USE OF ADSORBENT BEDS FOR ENERGY STORAGE IN DRYING OF HEATING SYSTEMS

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Abstract—Energy storage is an important feature of many solar energy systems. Because of the small temperature potentials available from flat plate collectors, large masses and volumes are involved when energy is stored by raising or lowering the temperature of a tank of fluid or bed of gravel. This paper proposes energy storage in the form of heat of adsorption in beds of adsorbent material. This is most readily achieved by nominating water as the adsorbate so that water vapour is transferred to or from the absorbent from the humid air flowing through the bed. The large heat of adsorption means that the adsorption of a small mass of water liberates a large amount of energy which mostly is transferred to the air stream. It is shown that adsorbing materials can occupy a much smaller volume than non-adsorbing materials for the same quantity of energy stored, and that thermal insulation can be dispensed with. Provided that the container is impervious to water vapour, energy can be stored indefinitely.

1. INTRODUCTION

In many solar energy systems, the requirements of the system and the intermittent incoming radiation demand that an energy store be included. Common systems used in storing thermal energy include water tanks[1, 2] or gravel beds[3-5] where energy is added to or subtracted from the store by raising or lowering the water or gravel temperature.

With flat plate collectors limited to delivering energy at around 40°C above ambient temperature, such stores can become very large. Supposing that 1 × 10⁶ kJ is to be stored using a temperature rise of 28°C, then the volume of a water tank must be about 9 m³ and a gravel bed 32.5 m³. Devices of such a size require expensive containers, need considerable thermal insulation and pose severe problems in weather-proofing and providing an attractive appearance.

Important considerations in the design of an energy store for a solar energy system include: the volume and mass of the store, the cost of the storage material, container and insulation, the length of time energy can be stored, the effect of repeated cycling or ageing on the storage material and, for an air handling system, the quality of air leaving the store.

The authors' attention was drawn to adsorption as a method of storing energy during the testing of a large gravel bed thermal store[3]. The test results showed that adsorption of water by the gravel from the humid air flowing through gave an effect similar to an increase in the gravel specific heat of 25 per cent. This led to speculation that materials which adsorb comparatively large quantities of water would store even larger quantities of energy per unit mass and volume.

The concept of an adsorbent energy store is quite simple and the operation can be outlined as follows: During the charging period hot air from the solar air heater is passed through a porous adsorbent bed, heating the bed and carrying off the adsorbed water in the form of water vapour. Energy is stored in the form of heat and in what might be called “dryness” or the capability of adsorbing water vapour from a moist air stream. Energy is extracted from such a store by passing ambient air through such a dry bed. Thermal energy is initially extracted by cooling of the bed. As the bed cools water vapour from the air stream tends to be adsorbed and heat is generated due to the heat of adsorption (of the order of the latent heat) which is then transferred from the bed material to the air stream thus simultaneously drying and heating the air stream. With suitable adsorbent materials this second form of storage can be many times larger than the energy stored as sensible heat. Also, as will be discussed further in the next section, since most of the energy needed to heat the air is supplied by the latent heat of the water vapour adsorbed by the bed from the air stream, the total amount of energy available from the store is little affected by the store temperature. Hence the store can be allowed to cool to ambient temperature and, if the container is impervious to water vapour, energy can be stored indefinitely.

The warm dry air coming from such a store is ideal for many drying processes but may not be completely satisfactory for heating applications because of its low humidity and because the temperature level reached is dependent upon the moisture content of the ambient air.

2. THE BEHAVIOUR OF BEDS OF ADSORBENT MATERIAL

The behaviour of beds of adsorbent materials subjected to changes in the state of the air passing through is complex. Many factors affect the behaviour, some are derived from the thermal and adsorption properties of the materials and others, such as bed geometry and particle
size, are under the control of the designer. To make the system analysis as elementary as possible, an ideal model only takes into account those effects due to thermal and adsorption properties and is also applied to non-adsorbent materials so that valid comparison can be made between the two types of materials.

The model is based on the following assumptions:
(i) Surface transfer coefficients are high enough for there to be no potential differences between the air and adjacent bed material.
(ii) Heat and water vapour diffusivities of the bed material are infinite along planes normal to the fluid flow direction.
(iii) There is no diffusion or dispersion in the fluid flow direction.
(iv) Adsorption of water vapour is without hysteresis.
(v) The fluid pressure is constant.

