. \(\beta\) is a constant that represents the efficiency of energy transfer from gas molecules to solid surface. The value of this constant ranges from 1.5-2. \(l_p\) is the mean free path of gas particles at ambient pressure, \(D\) is the effective pore diameter, \(P\) is pressure and \(P_0\) represents atmospheric pressure.
Figure 1: Thermal conductivity of fly ash measured as a function of pressure. The contrast between the superimposed Kaganer relation and fly ash data shows the significance of the coupling effect.

Figure 1 shows the thermal conductivity of fly ash plotted as a function of gas pressure. This material has a similar morphology with GB but it is typically composed of larger amounts of alumina and has a lower porosity. Hence, coupling effect is easily observed in this material compared to GB. Below 100 Pa, gaseous thermal conductivity is negligible and heat is primarily transferred solid contact area. Thus, the superimposed Kaganer relation represents the sum of contributions between the gas phase and solid contact area. The coupling effect is described as the phenomenon whereby thermal conductivity of the material exceeds the superimposed Kaganer relation. Additional heat conduction is observed because of the interaction between the solid and gas phase. Thus, this effect is typically linked to the porosity and intrinsic solid thermal conductivity of the particles, which is the prime difference between fly ash and GB. [12-15].
3.5 Results and discussions

The thermal conductivity of glass bubbles of different grades were measured from 26 Pa to atmospheric pressure (101325 Pa). The results are plotted in Figure 2.

![Figure 2: Thermal conductivity versus air pressure of various GB. Numbers in parenthesis represent porosity of each sample.]

The difference between the three grades of GB are the density of the particles, since the particle size distributions and compositions are almost identical. Thus, the resulting porosities vary with different grades. The thermal conductivity versus pressure curves experimentally verifies that coupling effect is controlled by porosity [12-15]. The magnitude of the coupling effect is small because GBs have very high porosities. Compared to FS, the thermal conductivity of GBs starts to increase at a much lower pressure due to its larger pore size distribution.

Compacted GB/FS composites were made using K20 GB to study its applicability in VIPs. Figure 3 shows the thermal conductivity curves of the GB/FS composites. A pure FS sample was included as a benchmark for the composites. The results indicate that up to 20% GB can be added into FS to yield thermal conductivity that closely resembles pure FS. Above that, the thermal conductivity curves quickly deviates from that of FS.
The fact that the thermal conductivity of 10% and 20% GB is equal to pure FS at 1000 Pa verifies that air trapped inside GB do not contribute to gaseous thermal conductivity. Given the size of GB (20 – 100 µm), the gaseous thermal conductivity should have increased well before 1000 Pa based on the Kaganer relation if there is significant contribution from the gas trapped in the glass bubbles.

Figure 3: Thermal conductivity as a function of air pressure for GB/FS composites. The composition is given in volume percentage.

Figure 4: Thermal conductivity of GB/FS composites at 1000 Pa. 0% GB is analogous to pure FS.
1000 Pa is essentially the pressure where gaseous conduction in macropores is operational. Hence, the volume fraction of macropores in the composites correlates with the thermal conductivity as illustrated in Figure 4.

Figure 5 suggests that macropores in the composites are gradually decreasing as the amount of GB is reduced and at 20% GB, there is sufficient FS to completely fill all the macropores. Thus, further reducing the GB content produced the same thermal conductivity at 1000 Pa. This result implies that a composite can retain the thermal conductivity of pure FS, as long as macropores are eliminated.
The application of GB was also extended DE/FS composites, which in the previous study was shown to be potential low cost alternative for VIPs. Figure 6 shows the results of the addition of GB into 60/40 DE/FS composite.

Figure 6: Variation of thermal conductivity 60/40 DE/FS composites with the addition of GB as a function of gas pressure.

