A calorimetric test of adsorbent-coated fins

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Highlights

- Calorimetric assessment of adsorption rates has been attempted on finned adsorbents.
- The method detects differences in adsorption rate between different substrates: flat plates, aluminium and steel fins.
- The results have implications for the performance enhancement of adsorption heat pumps.
Abstract

Adsorption heat pumps often use coated prismatic fins. This paper concerns a calorimetric test of different types of coated fins. Samples of substrate-plus adsorbent were kept at constant temperature by a thermoelectric module (TEM) but subjected to a step change in vapour pressure (large pressure jump, LPJ). The TEM had been calibrated to yield the quantity of heat transferred to the TEM and hence the heat rejected by the sample. The TEM was mounted on the outer surface of the test vessel in order to eliminate the impact on the sample of degassing and corrosion of the TEM by the water vapour used.) The plot of heat rejected from the fin base versus time fitted an exponential function. Thereupon a ratio of characteristic times indicated performance of coated fins (the numerator referred to the fin and the denominator to an isothermal flat plate). The ratio was 1.07 for 3-mm-diameter beads adhered to aluminium fins and this demonstrated an example where the axial temperature gradients in the fin were unimportant. In a steel fin a larger ratio of characteristic times (~ 2) demonstrated the impact of strong axial temperature gradients. Crudely inferred values of specific cooling power (SCP) were broadly comparable to values reported for other combinations of substrate, adsorbent and adsorbate.

Keywords

Adsorption heat pump; silica gel; calorimeter; extended surface.
### Nomenclature

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<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
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<tbody>
<tr>
<td>$A_c$</td>
<td>Cross sectional area of fin (uncoated)</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_o$</td>
<td>Pre-exponential factor</td>
<td>Pa$^{-1}$</td>
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<tr>
<td>$c_p$</td>
<td>Specific heat capacity (constant pressure)</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$C$</td>
<td>Geometric factors used to calculate heat loss</td>
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<tr>
<td>$h_{ads}$</td>
<td>Enthalpy of adsorption</td>
<td>J kg$^{-1}$</td>
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<tr>
<td>$k_f$</td>
<td>Thermal conductivity of substrate</td>
<td>W m$^{-1}$ K$^{-1}$</td>
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<tr>
<td>$L$</td>
<td>Fin length</td>
<td>m</td>
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<td>$m$</td>
<td>Complex wave number</td>
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<tr>
<td>$m_x$</td>
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<tr>
<td>$T$</td>
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<td>K</td>
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<tr>
<td>$V_r$</td>
<td>Fin volume (uncoated)</td>
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<tr>
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<td>Adsorption loading</td>
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<tr>
<td>$X^*$</td>
<td>Adsorption capacity</td>
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<tr>
<td>$z$</td>
<td>Distance from fin root</td>
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### Greek Symbols

<table>
<thead>
<tr>
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<tr>
<td>$\alpha$</td>
<td>Heat transfer coefficient</td>
<td>W m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>kg m$^{-3}$</td>
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</table>
\( \tau \) Characteristic time \( s \)

\( \omega \) Angular speed \( \text{rad s}^{-1} \)

Subscripts

- \( a \) Measured heat transfer at fin base
- \( b \) Base temperature
- \( f \) Fin property / area of fin flank
- \( I \) Refers to heat loss
- \( \text{LTJ} \) Refers to a test under the conditions for a “large temperature jump”
- \( r \) Refrigerant property
- \( x \) Refers to Stored Heat

Superscripts

- \( \text{fp} \) Refers to flat plate
- \( a+lx \) Raw heat measurement corrected for heat loss and heat stored in fin (substrate + adsorbent + adsorbate)
1. Introduction

This paper concerns a test of finned adsorbent by measurement of heat transfer.

The purpose of an adsorption heat pump is to convert low-grade heat into cooling, or to amplify higher grade heat (in effect, producing a boiler efficiency exceeding unity). Meunier [1] explains the operation and thermodynamic principles of the adsorption cycle. In essence, the mechanical work of compression is obviated by a generator or "thermal compressor"; it comprises a solid sorbent plus its heat exchange surfaces. Cooling the sorbent near to ambient temperature causes it to attract and adsorb refrigerant vapour from an evaporator; heating the sorbent forces vapour desorption and vapour transport into a condenser. Solid sorbents offer several advantages over liquid sorbents [2]: there is no requirement for a solution pump or a distillation column; there is no risk of crystallisation in the liquid phase; and the mechanically straightforward generator is manufactured from inexpensive steels. However, solid sorbents tend to exhibit low thermal conductivities, ~0.1 W m\(^{-1}\) K\(^{-1}\) when in a packed bed, and some means of enhancing heat transfer is needed. One method is to coat [3] or adhere [4] [5] [6] adsorbent to fins. Thereupon an apparently simple system has five components, base-substrate-adhesive-sorbate-sorbent. The aim of our work has been to develop a means of rapidly measuring rate of adsorption into coated fins.

