

SOLAR ENERGY STORAGE USING CHEMICAL POTENTIAL CHANGES ASSOCIATED WITH DRYING OF ZEOLITES

RONALD A. SHIGEISHI,* COOPER H. LANGFORD and

BRYAN R. HOLLEBONE

Metal Ions Group and Chemistry Department, Carleton University,
Ottawa, Canada K1S 5B6

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Abstract—Compact solar storage systems depend upon identification of systems which can store energy as chemical potential. Simple, noncorrosive, systems that operate at reasonably low temperatures are rare. The use of the heat of adsorption of moisture on zeolite molecular sieves is discussed here. The advantages of zeolites are high heats of adsorption (as much as 80 kJ mol^{-1}), large maximum adsorption capacity ($0.2\text{--}0.3 \text{ kg H}_2\text{O/kg}$ adsorbent) and easy control of the store following from control of heat output by regulations of flows of moist air. The disadvantages are the relatively high upper temperature required to utilize maximal storage capacities (up to 250°C) and cost. There is reason to project falling cost.

Zeolite storage is compared favourably with respect to capacity to water, stone, and heat of phase change systems. Compared to salt hydrates, acid solution, and salt solutions any capacity advantage is supplemented by low corrosion and opportunity for long term storage. Zeolites are compared favourably to alternative adsorbent materials; alumina, charcoal, and silica gel.

The warm dry air output from a zeolite storage bed can be utilized not only in space heating but also in the drying of agricultural timber and fish products.

1. INTRODUCTION

The intermittent nature of solar radiation makes thermal energy storage a mandatory feature of a solar energy system. The methods used for this storage are conveniently divided into two groups according to the temperature required for their operation. Here, 300°C is taken as the demarcation between low and high† temperature. Below this value, two methods of storage are commonly used, sensible energy storage via the heat capacity of the working material and storage in the form of heat associated with a phase change or solution process. For any method of storage the choice of the material is subject to the following general constraints: (1) low cost material; (2) low cost and simplicity of design for the material container and auxiliary system required for delivery of energy to and from the storage unit; (3) non-toxicity of material; (4) minimum deterioration in performance or degradation of material with repeated cycling; (5) low volume and weight; (6) high energy density.

Sensible energy storage is simple in both concept and application. The cost of material in the case of water or gravel is minimal although very cold climates require antifreeze in water which adds considerably to the cost. The main disadvantage is low energy density which necessitates a large volume of storage material and a massive container. Unfortunately problems are usually associated with the phase change process. The most common type of compound considered for heat of fusion storage is a hydrated salt consisting of some combination of alkaline or alkaline earth positive ions and anions such

as Cl^- , PO_4^{3-} and SO_4^{2-} , as well as water. The advantages and disadvantages of hydrated salts are readily seen in sodium sulphate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ which has been studied extensively[1]. This is a commonly available cheap salt (1¢/kg) melting at 32°C with a latent heat of 78 kJ/mol . The main difficulty with the fusion process is the formation of a liquid and solid phase with the latter sinking to the bottom and becoming unavailable for the reverse process. Thickening agents have been added in order to produce a gel in which the solid phase cannot settle out but the results have been only partially successful. A second difficulty is the occurrence of supercooling. Nucleating agents have been added to overcome this problem but they appear to deteriorate over long periods. Furthermore, design problems exist because the solutions are very corrosive and heat exchangers must be specially designed to ensure that the material freezing rates can keep up with the rates of heat removal. In view of these difficulties and the uncertainty of success over a long time span search is underway for more suitable phase change materials[2].

Paraffin waxes have been used as phase change materials but these have half the energy density of salts and are a potential fire hazard[3]. Thermal storage in the form of heats of solution have been attempted as in the case of sulphuric acid-water solutions and various saturated salt solutions[4]. These studies are still in the preliminary stages but the materials are certainly corrosive.

Up to the present, low cost and simplicity of design have been the paramount considerations. For these reasons operational systems have relied on sensible energy storage in the low temperature range despite the low energy density.

*Author to whom correspondence should be addressed.

†High temperature "storage" can involve fuel synthesis.

