Adsorption-Enhanced Compressed Air Energy Storage

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The problem to be addressed in this paper is diurnal load leveling. This means storing energy over a period of hours while the demand for it is low, keeping it for at most a day and then delivering it to the grid when the demand for it is high, also over a period of hours. The system described below is expected to be most valuable if installed at the sites of industrial end users, particularly those with ample low-grade waste heat or substantial space heating and cooling requirements. It may also prove cost effective if installed at electrical substations or wind turbine farms augmented with passive solar collectors, and perhaps even large coal-fired or nuclear power plants.

Most diurnal load leveling today is done either by pumped hydroelectric or (less often) by underground compressed air energy storage (CAES) systems, although a variety of advanced battery technologies are under evaluation particularly for use at electrical substations. The former two kinds of energy storage systems have the disadvantage of being tied to geological formations, which prevents them from being installed near most existing power plants or industrial end users, while present-day battery systems are relatively expensive and also involve caustic, toxic or inflammable materials. Thus there is a significant unmet need for a low-maintenance, environmentally benign energy storage system that can readily be installed wherever zoning ordinances and land prices permit it, and for which the lifetime cost per unit energy stored approaches that of pumped hydro and underground CAES.

This paper presents a novel approach to the diurnal load-leveling problem. It may be described as a form of "advanced adiabatic" CAES [2], which stores the heat of compression and uses it to reheat the air during expansion, rather than using a gas-fired turbine for that purpose. The most significant innovation in the proposed system is its use of a porous material that adsorbs air in order to greatly reduce the cost of the compressed air storage tank, mainly by reducing the pressure needed to attain a reasonable energy density. This in turn dictates the use of a new kind of thermodynamic cycle for the charge-discharge process, which relies primarily on a temperature swing rather than a pressure swing as in all CAES systems heretofore considered. An efficient implementation of the temperature-swing cycle using an adsorption-based heat pump will also proposed in the following. The general idea behind this approach is diagrammed in Fig. 1 below.
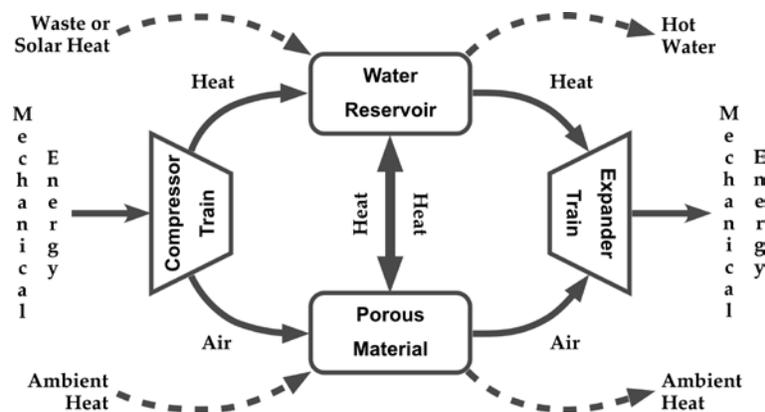

Figure 1. Schematic diagram of an adsorption-enhanced CAES system. In this system the heat of compression is stored in a water reservoir, while the compressed air is stored by allowing it to be adsorbed by a porous material. Adsorbed air is much more dense than gaseous air at the modest pressures, of order 20 bar, utilized by the system. At equilibrium, the amount of air adsorbed by a porous material at any the given pressure increases with decreasing temperature. Accordingly, the porous material is progressively cooled while charging the system to promote adsorption, and the heat taken from it is likewise stored in the water reservoir. To discharge the system, these processes are reversed. That is, heat is pumped from the hot water reservoir into the porous material to raise its temperature and so cause air to be desorbed from it, while additional heat is pumped into the air so that the input mechanical energy is fully regenerated during expansion. The dashed arrows indicate some alternate modes of operation. First, if low-grade waste or solar heat is available, it can be added to the hot water reservoir to compensate for heat lost during storage. Depending on the temperatures utilized, a portion of the heat needed may also be obtained from the environment, allowing some of the hot water to be used for other purposes. If enough low-grade heat is available it may further be more economical to dump some of the heat taken from the porous material into its environment while charging the system, rather than storing it for subsequent use while discharging it.

