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Review of Regenerative Adsorption Heat Pumps

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NASA is again considering a permanent lunar base as part of its new "Exploration Vision." Because the lunar surface reaches 100°C near the equator during the lunar day (14.75 Earth days) and −100°C during the lunar night (also 14.75 Earth days), some type of heat pump is needed to elevate the temperature of absorbed sunlight and interior waste heat in order to reject it to space. An earlier investigation by M. A. Lambert ("Conceptual Design of a Regenerative Adsorption Heat Pump for a Lunar Base," AIAA Paper 99-0465, 1999) identified adsorption (solid–vapor) heat pumps as one of two technologies best suited to this application, the other being a mechanical vapor compression device with a high-efficiency centrifugal compressor. In order to properly preface the creation of a detailed design for an adsorption heat pump, this investigation reviews the state of the art in adsorption heat pumps, specifically the recently developed, much more efficient, regenerative variants. The principal figures of merit are the coefficient of performance for cooling (COP_C) and the specific cooling power. Nonregenerative adsorption heat pumps exhibit a COP_C of only 0.3 to 0.4, whereas regenerative designs have achieved a COP_C of 1.1 with 70% regeneration of waste heat. Attention has focused on maximizing overall heat transfer coefficient and minimizing nonadsorbent mass of the most critical component, the adsorption bed, while maintaining adequate vapor permeability. This involves establishing a thermal wave temperature gradient traversing the bed, which minimizes the temperature difference for heat transfer and entropy generation. A number of novel designs have resulted. The most studied adsorbents are zeolites (a class of highly nanoscopically porous minerals), activated graphite, and silica gel. The refrigerants receiving the greatest attention are ammonia, methanol, and water.

Nomenclature

A_{ads} = contact area between the adsorbent and heat exchanger (m^2)
C_p = specific heat, kJ/kg-K
COP_C = coefficient of performance for cooling
h_{cont} = thermal contact conductance, W/m^2-K
h_f = heat transfer coefficient of heat transfer fluid, W/m^2-K
h_{fg} = heat of vaporization, kJ/kg
h_{sf} = heat of sublimation, kJ/kg
k_{ads} = thermal conductivity of adsorbent, W/m-K
k_f = thermal conductivity of heat transfer fluid, W/m-K
m_{ads} = mass of adsorbent, kg
T_{lift} = temperature difference between evaporator and condenser, $T_{\mathrm{lift}} = T_{\mathrm{evap}} - T_{\mathrm{cond}}$, K
U = overall heat transfer coefficient for a heat exchanger, W/m^2-K
α_{w-d} = ratio of nonadsorbent ("dead") to adsorbent ("live") mass
η_{Carnot} = Carnot (ideal) thermodynamic efficiency
θ_o = dimensionless outlet temperature for adsorbent bed
μ_f = dynamic viscosity of heat transfer fluid, N-s/m^2
ρ_f = density of heat transfer fluid, kg/m^3
ω = nondimensional switching frequency for heating and cooling an adsorbent bed

I. Adsorption Heat Pump for Permanent Lunar Base

NASA is redirecting its manned spaceflight program to extend beyond Earth orbit, as part of its recently announced "Exploration Vision." The first step will be to establish a permanent lunar base to research the effects of reduced gravity and other aspects of living in space on human health and to serve as a starting point for manned interplanetary exploration.

The lunar environment is extremely harsh. The lunar day lasts 29.5 Earth days. During the lunar daylight period (14.75 Earth days), surface temperatures can soar to 100°C at the equator, whereas during nighttime, temperatures can plummet to −100°C. These temperature extremes are why the six Apollo landings occurred at locations corresponding to early morning or late evening, where temperatures were closer to room temperature, requiring less complex and bulky thermal control equipment. The Apollo landings lasted less than one Earth day ($\approx 1/15$ lunar day), during which the moon rotated very little with respect to the sun, meaning that the sun was never very far above the horizon.

However, a permanent lunar base would be subjected to the aforementioned extremes of temperature. The base could be buried under the very fine powdered basalt and granite covering the lunar surface (called *regolith*, meaning "top rock"), which has low thermal conductivity. The lunar regolith would mitigate the temperature extremes experienced by the structures. However, this would require bulky earthmoving (moonmoving) equipment and its associated considerable expense (for design and launch). Conversely, a heat pump could be used to elevate the temperature of heat absorbed from the sun as well as internally generated waste heat above the effective environmental temperature, permitting it to be radiated to deep space.

Lambert[1] performed a feasibility study of cooling technologies (heat pumps) in order to recommend the best option for controlling the temperature of a lunar base. The principal goal of that study was minimizing overall mass of the heat pump, including its attendant solar collectors (either photovoltaic or thermal) and radiators, because mass is proportional to launch cost. The two best options are a mechanical vapor compression heat pump using a very efficient ($\eta_{\mathrm{Carnot}} > 85\%$) centrifugal compressor and an adsorption (solid–vapor) heat pump. Centrifugal compressors are a mature technology and their efficiency is nearing the practical limit. But there is considerable room for improvement of adsorption heat pumps, which have been the subject of in-depth study for less than 20 years. This paper reviews and critiques the available literature on adsorption heat pumps, identifies the most important parameters affecting performance, and describes avenues for improving the state of the art. It begins with a brief survey of heat pump technologies.

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II. Heat Pump Technologies

A. Mechanical Vapor Compression

The mechanical vapor compression cycle (reversed Rankine cycle) is overwhelmingly the most prevalent heat pump technology in use today. The heart of such a system is the mechanically or electrically driven compressor, of which there are several variants:

1) Rotary vane is the simplest and least efficient positive-displacement compressor used in small (<1 ton $= 3.5$ kW) applications such as refrigerators.

2) Reciprocating (piston–cylinder), another positive displacement device that is the most common in use today.

3) Rotary scroll is also a positive displacement device, but is more efficient (15%), simpler, quieter, and more reliable than reciprocating models, which scrolls are rapidly replacing in new production and retrofits.

4) Centrifugal compressors are not positive-displacement but rather steady-flow devices. They are the most efficient, but most expensive, and are employed in large-scale applications (typically >50 t $= 175$ kW). They are reliable but noisy.

Mechanical vapor compression is the only technology employed in automobiles and in almost all residential and light commercial settings. It is also used extensively in the heavy commercial and industrial sectors.

Since their introduction in 1931, synthetic chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) (e.g., R-11, R-12, R-22, and R-123) and their hydrofluorocarbon (HFC) replacements introduced in the late 1980s (e.g., R-134a, R-407, R-410), are essentially the only refrigerants used in mechanical vapor compression (reversed Rankine cycle) heat pumps.

In refrigeration terminology, efficiency is referred to as the coefficient of performance for cooling (COP_C), a dimensionless parameter defined as the ratio of cooling capacity (kW) to required power input (kW). The Carnot efficiency of positive displacement compressors has not risen much above 60%, even with the advent of scroll compressors, which have largely replaced reciprocating (piston–cylinder) compressors in small-scale stationary applications (e.g., residences) and have been adopted by some automakers. The isentropic (Carnot) efficiency of centrifugal compressors has reached 85%.

B. Reversed Stirling Cycle

Another mechanical heat pump, which has been studied for quite some time, is the Stirling-cycle mechanical gas compression heat pump. The Stirling cycle utilizes a refrigerant that remains a superheated gas throughout the cycle, as opposed to the reversed Rankine cycle, in which the refrigerant exists as both a vapor and a liquid at different points in the cycle. Recent improvements[2] in the performance of Stirling-cycle gas compression systems (achieving $\mathrm{COP}_C = 3.0$) still do not approach the efficiency of reversed Rankine-cycle vapor compression designs (COP_C in excess of 4) utilizing positive-displacement compressors.

The perennial desire for greater efficiency has also spurred renewed interest in older heat pump technologies, most of which were abandoned in the 1930s because their performance was eclipsed by that of mechanical vapor compression systems employing CFC and HCFC refrigerants.

C. Liquid–Vapor Absorption

One common alternative technology is the heat-powered, liquid–vapor absorption heat pump, which Ferdinand Carre patented in 1859. Since then, absorption heat pumps have been widely used for making ice. Today, absorption heat pumps also serve as large commercial and industrial chillers, where they are more economical then mechanical heat pumps.[3]

The major difference between the liquid–vapor absorption system and the mechanical vapor compression system is the primary form of energy used to drive the cycle. The mechanical compressor is replaced by a liquid pump, which requires a fraction of the power ($\approx 5\%$) to pump the liquid working fluid to high pressure. A burner or solar collector or any relatively low-quality heat source from a power plant or industrial process adds a large amount of heat to the generator to desorb the refrigerant from the absorbent. The most common refrigerant/absorbent pairs are ammonia/water (NH_3/H_2O)[2] and water/lithium bromide (H_2O/LiBr).[4] Liquid–vapor absorption systems usually exhibit low COP_C, typically 0.65 to 0.70,[2–4] even with substantial recovery and reuse of waste heat.[3]

D. Solid–Vapor Adsorption

Another technology that was supplanted by the advent of mechanical vapor compression systems is the heat-powered solid–vapor adsorption heat pump. Solid–vapor adsorption refrigeration operates on a principle similar to that of its better-known counterpart, liquid–vapor absorption refrigeration. However, in solid–vapor heat pumps the refrigerant is adsorbed onto a solid desiccant (freeze-dried) rather than absorbed into a liquid (dissolved) as in liquid–vapor heat pumps. The heat source can be a combustible fuel, but they require only a low- to medium-quality heat source at typically 150 to 250°C, such as waste heat from an industrial process, engine exhaust, or solar energy.

The adsorption phenomenon was discovered in 1848 by Michael Faraday when he noticed a decrease in pressure as vapor was passed over a cold adsorbent (desiccant) and an increase in pressure as heat was supplied to the adsorbent.[5] Thus, the mechanical compressor can be replaced by one or more pressure vessels filled with consolidated, granular, or powdered adsorbent (desiccant), herein referred to as *adsorbent beds* or simply *adsorbers*. Refrigerant vapor leaving the evaporator at low temperature and low pressure is adsorbed in the cool desiccant bed, after which the bed is heated to high temperature to desorb the vapor at high pressure, whence it passes to the condenser. A single bed allows intermittent refrigeration during its heating phase. Cyclically and asynchronously heating and cooling two or more adsorbent beds (or "adsorbers") results in continuous cooling.

Solid–vapor adsorption heat pumps were used in domestic refrigerators and refrigerated railroad cars in the 1920s and 1930s.[6] These required no electricity, an important feature in the days before national electrification, but exhibited COP_C of only 0.3 to 0.4.

Three adsorbent/refrigerant pairs have received the most attention to date: zeolite (a class of highly nanoscopically porous minerals)/water, activated carbon/ammonia, and silica gel (SiO_2)/methanol (CH_3OH). However, different combinations, such as zeolite/ammonia and activated carbon/methanol, are also feasible.