The desirability of high energy density processes has led to the investigation of thermal storage in the form of heats of chemical reactions which are often an order of magnitude larger than latent heats. Moreover, energy stored as chemical potential is not subject to thermal loss through the insulation and promises indefinite storage periods. Most suitable chemical reactions, however, require temperatures in excess of 300°C [5]. In the initial step high temperature solar energy is used to drive the reaction in the endothermic direction. The energy stored in the products is then released on demand, usually by lowering the system temperature and catalytically driving the reaction in the exothermic direction. The criteria for the selection of an appropriate reaction are the magnitudes of the equilibrium and rate constants at the cycling temperatures. Both factors should be large in the endothermic heat storage step to ensure a rapid and complete reaction. In order that the reverse heat release reaction at a lower temperature proceed equally completely the equilibrium constant must decrease sharply with temperature. The rate of this reverse reaction may often be assisted by catalysts. A detailed discussion is given by Wentworth and Chen [5].

A comparison of the energy densities and volume of material required for the storage of 4.18×10^6 kJ ($\approx 4 \times 10^6$ Btu, $\approx 10^6$ kcal) is given in Table 1 for the three methods of storage. Except for the case of chemical storage, a 50°C temperature rise in storage material is assumed.

Heat of reaction storage is obviously in a class by itself. Of the remainder, the hydrated salt is almost three times as efficient on a volume basis and almost twice on a weight basis as water. But, a higher energy density, lower temperature system is clearly desirable.

2. ENERGY STORAGE BY ADSORPTION

Adsorption of a gas by a solid is a spontaneous process in which the system entropy decreases due to the loss of freedom of molecules in the adsorbed phase. From the second law of thermodynamics

$$\Delta G = \Delta H - T\Delta S$$

and since ΔG and ΔS are both < 0 , $\Delta H < 0$; i.e. adsorption is accompanied by the release of the heat of adsorption. The reverse process, desorption, is then endothermic.

The utilization of the adsorption-desorption cycle as a means of low temperature heat storage was first proposed by Close *et al.* [6] using water vapour as the *adsorbate* (material which is adsorbed) and silica gel as an (expensive) *adsorbent* (material on which adsorption occurs). In their simple system hot air from the solar collector is passed through the adsorbent bed raising its temperature and desorbing water. Bed "dryness" is then a measure of energy stored. To extract heat, moist ambient air is driven through the hot bed which initially provides sensible heat. When the bed has cooled sufficiently, adsorption of the water vapour on the air stream releases the heat of adsorption. The result is a warm, relatively dry air supply. A generalized analysis of the engineering performance of such a system was given [6]. The question left open was choice of suitable materials.

The sensible heat content of the bed depends on the adsorbate-adsorbent combination and the cycling temperatures. With a judicious choice, this is only a small part of the total heat storage and even if it were not used the energy density compares favourably with phase change systems since heats of adsorption are comparable to latent heats. The adsorbent bed may therefore without great loss in efficiency be cooled to room temperature to store energy indefinitely provided water vapour can be excluded. *This provides a decided advantage over phase change materials which require efficient insulation to maintain temperatures between set limits.*

3. CRITERIA FOR SELECTION OF ADSORBATE

Adsorption is generally characterized as physical or chemical depending on the type of force responsible for the process. Physical adsorption is due to "van der Waals" and other weak intermolecular forces which exist between all materials and hence are non specific. Heats of physical adsorption are therefore, comparable to

Table 1. Energy storing properties for three methods of storage

	water	gravel	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	$\text{NH}_4\text{Br}_{(s)} \rightleftharpoons \text{NH}_3(g) + \text{HBr}_{(g)}$
specific heat kJ/kg/°C	4.18	.84	2.09	
heat of fusion or reaction kJ/kg			251	1910
density kg/m ³	10^3	2.56×10^3	1.55×10^3	2.43×10^3
energy density kJ/kg	209	42	355	1910
energy density kJ/m ³	209×10^3	107×10^3	552×10^3	5540×10^3
weight required kg	2×10^4	10×10^4	1.18×10^4	$.22 \times 10^4$
volume required m ³	20	39	7.6	.90

latent heats. Chemical adsorption, on the other hand, being the result of chemical interactions identical to those leading to chemical bonds, is specific to those materials which show chemical affinity. While heats of chemical adsorption may be similar to heats of reactions thermal storage by such chemisorption is generally not feasible because of the minute quantities adsorbed and the high temperatures required in the desorption step.