Presently, the most suitable known kinds of porous materials that can facilitate the storage of pressurized air are the zeolite minerals. These have been widely used as a means of separating the nitrogen and oxygen constituents of air

for medical and industrial purposes, but their air adsorption capacities at the relatively high pressures involved in CAES have not yet been thoroughly studied. In addition, most of the data that does exist is proprietary and not accessible to the scientific community at large [5]. One exception to this rule is a study published by G. W. Miller in 1987 on the adsorption of air to a common faujasite-type zeolite variously known as NaX or 13X, which includes N_2, O_2 & Ar adsorption isotherms at four temperatures ranging from –70 to +50°C and pressures of up to 4 bar [3]. This study further provides analytic fits of the Langmuir and Sips isotherm formulae to these measurements, and evaluates the accuracy of several multicomponent isotherm formulae on a more limited set of mixed gas data. The availability of these analytic formulae makes it straightforward to extrapolate these data to air at the higher pressures of interest here. Interpolation and extrapolation to temperatures other than those for which measurements were made can in principle be done by the van't Hoff equation, although this is somewhat more problematic especially at higher pressures. Figure 2 plots the air adsorption isotherms, derived from Miller's data using his "extended Sips" multi-component formula, at the higher three temperatures used by Miller, along with the isotherm obtained from a van't Hoff type extrapolation of the same formula to 100°C.
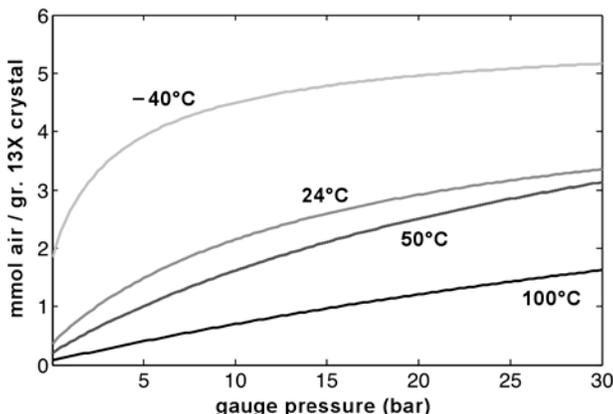

Figure 2. Extrapolated adsorption isotherms from Ref. [3] showing the amount of air adsorbed by the 13X zeolite as a function of gauge pressure at four different temperatures, derived as described in the main text.

In order to calculate the reduction in the volume needed to store a given quantity of air in the presence of a zeolite, one must first take into account the fact that zeolites are generally microcrystalline powders which are formed into pellets using an inert binder so that gases can flow readily through the packed adsorption bed. The binder typically constitutes of about 20% of the volume of the pellets, and the pellets typically fill about 80% of the volume of the packed bed. Accordingly, the density of zeolite in the bed is about 64% that in the crystal, with an additional 20% void fraction. Together with the above isotherms, this leads to the sampling of results from the effective "equation of state" for a packed zeolite bed seen in Table 1 below. Also shown in the table are the amounts of air released by a packed 13X bed over various (T, P)-swings divided by the amount of air that would be released over a simple pressure swing starting from the same maximum pressure at 25°C. It is readily seen that the increase in the density with which air can be stored in a packed 13X bed is significant especially at lower values of the operating pressure and when a large temperature swing is utilized; the additional benefit obtained from a combined temperature and pressure swing is not large by comparison.

table entries are dimensionless	0 bar	5 bar	10 bar	15 bar	20 bar	25 bar	30 bar
–40°C	45.0	96.7	111.8	119.9	125.3	129.4	132.7
24°C	9.0	37.3	54.2	65.9	74.7	81.5	87.1
50°C	5.2	25.6	41.2	53.8	64.4	73.5	81.3
100°C	1.9	10.7	18.6	25.8	32.4	38.4	44.0
P-swing at 24°C in a 13X bed over P-swing w/o 13X at 25°C	N/A	5.7	4.5	3.8	3.3	2.9	2.6
24 to 100°C T-swing in 13X bed over P-swing w/o 13X at 25°C	N/A	5.3	3.6	2.7	2.1	1.7	1.4
(T, P)-swing of (24, X) to (100, 0) over P-swing w/o at 25°C	N/A	7.1	5.2	4.3	3.6	3.2	2.8
–40 to 100°C T-swing at P=X in 13X bed over P-swing w/o at 25°C	N/A	17.2	9.3	6.3	4.6	3.6	3.0
(T, P)-swing of (–40, X) to (100, 0) over P-swing w/o at 25°C	N/A	19.0	11.0	7.9	6.2	5.1	4.4

Table 1. The first four rows are the volume units of air at STP that can be stored in a single volume unit of packed 13X pellet bed at various temperatures and pressures, assuming a binder & void fraction of 0.2 each and a 13X crystal density of 1.53 kg / L. Subsequent rows give the difference in the amounts of air stored at various pairs of (temperature, pressure)-values divided by the amount stored via a simple pressure swing at 25°C, which is the factor by which the air storage density is improved by using that (T, P)-swing in a packed 13X bed instead of an equivalent P-swing in a tank of the same volume at 25°C without the zeolite.

