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Long Term Thermal Energy Storage in Adsorbent Beds for Solar Heating Applications

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Abstract

Long term thermal energy storage in adsorbent beds is investigated as means to store excess solar heat from the summer and release it during the winter for residential heating applications. Adsorption is a reversible exothermic process which releases heat when mesoporous materials, called adsorbents, are exposed to gaseous species, called adsorbates. The adsorbate is adsorbed into the crystal lattice and energy is released. Since the process is reversible, heat can be used to regenerate saturated adsorbent, release the adsorbate and store energy. Adsorption thermal energy storage has many advantages over conventional thermal storage methods and can be combined with all types of solar panels. When incorporated into a solar heating system, the adsorption thermal energy storage system could provide solar heat year round and reduce the home's energy cost by up to 80%.

In this study, an activated alumina and zeolite 13X hybrid from Rio Tinto Alcan was identified as the best adsorbent when combined with water as the adsorbate, through an extensive screening procedure. The adsorption and regeneration cycles of the adsorbent were characterized using the prototype system. A maximum performance of 200 kWh/m^3 was recorded. A model for predicting adsorbent performance based on the regeneration temperature was created and then tested using a different adsorbent. The efficiency of the system was also calculated in order to identify critical design parameters. The adsorbent was modified by impregnating inorganic salt hydrates into the crystal lattice. The resulting modified adsorbents have a 25% increase in performance, with some adsorbents reaching 300 kWh/m^3. Using the performance and efficiency results of the prototype, the practical and economic feasibility of a large scale adsorption thermal energy storage system was investigated in various scenarios. Although adsorption shows several practical improvements over other forms of thermal energy storage, the cost of the systems remains a bottle neck to commercialization.

Résumé

L'emmagasinage à long terme d'énergie thermique dans des lits d'adsorbents est proposé comme méthode pour emmagasiner l'énergie de la radiation solaire durant l'été pour ensuite la libérer durant l'hiver comme source de chauffage résidentiel. L'adsorption est un processus exothermique réversible qui libère de l'énergie lorsque qu'un matériel mesoporeux, appelé adsorbent, est exposé à des composés gazeux, appelé adsorbate. L'adsorbate est adsorbé dans la matrice cristalline de l'adsorbent et de la chaleur est libérée. Puisque le processus est réversible, un adsorbent saturé peut être régénéré s'il est exposé à de la chaleur; l'adsorbate est libéré et l'énergie est emmagasinée. L'adsorption a plusieurs avantages comparativement aux autres méthodes d'emmagasiner l'énergie thermique et peut être combiné avec n'importe quel genre de panneaux solaires. Lorsqu'un système d'adsorption est incorporé dans un système de chauffage solaire, le chauffage solaire est disponible à l'année longue et les coûts de chauffage sont réduits par 80%. Suite à un criblage d'adsorbent et d'adsorbate, un mélange d'alumine activée et zeolite 13X préparé par Rio Tinto Alcan et l'eau sont choisies comme adsorbent et adsorbate pour les expériences. Les cycles d'adsorption et de désorption sont caractérisés en utilisant un système prototype. Une performance maximale de 200 kWh/m^3 est atteinte. Un modèle pour prédire la performance du système basé sur la température de régénération est conçu et confirmé avec un autre genre d'adsorbent. L'efficacité du système est calculé afin d'identifier les paramètres clés dans la conception. L'adsorbent est modifié en imprégnant des sels anhydres inorganiques dans la structure cristalline. Les adsorbents modifiés augmentent par 25% leurs performances et un des adsorbents modifiés performe à 300 kWh/m^3. En utilisant les résultats des expériences, une variété de scénarios sont conçus pour vérifier la viabilité pratique et économique de l'adsorption comme source de chaleur à l'échelle commerciale. Malgré que l'adsorption possède plusieurs avantages considérables comparativement aux autres méthodes d'emmagasinage d'énergie thermique, le coût du système crée un gros problème pour la commercialisation.

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Preamble:

The following is a paper-based thesis that contains 6 chapters. Chapters 2 and 3 are papers that have been submitted to refereed journals and contain their own referencing system independent from the rest of the thesis. Chapters 1, 4, 5 and 6 make up the remainder of the thesis. For consistency, the referencing style used for all chapters is that of the Journal of Renewable Energy.

1 Literature Review and Introduction

1.1 Introduction and Literature Search

Conservation and sustainability are integral parts of our society. They drive us to explore new sources of energy and find value in what used to be considered waste. As resources become depleted and prices for standard commodities, like oil, keep rising, clean sustainable technologies become more attractive and economically feasible.

Thermal energy storage is one of these resulting technologies. Thermal energy is a basic requirement of all industrial, commercial and residential operations. Instead of obtaining this energy from conventional sources, like fossil fuels, it can prove more profitable to collect it from unconventional sources, like solar radiation, incinerators or smelting plants, when it is abundant and store it until it is required. Solar heating is becoming increasingly popular as a source of heating. However, it is unreliable and not constant between day and night or from season to season. Regardless, there is a great supply of low to mid grade excess heat and there is a great demand for thermal energy storage systems to store it to provide heating. If an adequate long term storage system was developed, solar heating could be made available year round, bridging the gap in the solar heating service and rendering fossil fuel heating obsolete when compared with the abundance of solar energy.

The focus of this thesis is long term thermal energy storage combined with solar thermal energy collection but the proposed concepts can be applied to various other applications. All solar heating systems require three components;

- a solar collector to harvest the incident radiation
- a storage system that can contain the energy until it is needed and distribute it to the desired use
- a sink, like a room, home or building where the energy is given

1.1.1 Solar Thermal Collectors

There are two different types of solar collectors: photovoltaic solar collectors and thermal solar collectors. Photovoltaic solar collectors exploit the photovoltaic effect to produce electricity by using the energy available in solar radiation to excite electrons on a doped semi conductor and create a current. On the other hand, thermal solar collectors harvest the radiation of the sun as thermal energy, increasing the temperature of a transfer fluid flowing through the system. Although some thermal collection is involved in producing electricity, purely thermal collectors are the object of this thesis.

There are three basic types of solar thermal collectors; flat plate solar collectors, evacuated tube solar collectors and concentrating solar collectors. Each one of these can be made more efficient by adding glazing and one, two or even three axis tracking. Flat plate collectors are the most basic solar collector design. They are composed of dark colored plates with heat transfer tubes weaved on, below or through the collecting plate for the heat transfer fluid to pass through. As the plate heats up, it also heats up the fluid going through the tubes. These collectors are fairly inexpensive and simple but also have large surface areas which are prone to heat loss. As a result, they do not have a very good efficiency and reach temperatures below 100°C [34] which limits their operation to Domestic Hot Water (DHW) and space heating applications. Their low operating temperatures and sprawling design only make them useful in specific climates where the weather is not too harsh or cold.

Evacuated tubes are tubular solar collectors that have been encapsulated in a glass tube where a vacuum is applied. The heat transfer fluid flows through the inner tube and collects the energy. Because the vacuum is the ideal insulator, these systems are much more efficient and can reach temperature between 100-250°C [39]. They are more expensive than flat plate systems but are also more versatile and can be useful for DHW and space heating in a larger spectrum of climates.

Concentrating solar collectors use flat or parabolic mirror to concentrate the solar radiation from a large area to a small area which not only increases the amount of energy incident on that area, it also greatly reduces heat losses to the environment. The mirrors typically concentrate the solar radiation, up to 1000 suns in intensity, onto a point or a strip where a heat transfer fluid can extract the energy. These systems have the best efficiency of the three and can reach temperature of up to 500°C depending on design [34]. However, they have a more complex design which makes them more expensive and require more maintenance. Low end concentrating collectors can be used for DHW and space heating while high end collectors can be designed for industrial heating applications and steam production for electricity. It is also possible to combine the three types of collector in order to benefit from their inherent strengths (such as concentrating evacuated tubes).

Regardless of the collector type, each one harvests the thermal energy with a fluid. If that energy is not immediately utilized, it can be stored. These storage methods are usually sensible short term storage systems and the energy must be used within a few days or else it will be lost to the environment. Since solar heat is not constant year round, there is a huge excess of energy during the summer that is typically wasted since short term storage tanks have a storage capacity that is much lower than what is available. Furthermore, even if a plethora of storage tanks were available to store all the extra heat, it would not last long enough to be utilized. The inherent problem with solar collectors is this excess energy is present during the summer when it is not needed and a lack occurs during the winter when heating is required. With current technology, it is not possible to store the excess heat from the summer long enough to use it in the winter.

1.1.2 Thermal Energy Storage

There are three groups of thermal storage systems; Sensible Heat Storage (SHS), Latent Heat Storage (LHS) and Thermochemical Heat Storage (THS) [8][4][13]. In sensible heat storage systems, a material, like rock or water, is heated inside an insulated container that slows thermal leaking. The performance of this type of storage is measured by the temperature difference between the material and the ambient temperature. The amount of energy available can be calculated using $Q = mCp\Delta T$. Therefore a high heat capacity and a large temperature difference make for a good thermal storage system although these systems typically operate below 100°C. Examples of this type of storage systems are: Aquifer Thermal Energy Storage (ATES) [31], Borehole Thermal Energy Storage (BTES) [25] or water tank storage [20]. This method of storing energy is extremely cheap and is currently the dominant form of thermal energy storage. However, SHS systems have low energy densities, in the range of 40-60 kWh/m^3 [32], which requires large volumes to store sufficient energy for heating applications. The thermal energy is also sensibly stored and is constantly diffusing to the environment. As a result, large amounts of insulation are required to slow the heat loss to the surroundings. Most systems keep the energy for less than a week and even the state of the art systems do not last more than a few months, even with volumes above 30 000 m^3 [7]. These SHS systems have become widespread as short term thermal energy storage with small volumes. The systems can provide a limited amount of energy depending on the climate, which means that auxiliary heating systems are usually required, especially in northern regions.

Latent heat storage systems rely on the energy released or absorbed during the phase change of a material to store energy which is why they are typically referred to as Phase Change Materials (PCM). These materials are either free flowing or encapsulated for easy handling and placed in large heat transfer containers or they are infused into building materials like dry wall. These materials are mainly designed to maintain a constant temperature around the fusion temperature and are subject to continuous heat loss to the environment. Therefore, these systems also require a great deal of insulation and can not be used for long term thermal energy storage. Typical PCMs like paraffin waxes have energy densities around 55 kWh/m^3 [1] and are very good for cooling applications. Some PCMs, like molten salts, have been developed for high temperature (300°C and up) applications and can have energy densities as high as 300 kWh/m^3 [11]. The latter materials are best suited for steam production and would not be feasible in residential settings. Several prototypes of LHS systems are being developed and the paraffin waxes are starting to be commercialized, but these systems are not wide spread.

Thermo-chemical heat storage utilizes reversible exothermic/endothermic reactions or processes to store heat. Excess heat is used to perform the endothermic reaction which usually separates a product into reactants. Once the reactants are separated, the energy is stored as chemical potential. When the energy needs to be released, the reactants are brought together for the exothermic synthesis reaction and as the product is made, the energy is released. Since these systems store energy as chemical potential, they do not require insulation and the stored energy does not degrade with time. An example of this kind of thermal energy storage is NH_3 dissociation into H_2 and N_2 being developed by the Australian National University [14]. However, most reactions require very high temperatures (400°C and up) for both endothermic and exothermic reactions which makes them well suited for steam production, but not for typical heating applications [14]. Only a few experimental systems exist worldwide and the technology is still being developed.

As can be seen from the previous paragraphs, although thermal energy storage is an old concept, it is still young in terms of technology. There are some solutions that can cater to niche markets but widespread thermal applications, like residential heating applications, are out of range for currently available technology. The biggest hurdle is the lack of permanent long term thermal energy storage with charging temperatures below 250°C. The second hurdle is the need for more compact thermal energy storage systems that will not take up large volumes and could be retrofitted into existing homes. The commercialization target set by the international thermal energy storage community is a thermal storage system that has 8 to 10 times the energy density of water, around 480 kWh/m^3.

1.1.3 Theory of Heating

Energy supply for space heating in Canada is a 15 billions dollar industry [10]. Over 80% of residential energy comes from electricity or natural gas; 60% of the energy used in Canadian residences is for space heating and 20% is hot water heating [17]. An average house can expect to spend about $1140-1240 on space heating and about $400 on hot water heating every year [22]. These prices are projected to increase by up to 10% [16][35] a year because of the economic instability and the unpredictable fossil fuel market.

Energy consumption for heating varies depending on the house type, size and occupancy. Models have been developed to estimate energy consumption from heating and various other energy activities in order to optimize the design of integrated energy systems and energy saving practices. These models can be integrated into software suites, like HOT2000 that has been developed by Natural Resources Canada [2]. It employs the newest building standards and codes in Canada called R-2000 [30]. Using the regulations and the information provided about the home being simulated, the program builds a virtual home and produces reports on its energy consumption on a monthly basis over a full year. The software is linked to Canada's National Climate Archives which means the home's performance can be tested in different locations throughout Canada.

The total installed Canadian capacity of solar thermal energy has grown to just under 600 MW_{th} in 2006 [36]. There are 360 to 500 firms in Canada whose primary business is solar energy [15]. As of 2004, over 60% of those businesses were located in Ontario [15]. The solar heating industry in Canada has seen considerable growth recently and is projected to keep growing by at least 20% a year [12]. Also, Ontario has been a leader in clean energy incentives. The Green Energy Act will soon guarantee 1500 MW of newly installed clean distributed energy by 2015 and 3000 MW by 2025 as well as a 30% reduction in natural gas consumption by 2017 [38].

There are also millions of dollars in financial incentives from the provincial and federal government to develop renewable energy. For example, the Ontario Solar Thermal Heating Incentive Program provides up to \$440/m^2 of panel installed [24] and the Ontario Home Energy Savings Program provides up to \$10 000 for retrofitting houses with energy issues [23]. There are also added perks such as tax rebates and carbon credit obtained from CO_2 mitigation.