The use of fins in prototype AHPs is well known – for example the operation of annular tubes with heat sources in the range 333 K-to-353 K [7]. Finned designs have been employed for heat recovery from engine exhaust; selection of zeolite-13 X as adsorbent has permitted bed temperatures of up to 240°C during regeneration [8]. Proposed mathematical models of adsorbent heat exchangers [9] [10] covering intra-grain mass and heat transfer, the two dimensional temperature patterns in the sorbent layer, the thermal coupling to the substrate, and measured adsorption rates and adsorption capacities. (The adsorption capacities for small samples of adsorbent might well be assessed gravimetrically, nowadays by magnetic levitation balance [11] [12].) There is fair agreement with experimentation, but the predictions require a-priori knowledge on
many physical constants, and are complex and computationally intensive. (As an example of fair agreement, on Figure 7 of reference [10] the authors report confidence intervals of 20% relative error when plotting prediction versus measurement. Their experiments concerned a test section employing zeolite-water and silica gel-water pairs. Their Figure 7 refers to adsorbed mass and the input-to-output temperature differences of heating/cooling fluid.)

Rather than such extensive measurement and modelling, there is a persuasive argument for taking direct measurements from representative samples of AdHex (combined adsorbent and heat exchanger). One notes the “large pressure jump (LPJ)” method [13] where pellets are exposed to step changes in vapour pressure, and the isobaric large temperature jump (LTJ) where the pellet’s substrate is exposed to step changes in temperature, claimed to represent more truly the boundary conditions in the AHP [14]. More recent developments in gravimetric LTJ allow exchanger parts to be measured and sample masses up to about 500 g [15] [16]. An alternative calorimetric method [17] [18] offers direct measurement of component heating/cooling and eliminates interaction between heat transfer fluids and weight sensors. This has so far been used tentatively for a limited number of measurements with LPJ and LTJ [19]. Heat measurement with LTJ is more challenging than with LPJ because (1) without a guard heater that follows the changing sample temperature heat losses are appreciable (2) the measured heat rejection/addition includes changes in the sensible heat of the fin structure and therefore uncertainties owing to axial temperature gradients (3) parts of the test vessel touching the heating/cooling element cause additional direct heat losses. The heat losses in argument #3 can be mitigated by either heating the vessel walls to the same temperature as the sample (LPJ) or mounting the heating/cooling element in the test vessel (LTJ).

Calorimetric LTJ [19] is in principle most appropriate for the direct prediction of the coefficient of performance (COP) and specific cooling power (SCP) at laboratory scale [20]. Nonetheless, the aforementioned uncertainties necessitated extensive calculations with scope for error. (Nonetheless, such errors were not thought to be as significant as those caused by air ingress and the associated complications associated with Stephan flows.)
The calorimetric test employed in this paper permits comparison of the heat transfer dynamics of different coated surfaces; namely finned surfaces and a flat isothermal surface. To reduce heat losses from the adsorbent, LPJ-type boundary conditions were applied such that the temperatures of the fin base and the test-section-wall were equal and constant. (The thermoelectric module could then be located outside the test-section, additionally reducing the risk of degassing.) Nonetheless any deviation of the fin’s axial temperature profile from the fin-base-temperature would have indicated a heat loss from the adsorbent; the paper explains how the profile was estimated by a finite difference method to yield the corrected heat of adsorption (= measured heat transfer - estimated losses). The impact of different material choices became apparent when inferred heats of adsorption were fitted to characteristic times. When compared against a flat plate under otherwise identical conditions, the steel fin slowed the adsorption rate far more than the aluminium fin (typical rate reductions were 7% for aluminium and 50% for steel).