With these assumptions, Banks[6] shows that the equations describing the conservation of energy and water can be transformed to

\[ \frac{\partial F}{\partial \theta} + \frac{v}{1 + \mu \gamma_F} \frac{\partial F}{\partial x} = 0 \]

\[ \frac{\partial G}{\partial \theta} + \frac{v}{1 + \mu \gamma_0} \frac{\partial G}{\partial x} = 0. \]  \hspace{1cm} (1)

The properties \( F, G, \gamma_F \) and \( \gamma_0 \) are complicated functions of the system thermal and adsorption properties.

Equations (1) may be compared with the conservation equation for a non-adsorbing bed

\[ \frac{\partial H}{\partial \theta} + \frac{v}{1 + \mu \sigma} \frac{\partial H}{\partial x} = 0. \]  \hspace{1cm} (2)

An examination of eqns (1) and (2) shows that \( F \) and \( G \) can be regarded as potentials analogous to temperature, and the properties \( \gamma_F \) and \( \gamma_0 \) analogous to the specific heat ratio \( \sigma \).

In the case of a non-adsorbing bed, eqn (2) shows that if a step change occurs in the temperature of the air entering the bed, a temperature front passes through the bed. Since \( \sigma \) can be assumed independent of temperature, the temperature front gives a step temperature change. Correspondingly, in the case of the adsorbing bed subjected to a step change in the entering air state, eqns (1) show that two fronts pass through the bed. Banks[6] and Close and Banks[7], have demonstrated that these fronts are separated in time at a given position.

Charts taken from[7] may be employed to determine the behaviour of an adsorbing time for the system comprising silica gel, water and air.

The lines in Fig. 1 are constant \( F \) and \( G \) plotted on a psychometric or \( t \) vs \( w \) chart for atmospheric pressure and where equilibrium air states are used to identify adsorbent states. If a bed of silica gel is initially at state \( A \), and a step change from \( A \) to \( B \) (Fig. 1) occurs in the entering air state, then the two changes which occur in the bed are from \( A \) to \( C \) (a change in \( F \) at constant \( G \)) and from \( C \) to \( B \) (a change in \( G \) at constant \( F \)). The individual changes are governed by the appropriate eqn (1).

The outlet air temperature and absolute humidity as functions of time are shown in Fig. 3 assuming a bed mass of 2500 kg of dry silica gel and an entering air flow rate of 0.38 m\(^3\)s\(^{-1}\). The speeds of the fronts are determined by the values of \( \gamma_F \) and \( \gamma_0 \) (Fig. 2) since from eqn (1)

\[ \left( \frac{\partial x}{\partial \theta} \right)_F = \frac{v}{1 + \mu \gamma_F} \]

\[ \left( \frac{\partial x}{\partial \theta} \right)_0 = \frac{v}{1 + \mu \gamma_0}. \]

The smeared form of the change in \( G \), (Fig. 3) is due to the variation in \( \gamma_0 \) between \( C \) and \( B \) (Fig. 2).
For comparison purposes, the outlet air temperature from a bed of gravel (assumed non-adsorbing) and having the same mass, is shown in Fig. 3.

3. ENERGY STORAGE FOR DRYING PURPOSES

One use for stored energy is in the drying of timber or farm produce. A simplified model of an adsorbent store supplying warm dry air to a bed of moist material (load) which is to be dried can be examined with reference to Fig. 4.

![Fig. 4. Sketch illustrating the operation of an adsorbent energy store.](image)

The store is brought to state point A, Fig. 4 by air from a solar collector. Ambient air at state point B then enters the store and air leaving the store is delivered to the load also assumed to be at state point B.

Two assumptions in addition to those enumerated in the previous section, are made to simplify analysis of the store-load interaction, viz.

(vi) The store and load have the same properties, $F$, $G$, $\gamma_0$ and $\gamma_c$.

(vii) These properties are such that lines of constant $G$ and lines of constant bed water content $W$ coincide.

Banks[7] shows that this limit is approached by adsorbents which adsorb large quantities of water, and data in[8] shows that silica gel closely approximates this situation.