At the end of 2008, there were an estimated 1000 solar roofs in Ontario. As part of the Government of Ontario's Go Green initiative, they are aiming for 100,000 solar roofs designed to supply hot water and space heating within the next 11 years (5,000 by 2011, 60,000 by 2017) [3][21]. The potential market size for solar heating is every unobstructed roof; theoretically, this represents 1.8 million houses only in Ontario [3]. There are over 11 million households in Canada including multi-residential buildings [19]. The federal government and other provincial governments also have great incentive programs and plans to grow the renewable energy industry; British Columbia has also announced their "100,000 solar roofs by 2020" initiative [33]. Europe is already a world leader in the renewable industry with 15.4 GWth [9] of installed solar heating and will continue to grow. It plans to have 20% of its energy from renewable sources by 2020 [37].

1.2 Previous Work at the University of Ottawa

This project started as an undergraduate thesis at the University of Ottawa, Chemical and Biological Engineering Department under the supervision of Dr. Handan Tezel. In the fall of 2006, a preliminary study prototype was built in order to test the effect of relative humidity and cycling on a CECA 13X and water working pair which had been determined to be the best after an extensive literature search [5]. In the summer of 2007, a research assistant was commissioned to take the preliminary prototype and produce a more rugged system with an automated data acquisition system. In the fall 2008, a special directed study student started working on the system and did some adsorbent screening on CECA 13X as well as two other adsorbents with similar properties that had been identified and the results are in the process of being published [6]. The maximum system energy density reported was around 150 kWh/m^3. The energy density of the system is calculated by an Excel program which uses the data collected as well as mass and energy balances to determine the amount of energy released. The equations and procedure used to calculate the energy density can be found in Appendix 5. A schematic diagram of the system can be found in Chapter 2.

1.3 Objectives and Hypothesis

In previous work at the University of Ottawa, the validity of energy storage in adsorbent beds was demonstrated and some of the basic operating parameters were characterized. The objectives of the current thesis are to:

- Improve the design and performance of the system to obtain energy densities upwards from 150 kWh/m^3 by modifying adsorbents and modifying the equipment by adding a new heater, fogger, thermocouples and hygrometer to the experimental system.
- Characterize the energy densities for the system during adsorption.
- Characterize the regeneration process by varying operating parameters, such as flow and inlet humidity and the regeneration temperature.
- Obtain real life annual performance for solar panels during winter and summer months as well as space heating loads for a typical Canadian house.
- Using the Regeneration and Adsorption Characterization as well as the solar panel and household space heating information, perform an economic analysis for the

system and establish economically viable options for the use of long term thermal energy storage in adsorbent bed systems.

The hypotheses for the current work are;

- An energy density of 200 kWh/m^3 can be achieved with improvements to the system.
- It is possible to produce a model for regeneration based on the regeneration temperature and the amount of energy inputted into the system.
- When incorporated into a solar thermal heating system and a household, it is possible to provide heat all year round to residential establishments either through onsite panel and stationary bed installations or using mobile beds with concentrated solar farms for refuelling.

2 Adsorption Thermal Energy Storage for Solar Heating Application

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Abstract

Adsorption Thermal Energy Storage (TES) is a promising technology for long term thermal energy storage of solar heat. By using the exothermic reversible adsorption process, excess heat from the summer can be stored and then released for heating during the winter. The usefulness of the storage system relies heavily on the temperature and quality of the heat available for regeneration of the adsorbent as it affects the storage efficiency, the amount of water released from the adsorbent and in turn the performance or energy density of the storage system. In this study, a lab scale high throughput open loop forced air adsorption TES has been built. A series of adsorption experiments were performed to determine the effect of adsorption flow rate and cycling on the chosen best performing adsorbent, AA13X from Rio Tinto Alcan. Regeneration characterization experiments were performed to determine the effect of flow rate, temperature and feed air relative humidity on the regeneration and performance of the system. The results were compared with another adsorbent to verify the observed trend. Finally, the efficiency of the thermal storage system was calculated.

Keywords: Long Term Thermal Energy Storage, Solar Heating Storage, Adsorption, Seasonal Storage

2.1 Introduction

Solar radiation is a renewable source of energy which makes solar heating a very attractive alternative to residential heating with natural gas or electricity which makes up 80% of the residential energy consumption in Canada [2.15]. The biggest trouble with this technology is that the supply does not match the demand. The incident radiation on a typical Canadian home is up to two times more than its annual space heating and domestic hot water needs. However, the majority of that radiation occurs during the summer months when it is not needed. In all currently available commercial solar heating systems, the energy collected during the summer is stored in sensible heat storage systems, either small short term water storage tanks which last a few days or larger borehole systems that can hold the energy for 1 or 2 months, and the heat dissipates with time. Therefore, solar heating is not available when it is most necessary because there is no long term storage technology that can hold the energy long enough. There is also a great need for compact thermal storage systems that could be easily installed or retrofitted since the current options require exceedingly large volumes.

Adsorption thermal energy storage is a promising technology that could provide a long term storage solution that is more compact then conventional thermal storage methods. Adsorption is an exothermic physical process where a gas diffuses into the pores of a porous solid material and is trapped into the crystal lattice which releases heat. The gas is then considered to be in the adsorbed phase and the energy that is released during the adsorption process is called the heat of adsorption. The process is also reversible; when energy is applied to an adsorbent that is saturated with adsorbed gas, the endothermic desorption process (also referred to as regeneration) takes place; the gas is released and the energy is stored in the crystal lattice until the next adsorption process. Therefore, once the regeneration of the adsorbent takes place and the adsorbate gas is removed from the adsorbent, the energy is permanently stored in the material for an indefinite period of time as long as it is not exposed to the gas. Since the energy is not sensibly stored, the material can be kept at ambient temperature without degrading the energy [2.2].

There are a variety of adsorbents, such as activated carbons, silica gels, synthetic zeolites, natural zeolites and activated alumina, that can be combined with a variety of gases, like CO_2, NH_3, H_2O and hydrocarbons [2.22][2.14][2.10][2.5][2.17][2.19][2.1]. The heat of adsorption resulting from these combinations varies greatly depending on the interactions between the adsorbent and the adsorbate such as polarity, pore size, molecule size, surface area, presence of cations, pressure and temperature. These various characteristics are used in adsorption to perform various gaseous separations. The adsorbent/adsorbate working pair must be chosen carefully. For thermal energy storage, which is not a typical application of adsorption, the most desirable characteristics are high heat of adsorption and high energy density. Other desirable characteristics are a low regeneration temperature, no toxicity and no reactivity. Several working adsorbent thermal energy storage systems have been reported in the literature. *Gantenbein* [2.6] produced a working zeolite system which had an energy density of 106 kWh/m^3. Jaehnig investigated thermo-chemical energy storage using 200 kg of silica gel as the adsorbent [2.12]. *Hauer* [2.9] reported a successful full scale 7000 kg zeolite 13X storage system which heated a school and was charged by district heating over night to offset the peak energy demands and performed at an energy density of 124 kWh/m^3. *Janchen et al.* [2.13] studied a zeolite system with an energy density of 160 kWh/m^3. *Dawoud* [2.2] reports their working zeolite 13X system performing at 165 kWh/m^3. Even natural zeolite, which has a lower performance when compared to its synthetic counterparts, has been identified as a potential candidate for use in an adsorption thermal energy storage system [2.16]. The energy densities reported for all of these large scale systems are significantly lower than the theoretical energy or potential energy that could be achieved based on the heat of adsorption; practical performances of 124 kWh/m^3 are compared to theoretical performances of up to 250 kWh/m^3 [2.7][2.8].

Heat obtained from solar collectors or another source of excess heat can be used to regenerate the adsorbent and store energy in an adsorption thermal storage system. The adsorption and desorption processes can be cycled between summer and winter which makes the adsorbent bed a source of clean renewable heating and gives the user access to solar heating year round. Solar collectors are extremely varied in design and can have operating temperatures anywhere between 30°C and 500°C [2.21]. The regeneration temperature has been known to affect the amount of energy stored and therefore the energy density of adsorbent storage systems. Regeneration usually takes place at temperatures in excess of 250°C to assure complete regeneration. However, most commercially available solar collectors operate at temperature below 200°C. Therefore, information on system performance at a variety of low regeneration temperature is required in order to properly match an adsorbent system with a solar collector.

To date, most adsorbent system research has focused on the adsorption cycle and the maximum energy density that can be achieved when regenerated at exceedingly high temperatures. There is limited information in the literature about low regeneration temperatures and the resulting performance for the system. Therefore, a series of experiments were developed to not only to explore the maximum performance of the adsorbent, but mainly characterize the regeneration of the adsorbents at various temperatures, flow rates and relative humidities.

In our earlier studies, an extensive adsorbent screening process has taken place [2.3][2.4] in order to identify the best working pair. An Activated Alumina and Zeolite 13X hybrid combined with water as an adsorbate was chosen based on energy performance, availability, regeneration temperature and low toxicity.

2.2 Materials and Methods

Experiments were conducted using the same experimental setup as *Dicaire and Tezel* [2.4] with certain modifications. The hygrometer was calibrated and a new housing container was built to insure accurate readings. An ultrasonic fogger was installed in the bubble chamber to ensure 100% relative humidity during every run. New thermocouples were added into the system. More insulation was installed to ensure minimal heat loss during the experiments. Finally, the column was modified to house a larger volume of adsorbent and to have an L/D ratio of 1.8. The adsorbent identified in our earlier studies [2.4] which is a mixture of activated alumina and zeolite 13X (obtained from Rio Tinto Alcan from Brockville, Ontario, with commercial name ACTIGUARD 650PCAP, 8x14 mesh), referred to as AA13X, was selected as the adsorbent of choice for this series of experiments. Figure 2.1 is a schematic diagram of the experimental system used.

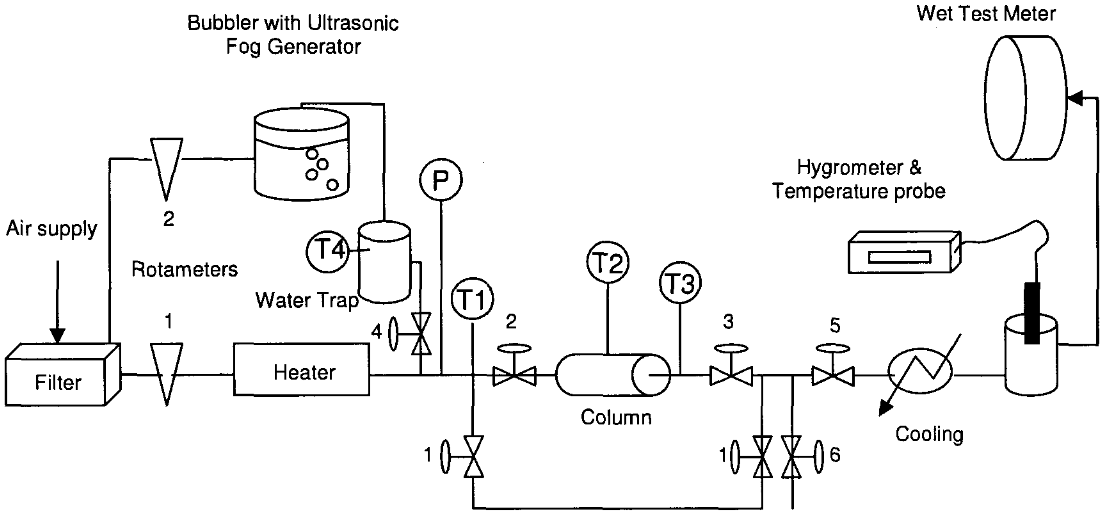


Figure 2.1: Schematic diagram of the experimental setup.

The air supply comes from the air compressor from the building supply which produces instrument quality air with little to no humidity. Rotameters 1 and 2 control the air flow into the system. The air going through Rotameter 2 goes through the bubbler filled with liquid water and gets saturated with water vapour. When rotameters 1 and 2 are combined, it is possible to produce air with varying flow-rates and relative humidity to feed into the system. All tubing in the system is ¼″ tubing. Polyethylene was used for the parts of the system with low temperature and stainless steel was used for the parts with high temperatures. The column is composed of 70 mm long of 38.1mm O.D. SS 314 pipe with ¼″ pipe welds at the entrance and exit. The column is welded shut but can be unscrewed at one end where a Teflon O-ring ensures a tight seal. The column has a total volume of 62.76 ml, a mass of 315.7 g when it is empty and has an L/D ratio of 1.8. The column holds approximately 55 g of the AA13X adsorbent. The bubbler is a 4 litre Erlenmeyer flask which contains a Hagen Exo Terra Ultrasonic Fog Generator which sits in 5 to 7,5 cm of water and fills the flask with an ambient temperature fog which saturates the air stream to above 95% relative humidity. This is one of the most efficient methods of producing completely saturated air [2.11]. The water trap captures the water which condenses from the vapours to prevent liquid water entering the system. The heater is an in-line air heater AHP-5051 from Omega which is connected to a rheostat which enables the user to regulate the temperature of the inlet air between ambient and 500°C with 400 Watts of power up to 10 SCFM. The hygrometer is a high temperature relative humidity and temperature probe transmitter (model HX-15 from Omega). The cooling coil preceding the hygrometer ensures that the air is at ambient temperature before the hygrometer takes a reading. This often causes condensation and the hygrometer container has been designed to trap the condensed liquid in a large volume ensuring that all the humidity leaving is measured by the hygrometer. Thermocouples T1 to T4, as well as the hygrometer, which has both a temperature and a relative humidity probe, are connected to a data acquisition system which is used to record data every 15 seconds during the experiments. By closing valves 2 and 3 and opening valve 1, it is possible to close off and by-pass the column, enabling the user to produce steady humidity before initiating the experiments. Valve 6 can be used as a purge for the system if necessary. The flow rates are measured using a Precision Wet Test Meter.

During adsorption experiments, the flow rate and the relative humidity into the column is controlled by Rotameters 1 and 2. Air from Rotameter 2 passes through the humidifier to ensure 100% relative humidity. If a different relative humidity is required, the flow from Rotameter 2 is combined with a flow from Rotameter 1 (which only has dry air) with different flow rates, to ensure the desired relative humidity is obtained going into the column. Steady conditions for flow rate and relative humidity are measured before the start of the experiment by using the bypass. To start the experiment, valve 1 is closed and valves 2 and 3 are opened, exposing the column to humidity.

