Effective thermal conductivity modeling of consolidated sorption composites containing graphite flakes

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1. Introduction

Heat-driven sorption technology, as a sustainable and clean solution for thermal management and heat storage, has drawn significant interest in academic and industrial research community. This interest has been intensified in the last decade as environmental and climate changes issues are becoming major global challenges. Numerous studies aim to improve material sorption performance, as it is at the core of sorption cooling or storage systems [1]. Due to the nature of sorption process, heat transport properties, e.g. thermal diffusivity and thermal conductivity, of the adsorbent material plays an important role in their performance, since increasing thermal diffusivity can enhance the heat transfer rate that leads to faster sorption/desorption cycles thus more efficient (more compact) heat-driven sorption chillers [2]. A key part of the sorption chillers design is developing adsorbent materials (or composites) with superior hydrophilicity, high water uptake capacity, low regeneration temperature (60–150 °C) [3], and high thermal diffusivity. Silica gel [4] and silicoaluminophosphate [5] have suitable adsorption properties at operating conditions of water-based sorption cooling systems, i.e. low temperature (30–90 °C) and pressure (1.2–5.6 kPa); however, these highly porous sorbents have low effective thermal conductivity 0.13 W m⁻¹ K⁻¹ [6]. Methods used to improve heat transfer in sorption beds include: (i) coating heat exchanger with adsorbent material [2], this will reduce the thermal contact resistance at the interface between the heat exchanger and the coated sorption material; (ii) growing adsorbent on the adsorber bed surface [7]; (iii) adding thermally conductive materials such as metals [8] and consolidating adsorbents in a thermally conductive porous matrix [9], which lead to an increase in the bulk thermal conductivity of sorption composite. The effective thermal conductivity of a wide range of adsorbents reported in the literature is shown in Table 1.

Tanashev et al. [9] measured the thermal conductivity of hygroscopic salts (CaCl₂ [10], LiBr and MgCl₂) confined silica gel (KSK) with 0.1–0.8 g/g water content using the transient hot wire method at 290–300 K and observed an increase in thermal conductivity from 0.1 to 0.5 W m⁻¹ K⁻¹ with increasing water content. Aristov et al. [11] measured the thermal conductivity of consolidated sorbents, silica gel (KSK) with 36.6 wt% CaCl₂ and silica gel (KSK) with 42.7 wt% LiBr and reported that the thermal conductivity increased significantly as the water uptake of the sorbent increased, while the effect of temperature and pressure on thermal conductivity was almost negligible. Restuccia et al. [12] developed and experimentally validated a theoretical model to predict the effective thermal conductivity of wet zeolite. The effective thermal conductivity of zeolite 4A was measured by a hot wire method at different temperatures and water content. All the above-
mentioned studies showed a significant effect of water content on the thermal conductivity of sorption composites. Fayazmanesh et al. [16] synthesized consolidate composite with addition of copper powder and graphite flakes. Graphite flake particles are distributed evenly in composite adsorbent when copper powder particle inhomogeneously distributed at the bottom surface of samples.

As shown in Table 1, composite adsorbent with expanded graphite has higher thermal conductivity compared to silica or zeolite based composites. This is while the thermal conductivity

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Thermal conductivity of some adsorbent materials.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>Thermal conductivity, W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Calcined silica gel (KSK)/CaCl₂</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>- Consolidated silica gel (KSK)/CaCl₂ (36.6 wt%)</td>
<td>0.12–0.16</td>
</tr>
<tr>
<td>- Consolidated silica gel (KSK)/LiBr (42.7 wt%)</td>
<td>0.1–0.13</td>
</tr>
<tr>
<td>Consolidated silica gel (15 wt% binder)</td>
<td>0.24–0.26</td>
</tr>
<tr>
<td>- Compressed silica gel (KSK)/CaCl₂</td>
<td>0.12–0.5</td>
</tr>
<tr>
<td>- Compressed silica gel (KSK)/LiBr</td>
<td>0.16–0.4</td>
</tr>
<tr>
<td>- Compressed silica gel (KSK)/MgCl₂</td>
<td>0.14–0.42</td>
</tr>
<tr>
<td>- Alumina/CaCl₂</td>
<td>0.12–0.41</td>
</tr>
<tr>
<td>Wetted zeolite 4A</td>
<td>0.17–0.25</td>
</tr>
<tr>
<td>- Consolidated composite activated carbon</td>
<td>1–4</td>
</tr>
<tr>
<td>- Consolidated silica gel (15 wt% binder)-graphite flake (6–20 wt%)</td>
<td>0.13–0.42</td>
</tr>
<tr>
<td>Consolidated composite activated carbon</td>
<td>0.9–2.5</td>
</tr>
<tr>
<td>- CaCl₂ (powder)</td>
<td>0.31–0.39</td>
</tr>
<tr>
<td>- CaCl₂ (pellet)</td>
<td>0.11–0.14</td>
</tr>
<tr>
<td>- Composite-KP50 expanded graphite (20%) and CaCl₂</td>
<td>0.4–0.47</td>
</tr>
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<td>- Consolidated composite- KP50 expanded graphite (20) and CaCl₂</td>
<td>0.31–0.47</td>
</tr>
<tr>
<td>- Different pressure applied for making consolidated samples (0–0.67–20)</td>
<td>- Dry samples</td>
</tr>
</tbody>
</table>
of silica-/zeolite-based composites are already increased considerably by adding activated carbon.