Equations (1) describe changes in the properties $F$ and $G$ which occur in the bed. As the bed and adjacent air are in equilibrium, changes in bed state at the bed outlet end give rise to equal changes in the equilibrium state of the outlet air. If the load is changed from the equilibrium state $B$ to the equilibrium state $A$, the load property $G$ has changed from $G_B$ to $G_A$. Since lines of constant $G$ are effectively lines of constant load water content $W$, the load water content has been changed from $W_B$ to $W_A$, which is drying of the load material. Hence the mass of water evaporated from the load, and consequently the mass of load which has been dried, is determined by the quantity of air having the property $G_A$ which can be delivered to the load.

Referring to Fig. 3 and considering an adsorbent store initially at state $A$ throughout, air entering at state $B$ leaves at state $A$ for a short period until the $F$ front reaches the bed outlet. At this time the air outlet property $F$ changes rapidly from $F_A$ to $F_C$, the property $G$ remaining constant at $G_A = G_C$. The exit air temperature and absolute humidity have dropped with the change in $F$ from $t_a$ to $t_c$ and $w_a$ to $w_c$. The air outlet state then remains constant at state $C$ for a long period of time, until the diffuse $G$ front reaches the end of the bed. The air outlet temperature after remaining constant at $t_c$ then falls slowly to $t_b$ while the air outlet absolute humidity rises to $w_b$. The time for which air [having the property $G_A(=G_C)$] is delivered, is the time taken for the $G$ front to reach the end of the bed. The time for which air of similar drying potential is delivered from the non-adsorbing store, is the time for which air is delivered at state $A$. By comparing these times it is possible to compare the two stores on the basis of stored energy for drying. This is conservative as far as the adsorbent store is concerned since air delivered at states between $C$ and $B$ as the diffuse $G$ front passes the end of the store, still has some drying potential.

The period over which air emerges from the adsorbing store before the $G$ front reaches the store outlet is given by the value of $\gamma_G$ at $C$ since, from eqns (1),

$$\frac{\partial x}{\partial t} = 1 + \mu \gamma_G \approx 1 + \mu \gamma_G$$

Hence, $\theta_w$, the period over which air is delivered with property $G_A$ is

$$\theta_w = \frac{M_w \gamma_G}{m_i}$$

Similarly, for the non-adsorbing bed

$$\theta_N = \frac{M_N}{m_i}$$

Putting $\theta_w = \theta_N$

$$\frac{M_N}{M_w} = \frac{\gamma_G}{\gamma_c}$$

To obtain some illustrative values of $(M_N/M_w)$ and the corresponding volume ratio $(V_N/V_w)$, state $B$ has been taken as 27.7°C and 0.018 kg water/kg dry air. State $A$ has the same absolute humidity and the temperature is varied. Values of $(M_N/M_w)$ and $(V_N/V_w)$ are shown in Table 1, assuming the specific heat of the non-adsorbing store to be 0.92 kJ kg⁻¹ K⁻¹.

<table>
<thead>
<tr>
<th>$t_a$ (°C)</th>
<th>$\gamma_G$</th>
<th>$M_N/M_w$</th>
<th>$V_N/V_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.6</td>
<td>15</td>
<td>16.4</td>
<td>8.2</td>
</tr>
<tr>
<td>56.0</td>
<td>19</td>
<td>20.7</td>
<td>10.4</td>
</tr>
<tr>
<td>51.8</td>
<td>22</td>
<td>24.0</td>
<td>12.0</td>
</tr>
<tr>
<td>47.6</td>
<td>27</td>
<td>29.4</td>
<td>14.7</td>
</tr>
<tr>
<td>41.3</td>
<td>37</td>
<td>40.3</td>
<td>20.2</td>
</tr>
</tbody>
</table>

The values of $(M_N/M_w)$ and $(V_N/V_w)$ shown in Table 1 indicate an order of magnitude advantage in both the volume and mass of the adsorbing over the non-adsorbing store. The advantage of the adsorbing over the non-adsorbing store is decreased as the temperature is increased, but this is caused by the form of the silica gel isotherm. For silica gel $(\partial W/\partial t)_a$ decreases as $t$ increases, so that as the temperature at $A$, Fig. 1, is increased, proportionately less water is adsorbed by the bed material. A different isotherm could change this effect.
so that the characteristics could be tailored to the characteristics of the collector and the load.