During a regeneration run, the flow rate is controlled through Rotameter 1 which passes dry air from the supply to the in-line heater. The heater is used to obtain a designated steady temperature. Once a steady temperature is reached, valves 2 and 3 are opened and the column is exposed to heated air between 80 and 250 °C. If required, humidity can also be added to the regeneration stream going into the column using Rotameter 2.

2.3 Results and Discussion

Figure 2.2 shows temperatures measured at different places in the experimental set-up for a typical adsorption run. The inlet temperature to the column and the hygrometer temperature at the end of the system stay fairly constant. The thermocouple on the column sees an increase and decrease in temperature as the adsorption mass transfer zone moves through the column. As the energy is released from the adsorbent, it heats up the air passing through as well as the adsorbent and the stainless steel column which contains it. The hot air temperature is then measured by the outlet thermocouple. The column is well insulated so although some of the heat released during the adsorption is used to heat up the column as well as the adsorbent itself, only a small amount will actually be lost to the environment while most of the energy that went to heating up the column and the adsorbent will eventually be transferred to the air and measured by the outlet thermocouple. At the beginning of the experiment, equilibrium favours adsorption of the water vapour by the dry adsorbent which releases large amounts of energy and results in high temperatures. As the adsorbent becomes saturated and the temperature of the adsorbent rises, adsorption capacity decreases, which lowers the driving force for adsorption. As the temperature of the column and adsorbent decreases, equilibrium continues to drive the adsorption process although under much lower driving force, since the adsorbent is becoming saturated. The experiment is concluded when the inlet and outlet temperatures are equal, suggesting that the adsorbent is completely saturated and equilibrium has been reached.

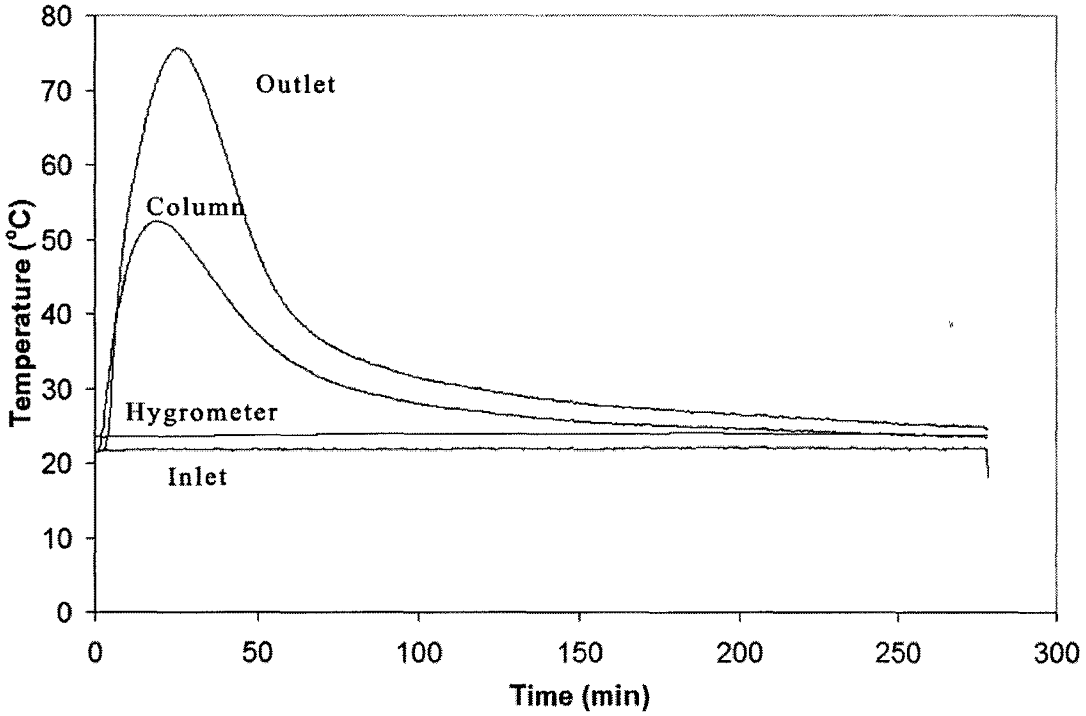


Figure 2.2: Typical adsorption run temperatures as a function of time at different places in the experimental set-up for AA13X as the adsorbent at 24 l/min flow-rate after regeneration at 250°C for 100% relative humidity at the inlet. Outlet = T3, Column = T2, Inlet = T1, Hygrometer = Hygrometer temperature probe

Figure 2.3 shows a typical breakthrough curve for an adsorption run of outlet humidity as a function of time, compared to the inlet humidity. Using the humidity measurements from the hygrometer, it is possible to tell when adsorption is taking place and when the adsorbent was saturated. As determined in our earlier studies [2.3], the maximum energy density can be reached when operating at 100% relative humidity; as a result, all the experiments were performed at 100% RH. The adsorption takes place at the beginning drying the air completely and the outlet humidity gradually increases as the adsorbent becomes saturated until the humidity value at the outlet reaches the same value as the inlet.

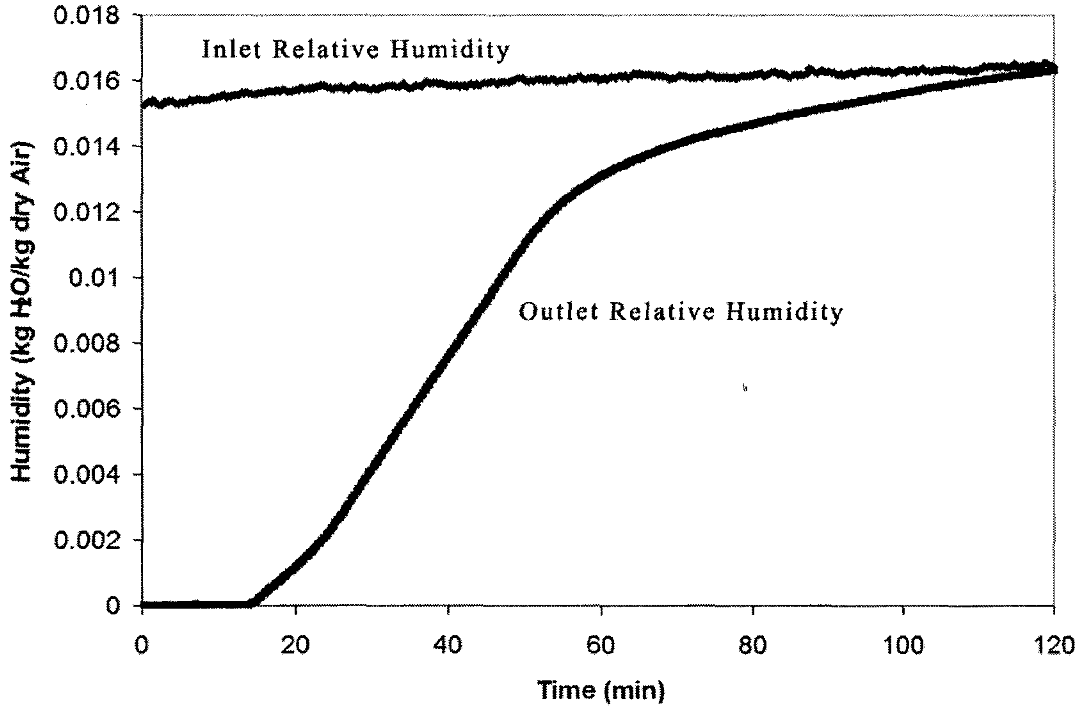


Figure 2.3: Typical adsorption run relative humidity at outlet and inlet of column as a function of time for AA13X adsorbent with 24 l/min flow-rate after regeneration at 250°C

Figure 2.4 and Figure 2.5 show the temperatures measured in the system and the outlet humidity for a typical regeneration run as a function of time respectively. As can be seen from Figure 2.4, the inlet air temperature is 250°C when it is introduced into the column. As the column is exposed to the heat, temperature increases and the saturated adsorbent releases the adsorbed water. Within the first 20 minutes, there is a small plateau where the temperature stays below 50°C during which the input energy into the system is not being used to heat up the system but to desorb the water. This step corresponds to the highest column outlet humidity values in Figure 2.5. Once the bulk of the water has been desorbed, the temperature in the column increases and the outlet humidity gradually reaches 0%. It is important to note that during the entire regeneration, the hygrometer temperature remains constant around 25°C due to the cooling coil since this temperature is required to have a reliable and consistent reading throughout the different runs. Another important thing to note about the regeneration experiments is their duration. In most of the literature, regenerations run overnight for at least 8 hours in order to get a complete regeneration. This system can regenerate the majority of the sample within an hour and completely regenerate the system within 2 to 3 hours. The reason for this discrepancy is that in most experiments the adsorbent is regenerated in ovens where the correct temperature is obtained, but there is no significant driving force to remove the water from the adsorbent. The system in this study uses hot dry air blown through the column to regenerate which not only supplies the heat but also supplies the purge with a constant concentration gradient to drive the water out of the adsorbent.

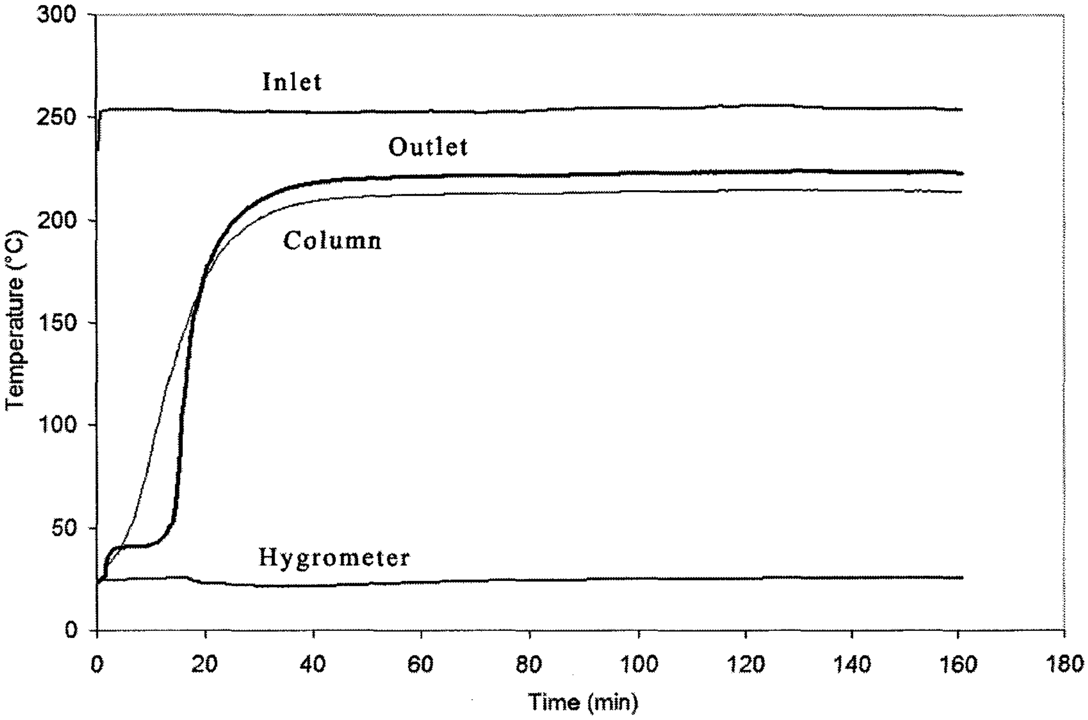


Figure 2.4: Typical regeneration run temperatures as a function of time at different locations in the experimental setup for AA13X adsorbent at 24 l/min flow rate with 0 % RH at the inlet.

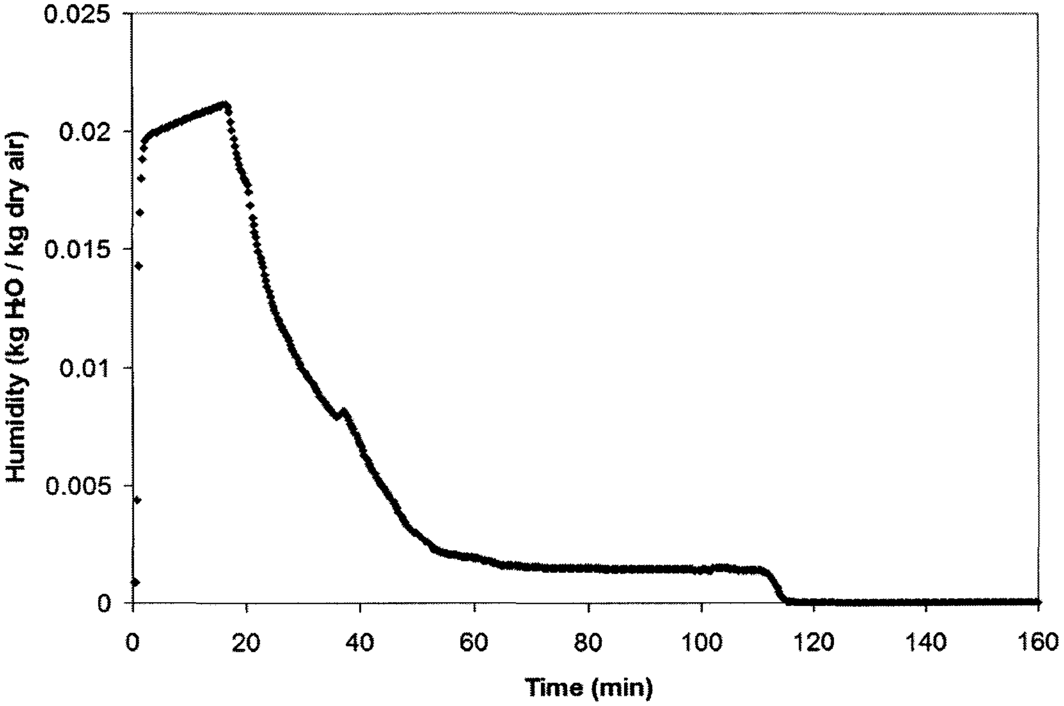


Figure 2.5: Typical regeneration run results showing relative humidity at the outlet of the column as a function of time for AA13X adsorbent at 24 l/min flow-rate with 0 % RH at the inlet.