Figure 6 illustrates that up to 10% (volume) of 60/40 DE/FS can be replaced with GB without forming any macropores. In terms of volume, 10% GB substituted DE/FS contains only 65% FS. For a given VIP with a typical barrier film (metalized polymer), it was found that the pressure increase in the panel approximately 100 Pa per year [21]. Thus, the insulation performance of 10% GB will only begin to degrade after 10 years of usage. To compare our measurements (TPS technique) with standard measurements, we assumed that the difference between the techniques can be compensated simply by shifting the thermal conductivity versus pressure curve in the vertical axis. In other words, we only compare the rise in thermal conductivity from high vacuum to atmospheric pressure. Under these circumstances, 10% GB (60/40 DE/FS) would still meet specifications as a super insulator by ASTM standards even after 30 years of use [22].
3.6 Conclusion

Multiple grades of glass bubbles (GB) were measured for their thermal conductivity as a function of gas pressure. The applicability of GB for long life-time vacuum insulation panels (VIP) was demonstrated by measuring composites of GB and fumed silica (FS). It was found that up to 20% (volume) of GB can be added into FS to obtain a composite with almost identical thermal conductivity as pure FS. This result was linked to the microstructure of the composite whereby FS formed a matrix surrounding the GB particles, which eliminated large interparticle pores between GBs. The application of GB was also extended to composites of diatomaceous earth (DE) and FS, producing a three-component composite. In this case, 10% (volume) of GB can be added before interparticle pores were introduced into the composite. This composite, which contains only 65% (volume) of FS, was estimated to have a service life of 30 years.

3.7 Acknowledgements

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3.8 References


CHAPTER 4
MODELLING THERMAL CONDUCTIVITY OF A SOLID FROM MEASUREMENT OF GRANULAR MATERIALS

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Abstract
A method of predicting the solid thermal conductivity of granular materials is demonstrated in this article. Measurements of the effective thermal conductivity of powder slurries were taken in different liquids and a model was employed to predict the underlying solid thermal conductivity. The present model utilizes the Zehner unit cell for separating the contribution of the solid and fluid phase from the effective thermal conductivity [6]. This technique predicts the thermal conductivity of ceramic and metal particles without the use of fitting parameters. Limited number of data showed that the thermal conductivity predicted for coarser particles showed better agreement with bulk values reported in the literature, differences ranging between 0-22%. The proposed technique also showed better agreement with literature for all samples when compared to the Horai method. Presumably, interfacial thermal resistance, which occurs at the solid-fluid interface will always be embedded in the thermal conductivity by the proposed technique making it more suitable for modelling effective thermal conductivity.
4.1 Introduction

Modelling the effective thermal conductivity of granular solids had steered a great deal of interest since the past century for its applications in geology and petroleum production [1, 2, 3]. In recent years, the emergence of aerogels and vacuum insulation panels lead to a renewed interest in this subject [4, 5]. Yagi et al. and Kunii et al. [1, 2] were the first to introduce a unit cell to represent heat flow across a granular solid (Figure 1 (a)). Their unit cell considered heat conduction across two particles in point contact, whereby thermal resistance circuit, which include series and parallel connections was applied to calculate the thermal conductivity of the granular material [1]. Effective thermal conductivity was mainly partitioned into conduction through void space by the fluid phase, contact area of the solid particles, and a combination of solid with stagnant fluid near the contact surface. This combination between solid and fluid will be addressed throughout the article as the composite region (Illustrated in Figure 1 as box bound by dashed lines).
Figure 1: Two dimensional schematic representation of unit cells proposed previously. Assuming one dimensional heat transfer in the vertical direction, the dotted box represents the composite region whereby thermal conductivities of the fluid and solid phase have to be considered. The area outside the composite region represents the fluid region with the only exception being the lumped parameter model. (a) Kunii model. (b) Zehner model (Further illustrated in Figure 2). (c) Modified Zehner model. (d) Lumped-parameter model.