Liquid–vapor absorption and solid–vapor adsorption both are physical processes (physisorption), dissolution in the former and van der Waals (secondary) bonding in the latter. The strongest form of van der Waals bonding, hydrogen bonding, is exhibited by the small polar molecules H_2O, NH_3, and CH_3OH, which yield the best performance in solid–vapor adsorption heat pumps. An adaptation of solid–vapor adsorption being developed[7–9] is the solid–vapor, chemi-sorption heat pump, in which chemical reactions bind the refrigerant to the adsorbent. Two systems are receiving attention. The "complex compound" heat pump employs an alkali or alkaline metal/halogen salt (e.g., NaCl) as the adsorbent and a small polar molecule (e.g., NH_3) as the refrigerant, also called the ligand.[8,9] In the metal hydride heat pump, intermetallic compounds (of transition metals and/or rare earth metals) serve as the adsorbent and hydrogen gas (H_2) as the refrigerant.[7]

Desiccant cooling is a related technology in that it also employs solid adsorbents. However, desiccant cooling involves an open cycle rather than a closed cycle and proceeds as follows. Outdoor air (needed to meet industrial and commercial ventilation requirements) is drawn through half of a large (up to 2 m diam), slowly rotating wheel filled with corrugated paper coated with desiccant particles, resembling a big air filter. The desiccant adsorbs excess moisture, lowering the humidity of incoming air. The heat of adsorption liberated in this process heats the dried intake air. This excess heat is discarded either in a heat exchanger using outgoing air as the cooling medium or by a conventional mechanical vapor compression device. Once a given sector of the desiccant wheel has become saturated by moisture adsorbed from incoming air, it rotates out of the intake flow and is dried or "regenerated" by outgoing air heated by a natural gas burner. Desiccant cooling is beginning to penetrate the industrial and commercial sectors in regions where there is significant humidity.[10]

However, desiccant cooling is unsuitable for a lunar base for the following reasons. First, obviously there can be no exchange of air with the outdoors. Thus a desiccant cooler would simply trade latent heat for sensible heat, so that some type of heat pump would still be required to reject the waste heat.

Second, desiccant coolers can only remove latent heat (i.e., moisture). However, the latent heat load in a lunar base would be very small compared to the total (latent plus sensible) heat load. Conceptual designs for a lunar base usually assume a total heat load of 100 kW.[1] A crew of 10 astronauts would generate less than 1 kW of latent heat. The only other sources of moisture would be cooking and showering. It would be rather easy to limit the amount of moisture released during food preparation by using closed containers for heating food. Showers would be enclosed and equipped with vents and small condensing coils to reclaim steam. Over 98% of the heat load would be sensible, coming mostly from electrical and electronic equipment and solar radiation, with 10 astronauts contributing about 1 kW of sensible heat.

E. Thermoelectric Refrigeration

Thermoelectric refrigeration was discovered in 1834 by Jean Charles Athanase Peltier. He applied an external voltage to a loop of dissimilar metal wires, thereby reversing the current with respect to that in a thermoelectric generator (discovered in 1821 by Thomas Johann Seebeck), and observed cooling at one of the junctions. The flowing electrons serve as the working fluid, transporting heat through the circuit, heating one junction while cooling the other junction. The modern Peltier device uses a series of solid state (semiconductor) p–n–p–n–p–n junctions instead of dissimilar metal wires. Peltier refrigerators are currently capable of transporting only a few hundred watts of heat and are useful for such purposes as cryogenic cooling of optical sensors, as well as for space heating and cooling on a very limited scale.[3] Peltier devices have a low COP_C,[3] relegating them to a very limited number of applications, where simplicity, reliability, and quietness are desirable.

Thus, there are three potentially feasible heat pump technologies suitable for space cooling and heating of a lunar base. These are 1) mechanical vapor compression, 2) liquid–vapor absorption, and 3) solid–vapor adsorption. The condenser, thermostatic expansion (or throttling) valve, and evaporator are common to all three systems; they differ only in the manner in which refrigerant vapor is compressed. However, Lambert[1] eliminated option 2), because a liquid–vapor absorption device would be considerably heavier than either of the other two.

III. Adsorption Heat Pumps

A. Simple Cycle Adsorption Heat Pumps Not Utilizing Heat Recycling

The adsorption phenomenon employed to realize refrigeration with solid–vapor heat pumps was briefly described in Sec. II.D. The present section begins with a more detailed description of the operation of a simple cycle (no recycling of heat) adsorption heat pump to establish a background for discussing recent efforts to improve efficiency by recycling heat.

The thermodynamic cycle for an adsorption bed is described by Meunier et al.[11] and is shown in Fig. 1. It proceeds as follows:

1) Beginning at the lower left corner of the heavy-lined parallelogram and moving clockwise, the bed is heated and desorbs refrigerant vapor isosterically (i.e., at constant total mass in the adsorber), thereby pressurizing the bed until the top left corner is reached. At this point the pressure is great enough to cause vapor to flow from the hot bed through a one-way valve (a check valve) to the condenser.

2) Isobaric heating continues, desorbing more refrigerant and forcing it into the condenser until the top right corner is reached.

3) The bed is then cooled isosterically (at constant total mass in the adsorber) until the pressure drops low enough for another one-way valve connecting it to the evaporator to open, allowing vapor to enter the bed.

4) Isobaric cooling continues until the bed is again saturated with adsorbed refrigerant, thereby completing the cycle (i.e., returning to the lower left corner of the parallelogram).

According to Miles et al.,[5] the coefficient of performance (COP_C) for actual built and tested simple cycle (no recycling of heat) adsorption heat pumps is 0.3 to 0.4, perhaps even 0.45. This is primarily due to the fact that heat rejected from the adsorbent bed during the cooling phase was simply discarded. A second reason for low COP_C and low specific cooling power (SCP) is that much of the mass of the device (the pressure vessel and its internal heat exchanger) is nonadsorbing, or so-called dead, mass that is unavoidably heated and cooled with the adsorbent but contributes nothing to the compression effect.

If the heat of desorption for the refrigerant/adsorbent pair is equal to the heat of vaporization of the refrigerant, h_{fg}, and the thermal mass of the bed container (or shell) and internal heat exchanger approaches zero, the theoretical COP_C is 1.0. However, the heat of desorption is more on the order of the smaller heat of sublimation, h_{sf}, and the thermal masses of the shell and heat exchanger are not zero. Thus, the highest COP_C for a nonregenerative device is 0.3 to 0.4.

B. Recycling Heat to Increase COP_C

Recent efforts to improve performance have centered on increasing COP_C by recycling otherwise wasted heat that is necessarily

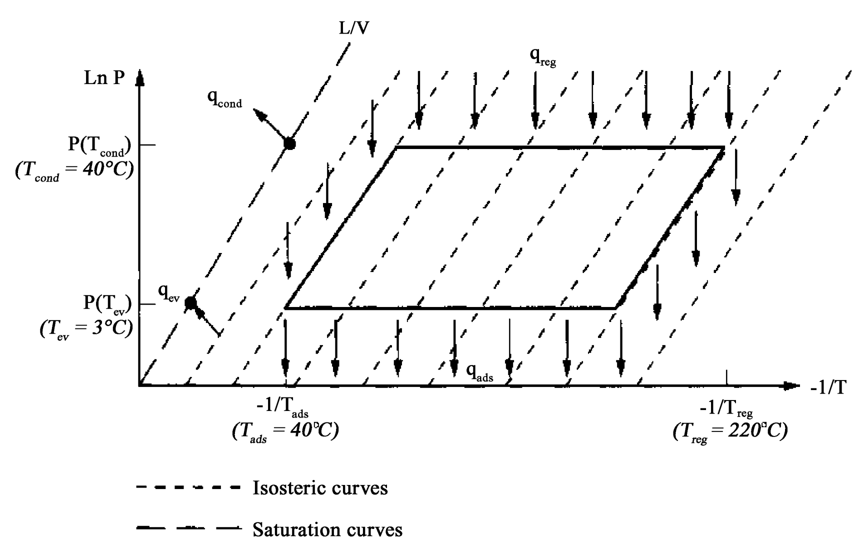


Fig. 1 Thermodynamic cycle for an adsorption bed.[11]

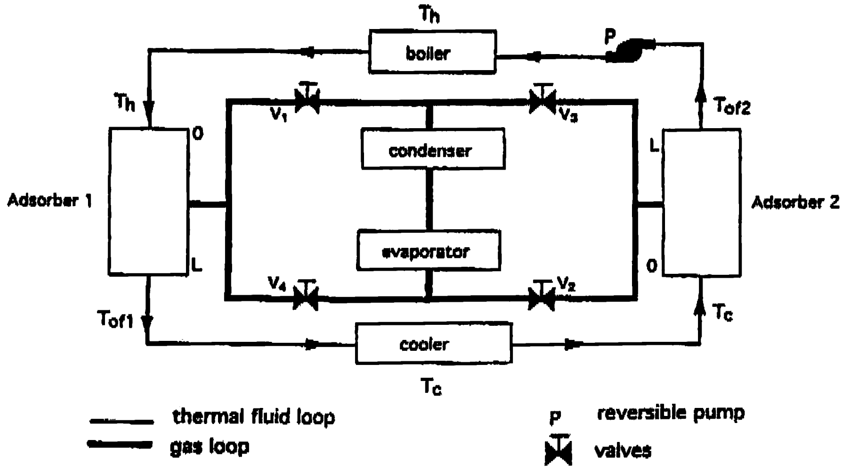
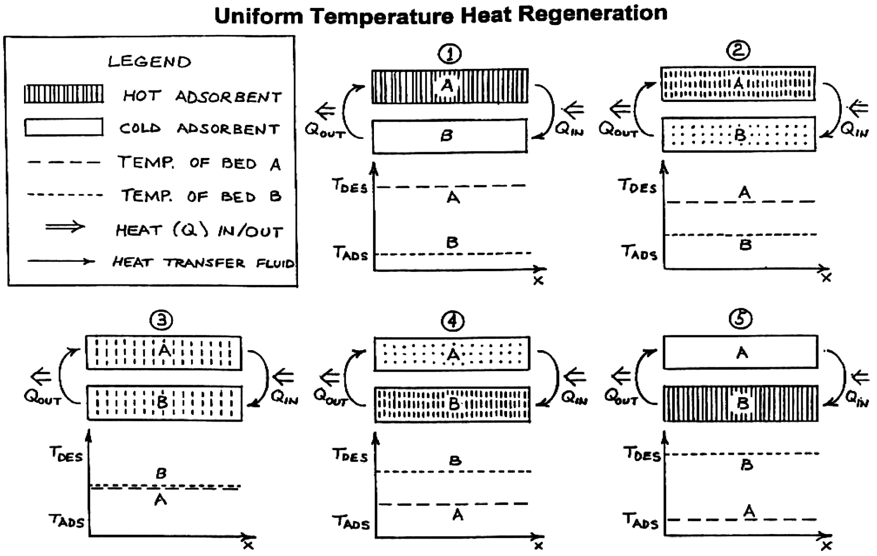