Although the improvements indicated in Table 1 are significant, it is important to realize that the increase in the energy density obtained through the use of a zeolite will actually be substantially better than the increase in the air storage density alone. One reason for this is that the combination of a temperature swing with a zeolite allows most of the stored air to be discharged without a large drop in the pressure, whereas the drop in pressure that accompanies the release of air from a conventional CAES system makes this rather more difficult to arrange [2]. More important, however, is the fact that the heating and cooling of a zeolite in equilibrium with gaseous air provides a means of converting heat to and from mechanical energy, in a fashion not fundamentally dissimilar to the conversion that occurs when boiling a liquid into a vapor at constant pressure. In the usual case of boiling water, less than 10% of the heat is converted into PV work, while the rest of the latent heat of vaporization winds up as sensible heat in the steam. The analogy between vaporization and the desorption of air from a zeolite, however, is far from exact, in part because the later process is supercritical, and in part because desorption is not a typical first-order phase transition in that the temperature rises continuously as it proceeds.
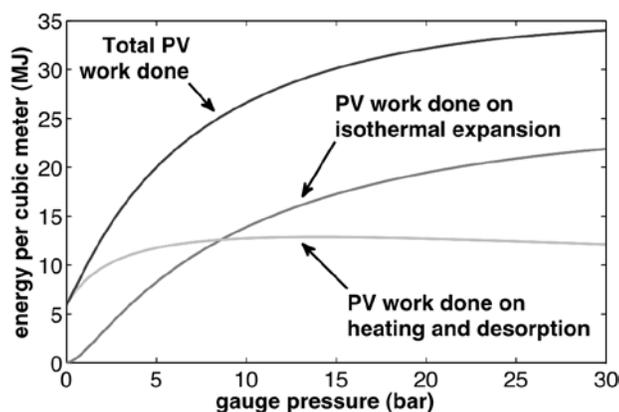
Figure 3. Plots of the PV work done on heating a cubic meter of zeolite pellet bed saturated with air from –40 to 100°C as a function of pressure, which is held constant during that process, together with the work done on subsequent isothermal expansion of this air down to ambient pressure after isobaric cooling to 25°C, and the total work done by the combined process, as predicted from the isotherms shown in Fig. 2.

In Fig. 3, we compare an estimate of the energy that could be extracted during the heating and desorption of air from a zeolite with an estimate of the energy that could be extracted by subsequently expanding this air, both as a function of pressure. The assumption of reversible isothermal expansion is of course excessively optimistic, as is the assumption that all the PV work done on desorption can be extracted in practice, but these estimates nevertheless show that the PV work done during desorption will be a substantial fraction of that done during expansion throughout the range of pressures under consideration here, and may even exceed it at pressures below 10 bar. Indeed these calculations imply that the PV work done during desorption will be 15 to 20% of the latent heat of adsorption, including the relatively small amount of work done by heating the desorbed air; a more precise number cannot be given without carefully considering the composition of the adsorbed air, which will be highly enriched with nitrogen (the heat adsorption of nitrogen to 13X is 25 kJ / mol, while that of oxygen and argon is 13 kJ / mol [3]).