The thermal conductivity at the composite region was taken as the series connection between solid and fluid. Kunii approximates the layer of fluid film in between the particles to have a uniform effective thickness, a step that highly simplifies the calculation for the composite region. Obtaining the effective thickness would require more detailed description of particle packing in the compact. Finally, the effective thermal conductivity is taken as the parallel connection between thermal conductivity of the fluid and composite region. However, Kunii et al. [1] used the volume fraction of the fluid and solid phase to represent the contribution from the fluid and composite region, which is not necessarily valid because a significant portion of the fluid phase lies within the composite region. An additional term is also included in the model to account for the heat
conduction at the point contacts between particles. Nonetheless, the contribution from particle contact is only important when the fluid thermal conductivity is very small compared to solid conductivity. Zehner et al. [6] made a similar analysis by using a cylindrical unit cell enveloping the two particles in contact (Figure 1 (b)). This model is superior compared to the previous one because a semi-empirical relationship was developed that partitions the contributions from the fluid and composite region. The thermal conductivity of the composite region for this model depended on particle geometry but was also calculated based on a series connection. Hsu et al. [7] modified the Zehner unit cell by including an area-contact rather than assuming point contacts between the particles (Figure 1 (c)). The same group also developed a model known as the lumped parameter model, whereby particles were assumed to be periodically arranged resulting in a unit cell shown in Figure 1 (d) [8]. An area-contact parallel and perpendicular to the direction of heat flow was introduced between solid particles. The solid-fluid contact term was incorporated to include the contribution of the parallel area-contact while the perpendicular area-contact was treated as a secondary composite region.

The modelling of effective thermal conductivity gained popularity among the aerogel community [4, 9, 10] in the past decade although its contribution in aerogels is less pronounced due to very small particle sizes (20-100 nm) as the length scales of nano-size particles are comparable to the mean free path of phonons causing the thermal conductivity of the particle to significantly decrease due to boundary scattering [11]. The contribution from the composite region to the overall thermal conductivity was termed by the aerogel community as the coupling effect. Swimm et al. [9] was the first group to include this effect into the model. They applied the Zehner unit cell and modelled the composite region by assuming spherical particles. Zhao et al. [10] provided a detailed list of models for gaseous thermal conductivities in a porous
media and they essentially used a similar model as Swimm but instead of analyzing individual particles (primary particles), they lumped groups of primary particles into a larger secondary particle that consist of micropores. Bi et al. [4] calculated the coupling effect for aerogels by applying a model by Cheng et al. [14], which is essentially the Hsu et al. [7] model except more geometries were analyzed. All three groups mentioned here modelled the coupling effect by applying the same thermal resistance circuit models that were developed before but use air as the fluid phase and plotted thermal conductivity as a function of gas pressure.

The models previously mentioned focused predicting effective thermal conductivity assuming that the solid and fluid thermal conductivities are known. However, for materials with complex compositions such as alloys and rocks, the solid thermal conductivity is not always a given value. Horai et al. [15] applied the Hashin and Shtrikman bounds [16] for predicting mixture properties to predict solid thermal conductivity of granular rocks. The thermal conductivity of granular rocks was studied using water as the fluid phase. However, the Hashin and Shtrikman bounds was originally derived for calculating effective magnetic permeability and hence, do not take the structure of a granular solid into account. Furthermore, Horai et al. assumed the effective thermal conductivity to be an average of the upper and lower bounds. This assumption does not hold when thermal conductivity of the solid is significantly larger than the fluid, which limits this technique to solids with low thermal conductivity.

In this article, we demonstrate a new technique to determine solid thermal conductivity of granular solids whereby its applicability extends to more conductive solids such as metals. Effective thermal conductivity of granular solids will be measured in several stagnant fluids with different thermal conductivity and a model, which combines the Zehner unit cell and Kunii approximation will be used to predict solid thermal conductivity. Unlike the previous models
mentioned before, particle contact parameters are not required because heat transfer at the particle contacts will be shown to be negligible when liquids such as alcohol and water is used as the fluid phase. The results obtained will be compared with those of Horai method and known thermal conductivity of solids reported in literature.