An examination of Fig. 4 allows the effect of thermal losses from the store to be determined. Suppose that thermal losses occur but no water or water vapour can escape from the bed. The bed temperature will decrease to \( t_9 \) in Fig. 4 (assuming \( t_8 \) to be the ambient temperature) but the water content \( W_A \) remains constant. The final state of the store is then given by state point \( E \), Fig. 4. Since the lines of constant \( G \) and \( W \) closely coincide, then the drying potential of the store has changed little. Hence, the occurrence of thermal losses has not appreciably affected the useful energy stored by the adsorbent bed, indicating that energy may be stored indefinitely.

There may be some advantages in operating the store following thermal losses. This will lead to the load being dried at lower temperatures than would be the case if drying was carried out with air at state \( A \) as delivered from a non-adsorbent store. The same argument applies but to a lesser degree to air delivered from a store at equilibrium state \( A \). This may lead to a reduction in such problems as thermal stresses or thermal stability in the load material.

4. SENSIBLE ENERGY STORAGE

The behaviour of an adsorbing store has thus far been examined in relation to its use for storing energy for drying. The following analysis shows that such a store also has volume and mass advantages over a non-adsorbing store when used for storing sensible energy; that is energy which is dependent on temperature level only.

Suppose that the store has been brought to state \( A \) (56°C, 0.018 kg water vapour/kg dry air). Energy supplied to the load from the store is to maintain it at temperature \( B \), Fig. 1. It is assumed that air at state \( B \) (29.7°C and 0.018 kg water vapour/kg dry air), is available to extract energy from the store and deliver it to the load.

Sensible energy delivered by the non-adsorbing store is,

\[
E_N = M_N C_v (t_A - t_B).
\]

Making the conservative assumption that the only useful sensible energy delivered by the adsorbing store is at \( t_C \), Fig. 1, then

\[
E_W = M_w (t_C - t_B) \gamma_{0,C} C_f.
\]

For the same quantity of sensible energy stored,

\[
M_w = \frac{t_C - t_B}{t_C - t_B} \left( \frac{\rho}{\gamma_{0,C}} \right)^{-1}.
\]

Using appropriate values,

\[
\frac{M_w}{M_N} = 13.5
\]

which is of the same order as values shown in Table 1.

5. HEAT RECOVERY

From the foregoing discussion, it is apparent that an adsorbing store needs to draw water vapour from the reject water vapour to the atmosphere. During the time energy is being stored water vapour is rejected to the atmosphere; on the other hand, when energy is removed from the store, moisture is gained from the air supply.

If the store was allowed to vent directly to the atmosphere, then energy rejected from the load or store would be lost and the overall system performance significantly reduced. A practical method of reducing the magnitude of this energy loss yet drawing on the atmospheric water vapour source/sink, is to introduce an air to air heat exchanger or regenerator into the circuit, as shown in Fig. 5. Rotary regenerative heat exchangers are used fairly extensively in air conditioning systems at present[8, 9].

![Fig. 5. Layout of system employing air to air heat exchanger.](image)

By using the control valve and dampers the four basic operating modes of the system can be achieved, viz.

(i) Collector supplying store only.
(ii) Collector supplying store and load.
(iii) Collector and store supplying load.
(iv) Store only supplying load.

This a satisfactory solution to the problems of the drying system, and need not represent an increase in cost as a drying system supplied by a conventional source benefits from a heat exchanger on the load exhaust line.

6. POSSIBLE MATERIALS

Thus far, silica gel has been used to illustrate the behaviour of adsorbing beds. At a cost of around $0.8 Aust. per kg dry, it is clear that gel is much too expensive to be used for energy storage.

A suitable material needs to adsorb or absorb large quantities of water and must also be cheap. A few materials have been examined to determine their suitability by measuring the amount of water adsorbed when exposed to a saturated atmosphere. By far the most promising to date comprises crushed gravel soaked in a solution of lithium chloride. The particular sample tested had a saturation water content of around 12 per cent, based on the dry weight of lithium chloride plus gravel, compared with about 40 per cent for silica gel. Clearly this value could be much increased using a more porous carrier material. However, lithium salts are expensive and it may be possible to use a hygroscopic salt such as calcium chloride which is extremely cheap.

The potential of these salts can be gauged by calculating the differential quantity of water adsorbed by lithium chloride when changed from states \( A \) to \( B \), Fig. 1. From
data in [10] this quantity is around 1 kg water/kg dry LiCl compared with around 13 kg water/kg dry gel for silica gel. It appears that further investigations of suitable salts and carrier materials is warranted.