2. Methods and material properties

Figure 1 shows the calorimeter developed in references [17] [18], equipped with finned sample. The essential component (Figure 1, part b) was a thermoelectric module (item 5) bonded to the sample base (item 4). The TEM maintained a constant base temperature (measured at item 1), particularly when vapour was introduced into the sample section. The rate of net heat absorption by the face of the TEM was influenced principally by the Peltier effect, ohmic heating inside the TEM, and conduction losses or gains between the two faces of the TEM. An average 10% error in heat measurement was derived, either by putting the different instrument errors into a Monte-Carlo model [18] or by comparing calorimetrically inferred adsorption capacities against gravimetric measurements [17]. Uncertainties in pressure measurement were estimated as 2.2 mbar and uncertainties in temperature measurement as 0.29 K.
In preparation for adsorption tests the adsorbent was isolated by closing the connecting valve (item 3 in Fig. 1a). Heating and vacuum were applied after which the adsorbent and water were brought to their set point temperatures. The connecting valve was then opened.

The adsorption capacity of the silica gel was previously fitted to Henry’s law [17].

\[ X^* = A_o \exp \left( \frac{h_{ads}}{R T_b} \right) p \]  \[ \text{[1.]} \]

where \( X^* \) is the adsorption capacity, \( h_{ads} = 2495 \text{ kJ kg}^{-1} \) is the heat of adsorption, \( A_o = 1.92 \times 10^{-12} \text{ Pa}^{-1} \) is a pre-exponential constant, \( T_b \) is the temperature of the base plate. (A Toth equation [21] applies when the adsorption capacity exceeds 30%.)

Figure 2 shows the samples and Table 1 gives geometric details. (The base (item 2) matches the aluminium end plate, item 4, on Figure 1a.) As in [17], beads of type-A silica gel of 3-mm diameter were bonded to the fin flanks with marine-grade silicone sealant to an estimated depth of 0.3 mm. Following preliminary tests, only the central fin was covered with silica gel. The fin height was restricted by the existing glassware. A wire-cut electrical discharge machine (WEDM) fabricated the first set of substrates from a single piece of aluminium, thereby removing any thermal resistance between fin root and base. A second, stainless steel SS304 substrate was intended to impose an appreciable axial temperature gradient (as would be true for a far longer aluminium substrate). Because the WEDM equipment could not operate with steel, the substrate was bonded to an aluminium base with a thermally conductive adhesive [22]. The bond thermal resistance, defined by

\[ R_c = A_c \frac{T(0^-) - T(0^+)}{Q} \]  \[ \text{[2.]} \]
was assessed experimentally by a variant of reference [23], described in the Appendix. (The two
temperatures above are those on either side of the bond, \( A_c \) is the cross sectional area of the
substrate, and \( R_c \) is the thermal resistance.)

3. Data Analysis

Two sets of analysis were adapted from previous work [17]: the calculation of adsorption capacities
from heat transfer for purposes of checking, and the assignment of characteristic time. A numerical
model of the fin was used to estimate axial temperature gradients and thus the terms for stored
sensible heat and heat loss from fin to side-walls.

In [17] silica gel was bonded to an isothermal plate and the heat load on the plate measured
following an LPJ. The plate and its surroundings held nominally the same temperature, the
temperature profiles in the adsorbent were small, and there were only small changes in stored
sensible heat in the plate (about 4\% of total). Therefore, with small discrepancies only the
measured heat transfer to the plate corresponded closely to the heat of adsorption (“That is,
temperature spikes in the plate corresponded to a temporary deviation of ~4\% of heat of
adsorption, and a (hypothetical) 10 K spike in the temperature of the silica gel would correspond to a
temporary deviation of 2\% of the heat of adsorption.”) The measured heat transfer could then be
checked against measured adsorption capacities according to

\[
Q_{a,fp}(t \rightarrow x) \approx m_x(X^* - X(0))\left(h_{ads} - c_{p,r}(T_b - T_v)\right)
\]

[3]

Where \( h_{ads} \) is the heat of adsorption, \( m_x \) is the dry mass of adsorbent, \( Q_{a,fp} \) is the heat transfer to
silica gel adhered to an isothermal flat plate, \( T_v \) is the estimated vapour temperature, \( T_b \) is the
temperature of the isothermal flat plate, \( X(0) = 0 \) is the initial loading, and \( X^* \) is the adsorption
capacity. Equation [3] was used to estimate adsorption capacity for checks against gravimetrically
measured values. The fitting equation followed Henry’s Law
\[ X^* = A_o \exp \left( \frac{h_{\text{ads}}}{R T_b} \right)p \]  

[4.]

where \( h_{\text{ads}} = 2495 \text{ kJ kg}^{-1} \) is the heat of adsorption, \( A_o = 1.92 \times 10^{-12} \text{ Pa}^{-1} \) is a pre-exponential constant, and \( R \) is the specific gas constant. (A Toth equation [21] applies when the adsorption capacity exceeds 30\%).) The timewise recordings of \( Q_{a_fp} \) followed an exponential recovery (to \( r^2 > 99\%) \) and characteristic time, \( \tau(T) \), were fitted to an Arrhenius expression.