Fig. 2 Simplified schematic of a regenerative solid-vapor adsorption heat pump.[11]


Uniform Temperature Heat Regeneration

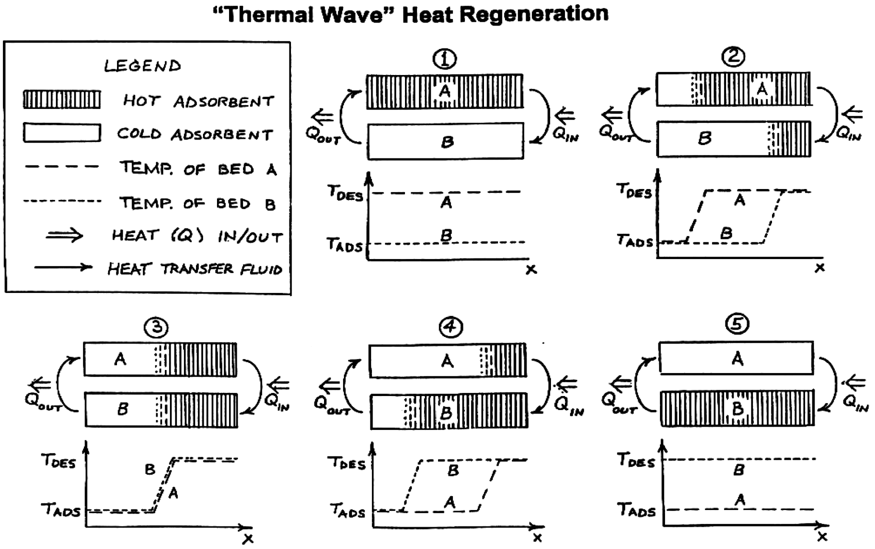

"Thermal Wave" Heat Regeneration

Fig. 3 Uniform-temperature heat regeneration (or heat recovery or double effect heating) and thermal wave heat regeneration.

rejected from the adsorbent bed being cooled by transferring it to the adsorbent bed being heated, thereby reducing the required external heat input (make-up heat). A heat transfer fluid (HTF, a mineral or silicone oil or even ethylene glycol) is used to transfer heat between beds (see Fig. 2). The effectiveness of heat recycling depends upon how the heat is transferred from the bed being cooled to the bed being heated, which is bounded by two extremes: 1) uniform-temperature heat recovery or double-effect heating and 2) thermal wave regeneration employing moving, steep temperature gradients. Figure 3 illustrates both concepts.

1. Uniform-Temperature Heat Recovery or Double-Effect Heating

When recycled heat is supplied uniformly to the adsorbent beds, it is called heat recovery or double-effect heating, and this can reduce the required make-up heat by about 40% in a two-bed device, boosting COP_C from 0.3 to 0.4 for simple cycle (no recycling of heat) adsorption devices to 0.5 to 0.65 [0.3/(1–0.4) = 0.5 to 0.4/(1–0.4) ≈ 0.67]. However, heat recovery supplies high-temperature heat from the hot bed at the beginning of the cycle, when only medium-temperature heat is needed to begin heating the cold bed. This large temperature difference creates a large amount of entropy. Also, once the beds reach equal temperature, heat recovery is no longer possible. The theoretical limit of heat recovery for a two-bed device is 50%, but the aforementioned 40% is the practical limit.[12]

2. *Moving Temperature Gradient Thermal Wave Regeneration*

Thermal wave regeneration results from employing moving temperature gradients or thermal waves that traverse the adsorbent beds to heat and cool them, and was first suggested by Tchernev and Clinch.[13] Thermal wave regeneration is more efficient than uniform-temperature heat recovery for a given number of beds, because heat is transferred across a smaller temperature difference, creating less entropy. This is because medium-temperature heat at the front of the thermal wave is used to heat cold adsorbent, and high-temperature heat at the back of the thermal wave is used to heat adsorbent already warmed by the medium-temperature heat. Tchernev and Emerson[14] demonstrated about 70% thermal wave regeneration of heat, elevating COP_C to about 1.1 [0.33/(1–0.7) = 1.1].

Improvements in regeneration would further elevate COP_C. The theoretical maximum efficiency for thermal wave regeneration is 100% for an infinitesimal temperature difference between the heat transfer fluid and the adsorbent; however, the practical limit for thermal wave regeneration has been estimated at 85%.[13,14] What may seem like a modest improvement in regeneration from, say, 70% to 80% would significantly boost efficiency. A 70% heat regeneration requires 30% make-up heat; an 80% heat regeneration requires 20% make-up heat, or $\frac{1}{3}$ less than 30% make-up heat, thereby increasing COP_C by a factor of 1.5.

C. Review of Literature on Regenerative Solid–Vapor Adsorption Heat Pumps

The adsorber is the most important component in a solid–vapor adsorption heat pump, and essentially all recent work on these systems has revolved around improving adsorber performance. Research groups in the United States, Italy, France, China, Japan, and Turkey have concentrated their efforts on designing several variants of internal heat exchangers for adsorbers with the goal of improving regeneration. Investigators also have striven to minimize the nonadsorbent mass of adsorbers, which diminishes the cooling effect and lowers SCP. They also have examined a number of adsorbent materials and processing methods.

The next several studies were conducted by Cacciola, Restuccia, and their colleagues at Messina, Italy. Cacciola and Restuccia[15] describe a serpentine, flat-pipe heat exchanger (Fig. 4) that winds its way between consolidated adsorbent bricks. The flat pipes are fabricated from two thin sheets of metal foil (0.1 mm thick) that are laid over one another and welded, brazed, or soldered at the edges.[16] Although such a design provides a relatively large contact area between the heat exchanger and the adsorbent bricks, it is very difficult to manufacture, in addition to being fragile and prone to punctures, ruptures, and leaks. The consolidated adsorbent bricks exhibit greater effective thermal conductivity than a poured bed of spherical adsorbent pellets, but their lack of porosity greatly impedes vapor transport, thereby severely degrading performance.

In a later study, Cacciola and Restuccia[17] used an analytical model to predict COP_C in the range of 0.75 to 0.85 for three adsorbent/refrigerant pairs: zeolite 4A/H_2O, zeolite 13X/H_2O, and activated carbon AC35/CH_3OH with evaporator and condenser temperatures of 5°C and 40°C, respectively. They predicted optimum desorption temperatures of 200°C for the zeolite/H_2O pairs and 120°C for the activated carbon/CH_3OH pair. The adsorption temperature was 35–40°C.

Restuccia and Cacciola[18] noted the limitations of the two methods utilized previously to enhance heat transfer: Concept 1), thick ($\geq$1 cm) consolidated adsorbent bricks (Fig. 4), and concept 2), thin ($\leq$500 μm) deposited layers of adsorbent on HTF tubes in a shell and tube heat exchanger. The HTF passes through the zeolite-coated tubes, while refrigerant vapor occupies the spaces in the shell. The former 1) is limited by poor vapor permeability, and the latter 2) by a high proportion of nonparticipating "dead" mass (e.g., all metal components of the adsorbers), which must be heated and cooled with the adsorbent but contributes nothing to the refrigeration effect. They suggested that thicker (1-mm) layers of adsorbent deposited on HTF tubes could enhance performance. They predicted $\mathrm{COP}_C = 0.37$–0.43 and SCP = 230–266 W/kg for zeolite 4A with water and $\mathrm{COP}_C = 0.52$–0.56 and SCP = 26–28 W/kg for activated carbon with methanol. They did not address the durability and adhesive strength of brittle adsorbents bonded to the HTF tubes. The tubes are metal and the adsorbent is a ceramic composite, so their dramatically different thermal expansion coefficients exacerbate stresses in the adsorbent arising from thermal cycling.

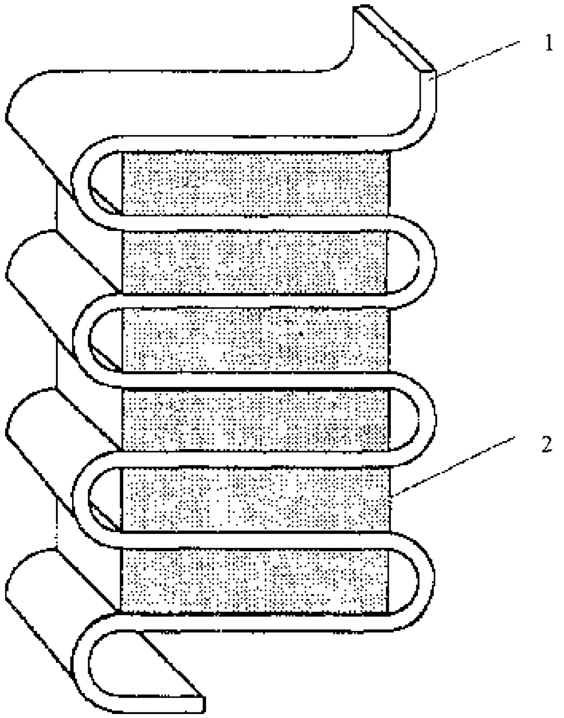


Fig. 4 Serpentine heat exchanger with consolidated bricks of zeolite adsorbent.[15]

Cacciola et al.[19] examined the effect of metal additives for increasing the effective thermal conductivity of the adsorbent bed. Such additives increase the ratio of dead mass to adsorbent mass and reduce SCP, thereby requiring more massive and expensive adsorbers, unless the ratio of the product of overall heat transfer coefficient and contact area over adsorbent mass, $U \times A_{\mathrm{cont}}/m_{\mathrm{ads}}$, is sufficiently increased.

The next several investigations[11,20–30] were performed by the research group at Orsay Cedex, France. Modeling assumptions used in practically all the work done by this group are given by Guillerminot et al.[20]:

1) Heat source and sink as well as evaporator and condenser are ideal.

2) Vapor pressure is uniform in the adsorbent bed, and the adsorbent and refrigerant are always in equilibrium.

3) Thermophysical properties (ρ, C_p, k, μ) of the metal, adsorbent, refrigerant, and HTF are independent of temperature.

4) Axial conduction in the metal and adsorbent is negligible.

5) Only three temperature profiles in the axial dimension along the fluid flow are considered: one for the HTF, one for the metal, and one for the adsorbent.

6) The pressure vessel and accessories are not considered in the heat balance.

7) The C_p of the adsorbed (freeze-dried) phase is equal to the C_p of the vapor phase, rather than the C_p of the liquid phase. However, there is great uncertainty in this assumption and there are scant data to shed light upon it.

In a numerical study, Ben Amar et al.[21] considered a concentric tube configuration in which HTF flows through the inner tube, and the adsorbent material is contained in the annulus between the inner and outer tubes (Fig. 5). This provides relatively little contact area between the adsorbent and the small, inner, heat exchanger tube.