It is further interesting to observe that the zeolite's ability to convert latent heat into PV work could potentially also be used to make up for some of the losses involved in compressing and expanding the air, due to the impracticality of carrying out these processes even approximately isothermally at any significant power level. Although precise estimates must await the development of detailed system designs, this possibility can be illustrated by the idealized processes shown in Fig. 4. This figure displays the PV-diagram of a thermodynamic cycle that involves three adiabatic compressions, each by 2.35 times the initial pressure and followed by isobaric cooling back to 25°C. The air at $2.35^3 = 13$ bar is then adsorbed by a zeolite bed which is cooled to –40°C for storage. To discharge the system, the zeolite bed is first allowed to warm up to –6°C in a sealed tank, which will raise the pressure therein by another factor of 2.35 to 30.5 bar. This is followed by isobaric heating to 107°C to desorb the air and adiabatic expansion back to a pressure of $2.35^2 = 5.5$ bar, which cools the air all the way back down to –40°C. Two more isobaric heatings to 25°C each followed with an adiabatic expansion by a factor of 2.35 then takes the air back to atmospheric pressure.
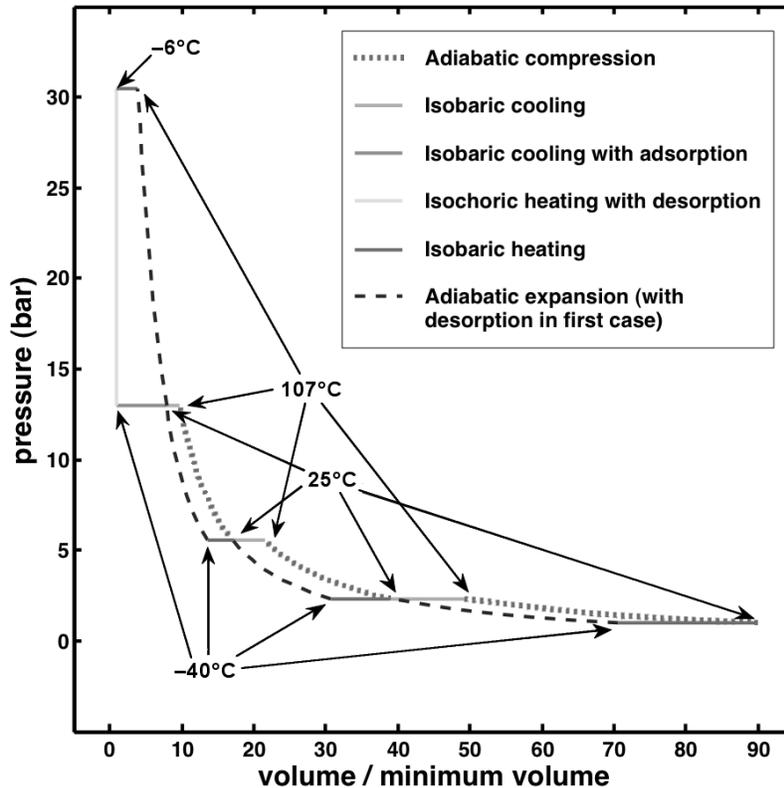
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Figure 4. The PV-diagram of an idealized thermodynamic cycle involving three adiabatic air compressions, each to a pressure 2.35 times the initial pressure and a temperature of 107°C, followed by isobaric cooling back to 25°C. After the last such compression and cooling, the air is adsorbed by a zeolite bed with cooling down to –40°C for storage. To recover the energy and make up for the losses inherent in the asymmetry of expansion vs. compression, the zeolite is initially allowed to warm up to ca. –6°C, which is predicted to raise the pressure by another factor of 2.35 to 30.5 bar (absolute). The zeolite is then heated to 107°C while the air is drawn off and likewise heated to 107°C, then adiabatically expanded by a factor of $2.35^2 = 5.5$ and a temperature again of –40°C, then isobarically heated back to 25°C. Two more adiabatic expansions by a factor of 2.35 and isobaric heatings from –40 to 25°C then completes the cycle. The area inside the closed loop in the upper left of this diagram represents the additional energy extracted by heating the zeolite at the higher pressure of 30.5 bar, and is approximately equal to the sum of the areas of the other three loops in the diagram which represent the energy lost due to the asymmetrical nature of the compression and expansion processes.

It may be observed that the energy harvested in the initial desorption and expansion steps (the area inside the upper-left-hand closed loop in the diagram) largely compensates for the energy not recovered in the subsequent adiabatic expansion and isobaric heating steps (the remaining three loops in the diagram); the ratio of the energy harvested to the energy lost is about 75%. Note also that both the cooling of the air after each compression and heating of the air after each expansion are largely spontaneous processes (depending on the ambient conditions), and hence can be implemented inexpensively without heat storage and recovery. In fact, save for the compressions, the cooling of the zeolite bed to –40°C while charging the system, and the heating of the zeolite bed to 107°C during discharge, all of the processes operating in this cycle should be largely spontaneous in most settings. This observation was, in part, the reason for our choice of minimum and maximum temperatures over the cycle of –40 & 107°C, which roughly symmetrically bracket common ambient temperatures.