A statistical analysis to determine the error and standard deviation of the system was performed. The average energy density of AA13X after a complete regeneration at 250°C is 197 ± 7 kWh/m^3. This statistical information is considered to be representative of the standard deviation of the system and has been used as the basis for comparison in other sections in order to determine if a statistically significant change is caused by a parameter. The complete procedure and analysis can be found in Appendix 1.

Cycling experiments were performed on the adsorbent through the series of experiments to determine the effect of re-using (doing adsorption and regeneration runs) on the same adsorbent. In total, over 50 adsorption cycles were performed on a single sample of adsorbent without any loss in performance that could be distinguished from the typical experimental variation as can be observed in Figure 2.6. Not all experiments are included because several parameters were varied during some of these experiments and only the ones with identical conditions can be compared. This is similar to the results obtained in the literature for lower cycling numbers. This confirms that it is possible to completely regenerate the adsorbent after it has been saturated and that it would be possible to recharge the adsorbent over many cycles without losing any performance.

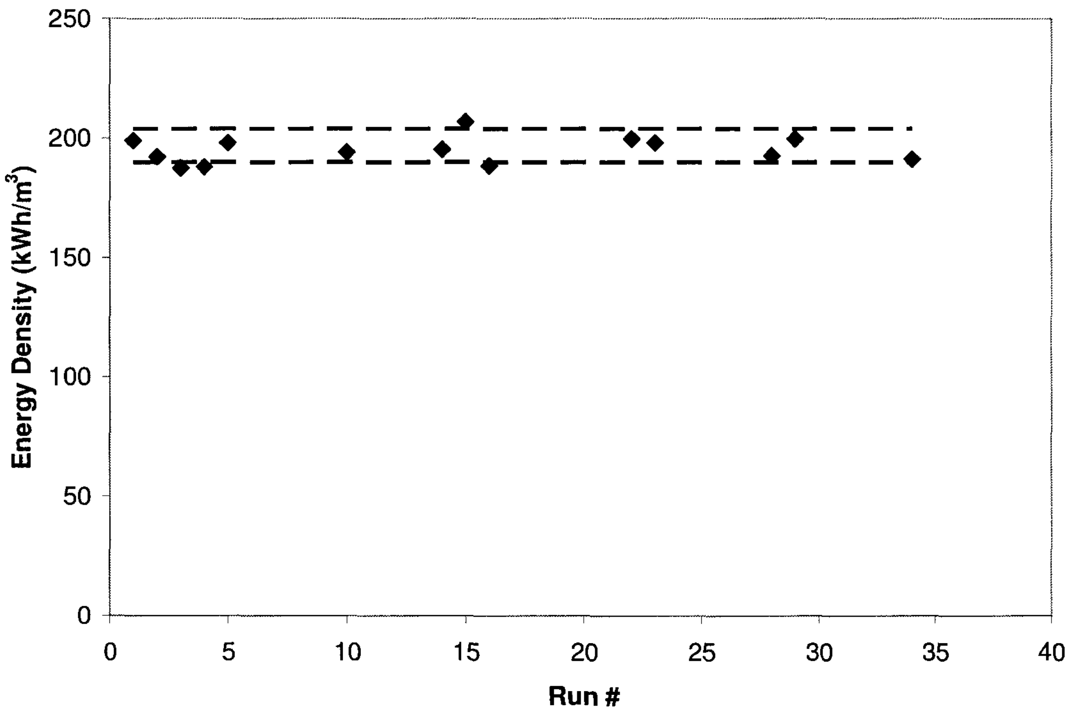


Figure 2.6: Cycling experiments for AA13X adsorbent with 24 l/min flow-rate and 100% RH after regeneration at 250°C. Dashed lines represent standard deviation around mean.

Experiments were also performed to investigate the effect of the adsorption flow rate on the overall energy density of the adsorbent. It can be clearly seen in Figure 2.7 that in a properly insulated column, the energy density is not affected by the flow rate and remains constant around 200 kWh/m^3.

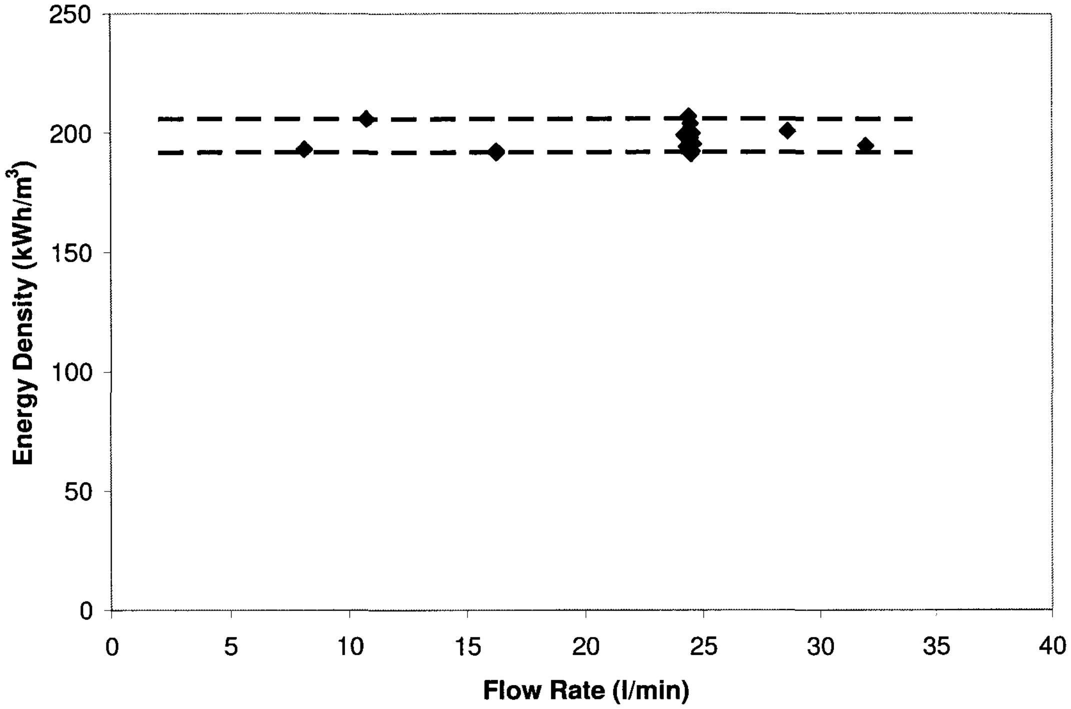
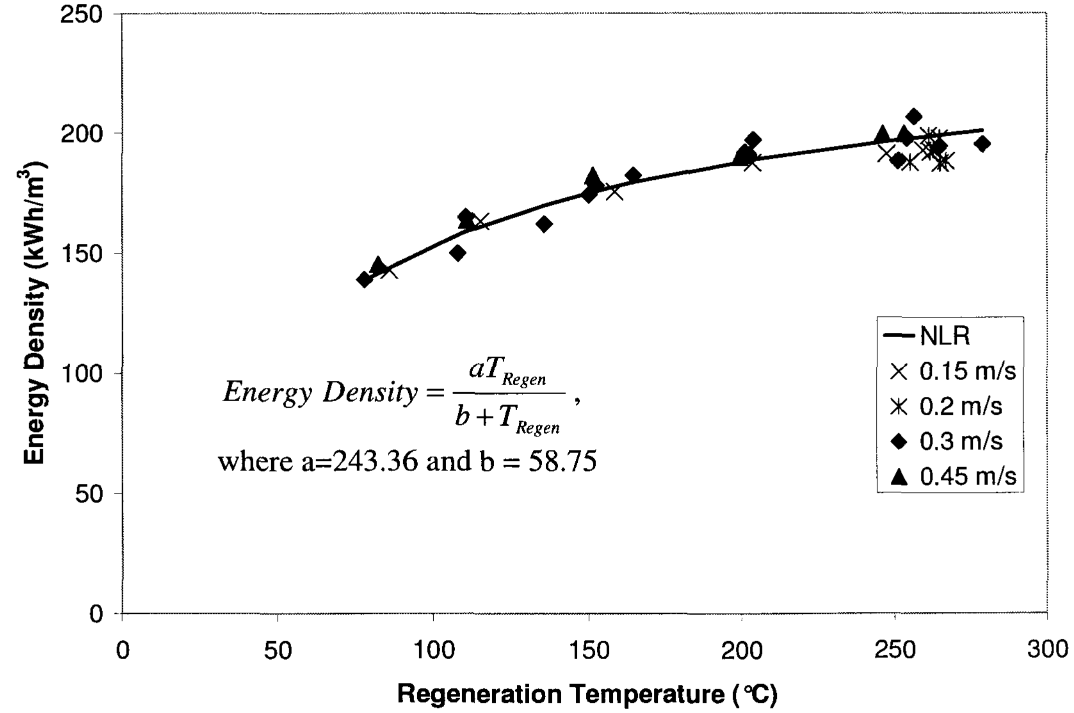


Figure 2.7: Effect of desorption flow rate on energy density for AA13X adsorbent with 100% RH after regeneration at 250°C. Dashed lines represent standard deviation around mean.

After the study of the adsorption parameters, the regeneration parameters were studied in more detailed. The effects of regeneration temperature and regeneration flow rate on the energy density are displayed in Figure 2.8. It can clearly be seen that the regeneration temperature has a non linear relationship (shown in this figure as NLR) with the energy density which reaches a plateau around 250°C for the regeneration temperature. This type of trend is to be expected since the bulk of the water in the macro pores of the adsorbent will be easily removed at lower temperatures and the water molecules in the micro pores will require higher temperature and more energy to be removed. A similar trend can be seen in Figure 2.9 which displays the amount of water removed from the adsorbent as a function of the regeneration temperature. The similarity in the trends for these two figures is to be expected since the adsorption of water is responsible for releasing the energy. The higher the amount of water released during the regeneration, the higher will be the water adsorbed during the next adsorption cycle, increasing the heat effects during adsorption, which will increase the energy density of the system.

Both Figure 2.8 and Figure 2.9 include the effect of regeneration flow rate on the energy density/water removed. Flow rates of 8 litres/min, 10 l/min, 16 l/min and 24 l/min were used which correspond to superficial velocities of 0.15 m/s, 0.2 m/s, 0.3 m/s and 0.45 m/s which are similar to what is found in the literature [2.20]. As can be seen in the graphs, the regeneration flow rate had no effect on the energy density or the water removed during regeneration since each flow rate data point in these figures is within the standard deviation of the non linear regression curve.



$$Energy\ Density = \frac{aT_{Regen}}{b + T_{Regen}},$$

where a=243.36 and b = 58.75

Figure 2.8: Energy density for AA13X adsorbent as a function of the regeneration temperature at different superficial velocities in the column. NLR stands for Non-linear regression curve to show the trend.

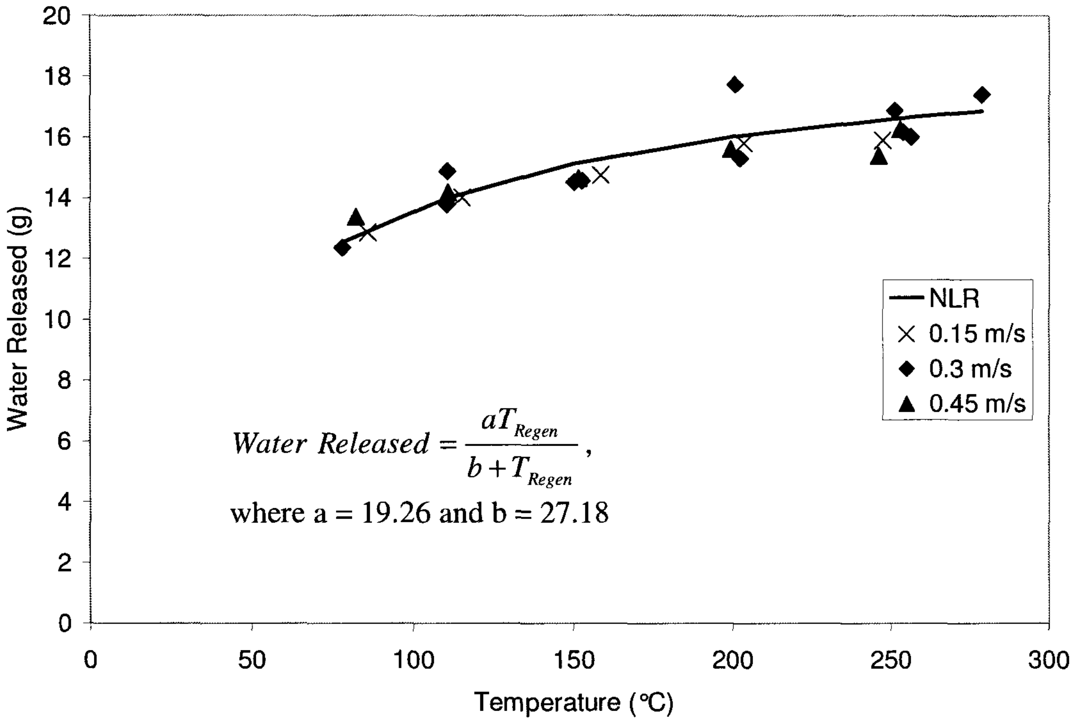


Figure 2.9: Water released during regeneration of AA13X as a function of regeneration temperature for different superficial velocities in the column. NLR stands for Non-linear regression curve to show the trend.

These trends were analyzed in order to produce a non linear model using the equation: EnergyDensity = a*$T_{regeneration}$ / b+$T_{regeneration}$. This model is being suggested as a tool for adsorbent energy density characterization. The concept is that this model could be applied to any adsorbent if the “a” and “b” constant were determined. Therefore, extensive characterization experiments would not be necessary to determine the energy density of an adsorbent as a function of regeneration temperature if the “a” and “b” parameters could be determined from typical adsorbent qualities, such as BET surface area, heat of adsorption and pore size.