4.2 Theory

Horai et al. (1969) first used the Hashin and Shtrikman (HS) bounds to model thermal conductivity of rock forming minerals [17]. Rocks were first crushed into smaller particles and mixed with water. The effective thermal conductivity of the sample was then measured using a needle probe. The HS bounds represents the upper and lower limit of the effective thermal conductivity for a given mixture and the separation between the bounds is proportional to the difference in thermal conductivity between the solid and fluid phase. Upper and lower bounds for thermal conductivity of the solid-water mixture are given by:

\[
k_U = k_m + \nu \left( \frac{1}{k_w - k_m} + \frac{1-\nu}{3k_m} \right)^{-1}
\]

\[
k_L = k_w + (1-\nu) \left( \frac{1}{k_m - k_w} + \frac{\nu}{3k_w} \right)^{-1}
\]

Whereby \(k_m\) is the solid thermal conductivity, \(k_w\) is the thermal conductivity of water and \(\nu\) is the volume fraction of water. \(k_U\) and \(k_L\) represent the thermal conductivity at the upper and lower bounds. The solid thermal conductivity was solved from the HS bounds by assuming effective thermal conductivity is equal to the average of the upper and lower bounds. This assumption is only appropriate when the separation between the upper and lower bound is sufficiently small because this limits the amount of error associated with the effective thermal conductivity.
conducivity. In other words, given that fluids typically have low thermal conductivity, the technique is not suitable for highly conductive solids such as metals.

The technique introduced in this article utilizes the Zehner unit cell for a bed of packed spheres in order to separate the solid and fluid contributions to overall thermal conductivity. The unit cell is cylindrical in shape and consists of two spherical particles connected by a point contact as shown in Figure 2. The model presented here will take advantage of the thermal conductivity at the composite regions (labelled as inner cell in Figure 2) whereby both the solid and fluid thermal conductivities have to be taken into account.

Figure 2: Zehner unit cell with composite region in cylindrical shape.

The cylinder is divided into two sections, outer and inner cells. The outer cell represents a region of pure fluid conduction, the inner cell has both solid component and fluid component, which constitute the composite region. For heat flow in the vertical direction, the outer and inner cylinders are concentric while within the inner cylinder, the solid and fluid components are
connected in series. Thus, the effective thermal conductivity of the unit cell can be written as parallel resistance circuit between the outer and inner cell,

\[ k_{\text{eff}} = f_0 k_o + f_i k_i \]  

(3)

Where \( k_{\text{eff}} \) is the effective thermal conductivity of the unit cell, \( k_o \) and \( k_i \) are the thermal conductivities of the outer and cells respectively and \( f \) corresponds to the fraction contributed by each cell. Equation 3 neglects the heat transfer at the contact points between particles because this heat conduction mechanism is insignificant especially when a liquid is used for the fluid phase rather than air as the effective thermal conductivity becomes much greater in comparison. This is experimentally verified by taking measurements of several granular solids in vacuum as shown in Figure 3.

![Figure 3: Thermal conductivity measured as a function of air pressure for granular solids.](image-url)
Thermal conductivity of all 4 materials converge at 0.02 W/m.K as pressure is reduced to 26 Pa because heat conduction is limited at the particle contact points. Typically, the effective thermal conductivity is 2 orders of magnitude higher than this value when a liquid is used as the fluid phase instead of air.

Zehner et al. [6] determined semi-empirically that porosity (\( \emptyset \)) is related to cell coefficient, \( f_i \), as shown below.

\[
f_i = \sqrt{1 - \emptyset}
\]  

(4)

Thus, Equation 3 transforms into

\[
k_{eff} = (1 - \sqrt{1 - \emptyset})k_o + (\sqrt{1 - \emptyset})k_i
\]

(5)

\( k_o \) can be taken as the thermal conductivity of the fluid while \( k_i \) incorporates both solid and fluid phases. The Kunii approximation is adopted whereby the solid component within the inner cell is approximated to be cylinders rather than spheres as illustrated in Figure 4. The net consequence of this approximation is that volume fraction in the direction of heat flow now has a fixed thickness and an average thermal conductivity can be assigned (Figure 4 (a)).
Figure 4: (a) 2 dimensional representation of the approximation from sphere to cylinder. Only half of the cell needs to be analyzed because the cell can now be simplified into two equal halves represented by the dotted line. (b) 3 dimensional view of the modified unit cell. This model is a combination of the Zehner et al. and Kunii et al. models.