Ben Amar et al.[21] also noted that there is an ideal degree of compaction or consolidation of the adsorbent that increases thermal conductivity but does not sacrifice too much vapor permeability. Their simulation predicted maximum $COP_C = 1.07$, $SCP = 142$ W/kg, and approximately 70% regeneration at cycle time 900 s for zeolite NaX/H_2O, as well as a maximum $COP_C = 0.99$, $SCP \approx 140$ W/kg, and approximately 75% regeneration at cycle time 600 s for activated carbon AX21/NH_3.

Pons et al.[22] performed experiments with an arrangement opposite to that considered by Ben Amar et al.,[21] as shown in Fig. 5. That is, Pons et al.[22] pumped HTF through a narrow annular passage that surrounded an inner cylinder of adsorbent. This arrangement is shown in Fig. 6. They achieved regeneration of 45% to 70% and maximum regenerative $COP_C = 0.89$ with $SCP = 35$ W/kg. They utilized a patented consolidated adsorbent, a mixture of powdered zeolite 13X and expanded natural graphite. The addition of graphite resulted in a thermal conductivity of $k = 5$ to 15 W/m-K. The contact conductance between the inner pipe wall and the adsorbent ranged from $h_{\text{cont}} = 200$ to 3000 W/m^2-K. Pons et al.[21] determined that the permeability of the consolidated adsorbent is about three orders of magnitude lower (10^{-3}) than that for packed beds of spherical pellets. Therefore, they drilled holes in the adsorbent brick to increase vapor transport, but this did not solve the problem.

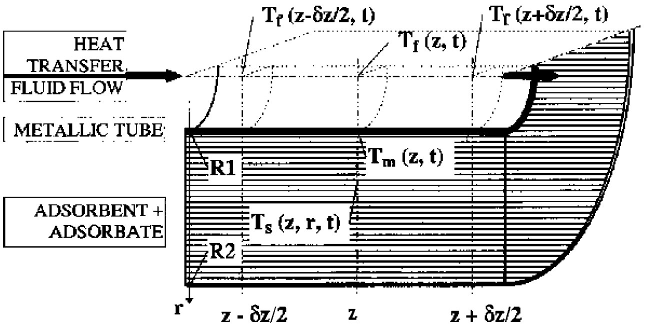


Fig. 5 Cut away of a segment of the adsorber used by Ben Amar et al.[21]

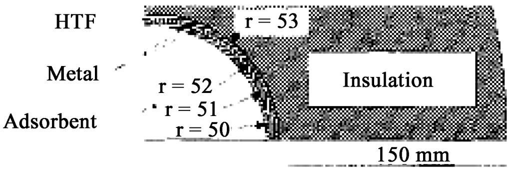


Fig. 6 Cross-section of a segment of the adsorber used by Pons et al.[22]

Meunier and Douss[23] built a regenerative, cascading system consisting of a pair of zeolite/H_2O adsorbers and a single activated carbon/CH_3OH adsorber. They reported a COP_C of 1.06 and SCP of 37 W/kg.

Poyelle et al.[24,25] describe the model and experimental data for an adsorption heat pump having the same configuration (Fig. 5) as previously developed by their research group.[21]

Guilleminot et al.[26] mixed zeolite and naturally expanded graphite powders with a binder and then compressed the mixture. This consolidated adsorbent exhibited 50 times the thermal conductivity and 10 times the thermal contact conductance of packed beds of zeolite pellets. But its permeability was four orders of magnitude lower (10^{-4}) than that of packed beds of granular zeolite, which severely impeded vapor transport, making mass transfer the governing phenomenon. This limited COP_C to 0.41–0.68, whereas SCP was 115–135 W/kg. Their adsorber has the same general layout as the one used by Ben Amar et al.,[21] described earlier and shown in Fig. 5.

Pons[27,28] demonstrates that there are two important parameters governing COP_C. The first is the global NTU (number of transfer units) for the heat transfer path within the adsorber, consisting of the convection resistance between the HTF and the wall, the conduction resistance through the wall, and the contact resistance between the wall and the adsorbent. There is another resistance that Pons ignored, namely, the conduction resistance through the adsorbent to the individual adsorption/desorption sites, which may comprise the principal limitation on COP_C depending on the thickness of the adsorbent and adsorber geometry. The second parameter identified by Pons[27,28] is the dimensionless outlet temperature, θ_o, of the HTF at the end of the cooling cycle. Figure. 7 illustrates the effect of NTU on both θ_o and COP_C.

Pons[27,28] also notes that none of the thermal wave devices tested up to that time by other research groups had achieved greater than 50% Carnot efficiency. For the configuration of Pons et al.,[22] Pons[27,28] predicted a maximum achievable COP_C of 1.6 with a corresponding Carnot efficiency of about 60%. Figure 8 shows that the regeneration factor (fraction of heat that is reused) rises with increasing dimensionless outlet temperature, θ_o. Figure 9 depicts typical temperature profiles in the adsorber at the end of the heating and cooling phases. Figure 10 shows the trend for θ_o and its impact on COP_C, which drops with increasing θ_o. The inverse relationships of regeneration factor and COP_C versus θ_o tend to counteract each other in the overall performance of the adsorber.

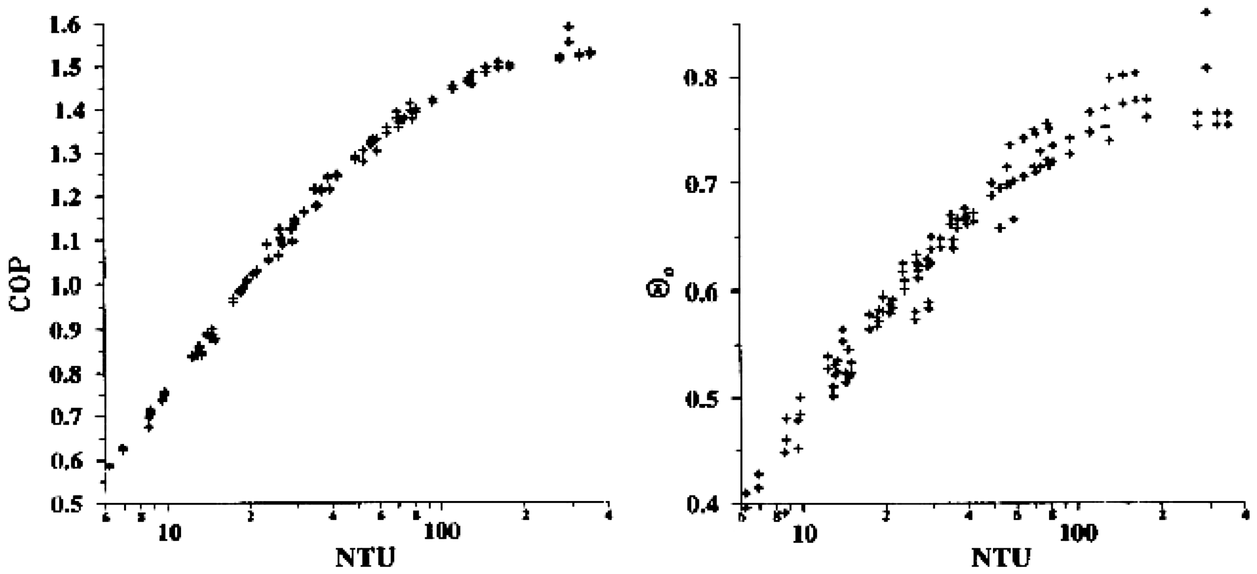


Fig. 7 Correlation between COP and NTU (left) and between θ_o and NTU (right).[27]

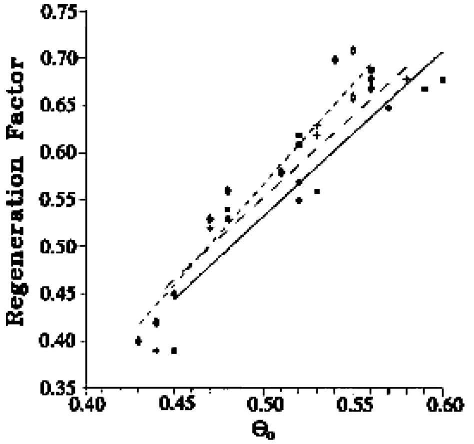


Fig. 8 Dependence of regeneration factor on dimensionless outlet temperature θ_o for various HTF flow rates, 150 g/min(■), 200 g/min(+), 250 g/min(◇).[22]

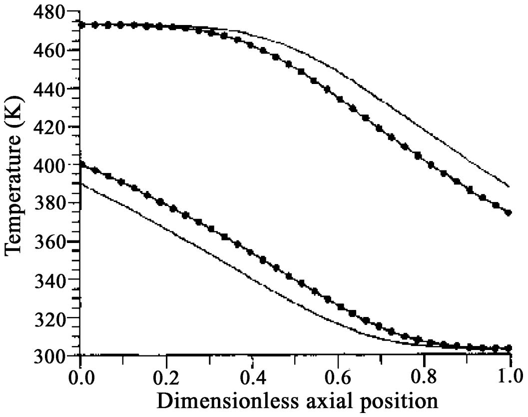


Fig. 9 Typical calculated temperatures profiles in the adsorber at the end of the heating and cooling phases: HTF (solid lines) and adsorbent (dots and lines).[27]

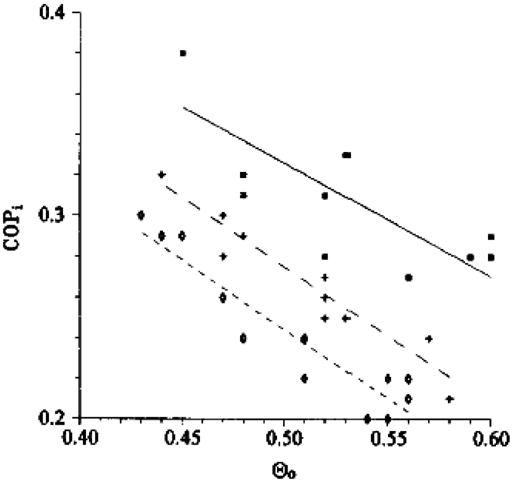


Fig. 10 Correlation between COP of cycle and dimensionless outlet temperature, θ_o for various flow rates, 150 g/min(■), 200 g/min(+), 250 g/min(◇).[22]

Meunier et al.[11] performed a Second Law analysis to determine the Carnot efficiencies and relative amounts of entropy production for 1) a nonregenerative or simple cycle, 2) a uniform-temperature regenerative cycle, and 3) a thermal wave regenerative cycle.

For intermittent, nonregenerative cycles with one adsorber, $COP_C = 0.53$, $\eta_{\text{Carnot}} = 19\%$, and 97% of entropy production is due to thermal coupling between the isothermal external reservoirs (the heat source and sink) and the temperature-varying adsorbers, whereas internal entropy production (e.g., throttling in the expansion valve, pressure drops, and internal heat transfer) accounts for the remaining 3%.