1-mm-diameter beads (\( \tau \) measured in seconds)
\[
\tau(T) = \frac{1}{162.6} \exp \left( \frac{3401.3}{T_b} \right)
\]

[5.]

3-mm-diameter beads (\( \tau \) measured in seconds)
\[
\tau(T) = \frac{1}{7.85} \exp \left( \frac{2730.3}{T_b} \right)
\]

[6.]

The heat of adsorption and the measured heat transfer at the fin root must be balanced against other terms (see also [19] [20]).
\[
Q^{(a+lx)}(t) = Q_a(t) + Q_l(t) + \sum Q_{x,i}(t)
\]

[7.]

where \( Q_a(t) \) is the measured heat rejection to the TEM, \( Q_l \) is the heat loss from the sample to the side walls of the vessel, \( Q_a \) allows for sensible heat storage in the substrate \( i=1 \), silica gel \( i=2 \) and adsorbed phase \( i=3 \). Term \( Q^{(a+lx)} \) equals the heat of adsorption. Characteristic times were fitted to measured term \( Q_a(t) \) directly, for comparison with data for flat plates. Numeric estimates of axial temperature profiles allowed estimates of \( Q_{x,i} \) and \( Q_a \) and hence (from Equation 8) of heat of adsorption \( Q^{(a+lx)} \). The adsorption heat replaced \( q^{(a,b)} \) in equation [3] enabling \( X^* \) to be checked against gravimetric measurements.
The description of the model of axial temperature profile follows. The rate of heating due to adsorption was taken as constant along the fin and incorporated into the general conduction equation [24].

\[
\sum_{i} \frac{m_i c_{p,i}}{V_f} \frac{\partial T(t,z)}{\partial t} = k_f \frac{\partial^2 T(t,z)}{\partial z^2} + \frac{\partial^2 Q^{(a+lx)}}{\partial t \partial V_f} - \frac{\partial^2 Q}{\partial t \partial V_f} \tag{8.}
\]

The fin tip was treated as adiabatic whereas the root was treated as being at fixed temperature (if aluminium) or the Robin type boundary condition in Equation 2 applied (if stainless steel). One term in Equation 8, \(\frac{\partial^2 Q^{(a+lx)}}{\partial t \partial V_f}\), required a predictor-corrector method as follows.

1. The measured heat rejections, \(Q_a(t)\) were divided into \(k = 1, 2, \ldots K\) segments of duration \(\Delta t = 100\) s, each with start time \((k-1)\Delta t\) and end time \(k\Delta t\).

2. For each segment \(k\), the heat of adsorption \(\Delta Q^{(a+lx)}\) was guessed and treated as an effective volumetric heating term such that in Equation 8 \(\frac{\partial^2 Q^{(a+lx)}}{\partial t \partial V_f} \rightarrow \Delta Q^{(a+lx)}/V \Delta t\). Equation 8 was solved by the explicit finite difference method for the duration of the time segment.

3. The value of \(\Delta Q^{(a+lx)}\) was corrected and step 2 repeated until the predicted heat rejection at the fin root matched the corresponding measurement, \(Q_a\).

Aluminium fin, prediction satisfactory when

\[
k_f A_c \int_{(k-1)\Delta t}^{k\Delta t} \frac{\partial T(0)}{\partial z} \, dt = Q^a (k\Delta t) - Q^a ((k-1)\Delta t) \tag{9.}
\]

Steel fin, prediction satisfactory when

\[
A_c \int_{(k-1)\Delta t}^{k\Delta t} \frac{(T(0^+) - T(0^-))}{R} \, dt = Q^a (k\Delta t) - Q^a ((k-1)\Delta t) \tag{10.}
\]

4. This procedure was repeated for \(k = 1, 2, 3, 4\) ...
The natural convection component of heat loss was

\[
Q_{\text{conv}}(t) = \frac{A_f}{1 + \frac{1}{\alpha_f C_1 \alpha_{\text{side}}}} \int_0^t (T_{f,\text{avg}}(t') - T_b(t')) \, dt'
\]

[11.]