Thermal conductivity of the inner cell can now be expressed as a series resistance circuit,

\[
\frac{1}{k_i} L_{total} = \frac{1}{k_1} L_1 + \frac{1}{k_2} L_2
\]  

(6)
$L_1$, $L_2$ and $L_{total}$ are the effective lengths for the solid component, fluid component and total length (Figure 4 (a)), $k_1$ is the thermal conductivity of the solid component and $k_2$ is the thermal conductivity of the fluid component of the inner cell. Thus, $k_2$ can be assumed to be equal to thermal conductivity of the fluid, $k_f$.

Assuming that $L_1 >> L_2$, ($L_{total} \approx L_1$) and dividing Equation 7 by $L_{total}$ will result:

$$\frac{1}{k_i} = \frac{1}{k_1} + \frac{1}{k_f} \frac{L_2}{L_{total}} \quad (7)$$

Substituting Equation 7 into Equation 5,

$$k_{eff} = (1 - \sqrt{1 - \varnothing}) k_f + (\sqrt{1 - \varnothing}) \left( \frac{1}{k_1} + \frac{1}{k_f} \frac{L_2}{L_{total}} \right)^{-1} \quad (8)$$

Thermal conductivity of the inner cell, $k_i$ can be calculated from measured thermal conductivity, $k_{eff}$, and porosity of the powder using Equation 5. Then plotting $\frac{1}{k_i}$ against $\frac{1}{k_f}$ as shown in Equation 7, will produce a straight line with its slope equal to $\frac{L_2}{L_{total}}$ and the intercept $\frac{1}{k_1}$ yields $k_i$, thermal conductivity of the solid particle. Thus, this model allows determination of the thermal conductivity of solid phase. It essentially requires information about the porosity of the compact and the measured effective thermal conductivity values in several non-reactive liquids.

**4.3 Experimental**

The Thermal Constants Analyzer (Hot Disk TPS 1500) which utilizes the transient plane source (TPS) technique was used to measure thermal conductivity. Details of the technique are described by Gustafsson. [18] The particle size distribution of the samples was assessed qualitatively with scanning electron microscopy (JEOL JSM-6060LV) and quantitatively by light blocking centrifugal sedimentation technique (Horiba CAPA-700). Surface area of the powders
was determined by BET method from nitrogen sorption measurements (Micromeritics ASAP 2010). A set of 12 powders with a broad range of bulk thermal conductivities (2-400 W/m.K) were used to experimentally verify the model presented above. The powders used had a variety of particle sizes as this was not accounted for in the model. Conversely, porosity is required in order to make proper calculations. This value is computed by comparing the powder’s tap density with its corresponding true density. Each powder is tested in five liquids with varying thermal conductivities. The five liquids were selected from the following list: water (0.599 W/m.K), ethylene glycol (0.256 W/m.K), ethanol (0.166 W/m.K), acetone (0.157 W/m.K), isopropanol (0.14 W/m.K), toluene (0.133 W/m.K), and heptane (0.126 W/m.K) [19].

Table 1 summarizes the powders measured in this study. The average particle radius ranged from 1-1250 µm. The surface density is defined in this study as the product of the specific surface area and tap density. This value is a measure of surface area per volume of powder, which embodies quantitative information of the amount of solid liquid interfaces present in the sample. The specific surface area of larger particles were estimated using the equation below as their surface area is too small to be determined by nitrogen gas adsorption.

\[
A = \frac{3}{\rho r}
\]  
(9)