For uniform-temperature regeneration with two adsorbers, $COP_C = 0.809$, $\eta_{\text{Carnot}} = 30\%$, and external coupling entropy production is reduced to 70% of the total entropy production with most of the balance due to regeneration (22%). This performance improves asymptotically with the number of adsorbers. For 11 adsorbers, $COP_C = 1.465$, $\eta_{\text{Carnot}} = 54\%$, and external coupling entropy production is further reduced to 58% of total entropy production with 31% due to regeneration.

For thermal wave regeneration the maximum performance is $COP_C = 1.52$, $\eta_{\text{Carnot}} = 56\%$, and external coupling entropy production is 52% of the total entropy production. Performance of thermal wave cycles is highly dependent upon how the cycle is achieved.

Pons and Poyelle[29] describe the additional refinement of the regeneration process of shunting refrigerant vapor from the higher pressure, hot adsorber that is being cooled to the lower pressure, cool adsorber that is being heated, during the early part of each half-cycle. This is to take advantage of the fact that it is more efficient to reverse the flow of HTF before the adsorbent is fully heated or cooled, as demonstrated by Pons.[28]

Pons and Szarzynski[30] examined the effect of variable density and specific heat of the HTF. They noted that for a common (mineral oil) HTF, ρ_f and C_p changed by −20% and +45%, respectively, from 45 to 290°C, a temperature range typical of adsorption heat pumps. They concluded that changes in ρ_f have little effect on performance, but not accounting for changes in C_p can lead to marginally overpredicted COP_C. Pons and Szarzynski[30] also assumed that k_f was unchanged, but did determine that the decrease in viscosity, μ_f, caused a near doubling of the heat transfer coefficient, h_f, of the HTF. They also related COP and SCP to NTU (Fig. 11).

In a similar effort to enhance heat transfer into and through the adsorbent bed, Lang et al.[31] sprayed zeolite particles on a metal matrix.

Miles et al.,[32] utilizing earlier models developed by their research group,[12,33] built a bench-scale test unit and achieved $COP_C = 0.8$ for the activated carbon/NH_3 regenerative heat pump. Other members of this research team modeled adsorbent conductivity and permeability and temperature effects in an effort to increase COP_C of their design.[34,35]

Ito et al.[36,37] and Watanabe et al.[38] constructed heat pumps that employed silica gel and graphite adsorbents and ethanol refrigerant. Their units did not perform notably, with $COP_C < 1.0$.

Zheng et al.[39,40] developed a dimensionless model of an adsorption heat pump and performed parametric studies for a range of cycle times, adsorbent conductivity, and contact conductance between the heat exchanger and the adsorbent. They observed that for a given NTU, there is an optimal nondimensional switching frequency (bank cycle time) that nets the highest COP_C. This nondimensional switching frequency is some fraction of the maximum output capacity at a given temperature lift. It was also noted that the ratio of live to dead mass has a pronounced influence on the selectivity of the switching frequency in improving COP_C. That is, the smaller the ratio of dead

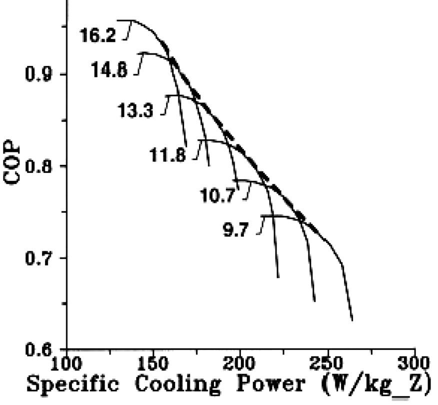


Fig. 11 COP vs SCP for various NTU.[30]

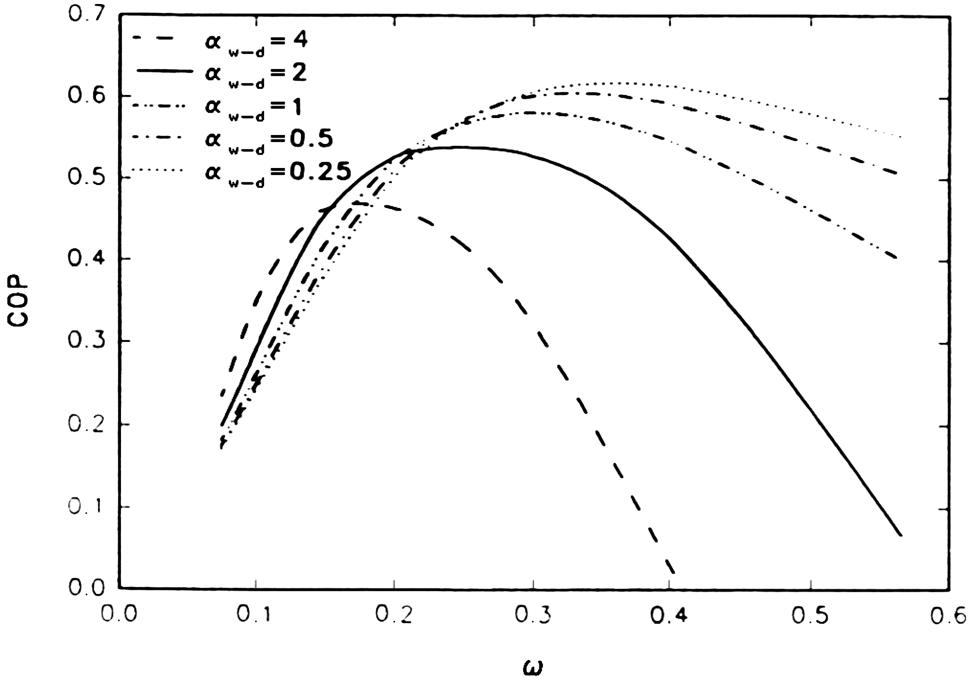


Fig. 12 COP_C vs nondimensional switching frequency (ω) for various ratios of dead to live mass (α_{w-d}). (Ref. 39).

to live mass, the greater the improvement in COP_C and the closer the optimal switching frequency is to unity (Fig. 12).

Jones[41] determined the thermal characteristics of four activated carbon/NH_3 adsorbent beds and predicted $COP_C \approx 1.0$.

Critoph,[42] Saha et al.,[43,44] Harkonen and Aittomaki,[45] and Hajji[46] developed numerical models to simulate thermal performance, including limitations, of adsorption heat pumps.

Saha et al.,[43,44] examined a three-stage cascaded silica gel/water heat pump. They noted that cooling capacity, SCP, COP_C, and η_{Carnot} are strongly affected by the overall thermal conductance (i.e., NTU) of the adsorbers, confirming the first observation by Pons,[27,28] as well as the ratio of adsorbent ("live") mass to inert ("dead") mass. They also noted that both of these parameters must be increased in order to significantly improve performance. Evaporator conductance had a minimal effect on performance, and condenser conductance had almost no effect.

Teng et al.[47] and Tchernev[48] provide very insightful overviews of adsorption cooling principles and technology. Tchernev and Clinch[13] and Tchernev and Emerson[49] developed the most promising prototype to date, which attained 70% regeneration and $COP_C = 1.1$. They utilized a serpentine flat-pipe heat exchanger similar to that employed by Cacciola and Restuccia.[16,19]

Ramotowski and Shamsundar[50] constructed a zeolite $13X/H_2O$ dual-adsorber heat pump. Each adsorber consisted of a cylindrical shell containing a helically wound stainless steel tube, which served as the heat exchanger. The shell was filled with spherical pellets of zeolite that occupied the spaces surrounding the helical tubing. The tubing had relatively little surface area and the adsorbent bed had very low thermal conductivity and contact conductance.

Wojcik et al.[51] modeled thin (≤ 500 μm) layers of type A zeolite synthesized on the stainless steel HTF tubes in a shell and tube heat exchanger. Water was the refrigerant. This configuration was being considered by a number of researchers, such as Lang et al.,[31] Restuccia et al.,[16] and Cacciola et al.,[19] to alleviate two problems associated with consolidated adsorbent bricks, namely poor vapor transport and high contact resistance between the adsorbent and heat exchanger surfaces. Wojcik et al.[51] determined that thin, synthesized zeolite layers introduce different problems. The low ratio of adsorbent mass to void volume precludes adequate pressurization to force sufficient vapor into the condenser. The low ratio of adsorbent mass to heat exchanger mass results in a large percentage of "dead" mass, which must be heated and cooled with the adsorbent but contributes nothing to the cooling effect. They suggested using zeolite Y instead of zeolite A, because the former can be deposited in thicknesses exceeding 1 mm. However, Wojcik et al.[51] cautioned that the adhesive strength is very poor, and that vibrations during transport and thermomechanical stresses during temperature cycling could likely cause debonding.

Anyanwu et al.[52] modeled, designed, constructed, and tested a solar adsorption refrigerator using activated carbon and methanol. They were more interested in developing a system that could be operated in remote, undeveloped areas than in high efficiency. Thus, their COP_C was only 0.06. They noted little dependence of COP_C on adsorbent thermal conductivity or contact resistance between the adsorbent and tubes bonded to the solar collector plate.

Vasiliev et al.[53] modeled, constructed, and tested a design utilizing carbon fiber adsorbents with ammonia. In a follow-up investigation[54] they added $CaCl_2$ salt, which reacts with ammonia, thus creating a complex compound reaction to augment the physical adsorption of ammonia on the carbon fibers. They were able to adsorb 40% ammonia on non-chemisorption-enhanced activated carbon fibers by weight. In their nonregenerative solar-powered system with a source temperature of around 130°C rejecting to ambient (23°C) and maintaining a refrigeration temperature of -5°C they were able to achieve a COP_C of 0.3.

Vasiliev et al.[53] also evaluated operating at elevated adsorber temperatures and cascading a cycle employing zeolite NaX and ammonia. They modeled the process as isobaric with infinite permeability. Their design was quite complicated, incorporating a solar collector (mirror), two adsorbent bed canisters connected by the heat recovery loop, a two-phase heat transfer system (vapor-dynamic thermosiphon), one condenser, two evaporators, and two cold panels (loop heat pipes) inside the refrigerator cabinet.

Alam et al.[55] demonstrate how to optimize the overall conductance, $U \times A_{\text{ads}}$, of the four heat exchangers in an adsorption heat pump: the condenser, the evaporator, the adsorber being heated, and the adsorber being cooled. They also optimized the collector size for a solar powered device.

Sami and Tribes[56] modeled the performance of a dual-adsorber heat pump using AC35 activated carbon and methanol with uniform temperature heat recovery. Their model accounted for nonideal evaporator and condenser by modeling them as air-cooled, finned heat exchangers.