This model was tested by performing regeneration experiments at various regeneration temperatures for another adsorbent: natural clinoptilolite from Ash Meadows. The results are shown in Figure 2.10 and compared to the data obtained for AA13X under the same conditions. Regenerations were performed at the same temperatures and a similar non linear trend can be seen. The heat of adsorption of clinoptilolite is significantly lower than that of the AA13X adsorbent which explains the difference in the energy densities at each temperature, but the trend still stands.

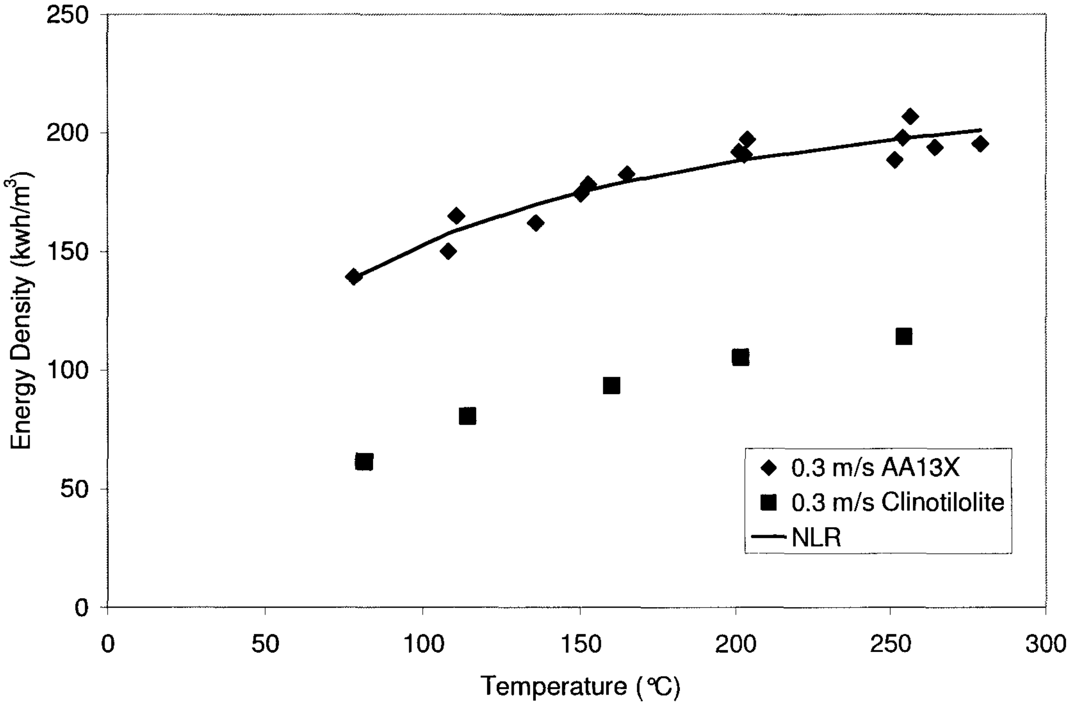


Figure 2.10: Energy density of AA13X and Clinoptilolite with 100% relative humidity after regeneration as a function of regeneration temperature. NLR stands for Non-linear regression curve to show the trend.

The air being used for the regeneration experiments was instrument quality air that contains no detectable amount of humidity. Since the concentration gradient produced from this dry air can also cause a strong driving force for regeneration of saturated adsorbent, it was necessary to verify the affect of regenerating the adsorbent with ambient humidity air. Regeneration experiments were performed on the adsorbent using air with 50% relative humidity at 25°C. The results are show in Figure 2.11.

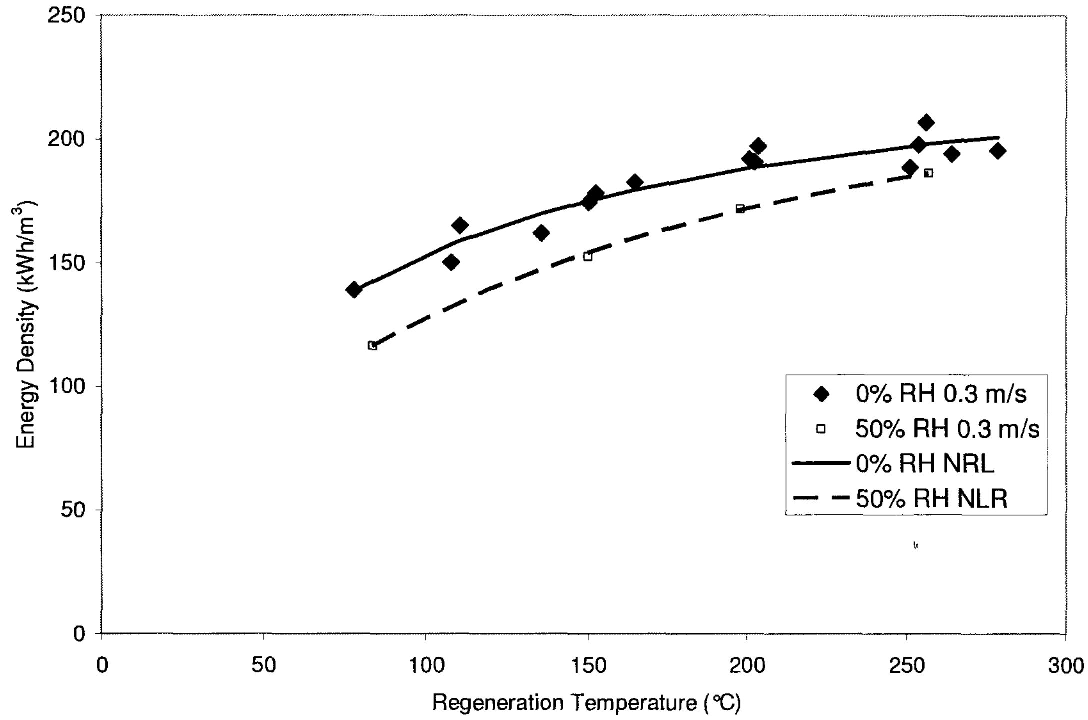


Figure 2.11: Energy density of AA13X after regeneration with 0% RH air and 50% RH air as a function of the regeneration temperature. NLR stands for Non-linear regression curve to show the trend.

Although a non linear trend can be seen in the 50% RH regeneration, the shape and location of the curve is slightly different from the 0% humidity regeneration on which the NLR is based. The discrepancy between the different humidity curves is fairly low at high regeneration temperatures and gets larger and larger as regeneration temperature decreases. At temperatures above atmospheric water evaporation, even if there is already 50% ambient relative humidity present, equilibrium favours water going from the adsorbed phase to the vapour phase, desorbing the water and regenerating the adsorbent. However, the humidity that is already present in the air will prevent complete regeneration in order to maintain equilibrium. Since adsorption capacity for water is higher at lower temperatures, the partial pressure of water is much smaller meaning that humidity already present in the air limits the amount of water that can be removed from the adsorbent in order to maintain equilibrium. This results in less complete regeneration and a lower energy density performance. Therefore, although it is possible to regenerate the adsorbent using humid air, the maximum regeneration requires air with negligible amounts of humidity.

The efficiency of the energy storage was also investigated in this study. Both the energy released during the adsorption and the energy absorbed by the adsorbent during the regeneration are calculated using an energy balance using data from the inlet and outlet conditions. The complete analysis is included in Appendix 5. The first three data series in the legend for Figure 2.12 show the amount of energy used (absorbed from the heating system) during regeneration as a function of the regeneration temperature for different superficial velocities. As regeneration temperature increases, heat absorbed from the heating system increases. The last three data series in this figure show the amount of energy released during the adsorption of water, following the regeneration at various temperatures. The middle data series show the theoretical amount of energy required to evaporate the water released from each regeneration run at various regeneration temperatures using heat of evaporation values. The values were obtained by multiplying the amount of water released by the theoretical heat of evaporation value obtained from the literature [2.18]. The resulting trends obtained are both linear increasing trends. The flow rate employed for regeneration has no effect on the amount of energy required during the regeneration and regeneration at a given temperature always requires the same amount of energy. The difference between the energy absorbed during regeneration and the energy released during adsorption can be attributed to heat loss to the environment and the energy required to heat the stainless steel column and the adsorbent itself while supplying heat for the regeneration. The amount of energy released at each temperature is very similar to the energy required to evaporate water at various regeneration temperatures. This is to be expected as the heat of adsorption is equal to heat of evaporation plus heat of binding.

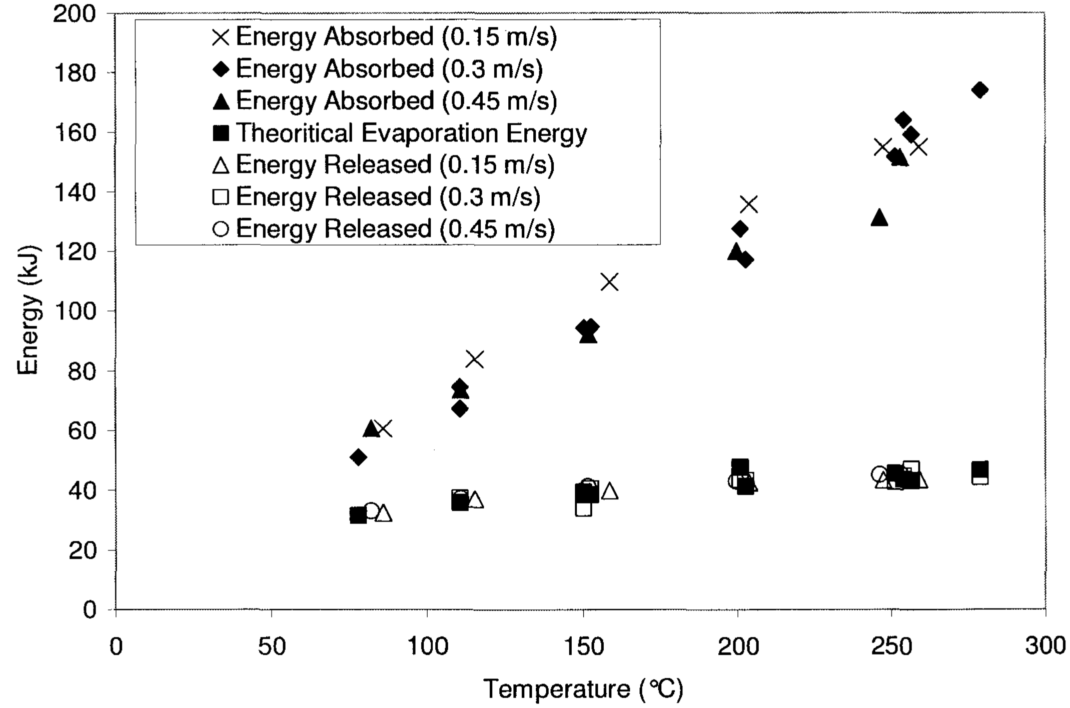


Figure 2.12: Comparison of energy absorbed from the heating system during regeneration and energy released during adsorption for AA13X as the adsorbent as a function of regeneration temperature for different flow-rates.

The thermal storage efficiency is defined by:

$$\eta = \mathrm{EnergyReleased}_{(\mathrm{adsorption})}/\mathrm{EnergyAbsorbed}_{(\mathrm{desorption})}$$

It is calculated by dividing the amount of useful energy released during an adsorption run by the amount of energy used during the regeneration. Figure 2.13 shows this calculated efficiency plotted against the regeneration temperature. The graph shows a linear trend with efficiency decreasing as regeneration temperature increases for all flow-rates studied. At lower regeneration temperatures, the efficiency is around 50% and steadily decreases with increasing temperature until around 30% at 250°C. This is due to the inherent higher heat loss to the environment for higher regeneration temperatures. Once again, the regeneration flow rate during these experiments had little to no affect on the storage efficiency.

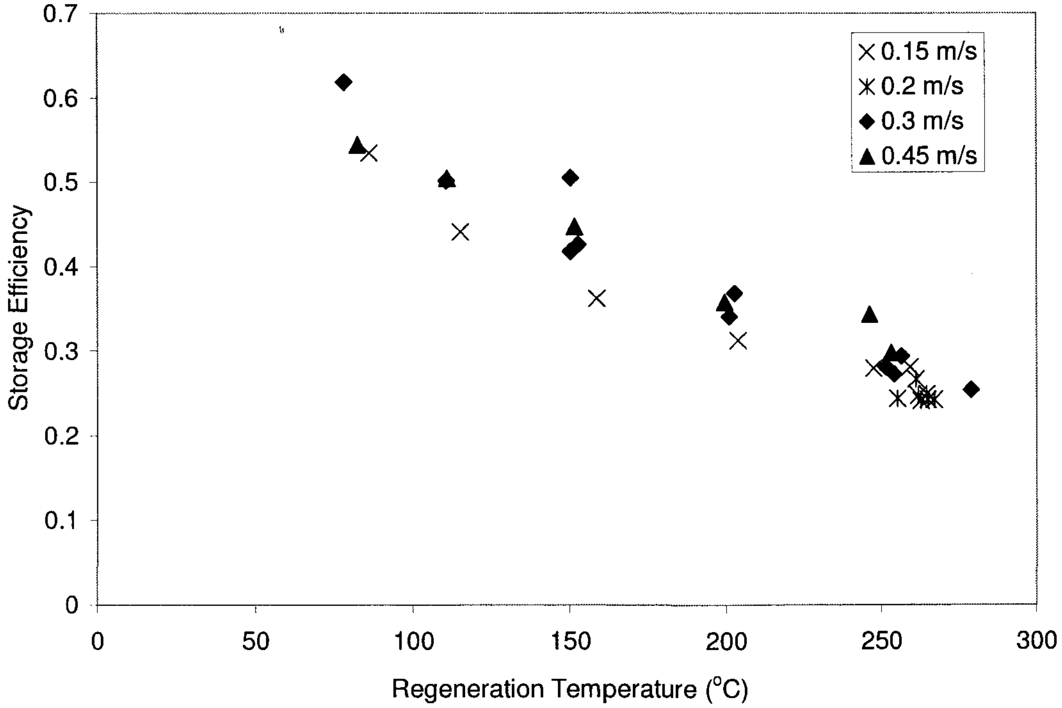


Figure 2.13: Thermal storage efficiency for AA13X adsorbent using 100% RH as a function of the regeneration temperature at different flow rates.