Whereby \(A\) is the specific surface area \((\text{m}^2/\text{g})\), \(\rho\) is the density \((\text{g/cm}^3)\) and \(r\) is the radius \((\mu\text{m})\) of the particle.
Table 1: Characterization data of granular solids used in this study. Surface density is the product of tap density and specific surface area. It is equivalent to volumetric specific surface area.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tap density (g/cm³)</th>
<th>Specific surface area (m²/g)</th>
<th>Surface density (cm⁻¹)</th>
<th>Average particle radius (µm)</th>
<th>True density (g/cm³) [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>1.95</td>
<td>&lt;0.01⁸</td>
<td>21</td>
<td>500ᵃ</td>
<td>5.60</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.26</td>
<td>0.01ᶜ</td>
<td>174</td>
<td>100ᵃ</td>
<td>2.17</td>
</tr>
<tr>
<td>Ni</td>
<td>4.82</td>
<td>0.01ᶜ</td>
<td>464</td>
<td>35ᵃ</td>
<td>8.90</td>
</tr>
<tr>
<td>SiO₂ (quartz)</td>
<td>1.71</td>
<td>0.01ᶜ</td>
<td>194</td>
<td>100ᵃ</td>
<td>2.64</td>
</tr>
<tr>
<td>KBr</td>
<td>1.52</td>
<td>0.01ᶜ</td>
<td>166</td>
<td>100ᵃ</td>
<td>2.75</td>
</tr>
<tr>
<td>Nb</td>
<td>5.56</td>
<td>&lt;0.01ᶜ</td>
<td>39</td>
<td>500ᵃ</td>
<td>8.57</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.88</td>
<td>&lt;0.01ᶜ</td>
<td>11</td>
<td>1250ᵃ</td>
<td>3.97</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.97</td>
<td>7.20ᵈ</td>
<td>69840</td>
<td>0.5ᵇ</td>
<td>6.95</td>
</tr>
<tr>
<td>ZrB₂</td>
<td>1.39</td>
<td>2.20ᵈ</td>
<td>30580</td>
<td>1ᵇ</td>
<td>6.09</td>
</tr>
<tr>
<td>Cu</td>
<td>5.20</td>
<td>0.06ᵈ</td>
<td>3120</td>
<td>1ᵇ</td>
<td>8.92</td>
</tr>
<tr>
<td>430 L stainless steel</td>
<td>4.44</td>
<td>0.10ᵈ</td>
<td>4440</td>
<td>2ᵇ</td>
<td>7.74</td>
</tr>
<tr>
<td>Al</td>
<td>1.00</td>
<td>0.03ᶜ</td>
<td>317</td>
<td>35ᵃ</td>
<td>2.70</td>
</tr>
</tbody>
</table>

ᵃ Determined by image analysis from SEM micrographs.ᵇ Measured by light blocking centrifugal sedimentation.ᶜ Estimated using Equation 9.ᵈ Measured by nitrogen sorption.

4.4 Results and discussions

Thermal conductivities, \( k_i \) and \( k_f \) for each liquid are computed from the effective thermal conductivity using Equation 3. A linear trend line is produced by plotting \( \frac{1}{k_i} \) and \( \frac{1}{k_f} \), to determine the thermal conductivity of the solid phase, \( k_f \).
Figure 5: Plot of $\frac{1}{k_i}$ versus $\frac{1}{k_f}$ for various powder slurries. The inverse of the y-intercept of each trend line represents the corresponding solid thermal conductivity while the slope of each line is equivalent to $\frac{L_2}{L_{\text{total}}}$. 

The value of the slopes in Figure 5 ranged from 0.05-0.14, which validates the assumption that $L_1$ is approximately equal to $L_{\text{total}}$. Furthermore, the coefficient of determination for each set of data is above 0.9. Water is not used in some cases due to the reactivity of the sample. For example, NaCl and KBr are soluble in water while copper and niobium were excluded because they were found to be partially hydrophobic.
Table 2 summarizes the predictions using the present model in comparison with the Horai model and literature values. Our model accurately predicted (<10% difference) the thermal conductivities of NaCl, Ni, KBr and Al₂O₃. However, predictions for SnO₂, ZrB₂, Cu and stainless steel were not accurate, differing from literature values by as much as 80%.