Tatlier et al.,[57] and Tatlier and Erdem-Senatalar[58] provide a very good synopsis of attempts at increasing the contact conductance between the HTF tubes or conduits and the adsorbent, as well as

Table 1 Adsorption devices built and tested by Gui et al.,[60] Lu et al.,[61] Wang,[62] Wang et al.,[63] Wang,[64] Wang et al.,[65–68] and Qu et al.[69]

Adsorption systems	Performance details	Remarks
Solar ice maker (activated carbon–methanol)	$COP_{solar} = 0.11–0.13$, 5–7 kg ice/m^2 solar collector.	Tested
Hybrid solar water heater and ice maker/refrigerator (activated carbon–methanol)	2 m^2 vacuum solar collector yields 60 kg 85–100°C hot water and 5 kg ice, or keeps a 120-liter cold box with a temperature lower than 5°C for 50 h.	Tested
Low-temperature waste heat source driven ice maker (activated carbon–methanol)	With a 100°C heat source, 5.2 kg ice/kg adsorbent per day per adsorber has been achieved.	Tested
Low-temperature waste heat source driven air conditioning system (activated carbon–methanol)	With a 100°C heat source, COP = 0.5 and SCP = 150 W/kg adsorbent for air conditioning has been achieved; COA = 1.3–1.5 and SHP = 300–500 W/kg adsorbent for heat pumping has been obtained with a temperature lift about 30°C.	Tested
Bus air conditioning driven by the exhaust gases (activated carbon–ammonia)	A 5-kW prototype has been constructed and will be tested soon; a 20-kW system will be designed.	To be tested
Adsorption air conditioning system for train locomotive driver (zeolite–water)	A 5-kW system has been constructed. Continuous cooling is achieved by cold storage, though only one adsorber is used in the system.	To be tested
Solar air conditioning (zeolite–water, activated carbon–methanol)	A 8-m^2 solar adsorber yields 8 h cooling for a 20-m^2 room. Plate type and tube type adsorbers will be tried and tested.	To be tested

the effective thermal conductivity of the adsorbent. They go on to describe a process for depositing thin films of zeolite on steel tubing, analogous to that described by Cacciola et al.[19] and Lang et al.[31] Tatlier and Erdem-Senatalar[59] presented a follow-up study regarding the optimization of such coatings. It addressed the concern raised by Wojcik et al.[51] that very thin zeolite coatings on the adsorber structure limit performance. Tatlier and Erdem-Senatalar[59] calculated that very thin ($<500\ \mu$m) zeolite coatings are a viable design concept for adsorbers, even those with unused/zeolite volume ratios greater than 4 to 1 (80% void space).

Gui et al.,[60] Lu et al.,[61] Wang,[62] Wang et al.,[63] Wang,[64] Wang et al.,[65–68] and Qu et al.[69] have performed extensive research on adsorption heat pumps, which is summarized in Table 1. Wu et al.[66,68] performed dynamic analysis of the mass and heat recovery process for a continuously operating heat pump and concluded that low heat transfer coefficients in the adsorber severely limit the recoverable adsorption heat. Lu et al.[61] also developed a 4.1-kW locomotive air conditioning system utilizing the zeolite–water pair.

Wu et al.[67] constructed an activated carbon–methanol adsorption heat pump and achieved an experimental COP_C of 0.4. This system achieved a SCP of 150 W/kg adsorbent. For this system, it was observed that the refrigeration capacity was indirectly proportional to the rate of temperature drop in the adsorber. This is equivalent to having the desorption rate in the desorbing bank equal the adsorption rate in the adsorbing bank. It was also observed that the longer the cycle time the greater the COP_C and SCP.[60,64–67]

Many different designs have been tried for the adsorber. Some investigators have employed the shell and tube heat exchanger, while others used a serpentine flat pipe winding between a stack of consolidated adsorbent bricks.[13,14,16,19,49] Wang et al.[63] proposed a spiral strip or tape type adsorber coupled with a solar collector (Fig. 13). This system was used with activated carbon–methanol to generate 1 kg of ice per kg of carbon per day.

Zhu and Wang[70] tested various means of improving heat transfer in absorbers. They demonstrated that increasing contact pressure and utilizing a conductive adhesive on the interface between the adsorbent and heat exchanger significantly increased overall heat transfer in the adsorber. Increased contact pressure in the range of 20–25 kPa resulted in a 66% reduction in contact resistance, whereas the conductive adhesive reduced contact resistance by 30–40%.

Miltkau and Dawoud[71] created a one-dimensional computer model of the adsorption/desorption diffusion process and observed that reducing the thickness of the zeolite layer by 50% reduced the adsorption time by 75% and the desorption time by 66%. They concluded that to achieve high SCP values the thickness of the zeolite layer should not exceed 2.5 mm, as is shown in Fig. 14.

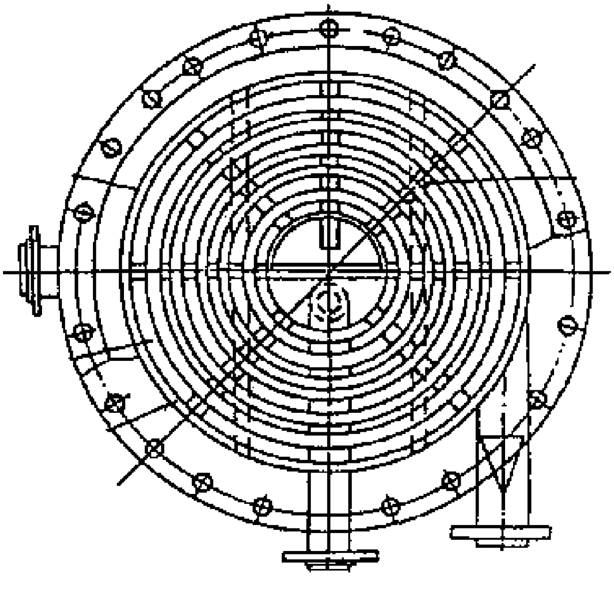


Fig. 13 Spiral or tape type adsorber proposed by Wang et al.[63]

Cerkvenik et al.[72] studied the relationship of performance to heat exchanger size for heat-driven heat pumps. They concluded that the main cause of the traditionally low COP_C for heat-driven heat pumps is the lack of a high-conductance adsorber coupled with a high proportion of inert mass, confirming the conclusions of Saha et al.[43,44]

Turner[73] and Zhang and Wang[74] examined the effects of porosity on coupled heat and mass transfer. Zhang and Wang[74] concluded from their model that performance can be limited by poor mass transfer through the adsorbent if its permeability is too low. The minimum necessary permeability is determined by the design of the overall adsorption system and includes geometry, temperature differences, and thermal resistances through various components in the adsorber.

Zhang[75] constructed and tested an adsorption air conditioner for an automobile, powered by the waste heat from its diesel engine. Pelletized, consolidated Zeolite 13X and water were used as the working pair in the nonregenerative single adsorber. The adsorber

Table 2 Various zeolites and some of their relevant characteristics[77]

Zeolite	Chemical structure	Activated density	Cavity volume	Pore aperture	Thermal conductivity[a]	Molecules adsorbed
		(kg/m^3)	(cm^3/g)	(_)	(W/m-K)	(Includes all of previous line)
3A	$K_6Na_6[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$	1460	0.30	3.20	0.7	H_2O, NH_3
4A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$	1330	0.30	3.5–4	0.7	H_2S, CO_2, SO_2, C_2H_4, C_2H_6, C_3H_6, ethanol
5A	$Ca_6Na_6[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$	1330	0.30	4.20	0.7	n-C_4H_9, n-C_4H_{10}, C_3H_8 to $C_{22}H_{46}$, R-12
13X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$	1290	0.36	8.0	0.7	C_6H_6, C_7H_8
Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 264H_2O$	1300	0.35	8.0	0.7	Same as Type X
B	$Na_4[(AlO_2)_6(SiO_2)_{10}] \cdot 15H_2O$	1470	0.15	3.5	0.7	Same as type 3A
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$	1720	0.14	6.6	0.7	Same as type 5A

[a] estimated for adsorbent powder mixed with binder (e.g., silica gel) and consolidated.

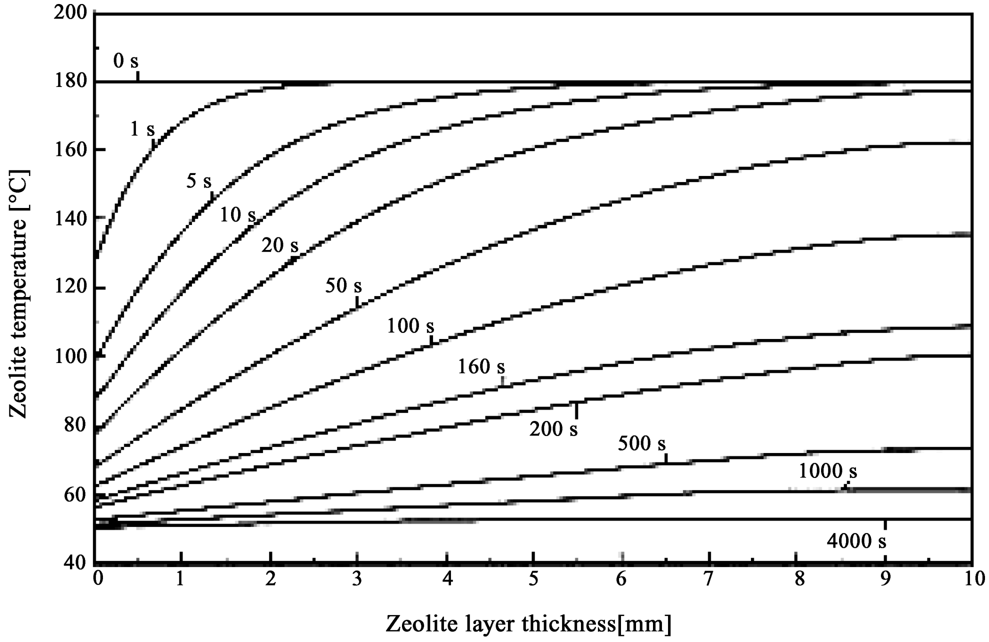


Fig. 14 Zeolite temperature as a function of time and distance from heat exchanger.[71]

was a pair of concentric pipes with adsorbent pellets filling the annulus and exhaust or cooling air passing through the inner pipe. Twelve thin radial copper fins were brazed to the outside of the exhaust/air pipe to enhance heat transfer to the adsorbent. This system exhibited an experimental COP_C of 0.38 and an SCP of 25.7 W/kg. This is contrasted to a COP_C of 0.5 for an absorption (liquid–vapor) heat pump using lithium bromide/water that was constructed and tested by Boatto et al.[76]

Breck[77] presents a much cited and thorough treatment of zeolite chemistry and characteristics. Worm et al.[78] and Bish and Ming[79] describe the fundamentals of heat transfer in zeolites and other porous media. Miura and Morimoto[80] provide adsorption data for carbon and graphite. Relevant data from these studies can be found in Tables 2 and 3.