where the side walls were at the same temperature as the fin base, \( T_b \). The heat transfer coefficients, \( \alpha_f \) and \( \alpha_{\text{side}} \) were established from [25] for both laminar and turbulent natural convection from vertical surfaces. The geometric term was set to \( C_1 = 1 \) for the aluminium substrate (exchanging heat with neighbouring, uncoated fins) and \( C_1 = 3 \) for the steel substrate (exchanging heat with the glass side walls). The component of loss caused by net thermal radiation was estimated as

\[
Q_{\text{rad}}(t) = \frac{1}{1 + \frac{C_2}{\varepsilon_{\text{sigel}} - \varepsilon_{\text{side}}}} \int_0^t \left[ A_f \sigma (T_{f,\text{avg}}^4 - T_b^4) \right] \, dt'
\]

[12.]

where \( \varepsilon_{\text{sigel}} = 0.92 \) is the total hemispherical emissivity of the silica gel coated substrate [26]. Transfer to the neighbouring uncoated aluminium fins was taken as equivalent to that between infinite parallel plates [27]; \( C_2 = 1 \) and \( \varepsilon_{\text{side}} = \varepsilon_{\text{al}} = 0.095 \) [27]. For transfer from the steel fin to glass side walls \( C_2/\varepsilon_{\text{side}} \rightarrow 1 \) forcing the term in square brackets to \( \varepsilon_{\text{sigel}} \). (The fin’s view was to the side walls; their surface area somewhat exceeded that of the fin and in any case the emissivity of glass in the infrared spectrum is close to one.)

4. Results

Figure 3 shows the heat rejection from finned adsorbents versus time. The results refer to constant base temperatures between 303 K and 333 K, bead diameters of 1-mm and 3-mm, and substrates formed from steel or aluminium. In all instances an exponential recovery, shown as a
dotted line, provides a fair fit ($r^2 > 0.99$). The heat rejection at $t \to \infty$ yielded adsorbent loadings (see Equation 3, setting $t \to \infty$).

Figure 4 shows computed adsorption capacity as a function of pressure, for a series of base temperatures ($T_b$). Part (a) applies to flat plates [17] whereas parts (b) and (c) apply to finned adsorbents. All data are compared against fits to both gravimetric tests [21] and fits to the calorimetric evaluation show on part (a). The consistency of adsorption capacities, from experiment to experiment, provided a further check on the quality of measurement.

Figure 5 shows predictions of all heat transfer terms and Figure 6 the corresponding axial temperature profiles. The predictions pertain to the greatest expected heat of adsorption ($Q^{(a+lx)}$): larger beads caused the greatest mass of adsorbent ($m_x$) and the lower base temperature ($T_b$) caused the greatest adsorption capacity ($X^*$). The measured $T_b$ and the measured heat transfer ($Q_{x}$) formed the boundary conditions of the simulation. The higher thermal conductance of the aluminium substrate ensured reduced heat loss ($Q_{l}$), reduced storage of sensible heat ($Q_{s}$), and smaller temperature changes at the tip and middle of the fin. Note that the temperature difference across the adhesive bond on Figure 6a, comprising - at peak temperatures - 52% of the difference between the base plate and fin tip, highlighted the importance of good conductance from base to root of fin.

The Arrhenius type plot on Figure 7 shows characteristic times for a coated flat plate, a coated aluminium substrate and a coated steel substrate. The differences between the best fits relating to the flat plate and the best fits relating to the aluminium substrate were small and between 4.8% and 7.1%. On the other hand the differences between flat plate and steel substrate were clearly evident from raw data. Figure 8 shows similar data for smaller, 1-mm-diameter beads. Table 2 shows the data as ratios of characteristic time (for identical vapour pressure at $T_b$): the numerator pertains to the fin and the denominator pertains to the flat plate. Clearly the dynamics of the fin with steel substrate were slower owing to the larger temperature gradients therein (see also Figure 6). At the higher values of the base temperature, $T_b$, (to the left of the x-axis on Figures 7 and 8) the characteristic time was smaller in all cases. At higher $T_b$ characteristic times associated with
the larger beads approached slightly the flat plate values ($\tau/\tau^p \to 1$), but the characteristic times associated with the smaller beads departed slightly. It is not immediately obvious whether higher $T_b$ should have increased or decreased rates of heat of adsorption because both characteristic time and adsorption capacity were reduced (Equations 1 and 6).

5 Discussion

This section covers the implications of results for practical chillers, the choice of boundary condition in tests, and the scale of measurement uncertainty.