The inaccurate predictions were attributed to the surface density of the samples given in Table 1. The model derived in the theory section assumes that there is no interfacial thermal resistance between the solid phase and the fluid phase. This is also supported by the fact that the model under predicts thermal conductivity for all samples. The effect of interfacial thermal resistance is especially pronounced in samples with fine particle size due to their larger surface density compared to coarse particles, which resulted in large deviations from the literature values.

On the positive side, with the effects of interfacial thermal resistance embedded into the predicted thermal conductivity, these values could potentially be more appropriate for modelling effective thermal conductivity. The only exception among the samples tested is aluminum. During the
course of the experiment, it was observed that the aluminum sample reacted with the liquids. This was verified using energy-dispersive x-ray spectroscopy whereby oxygen content increased by approximately two-folds after exposing the powder to water suggesting that the surface of aluminum had undergone a reaction with the liquids used. This explains the inaccurate prediction of the thermal conductivity of this material despite having a relatively low surface density. Thus, liquids that react with reactive powders will not produce accurate thermal conductivity values and should not be employed.

The Horai model, which utilizes the Hashin and Shrikmann bounds were found to be accurate for samples with lower thermal conductivity. For example, thermal conductivity of NaCl, quartz, KBr and alumina from the Horai model are within an acceptable range. However, highly conductive materials such as nickel suffered from 85% error compared to the present model, which predicted a value within 6% of that reported in literature. As mentioned in the theory section, the Horai method is only suitable for solids with low thermal conductivity because of the limitations of the HS bounds. To summarize, the present model showed better agreement with literature for all samples tested in this study compared to the Horai model.
4.5 Conclusion

The Zehner unit cell was coupled with the Kunii approximation to produce a practical model, which allows the prediction of the thermal conductivity of a solid from its powder or granular form [1, 6]. The technique requires only effective thermal conductivity measurements and porosity. The powders used in this study were immersed in common liquids to produce a range of effective thermal conductivities. Coarser particles were shown to be more accurately predicted by the model due to insignificant interfacial thermal resistance between the liquid and solid compared to fine particles. Predictions of coarse particles were in good agreement with literature values for materials with a wide range of thermal conductivity, from zirconia (0.8-2.2 W/m.K) to nickel (90 W/m.K).

4.6 Acknowledgement

We would like to thank A. Quah and M. Lee for their assistance in schematic illustrations of the unit cells. We would also like to thank L. Jones for supplying metal samples. This project was supported by Iowa Energy Center, Grant #13-04.

4.7 References


CHAPTER 5
GENERAL CONCLUSIONS

A major hurdle preventing the widespread implementation of vacuum insulation panels (VIP) for appliances, transportation and building systems is the excessively high cost of this product relative to traditional insulation. Fumed silica is the most common core material and it constitutes more than half the cost of a VIP. Efforts in reducing the cost of VIP by using low cost core material can be found in literature, however life-time is typically sacrificed because these materials are more sensitive to vacuum degradation in the panel. Thus, the prime objective of this thesis was to formulate a low cost core material for long-life VIP applications, in particular we focused on granular materials. Assuming that radiation heat transfer is negligible, heat conduction across a granular solid can be broken into three paths: solid contact, fluid, and coupling between solid and fluid. When no fluid phase is present (vacuum), heat conduction becomes tremendously low because the only remaining path for conduction is through the solid contacts, which is the operating principal of VIP. For porous particulate materials such as fumed silica, the solid contact area is exceedingly small leading to very low solid thermal conductivity. Thus, as long as an appropriate vacuum is maintained, most granular materials display great insulating ability. This is experimentally shown in Chapter 4 whereby the thermal conductivities of metal powders were measured in vacuum. However, long-life VIP core materials need to retain thermal insulation characteristics upon degradation of vacuum. As gas diffuses into the panel, the thermal conductivity of these metal powders quickly rises above that of traditional insulation materials.