IV. Critique of State of the Art

Research groups in the United States, Italy, France, China, and Japan have concentrated their efforts on devising improvements to the all-critical adsorbers, with the primary goal of improving efficiency (COP_C), which requires increasing the percentage of recycled heat. Several of these investigators agree in identifying the two most important parameters that must be improved in order to increase COP_C: 1) the ratio of adsorbent (live) mass to nonadsorbent (dead) mass, which must be maximized, and 2) the overall heat transfer rate (defined in terms of NTU), which must also be maximized. Because they have been working to maximize COP_C for stationary applications (e.g., in residences), little effort has been directed toward increasing SCP, which is at least as important as COP_C for transportation and space applications.

Some designs suffer from a low live-to-dead mass ratio, the first of the two critical governing parameters identified above. Those that do not suffer markedly in this regard pose significant problems in manufacturability, reliability, and expense, owing to their intricate, delicate configurations or subatmospheric pressures that allowed air leaks into the system.[15,16,19,47] For example, the serpentine thin metal foil heat exchangers described by Cacciola and Restuccia,[15] Restuccia et al.,[16] Cacciola et al.,[19] Tchernev,[48] and Tchernev and Emerson[49] are susceptible to mechanical failure.

All previous designs suffer to one degree or another from inadequate heat transfer rate (NTU is too small), the second of the two critical governing parameters. One aspect of some designs that limits their performance is that they do not distribute heat effectively. Previous adsorber configurations have inadequate contact area between the heat exchanger and a given volume of adsorbent. This feature may be described alternately by the characteristic length (volume/area) of the heat transfer path from the heat exchanger to any position within the adsorbent. This is exacerbated by the typically high contact resistance across the interface.

Another limitation of previous designs is that none embodies a satisfactory method for increasing the poor thermal conductivity of zeolite or activated carbon adsorbents while retaining sufficient permeability to refrigerant vapor. Consolidating adsorbents into bricks increased conductivity and marginally reduced contact resistance but decreased permeability by three to four orders of magnitude. Binders used in consolidation occlude pores, limiting adsorption potential. Some designs use packed beds of spheres, resulting in a very low effective thermal conductivity for the adsorbent. None of

Table 3 Partial list of refrigerants and their adsorptivity (kg/kg) in various adsorbents at 1 atm and 25°C (298 K) (Ref. 77)

Refrigerant	3A (K) (wt%)	4A (Na) (wt%)	5A (Ca) (wt%)	13X (Na) (wt%)	X (Ca) (wt%)	Y (Ca) (wt%)	Mordenite (mineral) (wt%)	Carbon fiber (wt%)	Silica gel (wt%)	Activated alumina (wt%)
Water	26	27	26	30	36	34	15		33	15
Ammonia	15	15	16	16	22	21		62	13	
Methanol	0	19	18.5	23				55	~50	
Sulfur dioxide	29	29	29	44			24			
Carbon dioxide	18	18	18	39	29	15	12.6			
Carbon monoxide				16.5	7	0	12.5			
Methane	0	5.8		8	2.9		0	51		
Ethane	0	6	6.5	9			0	10	1.5	
Propane	0	0.5	10	14			0	21	6	
n-Butane				18						
Isobutane		0		12.5			4.9			
Hydrogen sulfide	17	24	17	34						
Ethylene				14.7			3.4			
Cyclopropane				14						
Acetylene	0	9	9	12						
Propylene	0	11		12				21	9	
Ethylene	0	8	7.5	10.5				9.5	4	
Acetone				yes				61		
n-Heptane	0	0	14	21	20		6	39	26	
Benzene	0	0	0	18		25		44	35	

Table 4 Performance of regenerative adsorption heat pumps

Investigation	COP_C	SCP (W/kg)	Regeneration	Comments
Cacciola et al.[19]	0.75–0.85			Predicted
Ben Amar et al.[21]	1.07	150–80		Predicted
Pons et al.[22]	0.89	35–45	40–70%	Experimental
Meunier et al.[11]	1.06	37		Experimental
Miles et al.[32]	0.80	220		Experimental
Jones[41]	1.0	590		Predicted
Guilleminot et al.[26]	0.41–0.68	115–135		Experimental
Tchernev and Clinch[13] and Tchernev and Emerson[14,49]	1.1		75%	Experimental

the studies reviewed considers settling of the adsorbent particles or pellets, which may cause the adsorbent to lose contact with the heat exchanger.

Performance parameters (COP_C, SCP, %regeneration) for the investigations described above are compiled in Table 4. Note that the greatest experimental $\mathrm{COP}_C = 1.1$ achieved to date[13] is about 72% of the maximum $\mathrm{COP}_C = 1.52$ (with $\eta_{\mathrm{Carnot}} = 56\%$) predicted by Meunier et al.[11] for thermal wave regeneration, which leaves considerable room for improvement.

V. Design Criteria for Adsorption Heat Pumps

A. Adsorber Design Criteria

As determined by a number of investigators, the two principal impediments to obtaining better performance (i.e., greater COP_C and SCP) from an adsorber are a low overall heat transfer coefficient, which results in a small NTU, and a large proportion of dead mass. A number of issues must be addressed in order to significantly improve performance:

1) The thermal mass of any nonadsorbent components must be minimized. The pressure vessel encasing the adsorbent bed and its internal heat exchanger are heated and cooled but provide no vapor compression effect. Therefore, any high-COP_C design must minimize this dead mass. In addition, SCP is measured as the cooling power in watts/kilogram; reducing dead mass is a direct means of dramatically increasing SCP.

2) The contact area between the adsorbent and the heat exchanger must be maximized, and the contact resistance and path length from the heat exchanger to any point in the adsorbent must be minimized.

3) Adsorbents must be identified with the optimal combination of high adsorptivity (kg refrigerant/kg adsorbent), smallest possible temperature range for adsorption and desorption, and high thermal conductivity. The selected adsorbent must be processed (e.g., consolidated by combining it with binders and/or compacted) in such a way as to obtain an effective (extrinsic) thermal conductivity that is the greatest possible fraction of its intrinsic thermal conductivity, while simultaneously maximizing the permeability.

4) The ideal refrigerant must be chosen for the expected operating temperature range, paying specific attention to the associated vapor pressures in order not to require an excessively robust pressure vessel (i.e., bed shell) or the attainment of a low vacuum, which is prone to leakage and atmospheric contamination.

B. Selection and Processing of Adsorbents

Adsorbents must be identified with the optimal combination of high adsorptivity, small temperature range for adsorption/desorption, and high conductivity.

Zeolites are commonly used in adsorption heat pumps, due to their excellent adsorption characteristics. They are aluminosilicate minerals possessing highly nanoscopically porous, cage-like, crystal lattices (see Fig. 15), which allow them to adsorb small, polar molecules at standard temperature (22°C) and pressure (1 atm), giving them excellent adsorption characteristics. That is, their isosteres (Fig. 1), which are lines of constant ratio of adsorbed refrigerant mass to adsorbent mass, kg/kg, on a pressure-versus-temperature plot are close together, meaning that a small change in adsorbent temperature causes a large amount of adsorption or desorption.

Synthetic zeolites (e.g., 3A, 4A, 5A, 13X, NaX, NaY) have been studied most, but natural zeolites, such as clinoptilolite (found in Oregon and Turkey), chabazite (Arizona, southern Italy, Russia), gmelinite, heulandite, and mordenite may be better absorbers. Table 2 contains a partial list of synthetic zeolites and some of their properties. Most zeolites have low thermal conductivity, on the order of 0.1–1.0 W/m-K, which slows the adsorption and desorption process, thereby limiting SCP.

Table 5 Thermophysical properties of selected refrigerants at atmospheric pressure[2]

Refrigerant	Chemical formula	Melting point (°C)	Boiling point (°C)	Heat of vaporization (kJ/kg)	Heat of fusion (kJ/kg)	Density of liquid (kg/m^3)	Volumetric heat of vaporization (liquid) (MJ/m^3)	Thermal conductivity of gas (at STP) (W/m-K)	Specific heat of gas (Cp) (at STP) (J/kg-K)	Thermal diffusivity of gas (at STP) (m^2/s)*10^{-5}	Thermal diffusivity of liquid at 300°C, 1atm (m^2/s)*10^{-5}
Water	H_2O	0	100	2257	333.7	997	2251	*0.0181	*2041	*35.1	0.0130
Ammonia	NH_3	−77.7	−30	1368	322.4	682	932	0.0246	2200	1.550	0.0178
Methanol	CH_3OH	−97.7	65	1100	99.2	787	872	0.02	1550	1.056	
Ethanol	C_2H_5OH	−114.2	79	838	109	783	665	0.0147	1830	0.069	0.00889
Methyl amine	CH_3NH_2		−6	836		703	588				
Acetonitrile	C_2H_3N		81	766		782	599				
Formaldehyde	HCHO		−19	768		815	626				
Sulfur dioxide	SO_2	−76	−10	368		883	534				0.0104
Carbon dioxide	CO_2	−79	−56	230.5	18.4	298	171	0.0166	852	1.090	0.004**
Carbon monoxide	CO										
Methane	CH_4	−182.2	−161	512	58	446	248	0.0121	2070	0.327	
Ethane	C_2H_6		−88	488	45			0.0218			
Propane	C_3H_8	−188	−42	426	80	581	248	0.0183			
n-Butane	C_4H_{10}	−138.5	0	385	80	601	231	0.016			
Isobutane	C_4H_{10}	−160	−12	376	106	594	218	0.0163			
Halocarbon R-134a	CF_3CH_2F	−96.6	−26	217	27	1374	298	0.00952	784	0.231	2.9510475
Hydrogen sulfide	H_2S	−86	−60	213	187			0.0147			
Ethylene	C_2H_4	−169	−104	480	119			0.204			
Cyclopropane	C_3H_6	−128	−33	477	129						
Acetylene	C_2H_2	−98	−84	687	96.5			0.0213			
Propylene	C_3H_6	−185	−48	437	71						
Isobutylene	C_4H_8-i	−185	−6	391	69						
Methyl chloride	CH_3Cl										

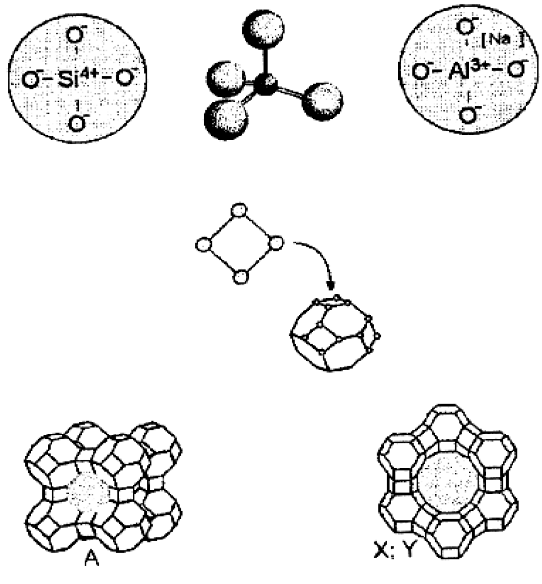


Fig. 15 Structure of zeolite.[77]

Silica gel (SiO_2), exhibits somewhat greater thermal conductivity, ranging from 1.4 W/m-K (for fused, i.e., amorphous, silica) to 8.3 W/m-K (for crystalline quartz). For most refrigerants, silica gel desorbs at below 150°C. Silica gel also exhibits a great affinity for methanol, adsorbing up to 50% by mass. This is greater than its affinity for other refrigerant candidates, such as water (33%) or ammonia (13%).