2.4 Conclusions

Thermal energy storage in adsorbent beds has been demonstrated in this study. It has been shown that flow rate has a negligible effect on regeneration and adsorption. Cycling experiments were performed which demonstrated that re-using or cycling adsorbent up to 50 runs has no effect at all on the energy density and that the adsorbent will not loose performance when re-used many times. Regeneration and performance as a function of regeneration temperature has been characterized for two adsorbents which both suggest that similar non linear models that could potentially be applied to other adsorbent systems to determine their energy density or performance depending on regeneration temperature without having to perform extensive experiments. The effect of humidity during regeneration was investigated and its affect on regeneration results has been quantified. Finally, the efficiency of the thermal storage system was calculated as a function of regeneration temperature.

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2.6 Abbreviations

AA13X: Hybrid adsorbent which is a mix of Activated Alumina and Zeolite 13X

L/D: Length over Diameter ratio

NLR: Non Linear Regression

OD: Outside diameter

RH: Relative Humidity

SCFM: Standard Cubic Feet per Minute

SS: Stainless Steel

TES: thermal Energy Storage

η: Thermal Efficiency

3 Improvements to Adsorption Thermal Energy Storage Systems using Hydrated Salt Impregnation

Chapter 3 was written as a paper which has not been submitted at the time this thesis was submitted.

Abstract

Salt hydration reactions and adsorption processes are promising candidates for long term thermal energy storage applications. It is hypothesized that by combining inorganic salts with adsorbents, higher energy storage densities can be achieved. A zeolite 13X and activated alumina hybrid adsorbent was identified for having a high energy density with water as the adsorbate. Magnesium sulphate, magnesium chloride and lithium chloride salts were chosen for their reaction properties and their hygroscopic nature. The salts were impregnated into the hybrid adsorbent by submerging the adsorbent in a 37.5% wt salt solution at 60-80°C for 24 hours and then drying it in an oven at 250°C. 15 adsorption and desorption cycles were then performed on these impregnated adsorbents to determine their stability, performance and cycling behaviour. On average the modified adsorbents had an increase of 25% in their energy density compared with the unmodified adsorbent. The highest performance recorded was 309 kWh/m^3 which represents a 50% increase over the unmodified adsorbent performance.

3.1 Introduction: Inorganic salts

Adsorption thermal energy storage systems have been around since the late 1970s [3.4]. During the oil crisis, they seemed to be a promising technology that could lessen dependency on foreign energy sources. Several adsorbent and adsorbate pairs were identified as having potential and some tests were performed. The experiments were fruitful and several patents were filed on these types of systems [3.19][3.20][3.12]. But as the oil crisis faded and fuel prices returned to normal levels, interest in adsorption thermal energy storage systems diminished before it could be fully developed. Towards the 1990s, as the effects of global warming and the fear of depleting oil reserves set in and new movement of renewable technologies was born. The concept of adsorption thermal energy storage was dug up and several institutes and associations began exploring various combinations of adsorbents and adsorbates. This time, a lot of emphasis was put on the screening of adsorbents and determining the best working pair. Various combinations of adsorbent and adsorbate pairs were tested and typically Zeolite 13X or Silica gel with water as the adsorbate were chosen based on toxicity, availability and performance [3.7]. The next goal was to build prototype systems to store and extract the energy from the adsorbent beds and attempt to reach high energy densities. Although these systems worked, their energy densities per volume seldom surpassed 150 kWh/m^3 which made them too bulky for commercialization [3.11][3.15][3.13][3.16][3.6]. Towards the beginning of the 2000s, minds turned to thermo-chemical material and exothermic reactions as means of thermal energy storage, like ammonia synthesis [3.21], boron [3.1] and inorganic oxides [3.5]. A set back that quickly appeared was that most reactions with pertinent energy densities require high temperatures in the range of 400-600°C to occur which could be useful for high temperature steam production, but not useful for lower temperature heating applications. Hydration reactions of inorganic salts seemed to be suitable for lower temperature applications. Using calorimeters and small powder samples, several salts were identified as having energy densities between 400-1500 kWh/m^3 which dwarfed zeolite energy density values [3.2][3.14]. Systems to exploit the energy density of salts are currently being developed with some difficulty. Salts require high surface area for the hydration reaction and are usually in powder form causing large pressure drops in reactors. Additionally, some hydrates only release their maximum energy in special pressure conditions.

In order to maximize the energy storage potential of salt hydration, it is necessary to allow ample surface area for the reaction, perhaps by supporting the salts on a mesoporous material or lattice. However, any lattice that is not participating in the reaction is wasted space and makes the system more voluminous than it needs to be. This problem could be avoided by combining salts and adsorbents, two materials which released heat when combined with water, by impregnation which would combine the benefits of both materials. It is hypothesized that an impregnated salt would have the conditions and surface area required to react to its fullest and the adsorbent would provide an easily manipulated lattice that will participate in the energy storage process, producing a more compact thermal storage system. This paper explores this theory.

Impregnation is a simple method of modifying porous materials which typically involve the addition of an inorganic salt to the crystal lattice of the adsorbent. The goal is to improve certain material properties by incorporating a salt that possesses desirable properties. The details may vary, but most methods follow similar procedures [3.24] [3.16] [3.10] [3.2] [3.27] [3.17]. An aqueous salt solution of varying concentration and temperature is produced. The adsorbent to be impregnated is immersed in the solution for a varying amount of time to allow the dissolved salt to penetrate into the porous material. Finally, the adsorbent is removed from the solution and dried by evaporation or vacuum distillation during which the salt crystals bind with the adsorbent. Some methods also include a calcination step to ensure that the salt is fixed to the adsorbent structure.

3.2 Materials and Method

The adsorbent to be impregnated was chosen after an extensive screening procedure in our earlier studies [3.8]. The properties of the adsorbent are listed in Table 3.1. The chosen salts are

- **Magnesium sulphate** as it is identified in literature as the most promising salt with a reported energy density of up to 777 kwh/m^3[3.26][3.28][3.25][3.29][3.14],
- **Magnesium chloride** because it is similar to magnesium sulphate and has 6 degrees of hydration (magnesium chloride hexahydrate) [3.2][3.9],
- **Lithium chloride** because of its hygroscopic nature [3.23].

Table 3.1: Adsorbent information

Adsorbent	Supplier	Product Name	Mesh size
AA /13X	Rio Tinto Alcan, Brockville, Ontario, Canada	ACTIGUARD 650PCAP	8x14

These salts were impregnated into the adsorbent using the following procedure. 1.2 kg of salt was dissolved into 2 litres of distilled water to produce a 37.5 % wt solution which is approximately the highest possible concentration due to solubility of the salts [3.22]. The solution was heated to 80°C. 130 g of AA13X adsorbent was added to the solution and left to soak at 80°C for 24 hours with continuous stirring. The adsorbent was then drained and placed in an oven at 250°C to dry for 4 hours. Details for the resulting adsorbents are listed in Table 3.2.

Table 3.2: Initial and final data for salt impregnated hybrid adsorbents

Salt	Initial adsorbent weight (g)	Final adsorbent weight (g)	Salt % wt
$MgSO_4$	136.1	160.3	15.1
$MgCl_2$	128.5	149.1	13.81
LiCl	129.7	150.5	13.8

Once dried, adsorption and regeneration runs were performed to determine the energy density using the same procedure and equipment as outlined in the previous paper [3.7]. 7 cm of 1.5" stainless steel tubing with a volume of 62.5 ml was filled with the adsorbent. Adsorption experiments exposed the adsorbent to 100% relative humidity air at ambient temperature with a flow rate of 24 l/min. Desorption experiment exposed the adsorbent to 0% relative humidity air at 250°C with a flow rate of 24 l/min.

3.3 Results and Discussion

Each modified adsorbent was tested for 15 consecutive cycles where each cycle includes one adsorption and one desorption. The salts in their anhydrous state are solid powders with a high melting point. When water is added to form hydrates, each level of hydration has different properties and the melting point of the salt is modified. The salts are so hygroscopic that if left out in ambient humidity, they will pull humidity from the air and form a liquid. Magnesium chloride and lithium chloride are often used as desiccants for clothing or used in dehumidification devices for residential use. These properties were of concern as the impregnated adsorbents were being exposed to humidity as part of the reaction process and the system is not designed to accommodate liquids. As a result, the first run for each modified adsorbent was unquantifiable because of the accumulation of liquid in the system as was expected due to salt hydrate properties. The freshly modified adsorbent pellets had an excess coating of salt on their surface which condensed the humidity in the air and resulted in liquid creeping through the system. Following the first experiment, the system was taken apart and cleaned and the subsequent experiments did not produce liquid and were quantifiable. The results for the magnesium sulphate and the magnesium chloride impregnation are displayed in Figure 3.1.

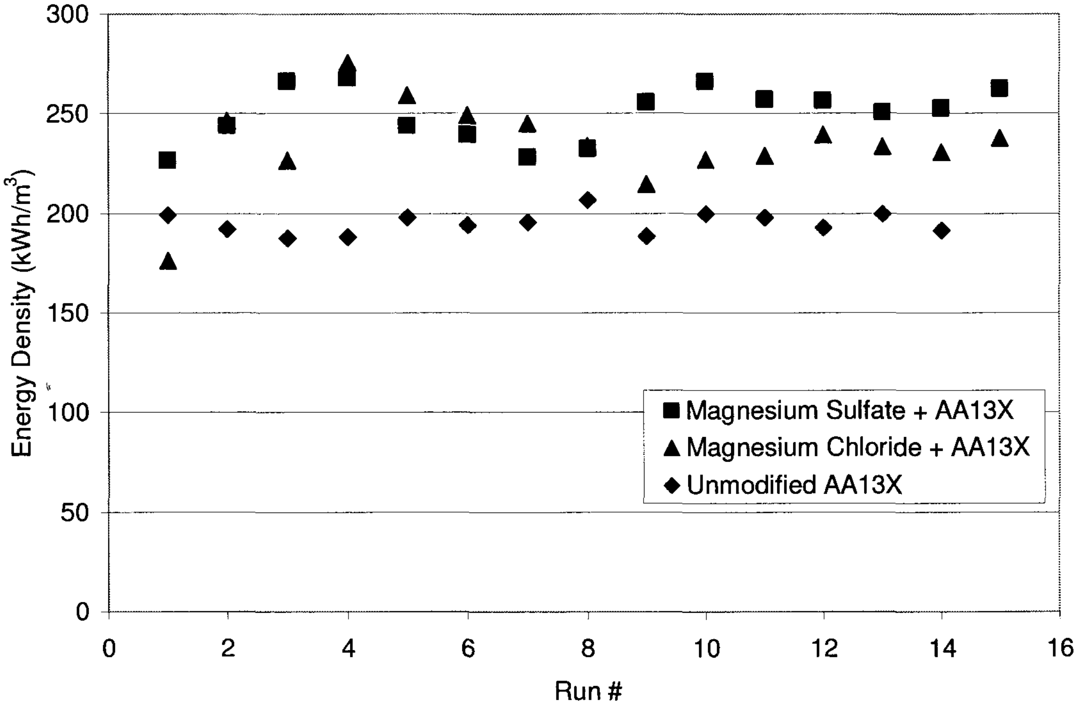

Figure 3.1: Energy Density for the modified adsorbents as a function of the number of cycles compared to the unmodified adsorbent.

Although the energy density values varied a great deal, the modified adsorbents showed a definite improvement over the unmodified adsorbent. Both modified adsorbents reached maximum energy densities above 260 kWh/m^3, with $MgSO_4$ averaging 250 kWh/m^3 and $MgCl_2$ averaging 235 kWh/m^3. This represents a 17-25 % increase from the plain adsorbent. The amount of water adsorbed during the experiments also increased by approximately the same percentage. The variations in the results were also different than the original adsorbent. Not only were the standard deviation values doubled for magnesium sulphate and tripled for magnesium chloride, the variation seem to follow an oscillation trend which eventually tails off to a more constant value. This type of oscillation had been seen with unmodified adsorbent but never with the same amplitude. A common cause had to be identified.

The reason for the oscillation was hypothesized to be swelling in the adsorbent. When the column is loaded, it is packed with as much adsorbent as possible in order to get the highest energy density available for the system. However, this does not leave much space for the possible swelling of the adsorbent due to adsorbed water. As a result, adsorbents and salts swell during the adsorption process which increases the pressure drop through the column and creates fissures and grinding of the adsorbent. Fissures are good because they increase the surface area of the adsorbent and thus can result in higher energy densities because new reaction sites are exposed. This is thought to produce the peaks in the oscillations. However, excessive fissures and grinding causes erosion of the particles which then leave the column as fine dust. This is thought to produce the lows in the oscillations. The continuous fissuring and erosion of the particles could produce the oscillating trend seen in Figure 3.1.

Accounting for swelling of the particles and leaving empty space in the column could prevent the erosion of the particles. This theory was tested using the adsorbent impregnated with LiCl salts. The 62 ml column was filled with 51 ml of adsorbent and then 15 cycles of experiments were performed. The results of those runs are displayed in Figure 3.2.