In choosing the best adsorbate previous criteria such as cost, availability, toxicity, etc. still apply. In addition to these the adsorbate must be capable of being adsorbed in large quantities and with a high heat of adsorption. This last is determined to a large degree by the polarity of a molecule. The more polar the molecule the greater the dispersion, polarization and quadrupole contributions to the "van der Waals" forces in both adsorbate-adsorbent and adsorbate-adsorbate interactions. This results in larger heats of adsorption and greater adsorbate-adsorbent affinity. Maximum heats may be achieved by adding the H-bonding interaction which occurs in the N-H...O and O-H...O systems.

Another prime consideration is the boiling point of the adsorbate. Since adsorption is similar to condensation of a gas, the lower the temperature at which adsorption occurs relative to its boiling point, the larger the amount adsorbed. Very little adsorption occurs in most cases at temperatures above the boiling point of the gas. Since the desirable lowest adsorption temperature for storage systems is room temperature, the boiling point should be substantially higher than 20°C.

Among the common polar gases such as H₂O, NH₃, CO, SO₂ etc. there is little doubt that water is the most suitable adsorbate. Aside from low cost and ease of handling it has a high latent heat, a substantial dipole moment, hydrogen bonding capability and a convenient boiling point for the adsorption-desorption cycle. A further advantage as pointed out by Close and Dunkel [6] is the dual capability of heating and drying. The latter is of obvious industrial importance in the drying and processing of agricultural, timber and fish products.

4. CRITERIA FOR SELECTION OF ADSORBENT

There are four major classes of solid adsorbents in use today [7]. These are (1) aluminum oxide in the form of alumina gel and activated alumina; (2) carbon in the form of various charcoals and activated carbon; (3) silica gel, a porous material; (4) crystalline zeolites-aluminosilicates with a porous structure; usually in pellet or spherical form.

All of these are chemically inert, resistant to deterioration and commercially available in large quantities in various particle sizes to suit the desired packing density in the storage bed. Being highly porous with surface areas in the range of 3×10^5 – 7×10^5 m²/kg [8, 12] they satisfy one of the main requirements, the ability to absorb large quantities of water.

The adsorption of water at room temperature under equilibrium conditions for these four classes of adsorbents is shown as a function of relative humidity in Fig. 1 [9, 13, 14]. The molecular sieves obtained from the Linde Company are labelled 13X, 4A and 5A. The first two are sodium aluminosilicates which differ slightly in void volume with 13X being larger, while 5A is identical to 4A except that sodium is replaced by calcium. Strictly on the basis of maximum capacity, silica gel and charcoal are best. Charcoal, however, unlike the others shows no preferential adsorption of water vapour. On the contrary, organic vapours in general displace water vapour from carbon. Carbon adsorbents therefore are unsuitable unless impurities in the air stream are eliminated. The isotherms further show that the extent of adsorption depends on the moisture content of the air with molecular sieves being superior at low relative humidity while silica

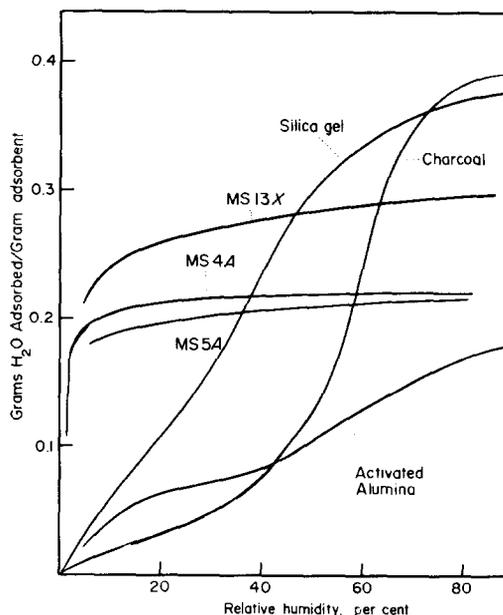


Fig. 1. Room temperature adsorption isotherms of water on various adsorbents as a function of relative humidity.