Graphite does not adsorb water as well as zeolites, but graphite adsorbs more ammonia than zeolites. Graphite adsorbs on its surface, rather than in pores, as is the case for zeolites. Fine graphite powder and graphite fibers have the highest surface-area-to-volume (and mass) ratios, making them more suitable for adsorption. But powdered graphite has low conductivity, whereas graphite fibers have very high conductivity (1950 W/m-K parallel to the lamellae, which resemble planar honeycomb structures, and 5.70 W/m-K perpendicular to the lamellae), making fibers the better form. A mixture of zeolites and fine graphite fibers may provide the optimal combination of adsorption characteristics and thermal conductivity.

A method for increasing thermal conductivity is compaction or consolidation of the adsorbent. However, permeability decreases with increasing compaction, suggesting an optimal intermediate density. Consolidation involves mixing the adsorbent with a binder, followed by heating to drive off the solvent, but the binder occludes some pores.

Different adsorbents have different advantages. Thus, if a versatile adsorber, which is adaptable for different refrigerants, is the primary goal, then zeolite CaX should be used with as little consolidation as is necessary to sufficiently enhance conductance. The binder for consolidation should be sodium metasilicate (silica gel). Adding about 10% carbon fibers will further enhance conductance while adding some adsorptivity. This allows utilizing the high adsorptivity of CaX for a broad range of adsorbents (any polar molecule with a nominal diameter less than 8 mm). If, however, a high-SCP heat pump is desired, then activated carbon fiber and ammonia should be utilized. The carbon fibers should be bonded to the heat exchanger tubing with a chemically stable adhesive such as epoxy or resin, but the adhesive should coat only a small fraction of the fibers' surface area in order to not adversely affect their adsorptivity.

C. Selection of the Proper Refrigerant

The ideal refrigerant must be chosen for the prescribed operating temperature range, paying due attention to the associated vapor pressures in order not to require an excessively robust containment structure (i.e., bed shell) or the attainment of a low vacuum, which is prone to leakage. Relevant thermophysical properties of some refrigerants are summarized in Table 5. For space heating (≈333 K), air conditioning (≈278–288 K), and food freezers (≈253 K), water, ammonia, and methanol are the best choices.

Table 3 lists the adsorptivity, at atmospheric pressure and room temperature, of several zeolites and other nonaluminosilicate adsorbents for various refrigerants. Characteristics of the most likely candidate refrigerants are as follows:

1) Water is nontoxic, nonflammable, nonpolluting, and stable and has the highest latent heat among common substances, making it nearly ideal, except for the fact that its vapor pressure is very low for the applications listed above, resulting in inordinately large condensers and evaporators. Water also freezes just a few degrees below the evaporator temperature, requiring precise control during operation and more elaborate protection measures when sitting idle in cold weather.

2) Ammonia has a relatively high vapor pressure for these applications, is toxic, flammable of some concentrations, nonpolluting, and stable, and has the second highest latent heat among common substances. However, when corrected for the necessary evaporator pressure, ammonia's latent heat drops by about 30% to 945 kJ/kg, making it less effective.

3) Methanol has a low vapor pressure for the temperature ranges of interest, is toxic, flammable, nonpolluting, and unstable beyond 393 K, and has the third highest latent heat among common substances.

4) Sulfur dioxide is a naturally occurring gas that is toxic in even very low concentrations and has a moderate latent heat.

The higher specific cooling capacity of ammonia makes it a better choice than water, methanol, and sulfur dioxide.

In addition to the functional characteristics of the refrigerants, consideration must be given to health and environmental effects of their use. Table 6 lists such characteristics.

D. Selection of Pressure Vessel Materials

The operating temperature range for an automotive adsorber may be as high as 600°C (873 K) at full throttle under heavy load, and as low as −20°C (253 K) when parked in cold weather.

1) Even the best aluminum alloys have very little strength beyond 300°C.

2) Copper, although having the second highest (after silver) thermal conductivity, lacks the high-temperature strength and creep resistance necessary to make it a viable choice for the pressure vessel material.

3) Brass has nearly the same strength as copper but has a lower melting point, and thus has inferior creep resistance compared with copper, thereby eliminating it as a viable material.

4) Stainless steel has excellent corrosion resistance and some alloys, such as 410, retain most of their strength at 600°C. However, stainless steel alloys have low thermal conductivities and are relatively expensive.

5) Low alloy, low to medium carbon steels (e.g., tool steels) possess high yield strengths (when quenched and tempered), have moderate thermal conductivities, can withstand the high temperature range of an automotive exhaust system, and can endure the cyclic loading experienced as the adsorber is heated and compresses the refrigerant.

Mechanical and thermophysical properties of these materials are summarized in Table 7.

Table 6 Various refrigerants and their potential environmental impacts

Refrigerant	Formula	Toxic concentrations	Environmental considerations
Water	H_2O	inert	Most prolific molecule on planet
Ammonia	NH_3	toxic > 25 ppm, corrosive	Produced by decaying organic matter
Methanol	CH_3OH	toxic > 200 ppm, irritant	Produced by decaying cellulose
Ethanol	C_2H_5OH	toxic > 200 ppm, irritant	Produced by decaying carbohydrates
Formaldehyde	$HCHO$	toxic, carcinogenic	
Sulfur dioxide	SO_2	toxic > 2 ppm, corrosive	Sources: volcanism, combustion of coal
Carbon dioxide	CO_2	inert, asphyxiation > 5000 ppm	Produced by combustion and respiration
Carbon monoxide	CO	toxic > 25 ppm, carcinogenic	Fossil and biomass combustion byproduct
Methane	CH_4	asphyxiant, explosive hazard	Naturally occurring atmospheric gas
Ethane	C_2H_6	asphyxiant, explosive hazard	Atmospheric gas which captures free radicals
Propane	C_3H_8	asphyxiant > 1000 ppm	Paraffin hydrocarbon gas, heavier than air
n-Butane	C_4H_{10}	asphyxiant > 800 ppm	Paraffin hydrocarbon gas
Isobutane	C_4H_{10}	asphyxiant	Paraffin hydrocarbon gas
Halocarbon R-134a	CF_3CH_2F	asphyxiant, toxic > 50,000 ppm, irritant	Synthetic refrigerant
Hydrogen sulfide	H_2S	toxic > 10 ppm, irritant	Byproduct of decomposing organic mater
Ethylene	C_2H_4	asphyxiant	Alkene of the paraffin ethane
Cyclopropane	C_3H_6	asphyxiant	Cycloparaffin
Acetylene	C_2H_2	asphyxiant, irritant	Alkene of the paraffin ethane
Propylene	C_3H_6	asphyxiant	Alkene of the paraffin propane
Isobutylene	C_4H_8-i	asphyxiant	
Methyl chloride	CH_3Cl	toxic > 50 ppm, irritant	Sources: seaweed, occasionally volcanism
Acetaldehyde	C_2H_4O	toxic > 25 ppm, irritant	Plastics mfg byproduct
Acetone	C_3H_6O	toxic > 750 ppm, irritant	

Table 7 Some common metals and alloys for adsorber construction

Material	Alloy	Melting temp. or range (°C)	Density (g/cm^3)	Yield strength (MPa)	Coeff. of thermal exp. (°C^{-1} × 10^{-6})	Thermal conductivity (W/m-K)	Specific heat (J/kg-K)
Aluminum	pure (>99.5%)	646–657	2.71	17	23.6	231	903
Aluminum	Alloy 2014	507–638	2.80	97	22.5	192	~900
Aluminum	Alloy 2024-T3	502–638	2.78	345	23.2	121	875
Steel (low-C)	Alloy 1020	1495–1520	7.86	295	11.7	52	434
Steel (med-C)	Alloy 1040	1495–1505	7.85	350	11.3	52	434
Steel (high-C)	Alloy 1080	1385–1475	7.84	380	11.0	48	434
Low alloy steel	Alloy 1022	1495	7.86	360	14.0	50	472
Low alloy steel	Alloy 4130	1537	7.85	435	11.9	43	477
Low alloy steel	Alloy 4340	~1537	7.85	470	12.6	45	475
Stainless steel	446 (Ferritic)	1425–1510	7.50	345	10.4	21	460
Stainless steel	316 (Austenitic)	1370–1400	8.00	207	16.0	16	468
Stainless steel	410 (Martensitic)	1480–1530	7.80	275	9.9	25	460
Copper	pure (>99.95%)	1085	8.94	69	16.5	398	385
Brass	(70%Cu-30%Zn)	915–955	8.53	75	20.0	120	380
Bronze	(92%Cu-8%Sn)	880–1020	8.80	152	18.2	62	420

VI. Conclusions

The following has been gleaned from reviewing the literature. Each conclusion is expounded upon in Section 4.

1) Several investigations agree in identifying the two most important parameters that must be improved in order to increase COP_C: a) the ratio of adsorbent ("live") mass to non-adsorbent ("dead") thermal mass, which must be maximized, and b) the overall heat transfer rate (defined in terms of number of transfer units or NTU), which must also be maximized.

2) Some designs suffer from a low "live" to "dead" thermal mass ratio, the first of the two critical governing parameters identified above.

3) All designs suffer to one degree or another from inadequate heat transfer rate (NTU is too small), the second of the two critical governing parameters. Their adsorber configurations have inadequate contact area between the heat exchanger and a given volume of adsorbent.

4) None of the designs embodies a satisfactory method for increasing the poor thermal conductivity of zeolite or activated carbon adsorbents while retaining sufficient permeability to refrigerant vapor.

Recommendations for future designs are:

5) Zeolite CaX is the best adsorbent if water is the chosen refrigerant. If SCP is important, then activated carbon fibers and ammonia is the best working pair, because the working pressure range for ammonia is much higher than for water, and modestly greater than the range for halogenated synthetic refrigerants. If intermediate working pressures (between those for water and ammonia) are important, then silica gel or activated graphite and methanol form the best pair.

6) Ammonia and methanol allow for smaller heat exchangers (condensers and evaporators) than water, which is a concern where volume and weight are an issue (transportation and spacecraft).

7) Carbon steel (and perhaps low alloy "tool" steel) is adequate for pressure vessels for high temperature applications. Copper may be necessary for internal heat exchanger components, because of its high thermal conductivity. Aluminum may be adequate for pressure vessels and internal heat exchangers for relatively low temperature applications (below 250°C).

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