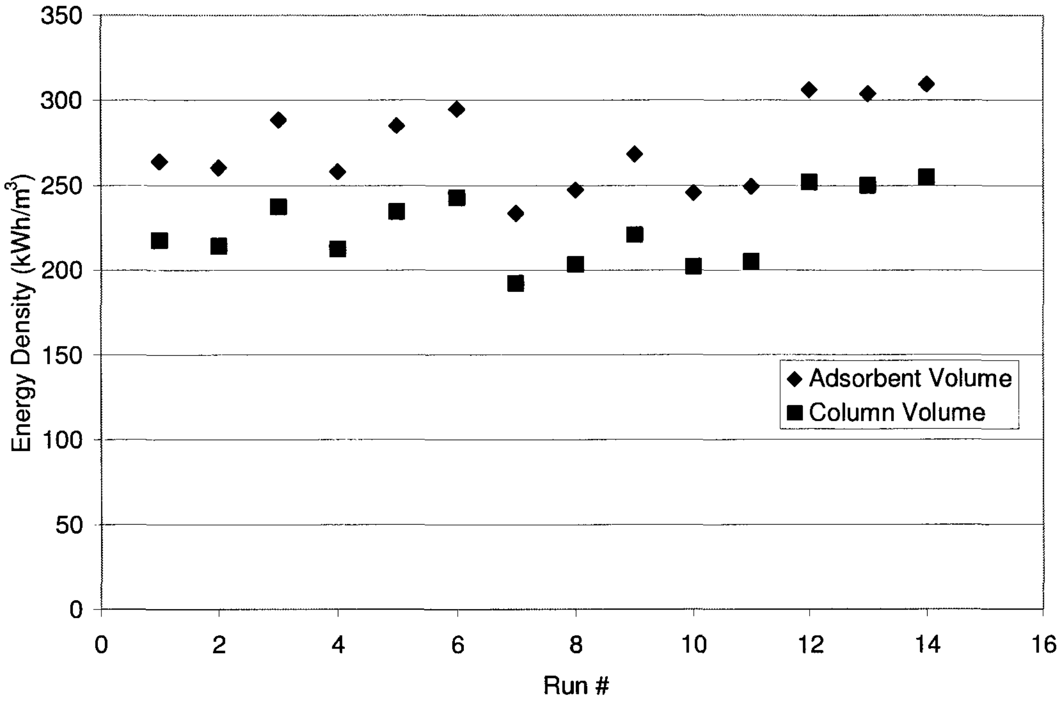

Figure 3.2: Energy density of adsorbent modified with lithium chloride calculated using Adsorbent Volume and Column Volume. Adsorbent volume is the volume of adsorbent place in the column (51ml). Column volume is the total volume of the column (62ml)

Lithium chloride had the best performance of all the salt impregnations. It reached a maximum performance above 300 kWh/m^3 and averaged 272 kWh/m^3. The oscillation trend does not seem to be present although the large variation between runs is still evident with a standard deviation that is double that of the unmodified adsorbent. This performance is based on the adsorbent volume which was 51 ml. However, if we consider the column volume and include the void space required to produce these results, the performance drops to 250 kWh/m^3, which is similar to the performance of the other salts. Although we were not able to quantify the swelling of the adsorbent and thus the actual working volume required, it is clear that more then 51 ml would be necessary. Therefore, a more representative energy density would be between the two data series in Figure 3.2.

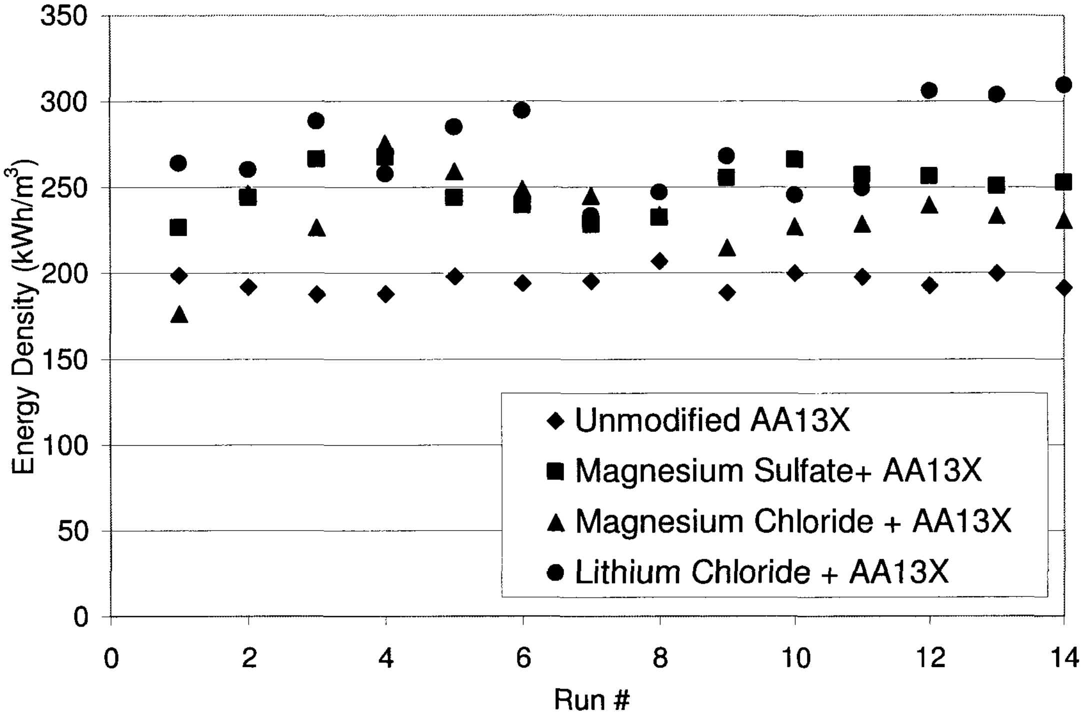

Figure 3.3; Comparison of energy density for all modified adsorbents and unmodified adsorbent

Figure 3.3 displays the results of all three modified adsorbents impregnated with salts and a set of data for unmodified adsorbent for comparison. Lithium chloride has the highest performance, followed by magnesium sulphate and magnesium chloride. Since the variations in values were so significant, a confidence interval was calculated using Equation E3.1 [3.18] for the three modified adsorbents. A confidence interval is a range of potential values to represent a value when there is a large amount of variations in the experimental reading. First, the average and standard deviation of the data set are calculated. Then, a range of potential other average values is calculated based on the standard deviation and an expectable level of certainty. This range, or confidence interval, has a certain probability of containing the real average which is more representative of the data set. The results for this statistical analysis are displayed in Table 3.3.

Table 3.3: Statistical analysis of energy density for modified adsorbents

	Energy Density Mean (kWh/m^3)	Standard Deviation (kWh/m^3)	Degrees of Freedom	Lower Limit (99%) (kWh/m^3)	Upper Limit (99%) (kWh/m^3)
$MgSO_4$	249.99	13.74	13	238.92	261.04
$MgCl_2$	234.93	21.97	13	217.24	252.61
LiCl	272.40	25.23	13	252.09	292.70

$$Limits = \overline{X} \pm t_{\alpha/2,n-1} \frac{Standard\ Deviation}{\sqrt{number\ of\ runs}},\ where\ t_{\alpha/2,n-1} = 3.012 \qquad \textbf{[E3. 1]}$$

The lithium chloride impregnated adsorbent has the highest performance without a doubt, but it also has the highest standard deviation. A 99% confidence interval was calculated for all the modified adsorbents which give ranges of potential values of the means based on their deviations. When intervals overlap, there is no significant difference between two means. All three confidence intervals calculated overlap around 252 kWh/m^3, which means that statistically the three means are potentially the same. Although a great improvement has been made on the adsorbent, it suggests that the results are related by a common denominator. AA13X has a standard pore size. The same concentration of salt was used for each impregnation. If the pores of AA13X had a maximum loading capacity for salts, it might be impossible to improve the adsorbent beyond its loading. Since there is a maximum amount of salt that can fit into the pores of the base adsorbent, there is also a maximum amount of water that can react with the salt as well as get adsorbed. Perhaps the salts were only achieving partial hydration. If each pore can only accommodate one salt molecule and a few molecules of water, each salt will improve the adsorbent by approximately the same value, regardless of how many hydration levels it has because of the limitation of the existing pores of the base adsorbent. The diameter of a zeolite 13X pore is 8.5 Å and a molecule of water is 2.7 Å while activated alumina has a wide pore size distribution [3.3]. Although the presence of a salt will increase driving force and add heat of reaction, the number of water molecules that can penetrate may be capped regardless of salt properties, especially if the salt is already taking up some of the pore volume. To exploit the salts' maximum potential, it may be more advantageous to use a mesoporous material that has larger pores, allowing more water to achieve complete hydration. However, materials with larger pores rarely adsorbed water very well which means the adsorbent would act like a support and not participate in increasing the energy density.

3.4 Conclusions

Magnesium sulphate, magnesium chloride and lithium chloride have been successfully impregnated into the base AA13X adsorbent. The salt impregnations have significantly improved the energy density of the base adsorbent but resulted in lots of variations in the performance. Lithium chloride reached the highest performance, at 300 kWh/m^3, of the three salt impregnations, however, the standard deviation for the performance is so large, that all salts can be considered to have approximately the same performance, somewhere in the 252 kWh/m^3 range. This suggests that the adsorbent pore size may be the limiting factor in exploiting the salt potential. Regardless, the impregnated salt adsorbents represent a 25 % improvement on energy density over the base adsorbent.

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4 Energy Discussions

In the previous chapters, discussion focused on the adsorbent and its maximum performance in relatively ideal conditions. In order to properly implement thermal energy storage, it is necessary to examine the energy flows through the system to ensure that there is a net gain. This chapter aims to discuss in depth the intricacies related to energy flows in the system such as heat loss, efficiency, limitations of the system and useful energy.

4.1 Liquid vs. Gaseous Adsorption

Since the total energy released is associated to the number of molecules that can be delivered to the binding sites, people often suggest using liquid water instead of gaseous vapours as the molecular density per volume is much higher. Although using liquids delivers molecules faster and energy is released more rapidly, the total energy released from this type of process is always considerably smaller than the amount released when adsorbing vapours. When water is adsorbed to the solid, it goes from the liquid or gaseous phase to the adsorbed phase. Since energy is released when the liquid water is adsorbed, the adsorbed phase necessarily has lower enthalpy than liquid water. Therefore, when either the liquid or gaseous water is adsorbed, it must release the difference in enthalpy between its starting state and its adsorbed state. Water vapour has much more energy to release than liquid water in order to reach the adsorbed phase because it has as much enthalpy as liquid water plus the enthalpy of evaporation.

Therefore, adsorbing one molecule of gaseous water will release considerably more energy than adsorbing one molecule of liquid water.

4.2 Heat Loss

The adsorbent column used in these experiments differs from the column used for *Dicaire and Tezel 2007* [6] as well as *Dicaire 2006* [5]. The previous column was slim and long with an L/D ratio above 8. It was determined that this column was not representative of the eventual system geometry and would not provide useful data for scaling. A new column, with an L/D ratio of 1.8, was built which is more characteristic of storage tanks. This new geometry was also chosen in order to minimize heat loss by having a thicker shorter column with less surface area per volume for heat loss than a long slender column. The new column also has a larger volume which allows for more comprehensive experiments towards an actual storage system. The entrance effects of using the new geometry were investigated and determined to have no effect on the energy density of the system.

The column was well insulated with two inches of fibreglass insulation as there is great concern for heat loss during these experiments. With these modifications to the original setup, it is believed that heat loss has been minimized for the following reasons:

- Some of the heat that is released during the adsorption will be used to heat up the adsorbent itself, the stainless steel column and the insulation. However, once the adsorption stops producing heat, these materials now have stored sensible heat that will be extracted by the flow of air through the column. Therefore, most of the energy that goes into heating these materials during the adsorption is not lost, only extracted as sensible heat later.

- Ambient air is being fed to the column at a considerably high flow rate. There is a great temperature driving force between this ambient air and the temperature inside the column. Although some of the heat can dissipate to the environment through the adsorbent, the column and the insulation, having a flow of ambient temperature air which we want to heat as an available heat sink within the column is a simpler heat transfer path. All the energy transferred to the air is measured in the energy balance between the input and output.

4.3 Complete System Energy Balance

In order to properly evaluate the system's usefulness, it is necessary to extend the control volume beyond the column, where the energy is absorbed and released, to include the entire system. This allows us to see all of the energy inputs/outputs and helps obtain more realistic values for efficiency. Table 4.1 lists the energy inputs and outputs for the system during the adsorption and desorption runs. All values were calculated using experimental data and performing energy balances which are outlined in Appendix 6. In Chapter 2, the energy absorbed during the regeneration runs ("Heating") and energy released during the adsorption runs ("Total Energy Released") were calculated and compared to determine the "Thermal Storage Efficiency". The two sources of energy overlooked in Chapter 2's efficiency analysis were the energy required to push air through the system ("Energy Flow") and the energy required to either humidify or dehumidify the air ("Energy Humidification/ Dehumidification"). The energy used for the flow rate was calculated using Bernoulli's equation, Equation [1] , which simplifies to Equation [2**Error! Reference source not found.**] for this system. The energy required for humidification/dehumidification was calculated based on evaporation energy of water at ambient temperature and conditions (feed air conditions based on seasonal norms: Adsorption = 0% relative humidity, Desorption = 50% relative humidity) for the amount of water adsorbed/desorbed during an experiments (roughly 16 g of water).

$$\frac{Q - W_s}{\dot{m}} = \left(\frac{v_2^2}{2} + gy_2 + u_2 + \frac{P_2}{\rho_2}\right) - \left(\frac{v_1^2}{2} + gy_1 + u_1 + \frac{P_1}{\rho_1}\right) \qquad [1]$$

$$W_s = \dot{m}\left(\frac{P_2 - P_1}{\rho}\right) \qquad [2]$$

The analysis was done on unmodified AA13X for a regeneration temperature of 250°C with a flow of 24 l/min and 8 l/min for adsorption and desorption. In the current calculation, an adsorption run requires enough energy to evaporate the full 16 grams of water which will be adsorbed and regeneration runs require enough energy to dehumidify the flow of air during the entire run.