Nevertheless, the biggest problem to be overcome in turning the foregoing observations into a practical energy storage device lies in the large amounts of heat that must be taken from the zeolite bed to make it adsorb large quantities of compressed air, and then returned to the bed again in order to desorb the air. This includes the sensible heat contained in the zeolite itself, in addition to the heat generated by adsorption of the air. The latter, together with the heat generated by compression, is expected to be at least twice the mechanical energy that can be recovered from the fully charged system, assuming a –40-to-100°C temperature swing as above. The heat capacities of zeolites, however, are comparable to those of sand or rock, or 800-900 J / kg-K. It follows that the heat capacity of a zeolite pellet bed is approximately 1 MJ / M^3-K, so that changing its temperature by 140°C requires about 140 MJ / M^3, or three-to-four times the recoverable mechanical energy. Even though about half of this heat would flow spontan-

eously to or from the environment while charging or discharging the system, taking the remaining heat from and returning it to the ambient environment could entail a substantial mechanical energy overhead.

Fortunately, there is an alternative. For even though an AE-CAES system needs a lot of heat, it needs that heat at rather modest temperatures. This makes it possible to use cheap, low-grade waste or solar heat to the warm the zeolite bed up to the 100°C or so needed to largely discharge the adsorbed air, rather than storing and recovering all the heat taken from the bed. An AE-CAES system's use of relatively low pressures, moreover, also means that such "low-grade" heat sources can be used to reheat the expanding air and so fully recover the stored mechanical energy. For example, an AE-CAES system installed at a wind farm could obtain much of the heat it needs from flat plate solar panels installed on or among the turbine towers. It may perhaps be argued that this is cheating, since the system is no longer a pure energy storage device, but the same is true of existing (underground) CAES systems, which use a gas-fired turbine to reheat the air and so are also not carbon neutral. Of course, there remains the problem of how to cool the zeolite to temperatures well below freezing in order to promote adsorption of the air, but it turns out that this too can be accomplished with inexpensive low-grade heat, and without the need to expend significant amounts of electrical or mechanical energy running the compressor of a conventional heat pump.

Curiously, this technology is once again based on adsorption, but this time of a refrigerant vapor rather than of air. Such adsorption refrigeration systems have certain advantages over conventional vapor-compression systems, needing in particular no mechanical energy for operation, but they are not presently commercially available even though thousands of laboratory prototypes have been built over the years [1]. The reason for this is certainly not their relatively low coefficient of performance (COP) since absorption refrigerators, which use a liquid rather than porous solid to soak up the refrigerant vapor, also have a low COP but are commercially available (the COP, in any case, is not a strictly fair comparison since the mechanical energy needed by vapor-compression systems is also ultimately obtained from heat, and with an efficiency well below unity). The most likely reason is therefore that adsorption refrigerators do not provide continuous cooling, but must be turned off while the adsorbent is being regenerated using low-grade heat (although a pair of such systems operated in tandem can still be used to provide continuous cooling). In the present application, however, their batch nature is actually an advantage.
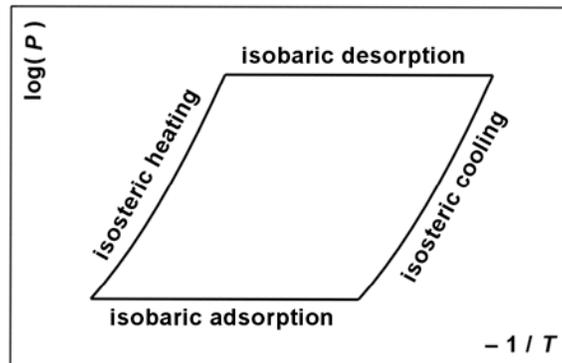

Figure 5. Clapeyron diagram showing the thermodynamic cycle typically used in adsorption refrigeration. Starting from the lower left, the adsorbent is first heated to raise the pressure by desorbing some of the refrigerant from it. In the next leg of the cycle, heating is continued while keeping the pressure constant by piping the refrigerant vapor through a condenser kept at ambient temperatures, thereby liquefying it. The liquid refrigerant is then stored in a tank until cooling is needed, while the adsorbent is cooled back to ambient temperatures thereby also bringing the pressure over it back down. Finally, the liquid refrigerant is drawn by the pressure differential through an evaporator and the resulting vapor adsorbed while continuing to cool the adsorbent. This carries heat away from the evaporator and its associated thermal mass, thus providing the desired refrigeration.