As an aside, a hygroscopic salt store need not be in the form of a packed bed. An air-solution contacting tower could be employed and energy stored in a tank in the form of a concentrated solution. This type of energy store has already been suggested for an air conditioning system[11].

7. CONCLUSIONS

The examples given in this paper show the large reductions in store volume that can be achieved using adsorbent materials. A further benefit is that if vapour proofing is employed but insulation is dispensed with, energy can be stored indefinitely. Furthermore, in this case where temperature sensitive materials are to be dried, the lower drying temperatures obtained with air from the adsorbing store can be of great advantage. Suitable materials at present available seem too expensive, and work appears necessary to develop new ones using hygroscopic salts and appropriate carrier materials.

Owing to the complex, transient nature of the processes described here, further studies will be necessary to extend the simple analysis presented here and verify the validity for practical systems of the conclusions reached.

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NOMENCLATURE

- \( C_i \): specific heat or air-water-vapour mixture, J kg\(^{-1}\) K\(^{-1}\)
- \( C_h \): specific heat bed material, J kg\(^{-1}\) K\(^{-1}\)
- \( E \): stored sensible energy
- \( F \): properties defined by eqn (1), K
- \( G \): properties defined by eqn (1), K
- \( M \): mass of bed, kg
- \( m \): air mass flow rate, kg s\(^{-1}\)
- \( n \): density of dry bed material kg m\(^{-3}\)
- \( t \): temperature, K
- \( V \): bed volume, m\(^3\)
- \( w \): air absolute humidity, kg water/kg dry air
- \( x \): coordinate in fluid flow direction, m
- \( y_c \): properties defined by eqns (1), K
- \( y_o \): properties defined by eqns (1), K
- \( e \): bed porosity
- \( \mu \): density ratio \( P(1-\epsilon)/\rho \)
- \( \sigma \): specific heat ratio \( C_h/C_i \)
- \( \rho \): air concentration, kg dry air/m\(^3\) mixture
- \( \theta \): time, s

Subscripts

- \( A \): at state points A, B and C
- \( C \): relating to non-adsorbing bed
- \( W \): relating to adsorbing bed

REFERENCES


Resumen—La acumulación de energía es una parte importante de muchos sistemas helioenergéticos. A causa de los pequeños potenciales térmicos obtenibles de los colectores planos se emplean grandes masas y volúmenes cuando se acumula energía por elevación o disminución de la temperatura de un tanque o un lecho de piedras. Este artículo propone la acumulación de energía en la forma de calor de adsorción en lechos de material adsorbente. Esto se obtiene fácilmente tomando el agua como adsorbato, de tal suerte que el vapor de agua se transfiera hacia o desde el adsorbente por el aire húmedo fluente a través del lecho. El gran calor de adsorción hace que una pequeña cantidad adsorbida de agua libere una gran cantidad de energía de la que la mayor parte es transferida a la oriente de aire. Se muestra que los materiales adsorbentes pueden ocupar un lugar mucho menor que los no adsorbentes para la misma cantidad de energía acumulada, y que la adsorción térmica puede ser prescindida. Con tal que el recipiente sea impermeable al vapor de agua, la energía puede ser almacenada indefinidamente.

Résumé—Le stockage d'énergie est un paramètre important de beaucoup de dispositifs solaires. A cause du faible niveau de température disponible à partir des capteurs plans, le stockage par élévaison ou abaissement de température d'un réservoir de fluide ou d'un lit de graviers, met en jeu des volumes et des poids importants. Cet article propose le stockage d'énergie sous la forme de chaleur d'adsorption dans des lits de matériaux adsorbants. Ceci est réalisé en
choisissant l'eau comme élément adsorbé, de telle sorte que de la vapeur d'eau soit transférée vers ou à partir de l'adsorbant, par l'air humide circulant à travers le lit. L'importante chaleur d'adsorption se traduit par le fait qu'une petite quantité d'eau libère une quantité d'énergie plus importante, dont la plus grande part est transférée au courant d'air. On montre que les matériaux adsorbants peuvent occuper un volume beaucoup plus petit que des matériaux non-adsorbants pour la même quantité d'énergie stockée, et que l'on peut se dispenser d'isolation thermique. A condition que le réservoir ne soit pas perméable à la vapeur d'eau, l'énergie peut être stockée indéfiniment.