The objective of this work is to develop a model to predict the effective thermal conductivity of consolidated composite adsorbent containing graphite flakes, considering random orientation of the graphite flakes. Assuming an effective medium theory (applied for thermal conductivity modeling of nano-fluid [13] and catalyst layer in polymer electrolyte membrane fuel cell [14]) and establishing upper and lower bounds, as asymptotes for thermal conductivity, a new model is developed for the effective thermal conductivity of consolidated adsorbent material containing graphite as a function of the volume fraction and orientation of the graphite flakes. Several consolidated samples have been fabricated in our lab and tested to validate the proposed model.

2. Experimental study

2.1. Sample preparation

Silica gel (SiliaFlash® B60, Lot 011112, Silicycle, Inc., Quebec, Canada) with irregular shaped grains (0.2–0.5 mm), average pore diameters of 6 nm and surface area (S BET) 514 m²/g was combined with different amount of graphite flakes (Sigma Aldrich, +100 mesh) and 40,000 MW polyvinylpyrrolidone (PVP40, Amresco) binder solution. The slurries were baked for one hour at 50 °C, and then heated to 180 °C for one hour to cross-link the binder. Table 2 shows silica gel composites based adsorbent prepared with different amount of graphite flakes 0–20 wt%.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Adsorbent</th>
<th>PVP</th>
<th>Graphite flakes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂-S6-0%G</td>
<td>4 g, 1.71 g</td>
<td>1 g</td>
<td>–</td>
</tr>
<tr>
<td>CaCl₂-S6-5%G</td>
<td>4 g, 1.71 g</td>
<td>1 g</td>
<td>0.35 g</td>
</tr>
<tr>
<td>CaCl₂-S6-10%G</td>
<td>4 g, 1.71 g</td>
<td>1 g</td>
<td>0.74 g</td>
</tr>
<tr>
<td>CaCl₂-S6-20%G</td>
<td>4 g, 1.71 g</td>
<td>1 g</td>
<td>1.67 g</td>
</tr>
</tbody>
</table>

Fig. 1. (a) Sample arrangement schematic in TPS 2500S. (b) Nickel double spiral insulated in a thin layer of Kapton sensor (Sensor 7577).

2.2. Thermal conductivity measurement

A thermal constants analyzer (TPS 2500S, ThermTest Inc., Fredericton, Canada) capable of precise measurement of thermal conductivity, diffusivity and specific heat was used for this study. The instrument has different sensor types and software modules to perform measurements on bulk materials (isotropic and anisotropic), thin films, powders and liquids. This apparatus uses the transient plane source method in accordance with ISO Standard 22007-2.2. In this study, a bulk sensor (7577) with a 2 mm diameter nickel double spiral insulated in a thin layer of Kapton is used for both transient heating of the sample and temperature measurements. A humidifier (P-10C-1C-2-0-031300-v7, Cellkraft AB, Sweden) is connected to thermal constant analyzer to control the humidity inside the TPS chamber.

For bulk material (isotropic) measurements, the sensor is placed on either side of a pair of dried identical samples. After 20 min for temperature and 2% RH humidity equilibration, measurements are...
performed on each sample three times at different locations, a standard deviation of 10\% has been measured. The sample-sensor assembly is shown in Fig. 1.

Effective thermal conductivity of the sample is calculated by

$$k_{\text{sample}} = \frac{\dot{Q}}{A \Delta T}$$

where $\dot{Q}$ is the power from the heat source, $\Delta T$ is the temperature rise between the sensor and sample, $A$ is the sensor area, and $t_{\text{sample}}$ is the sample thickness.

2.3. Geometrical parameters of the consolidated graphite-doped composite

Geometrical parameters, i.e. the particle size distribution and graphite flakes size should be measured to be used as input to the model. An optical microscope (Nikon Eclipse LV100) is used to measure the shape and size distribution of 100 graphite flakes, shown in Fig. 2.

Fig. 2 illustrates that the graphite flakes have irregular shapes which make it difficult to use one geometry and one size for geometric modeling. In this study, graphite flakes are assumed to have a disk shape with a diameter, estimated through statistical measurements. The statistical distribution of graphite flakes effective diameter is shown in Fig. 3. The average thickness and diameter for 100 measured graphite flakes is calculated to be 4.3 and 700 $\mu$m, with standard deviation of 7\%.

3. Model development

Fig. 4 shows a comparison between the existing models in the literature, listed in Table 3, and the present data for thermal conductivity.

As shown in Fig. 4, Maxwell and Hamilton-Crosser models can only predict the thermal conductivity for the sample with 5 wt\% and fail to predict higher graphite flake concentrations.