The use of an adsorption heat pump, possibly in tandem with a vapor-compression heat pump, thus offers the possibility of operating an AE-CAES system entirely off waste or solar heat, without any heat storage at all. Whether or not this is in fact the best way to operate the system will depend on the context in which it is used, but even when much of the heat is stored some additional heat from external sources will probably be needed to make up for the inevitable losses this involves. This leads to the intriguing possibility of actually deriving additional economic benefit from the heating and cooling power of the system, in addition to its mechanical or electrical power. For example, an AE-CAES system that was charged at night with low-cost off-peak electric power could provide heat or hot water to the building or factory in which it was installed during this process, and then regenerate the electric power during on-peak daytime periods while also taking some of the heat needed to discharge the system from the building or factory, simultaneously cooling it for air conditioning or cold storage purposes. This in turn

would greatly enhance the building or factory's ability to participate in demand-management programs, and could even greatly improve the economics of net-zero-energy buildings generally.

We close by considering briefly how much an AE-CAES system might cost. This will of course depend on the details of the system design, which we have not yet had the opportunity to explore in any depth. Hence to simplify matters we will assume that ample waste heat is freely available and that a single-stage adsorption refrigerator provides all the cooling power required, so that heat storage need not be used. Since an adsorption refrigerator is a simple device with few moving parts and needs only inexpensive adsorbent-adsorbate pairs such as activated carbon-methanol or zeolite-ammonia, we will also assume its cost is negligible. The air compressors needed by an AE-CAES system to reach the modest pressures it employs are very widely used to power pneumatic tools and machinery, and the DOE has estimated that with a ten year operating lifetime the cost of ownership of a compressed air system that operates 50% of the time is three-quarters electricity, one eighth maintenance and one eighth the compressor price [6]. At 5¢ per kWhr, the energy needed to produce 1000 ft^3 = 28.3 M^3 of air at 7-10 bar typically runs 15¢, which implies that a compressor with a capacity of 1000 cfm and reaching slightly higher pressures would use about 200 kW of power and have an upfront cost of about $50,000. The cost of the expander train should be about the same (although some of the same hardware might be used for both compression and expansion), leading to an estimate of $100k ($100,000) for the turbomachinery needed to store and deliver 1.0 MWhr each over 5 hours.

The only other significant cost component of an AE-CAES system is the pressured zeolite bed. The amount of steel needed to contain a given quantity of air is, to a first approximation, independent of the storage pressure: a lower pressure necessitates a bigger tank but with thinner walls, and vice versa. The steel in a standard gas cylinder costs about $50 / M^3 of capacity, so the steel needed to confine ca. 10,000 M^3 of atmospheric air, which will produce 1.0 MWhr on isothermal expansion from 100 bar, costs about $500k. This is why all existing CAES systems store their air underground, and it is also why AE-CAES can greatly reduce the cost of "surface CAES." The reduction in the cost of the tank provided by a zeolite, however, falls off rapidly as the pressure increases, simply because zeolites are largely saturated by air at pressures of a few tens of atmospheres (see Fig. 2). At the same time, however, the volume of the tank, and hence the amount of zeolite in it, needed to store a given quantity of air also falls off with increasing pressure. Thus the operating pressure of an AE-CAES system must be carefully chosen to minimize the cost of the zeolite plus the cost of the tank and of the compressors / expanders needed to deal with that pressure.

The cost of zeolites, however, is almost as diverse as their chemical structures and the associated quantity of air they can store. Naturally occurring zeolites can sell for as little as 25¢ / kg, but are generally less pure and so would be expected to store less air than their synthetic counterparts. Synthetics such as 13X, on the other hand, cost at least four times as much, although it has been reported that reasonably high-quality 13X can be made from fly ash for only a fifth the cost [4]. Assuming conservatively that a suitable material can be sourced in large quantities for $1 a kg and that the density of a pellet bed is about 1 ton / M^3, Fig. 3 implies that with a –40-to-100°C temperature-swing at 20 bar about 112.5 tons of zeolite would be required to store 1.0 MWhr, again using ca. 10,000 M^3 of atmospheric air. Also under those conditions Table 1 implies the cost of the tank would be reduced 4.6-fold, for a total of 500 / 4.6 + 112.5 = $221k. These rough estimates will doubtless come down as our work proceeds, but they are already comparable to any energy storage technology available today that can be deployed without geological restrictions.

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