In a practical chiller, aluminium fins would have two benefits. Compared against monolayers bonded directly to cooling/heating channels such fins would hold about six times as much silica gel per unit of base area with minimal impact on specific cooling power (calculation applies to hexagonally close packed spheres of 3-mm diameter). In comparison with packed beds, finned adsorbent would exhibit a higher specific cooling power but a decreased coefficient of performance; the additional aluminium would increase the dynamic loss of heat. In optimising performance one would seek a trade-off between low dynamic losses of heat (low substrate mass and thinner fins), good adsorbent mass per unit base area (longer fins) and high rate of refrigerant uptake (smaller axial temperature gradient, requiring shorter, thicker fins).

The large temperature jump (LTJ) offers truer representation of the boundary conditions in the AHP cycle [14]. On the other hand, LPJ beneficially maintained the sample’s base plate (part 4, Figure 1b) and side-walls at the same constant temperature, eliminating extraneous conduction losses. Furthermore, avoiding the step change in sample temperature mitigated heat convection and heat radiation to the side walls (Equations 11, 12). A limited set of calorimetric tests carried out under LTJ [19] presented two further difficulties. (1) Locating the TEM on the inside the containment vessel dealt with the aforementioned extraneous heat conduction losses but there might have been degassing from the TEM. (2) For example, for a 30 K temperature jump the sensible heat term on
Figure 5b, $Q_a$, would have comprised 12% of the heat of phase change and a corresponding uncertainty in total heat transfer.

Various characteristic times indicate both experimental uncertainties and a lower bound for SCP (Table 3). Characteristic times pertain to measured heat $Q_a$, the corrected heat of phase change $Q^{(a+lx)}$, the cooling of silica gel beads and the cooling of the aluminium or steel substrate. For cooling of the beads the characteristic time was the conduction time scale multiplied by a generous factor of 10 (to allow for complex topology). The time for axial conduction along the substrate was estimated by Equation 8 with zero heat of phase change, the end time counted as when the spatially averaged temperature was 306 K and within 3K of its asymptote (adsorption capacity was 16% less than at 303 K and adsorption characteristic time was 9% less). The characteristic time for LTJ was estimated by summing contributions, $\tau_{LTJ} < \tau^{(a+lx)} + \tau_{cond,fin} + \tau_{cond,sigel}$ (that is, adsorption was treated as if three processes occurred sequentially). Sapienza et al [15] estimate SCP for an 80% uptake of adsorbent.

\[ SCP_{80\%} = 0.5 \frac{X^*(303 K) - X^*(333 K)}{\tau_{LTJ}} h_f g \]  \[13.\]

The corrections required to obtain $\tau_{LTJ}$ seem modest for the flat plate and aluminium substrate. It is recalled that the steel substrate was chosen deliberately to exacerbate axial temperature gradients at the cost of SCP. The SCP is broadly comparable with Sapienza et al [15] where

SCP$_{80\%} = 0.56$ kW kg$^{-1}$ (for the LTJ (338K $\rightarrow$ 303 K) with SAPO24 monolayers of 2.4 mm to 2.6 mm diameter). For the ethanol-ACC pair [19], the characteristic times were comparatively short ($\tau_{LTJ} \in [159, 183]$ s) but nonetheless the corresponding SCP$_{80\%}$ was not remarkably higher (0.36 to 0.52 kW kg$^{-1}$).

Table 4 lists fractional random errors and systematic uncertainties that influence SCP.

(Random errors were taken as one standard deviation in measurement whereas systematic uncertainties were taken, pessimistically, as the corrections used to get $Q^{(a+lx)}$ or $\tau_{LTJ}$. In Equation 13 the approximation $\Delta X^* \propto Q^{(a+lx)}$ applied to error analysis.) With regard to the variance in
characteristic times Glaznev et al. [28] measured a 40% change in rate of moisture adsorption with very small amounts of air ingress (a partial pressure of 0.06 mbar). It is also possible that the silica gel degraded with repeated use, although a series of repeat tests discounted this. For the aluminium substrate the random errors are more problematic than the correction procedure whereas for the (highly non-optimum) steel substrate the correction procedure is more problematic. (Nonetheless, the large reduction in SCP would form sufficient evidence for the rejection of this particular prototype.)

Several developments might well benefit the accuracy of calorimetric test, particularly if LTJ is employed. These are: (1) the provision of guard heaters/coolers with independently controlled power supplies (2) vacuum-glazing of the test vessel to protect against air ingress (3) metering of mass flow of vapour (although difficult to achieve for gases of very low density) (4) protection of the TEM from degassing (the TEM might have to be manufactured separately because plastic and silicone components are located in proprietary units) (5) manufacture of miniaturised thermocouples breakthroughs (proprietary breakthroughs are typically ~6-mm diameter. The existing tactic of passing thermocouples through runs of epoxy resin [19] [20] might lead to degassing.)