3.1. Bounds of conduction for disk shape particle in basic unit cell

In this section, following the methodology introduced in [13], upper and lower bounds for steady-state through-plane heat conduction in consolidated composite containing graphite flakes...
samples are established for horizontally and vertically oriented disk-shaped flakes, as schematically shown in Fig. 5. A “unit cell” is considered to represent the geometry of the consolidated composite with the dispersed graphite flakes. The size of unit cell depends on the volume fraction of flakes in each sample, and it is calculated using the density of particles and continuous medium. The model is compared to experimental data collected from consolidated composite adsorbent samples, to ensure that the data lays between the upper and lower bound and it is then expanded for particles with a range of orientation angles in a continuous medium.

The assumptions used in development of the present are:

- Identical disk-shape graphite flakes are evenly dispersed throughout the composite.
- The contact between the graphite flakes and the sorption material is perfect, i.e. no thermal contact resistance is considered.
- The sorption material and graphite flakes have constant anisotropic properties, listed in Table 4.

The sorption material in the composite used in this study is CaCl₂-silica gel-PVP40.

3.2. Unit cell with disk particles

3.2.1. Lower bound: perpendicular to the heat flow

A lower bound for effective thermal conductivity, and its associated thermal resistance network, can be established by assuming isotherms perpendicular to the direction of heat flow, as shown in Fig. 6.

Based on the thermal resistance network shown in Fig. 6, the lower bound of effective thermal conductivity of the consolidated composite can be found from Eq. (2)
To calculate $R_2$ and $R_3$, a new parameter introduced named as $L_g$:

$$L_g = 2\sqrt{r^2 - d_e^2}$$

(3)

Then, the total $R_2$ and $R_3$ can be calculated from

$$R_2 = \frac{1}{2\tau} \int_0^\tau \left[ \frac{a - L_{g2}}{k_e} + \frac{L_{g2}}{k_p} \right] d(d_e)$$

(4)

The upper bound effective thermal conductivity can be calculated:

$$k_{\text{eff},u} = \frac{a \int_0^\tau \left[ \frac{a}{k_e} + \frac{L_{g2}}{k_p} \right] d(d_e)}{w \cdot k_e(wa - 2\tau) \int_0^\tau \left[ a \frac{a}{k_e} + \frac{L_{g2}}{k_p} \right] d(d_e) + 2ta}$$

(5)

4. Results and discussion

The established upper and lower bounds for effective thermal conductivity of consolidate adsorbent graphite flakes are shown in Fig. 8. As expected the experimental data fall between the two bounds.

In reality, the graphite flakes in the composite adsorbent are expected to be randomly oriented. The introduced upper and lower bounds are used, as two extreme cases, to predict the effective thermal conductivity of the consolidated composites. Using a similar approach, thermal resistance network and effective thermal conductivity can be calculated for consolidated composites containing graphite flakes disks with different angles, as shown in Eq. (6):

$$[k_{\text{eff},a}] = \cos^2(\theta) \cdot \frac{a \int_0^\tau \left[ \frac{a}{k_e} + \frac{L_{g2}}{k_p} \right] d(d_e)}{w \cdot k_e(wa - 2\tau) \int_0^\tau \left[ a \frac{a}{k_e} + \frac{L_{g2}}{k_p} \right] d(d_e) + 2ta} + \sin^2(\theta) \cdot \frac{k_e wa^2 [k_e(a^2 - \pi r^2) + k_p \pi r^2]}{[k_e a^2 + k_p (a^2 - \pi r^2)] \cdot (w - t) \cdot a^2}$$

(6)

The effective thermal conductivity model of disk particles in different angles compared to the measured thermal conductivity of S6-CaCl$_2$-G, is shown in Fig. 9.

Bound conduction model for disk shaped particles in consolidated sorbent composite shows good agreement with experimental model when the angle of the disk particles is 45°. The relative difference between the experimental data and the modeling result for low volume fraction disk shape thermally conductive additive (0–10 wt%) in continuous medium is 10%. As shown in Fig. 8, graphite flakes have a diameter range of 200–1300 μm which small particles help to make a path through consolidated sorbent composite and improve thermal conductivity.

5. Conclusion

Thermal conductivity of composite adsorbent containing graphite flakes was measured and its effective thermal conductivity with conduction bound method was modeled and measured at 35 °C (2% RH). The results showed thermal conductivity of consolidated composite increased significantly by adding thermally conductive particles.

In addition to the experimental measurements, a new analytical model was developed that can predict the effect of thermally conductive additive on thermal conductivity of consolidated adsorbent. The model captured the trend while different disk shape particles angle and size considered. This model is limited by geom-
etry of additive, volume fraction, the dispersion of particles in composite.

A pressure and temperature jump gravimetric test-bed is built to evaluate the effect of additives on consolidated sorbent performance. Durability of sorbent coated on graphite sheet with and without additives will be studied.

Conflict of interest

The authors declare that there is no conflict of interest.

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