Table 2. Capacity of molecular sieve 4A compared to silica gel and activated alumina

Relative Humidity	ratio: 4A to silica gel	ratio: 4A to activated alumina
5	6	5
10	3	4
20	2	3
30	1.2	2.4

gel is better at high values. This is also seen in Table 2[10].

Adsorption at temperatures greater than 25°C is of interest since the desorption step occurs at elevated temperatures and it may be desirable to begin the adsorption cycle before the bed cools to room temperature. The maximum amount of adsorption as a function of adsorption temperature, assuming a water vapour pressure of 10 mm Hg, is given in Fig. 2[11]. This shows the extremes of temperatures at which the adsorption-desorption cycle may be carried out to obtain a significant amount of net adsorption. Desorption from silica gel is virtually complete just above 100°C but the bed must be cooled to below 30°C for the substantial re-adsorption. This may be a problem for this and related materials since the adsorption process itself will warm

the bed considerably. In fact, commercial drying systems using silica gel (or activated alumina) require cooling rods in the bed to ensure isothermal operation; otherwise the bed temperature rises and drying capability is drastically reduced[15]. This would not be such a problem with molecular sieves since they do not exhibit a dramatic decrease in adsorption with increasing temperature. If molecular sieve 13X is used, desorption should occur at 150°C or higher. Even at this temperature there is ~0.05 g H₂O/kg adsorbent. If the bed is cooled to 50°C for the adsorption step there is a net adsorption of ~0.21 kg/kg adsorbent. For 4A the net adsorption between these temperatures is 0.13 kg H₂O/kg adsorbent.

Choice of an adsorbent must also be determined by the magnitude of the heat of adsorption. In reports on the use of adsorbent beds[6, 16] where silica gel (was the chosen, this factor appears to have been ignored. This is regrettable since it would be equivalent of choosing a chemical reaction solely on the extent of the reaction without consideration of the intensive parameter heat of reaction. For silica gel, activated alumina and charcoal the respective values are 46.0, 44.7 and 41.8 kJ/mol of adsorbed water[17, 18]. These values decrease only slightly with amount adsorbed. Heats of adsorption on zeolites depend slightly on the zeolite structure and show slightly greater variation with water content but are in general much higher. This is seen in Fig. 3 where the variation is plotted over the middle water content region for 4A and 5A[19]. For zeolite 13X the differential heats of adsorption are 94.9 and 70.6 kJ/mol for 0.03 and 0.24 kg H₂O adsorbed/kg adsorbent. At water contents below 0.03 kg H₂O adsorbed/kg adsorbent the heats are in excess of 125 kJ/mol reflecting the tenacity with which residual water is held.

With data on adsorptive capacity and heats of adsorption, energy storage densities may be calculated. To provide a comparison with Table 1 a temperature rise of 50°C and a storage of 4.18×10^6 are assumed in the relevant entries in Table 3.

The superior capability of adsorbent beds with respect

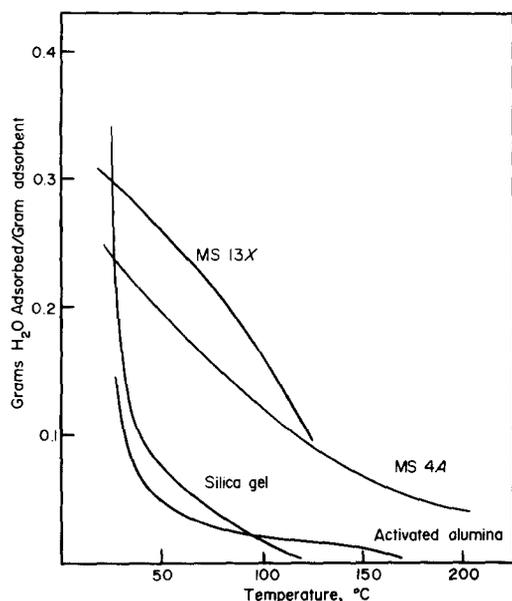


Fig. 2. Maximum amount of water adsorbed as a function of adsorption temperature. $P_{H_2O} = 24$ torr.