Kaganer relation shows that gaseous thermal conductivity is sensitive to pore size distribution of the granular material. Materials with smaller pore size are able to maintain high
thermal insulation with increase in gas pressure before the thermal conductivity increases appreciably. Thus, this property is highly desired for long-life VIP applications. Coupling conduction is affected by porosity, as well as intrinsic solid and gaseous thermal conductivities. Chapter 3 experimentally verifies the effect of porosity on coupling by comparing the thermal conductivity of glass bubbles with different porosities while Chapter 4 shows that the intrinsic solid conductivity is embedded in the effective thermal conductivity of a granular material.

Fumed silica (FS) fulfils all three criteria making it a highly suitable as a long-life VIP core material. A strategy was employed to reduce the use of FS was to make composites by mixing with alternative materials. Diatomaceous earth (DE) and glass bubbles (GB) were studied for their potential as VIP core materials. DE, which consist of mostly amorphous silica (80 – 90%) is a naturally occurring material with that is highly porous as seen under a scanning electron microscope (SEM). Results from mercury porosimetry and transmission electron microscopy showed that DE contains a wide range of pore sizes (0.01 – 10 µm). GBs are sodium borosilicate glass processed into hollow microspheres with particle sizes ranging from 30 – 100 µm. The pore size was qualitatively determined to be in the same range as the particle size via SEM. Mercury porosimetry was not performed on GB due to its fragility. Composites with a series of compositions were made to identify the optimum ratio. For DE/FS composites, the balance between cost and life-time was optimized at 60/40 (by mass). Volume fractions could not be expressed as true density of DE is not available and variable from batch-to-batch. GB/FS composites remains as long-life core materials up to 20/80 (by volume). Experimental results in Chapters 2 & 3 showed that long-life insulation requires sufficient FS to surround added DE or GB particles, thus filling majority of the large pores in the composite with nanoporous FS.
Through measuring the thermal conductivity of granular materials of different compositions, it was found that the intrinsic solid thermal conductivity played a large role in determining the effective thermal conductivity of the solid. Given that the contribution of the solid is embedded in the coupling effect, a model was successfully developed to predict the intrinsic solid thermal conductivity from effective thermal conductivity measurements. Assuming that conduction at the solid-solid contact is negligible, the Zehner unit cell [25] was used to separate the contributions of fluid and coupling conduction. The proposed model achieved an average accuracy of 10% for coarse particles (>75 µm). However, fine particles (<2 µm) were not as well predicted in comparison and this was associated with the fact that interfacial thermal resistance is not taken into account in the model. The effect of interfacial thermal resistance is more pronounced in fine particles because they contain more interfaces between solid and fluid compared to coarse particles.

In conclusion, this thesis explored the possibility for FS reduction using two potentially low cost alternatives, DE and GB. Furthermore, not only that the optimized compositions were found for DE/FS and GB/FS composites but the criteria for long-life VIP core materials was also established through the understanding of heat conduction mechanisms in a porous material. In addition, a practical method for determining solid thermal conductivity that is accurate for coarse particles was developed.
REFERENCES


APPENDIX

RELATIONSHIP BETWEEN THERMAL CONDUCTIVITY AND R-VALUE

R-value refers to the thermal resistance of a given material. Thus, it depends not only on thermal conductivity of the material but also its thickness. R-value is typically used in industry to compare the insulative ability of different materials. Also, this number is typically reported assuming one inch thickness unless otherwise stated.

\[ R = \frac{1}{k} \times t \]

Whereby \( k \) is thermal conductivity and \( t \) is the thickness of the material. In the US, it is customary to use imperial units instead of SI units when reporting this value. Conversion between the two units is given below.

<table>
<thead>
<tr>
<th>SI</th>
<th>US</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 , \frac{m^2K}{W} )</td>
<td>( 5.678 , \frac{hr ft^2.\circ F}{Btu} )</td>
</tr>
</tbody>
</table>

Hence, the R-value in imperial units for materials such as fiberglass and expanded polystyrene (30 – 40 mW/m.K) range from 3 – 5. VIPs (3 – 4 mW/m.K) on the other hand, can have R-values up to 50 in comparison.