6 Conclusions

This work concerns the rate of adsorption into silica gel beads coated onto extended surfaces. When boundary conditions followed a “large pressure jump (LPJ)”, a calorimetric test was sufficiently sensitive to detect a 5%-to-7% increase in characteristic time (the difference being between the flat plate and aluminium substrate/fin). Compared to the alternative large temperature jump (LTJ), the reduction in thermal energy storage and heat loss assisted accuracy for the case of the conductive aluminium substrate. Compared to steel, the far higher thermal
conductivity of aluminium makes fins more effective and accelerates the average rate of adsorption. The steel substrate represented a sub-optimum extreme with characteristic time about 60% greater than that of the flat plate. Subsequently, predicted fin temperatures increased up to 24 K above their initial value and in consequence heat loss and storage could equal 20% of heat of adsorption, to the detriment of accuracy. For the conductive aluminium substrate measurement errors outweighed uncertainties in crudely estimated characteristic times for LTJ. Thereupon, the inferred values of SCP were very broadly comparable to those reported for water vapour monolayers of SAPO or ethanol vapour on finned ACC.

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References


Appendix 1 Inference of the thermal resistance of a bond

The bond resistance $R_c$ was assessed by cycling sinusoidally the base temperature, $T_b$ (Figure A1). No beads were adhered to the fin, it was well insulated, and cyclic steady state was taken as 10 oscillations. The base temperature ($T_b \equiv T(0^-)$) was controlled well and to within 0.1°C of its set point. Consider principally axial conduction along a prismatic fin, with adiabatic tip from locations $z = 0^-$ to $z = L$.

\[ \rho_f c_f \frac{\partial T}{\partial t} = k_f \frac{\partial^2 T}{\partial z^2} \]  
\( \text{(A1.1)} \)

Let the temperature follow $T(z, t) = T_m + \theta(z) \exp(i \omega t)$ where $\theta(z)$ has a real value at $z = 0^-$ but a complex value elsewhere. If adiabatic conditions apply at the fin tip ($z = L$) then the solution is

\[ \theta(z) = \theta(0^-) \frac{\cosh(mL - mz)}{\cosh(mL)} \]  
\( \text{(A1.2)} \)

where term $m$ represents the complex wave number,

\[ m = \sqrt{\frac{i \omega \rho_f c_f}{k_f}} \]  
\( \text{(A1.3)} \)

The heat transfer follows from both the Fourier Biot law (at $z = 0^-$) and the thermal resistance (between $z = 0^-$ and $z = 0^+$, see Equation 2 in the main text). Equating the two estimates

\[ R_c = \frac{\theta(0^-) - \theta(0^+)}{k_f \theta(0^+) \Re(m \tanh(mL))} \]  
\( \text{(A1.4)} \)
Figure A1 Measurement of interfacial resistance (a) fin and thermocouple locations (b) cyclic variations in temperature (1) base plate (2) adhesive (3) steel fin. Thermocouple locations are at \( z = 0^+ \) mm (below interface), \( z = 0^-\) mm (above interface), and \( z = 3 \) mm.
### Table 1 Specification of fins

<table>
<thead>
<tr>
<th>Properties</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aluminium</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>170</td>
</tr>
<tr>
<td>Measurements (width x height x thickness, mm)</td>
<td>45 x 20 x 1</td>
</tr>
<tr>
<td>Root bonding method</td>
<td>Wire cut</td>
</tr>
<tr>
<td>Contact resistance (m²K/W)</td>
<td>0</td>
</tr>
<tr>
<td>Mass of silica gel (g)</td>
<td>4.000</td>
</tr>
<tr>
<td>Nominal diameter of beads (mm)</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 2 Ratio of characteristic times, fin to flat plate

| Diameter, mm | 3    | 1    | 3    | 333  | 303  | 333  | 1.07 | 1.05 | -   | -   | 1.75 | 1.71 | 1.99 | 2.09 |
|--------------|------|------|------|------|------|------|------|------|-----|-----|------|------|------|------|------|
| Base temperature, K                |      |      | 303  | 333  | 303  | 333  |      |      |     |     |      |      |      |      |      |
| Ratio of times τ/τₚ                |      |      |      |      |      |      |      |      |     |     |      |      |      |      |      |
| Aluminium                         | 1.07 | 1.05 |      |      |      |      |      |      |     |     |      |      |      |      |      |
| Stainless steel                   | 1.75 | 1.71 | 1.99 | 2.09 |      |      |      |      |     |     |      |      |      |      |      |
### Table 3 - Crude estimates of characteristic times and SCP