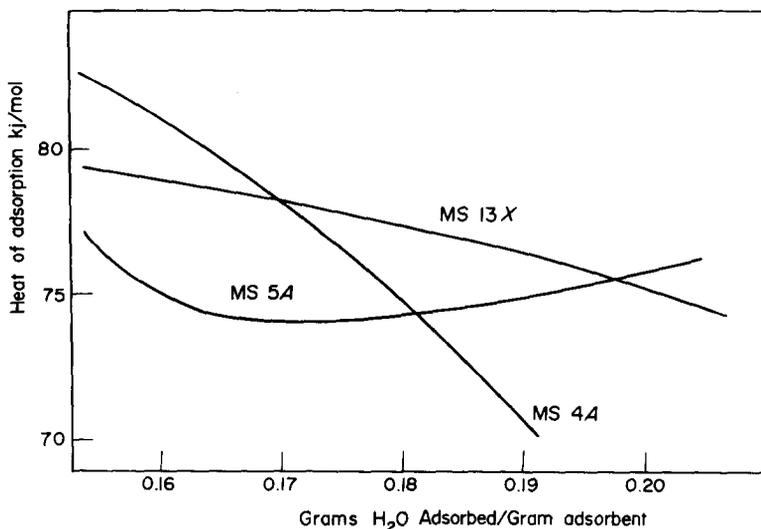


Fig. 3. Heat of adsorption as a function of amount of adsorbed water.

to sensible heat and phase change storage is seen in comparison of Tables 1 and 3. Of the adsorbents, the molecular sieves are superior with 13X being the best.

We also conducted experiments on other water adsorbents not discussed in Table 3. These included bentonite clay, drierite, boric acid, and magnesium sulphate. The latter two presented regeneration problems and vitiating the promise of their large storage capacities.

CONCLUSIONS

The combination of literature data and experiments reported here establish that energy densities of water-adsorbent bed storage systems can exceed systems using latent heat storage. This advantage accrues without reference to the additional advantage of corrosion problems and the possibility of long term storage without massive insulation. The importance of long term storage cannot be overemphasized when considering the feasibility of solar heat utilization in northern and irregular climates. It may also be of great importance to short term seasonally specific uses such as agricultural drying. The final advantage is specific to process drying applications, heat is delivered in dried air.

The major disadvantages of zeolite-moisture storage systems are cost and temperature. It is not yet possible to give a definite treatment of limitations. Studies of zeolite adsorption dynamics are in progress and prices are in flux. There are two principle causes for optimism. First, the use of zeolites in detergent formulations promises a reduction in prices to \$0.35 to \$0.44 per kg by 1982 [20]. A large scale energy storage market might lead to further price decrease. Second, lower cost focusing collectors are now appearing on the market (e.g. the "suntrek" R of Alpha Solarco).

EXPERIMENTAL

In order to check the adsorption properties of adsorbents, sample experiments were carried out on a variety of commercially available adsorbents. These included silica gel (granular form) activated alumina (powder), and three molecular sieves 4A, 5A and 13X either in spherical or pellet form.

Approximately 10 g of adsorbent was weighed out into a 800 ml beaker alongside a 30 ml beaker half filled with water. The larger beaker was covered with aluminum foil and the water uptake determined after various time periods. The adsorption curves under this static equilibrium condition are shown for the more suitable ad-

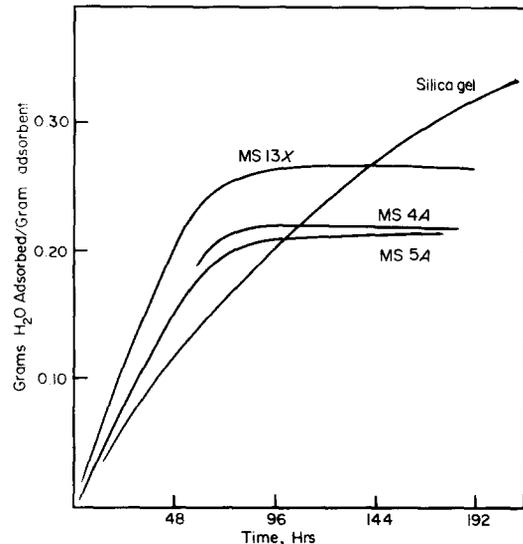


Fig. 4. Amount of water adsorbed at room temperature as a function of time.

Table 3. Energy storing properties for various adsorbents

	charcoal	activated alumina	silica gel	4A	5A	13X
Maximum capacity kg H ₂ O/kg adsorbent	.4	.19	.37	.22	.22	.30
Heat of adsorption (average) kJ/mol H ₂ O adsorbed	41.8	44.7	46.0	79.4	75.2	79.4
Energy stored kJ/kg adsorbent	920	472	945	970	920	1330
adsorbent specific heat kJ/kg/°C	1.09	1.00	.88	1.05	1.05	.92
energy density kJ/kg	1000	523	991	1020	974	1370
adsorbent density kg/m ³	480	890	670	780	680	600
energy density kJ/m ³	481×10 ³	464×10 ³	665×10 ³	796×10 ³	664×10 ³	823×10 ³
weight required kg	4170	8000	4200	4080	4290	3050
volume required m ³	8.7	9.0	6.3	6.0	6.3	5.1

Table 4. Amount of water adsorbed 24 and 48 hr after drying at 110, 150, 200, 250°C (kg H₂O/kg adsorbent)

	110°		150°		200°		250°	
	24 hrs	48 hrs						
Charcoal	.093	.14	.19	.14	.12	.16	.12	.16
Activated Alumina	.064	.11	.062	.11	.068	.12	.073	.13
Silica gel	.054	.10	.060	.11	.060	.12	.063	.11
4A	.053	.092	.052	.095	.072	.13	.067	.12
5A	.049	.082	.050	.089	.070	.12	.070	.12
13X	.086	.12	.091	.16	.10	.19	.12	.21

sorbents in Figs. 4 and 5. In the main, the final amounts adsorbed correspond well (within 10 per cent) to the literature values (see Fig. 1).

Of greater relevance to the energy storage question is the net amount of water adsorbed when the adsorbent is cycled at various temperatures. To obtain this information the adsorbent was first saturated with water and then dried at 110°, 150°, 200° and 250°C for 24 hr in an oven. After each drying, further adsorption was carried out. Time limitations limited the adsorption period to 48 hr. Results averaged over four cycles at each temperature are given in Table 4.

The amount reabsorbed is dependent on the type of adsorbent and the drying temperature. Charcoal aside, which is mentioned earlier is hydrophobic, the best adsorbent is molecular sieve 13X. The capacity of the others is about the same implying that the heat of adsorption is the dominant factor. For 13X if the drying temperature is limited to 110°C the energy density for heat of adsorption storage is 531 kJ/kg adsorbent, which is approximately *twice that of sodium sulphate decahydrate*. For molecular sieves 4A and 5A the values are 405 and 363 kJ/kg adsorbent respectively—still better than Na₂SO₄·10H₂O. At higher drying temperatures the energy densities for adsorbents would of course im-

prove. It should also be kept in mind that these figures are on the low side since drying the reabsorption is under static conditions. With an air flow through the bed the amount reabsorbed over a 48 hr period would be larger.

While energy density on a mass basis favours zeolites over sodium sulphate decahydrate, the reverse is true on a volume basis because of the relatively low density of zeolites. However, where the storage container is simple in design and easily constructed, the main cost of storage is the mass of storage material required. A high energy density on a weight basis is then economically advantageous.

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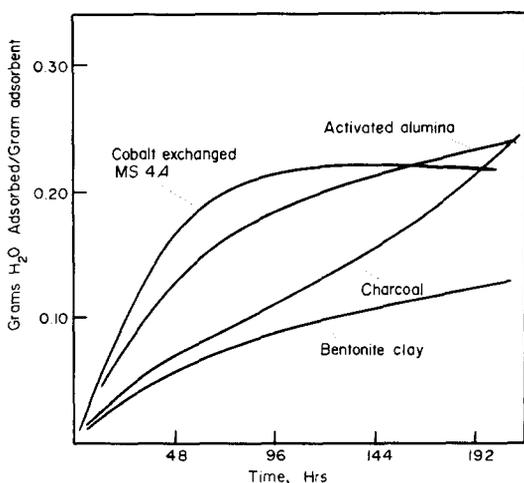


Fig. 5. Amount of water adsorbed at room temperature as a function of time. P_{H₂O} = 24 torr.

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