<table>
<thead>
<tr>
<th></th>
<th>Flat plate</th>
<th>Aluminium Substrate (Al6082)</th>
<th>Steel substrate (SS304)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Under LPJ</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measured $\tau_a$, s</td>
<td>1097</td>
<td>1181</td>
<td>1901</td>
</tr>
<tr>
<td>Inferred, $\tau_{a+lx}$, s</td>
<td>1097</td>
<td>1175</td>
<td>1763</td>
</tr>
<tr>
<td><strong>Under LTJ (333 K $\to$ 303K)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{\text{cond,fin}}$, s</td>
<td>-</td>
<td>20</td>
<td>434</td>
</tr>
<tr>
<td>$\tau_{\text{cond,spigel}} \sim 10 \frac{d_p^2}{\kappa}$, s</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Estimate $\tau_{\text{LTJ}}$, s</td>
<td>&lt;1142</td>
<td>&lt;1240</td>
<td>&lt;2242</td>
</tr>
<tr>
<td>$\tau_{\text{LTJ}} &lt; \tau_{a+lx} + \tau_{\text{cond,fin}} + \tau_{\text{cond,spigel}}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCP 80% (Equation 13), kW kg$^{-1}$ (adsorbent)</td>
<td>&gt;0.271</td>
<td>&gt;0.250</td>
<td>&gt;0.138</td>
</tr>
</tbody>
</table>

### Table 4 – Fractional errors and uncertainties relating to Specific Cooling Power (see Equation 13)

<table>
<thead>
<tr>
<th></th>
<th>Flat plate</th>
<th>Aluminium Substrate (Al6082)</th>
<th>Steel substrate (SS304)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Random measurement errors (fraction of total, 1 standard deviation)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_a$, observed from repeat measurements</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$\tau_a$, observed from repeat measurements</td>
<td>0.13</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>Error in SCP = Root sum of squares of above</td>
<td>0.16</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Systematic errors (as fraction of total)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat loss, $Q_a/\pi(\alpha+\lambda)$</td>
<td>-</td>
<td>0.013</td>
<td>0.260</td>
</tr>
<tr>
<td>Corrections to characteristic time, $\tau_{\text{LTJ}}/\tau_{\text{LTJ}}$</td>
<td>0.039</td>
<td>0.052</td>
<td>0.213</td>
</tr>
<tr>
<td>Uncertainty in SCP = Root sum of squares of above</td>
<td>0.039</td>
<td>0.054</td>
<td>0.336</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1  The schematic of calorimetric apparatus (a) general view with (1) evaporator section (2) adsorber section (3) connecting valve and (4) thermocouple locations (black dots) (b) detailed view of adsorber section with (1) thermocouple location (2) silica gel beads (3) nylon screws (4) base plate (5) thermoelectric module (6) heat sink and fan

Figure 2  Fin samples (a) fins wire cut from single piece of aluminium (b) single steel fin bonded to aluminium plate. Item (1) is thermocouple position

Figure 3  Heat rejection from the sample following contact with water vapour. The sample was initially under vacuum. Plate temperatures during experiments are indicated on each graph (a) 3-mm-diameter beads on aluminium (b) 3-mm-diameter beads on stainless steel (c) 1-mm diameter beads on stainless steel

Figure 4  Adsorption capacities inferred from heat rejection - 3-mm-diameter beads used in all instances (a) flat plate, reported by [17] with Wang’s gravimetric measurements [21] (b) aluminium fin, compared against best fits to [17][21] (c) Steel fin, compared against best fits to [17][21]

Figure 5  Predicted heat terms and measured heat transfer at fin root, $Q_a$. (a) Steel fin, with 3-mm-diameter beads attached (b) Aluminium fin, with 3-mm-diameter beads attached.

Figure 6  Predicted profiles of axial temperature. (a) Steel fin, with 3-mm-diameter beads attached (b) Aluminium fin, with 3-mm- diameter beads attached.

Figure 7  Overall rate constants for 3-mm-diameter beads

Figure 8 Overall rate constants for 1-mm-diameter beads

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(c) Steel fin, compared against best fits to [17][21]

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