Table 4.1: Energy and Power Inputs and Outputs for Adsorption and Desorption runs

	24 l/min	8 l/min
Adsorption		
Energy Flow (J)	72,000.00	15,000.00
Energy Humidification(J)	39,203.20	39,203.20
Total Adsorption Energy (J)	111,203.20	54,203.20
Desorption		
Energy Flow (J)	54,000.00	15,000.00
Heating (J)	160,000.00	160,000.00
Energy Dehumidification (J)	61,544.07	56,985.25
Total Desorption Energy (J)	275,544.07	231,985.25
Total Energy Released (J)	45,000.00	45,000.00

Four different measures of efficiency were determined for the system and are compared in Table 4.2. Overall efficiency is calculated using Equation [3]. It includes all energy inputs and compares them to the energy released.

$$Overall\ Efficiency = \frac{Energy\ Released}{Adsorption\ Energy + Desorption\ Energy} \qquad [3]$$

Renewable efficiency is calculated using Equation [4]. It represents the efficiency when the heating energy for the regeneration is removed from the calculation. This is done because regeneration comes from solar energy that would other wise be wasted and could be interpreted as impertinent for efficiency calculations.

$$Renewable\ Efficiency = \frac{Energy\ Released}{EFlow_{Adsorp} + EHumidification_{Adsorp} + EFlow_{Desorp} + EDehumidification_{Desorp}} \qquad [4]$$

Mechanical efficiency is calculated using Equation [5]. It compares the amount of energy required for the air feed for adsorption and desorption. This information is useful as it denotes the minimum electrical energy requirements to make the system function.

$$Mechanical\ Efficiency = \frac{Energy\ Released}{EFlow_{Adsorp} + EFlow_{Desorp}} \qquad [5]$$

Evaporation Efficiency is calculated using Equation [6]. It compares the amount of energy required to evaporate the water needed for the adsorption with the amount of energy released from the adsorption. This is the minimum amount of energy required to release the stored energy.

$$Evaporation\ Efficiency = \frac{Energy\ Released}{EHumidification_{adsorption}} \qquad [6]$$

Table 4.2: Efficiencies for entire system for 24 l/min and 8 l/min

	24 l/min	8 l/min
Overall Efficiency	0.12	0.16
Renewable Efficiency	0.17	0.27
Mechanical Efficiency	0.36	1.50
Evaporation Energy Efficiency	1.15	1.15

Both flow rates have similar efficiencies which is expected as the similar amounts of water, heat and air are used regardless of the flow rate. Some scenarios in Table 4.2 portray diminishing rates of energy return; this means that for each unit of energy put in, less then one unit of energy comes out. This is not problematic when considering Overall and Renewable Efficiency because the system is making use of otherwise wasted thermal energy collected during the summer.

Having a mechanical efficiency that is less than one is not economically feasible because it compares the amount of electricity put in compared to the amount of thermal energy released. Since electric resistance heaters are >90% efficient, it is never worth using 1 kWh of electricity to obtain only 0.5 kWh of heat from a heat storage system. This is the main difference between the flow rates. High flow rates create much higher pressure drops which require more power to overcome, reducing their efficiency and making the system unviable. At lower flow rates, less power is used to release the same amount of energy, bringing the efficiency above 150%. The high pressure drops generated at high flow rates are mainly due to the design of the current system. The system is composed of 6 m of ¼ inch SS tubing with valves, elbows and other fittings. As demonstrated in Appendix 6, it is the tubes and fittings that are responsible for the majority of the 18 000 Pa pressure drop at 24 l/min. Using lower flow rates reduces the pressure drop through the system to about 5 000 Pa. Another way to overcome this hurdle would be to use larger tubing, which even at high flow rates, would give a small pressure drop (1 000 Pa). Simply using ½ inch tubing instead of ¼ inch would have increased the efficiency above 200%. Therefore, this efficiency should be used as a guideline to ensure that the design of the thermal energy storage system does not draw more electricity than it produces heat.

Since overall efficiency and renewable efficiency are too broad and mechanical efficiency is a guideline that is very system design dependent, evaporative efficiency is the most representative of an adsorption thermal energy storage system. It speaks to the viability of all adsorption TES. Adsorption requires water vapours to unlock the stored energy and it is important to note its efficiency. Although water vapours may be readily available depending on conditions, if it is not it will have to be produced and a diminishing energy return rate would decrease the viability of such a system. Secondly, evaporation efficiency displays the efficiency of the system to convert low grade useless energy, such as enthalpy of humidity at 20°C, and convert it to higher grade useful energy, like dry air at 70°C. An evaporation efficiency above 1.0 ensures that adsorption TES is a valid storage mechanism.

4.4 Limitations of Adsorption Thermal Energy Storage Systems

Many have argued that calling the adsorption process a method of thermal energy storage is misleading. The issue is the semantics describing the macroscopic and microscopic scale. When adsorption takes place, it can be said that the energy is being released from the material, where it was stored. However, it has been clearly identified in the current and previous chapters that on the microscopic scale, the energy released during the adsorption process originates from the difference in enthalpy of the water between the gaseous and adsorbed phase. The water vapour enters the adsorbent with a high level of energy and releases an amount of energy equal to its heat of vaporization when it becomes adsorbed, effectively condensing it. Therefore, the energy did not come from the material, it came from the water. Similarly, when the saturated adsorbent is regenerated, it can be said that the energy is stored within the crystal lattice. However, the regeneration energy inputted to the system is used to dry the adsorbent, giving the water the energy required to vaporize and remove itself from the crystal lattice, leaving space for the adsorption process to be repeated. Therefore, the energy inputted into the system is not stored because it was used to vaporize the water and has left the system. The only thing stored in the adsorbent is the potential to released thermal energy.

The concept can be compared to a hydroelectric dam. The dam is often referred to as "electricity storage". However, the dam does not store electricity; it holds potential energy because of the height difference of its highest and lowest point. Similarly, the dry adsorbent holds the potential to release the enthalpy between the water's gaseous state and adsorbed state.

It is true that the energy is released form the water but it is only spontaneously released due to the adsorbent's nature and would not occur without it. Although technically inaccurate, the term thermal energy storage is used to represent the conceptual application of the system and this terminology has been the standard in the thermal energy storage field for over 30 years. However, when investigating the feasibility and practical applications of such systems, it is very important to understand the distinction.

The reason the origins of the energy released during the adsorption process is important is to understand the limitations of adsorption thermal energy storage systems. Although a plethora of thermal energy is important to regenerate the system and dry the adsorbent, it is the energy used to evaporate the water that truly limits the system operation and feasibility as that is the energy that is released. As identified in Chapter 2 and previously in this chapter, the amount of energy released is purely related to the vaporization energy of the water and is regardless of the amount of energy used to regenerate the adsorbent. Therefore, it is important to take into account where the vaporization energy to produce water vapour comes from, especially if the thermal energy storage system is to be used in winter when there are no readily available sources of humidity. If the humidity source is located within the building that is to be heated (i.e. ambient humidity in the building or humidity source within the building envelope), the overall heating has no net gains as there is no increase. An amount of energy is taken from the building to evaporate water, the water releases that same amount of energy taken from the building during adsorption process and then that energy is used to heat the building that originally gave the vaporization energy. No heating has occurred, the energy was simply moved around regardless of the temperatures reached during regeneration.

There are two possibilities to ensure a net energy gain. The first is to have an external energy source for vaporization. This could be a low grade district heating system or perhaps a geothermal well. It is important to note in this scenario, that the heat source must be of a low grade (close to ambient) because if it is of a higher quality, it should be used as the heating source instead of the long term thermal storage system. The second option is to use an energy source within the building envelop and develop an adsorbent that has a higher energy density then what is possible from releasing vaporization energy. An example of this are the salt impregnations in Chapter 3 that released more energy then what was needed to evaporate the water used in the system because the reaction taking place is more exothermic then adsorption. This limitation suggests that long term thermal energy storage systems either require thermo-chemical reactions to be feasible or that pure adsorption systems can only function when combined with an external energy source for evaporation.

4.5 Useful Energy Density

Energy density has been based on the amount of energy that was released from the adsorbent, regardless of the temperature at which it took place. The air fed to the system is at ambient temperature when it enters; it heats up to 70°C at the beginning of the experiment and gradually returns to ambient. Experiments were run until equilibrium was reached which was defined as a 3°C difference between the inlet and the outlet temperatures. Small cut off values are typical in thermal energy storage research as experiments are usually performed in differential calorimeters which will measure 0.1°C temperature differences. Using this evaluation method calculates the total amount of energy stored in the adsorbent. However, in practical applications there are specific operating temperatures that must be met and which can greatly affect the amount of useful energy stored or the useful energy density. Heat exchangers are designed with a minimum temperature difference of 10°C because anything below would require a large surface area for the exchange to take place. Air to air heat exchangers or heat recovery wheels for space heating are capable of operating with temperature differences as small at 3°C. However, if a system is required to heat outdoor air from 0°C to ambient, it will require a 20°C temperature difference. Water coming into a home from municipal pipes is typically fed at 10-15°C year round to prevent the pipes from freezing. If this water is to be heated for domestic hot water purposes, it will require a 30-40°C temperature difference to reach the necessary operating temperature.

As can be seen in the previous examples, the total energy stored in the adsorption thermal energy storage system is not necessarily representative of the useful energy, depending on the applications. It seems necessary to calculate useful energy densities for the system depending on the temperature difference required for the application. Figure 4.1 was created by calculating the amount of energy available using various minimum temperature difference between the inlet and the outlet. The energy density values were calculated using the procedure outlined in Appendix 5. However, only data with the minimum temperature difference was considered for each scenario. The scenario with a temperature difference of 3°C did not change as that was the typical cut off for experiments and represents the total energy available. However, when that minimum temperature difference is raised to 10°C, 20°C, 30°C or 40°C, the amount of useful energy available from the system is much smaller.

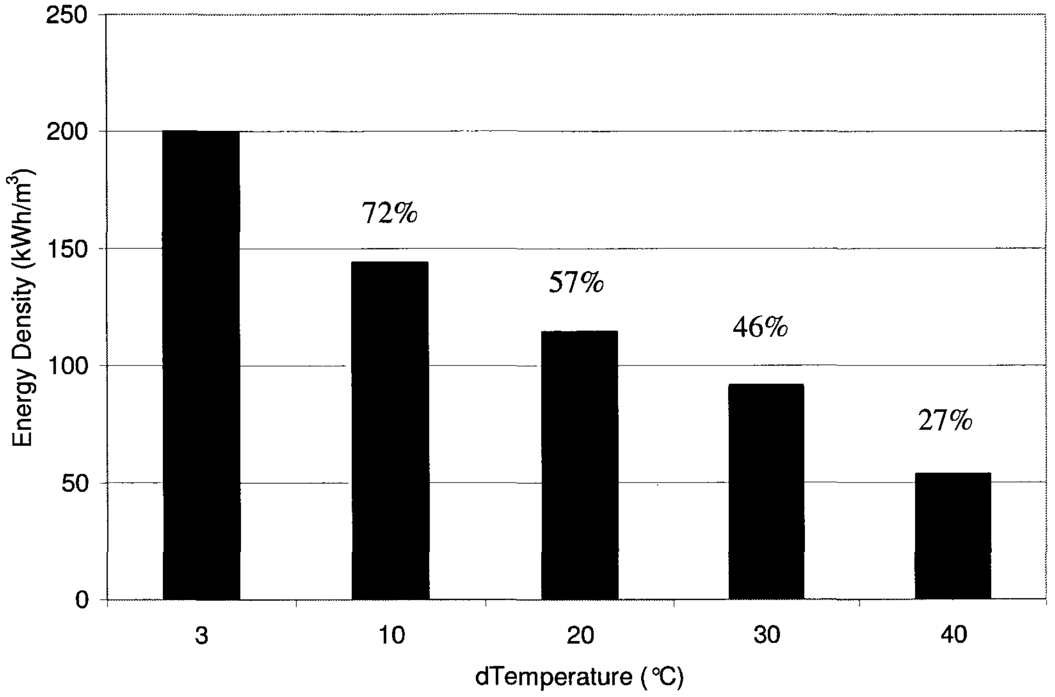

Figure 4.1: Useful energy density of AA13X depending on temperature difference required at the outlet of the system

Not all 200 kWh/m^3 of stored energy has the same quality and there is obviously much more low quality energy than high quality energy. In order to reach 40°C of temperature difference, you must raise the temperature one degree at a time. Therefore, the energy density decreases considerably when the temperature difference and quality of the heat required is increased. As can be seen in Figure 4.1, only 3/4 of the energy density is useful when a 10 degree difference is required and it drops dramatically to 27% for applications that require +40°C temperature differences. This is to be expected as, in any thermal system, there are always losses due to simply reaching the operational temperature.

4.6 Conclusions

This chapter has demonstrated some very important concerns with respects to energy flows in adsorption thermal energy storage systems. Although not completely discounting the feasibility of the system, the considerations brought forth by the efficiency, the limits of adsorption and the useful energy must be carefully contemplated to make any adsorption thermal energy storage systems feasible.

5 Practical Feasibility and Economic Analysis

As the technical considerations surrounding adsorption thermal energy storage have been discussed, practical applications for the technology will now be investigated. The data and values found in the previous chapters will now be extrapolated into full scale scenarios in order to determine the practical feasibility and the economic analysis. Potential applications for this technology include:

- Seasonal storage for residential, commercial or apartment buildings. This involves installing an on site adsorbent long term storage system and a solar panel system which includes a short term thermal storage system.
- Heat distribution system where excess heat from one place is stored and transported to another location. Ex: Excess heat from an incineration plant stored and brought to a district heating system
- Thermal energy storage for electricity generation

5.1 Residential Seasonal Storage System Scenario

Since the results of commercial, residential and apartment buildings are similar, the discussion will focus on seasonal storage systems for a residential building in Canada followed by the data for an apartment building. In all cases, the system will include solar thermal collectors, a short term solar heating storage unit and a long term thermal storage unit. Together, these three components are able to fulfill all heating requirements, making solar heating available year round.

HOT2000, developed by CanMET Energy Technology Center [2], was used to model typical heating requirements for Canadian homes. This software can build a virtual home and estimate the energy requirements of the home based on live weather data obtained from Canadian weather databases. This software is state of the art and uses R-2000 building codes to estimate energy requirements. An example of a report produced by the program can be found in Appendix 2. Solar collector data was obtained from our industry partner Menova Energy. The collector in question is a PS-35 power spar with purely thermal collectors. A copy of its monthly energy output can be found in Appendix 2. Figure 5.1 compares the monthly energy consumption for a typical Canadian home in Montreal with and without domestic hot water requirements and the output that can be obtained from a PS-35 power spar collector. Monthly energy balances, included in Appendix 2, were performed to see which months had excess energy and which months had an energy deficiency and how much long term thermal energy storage is required.

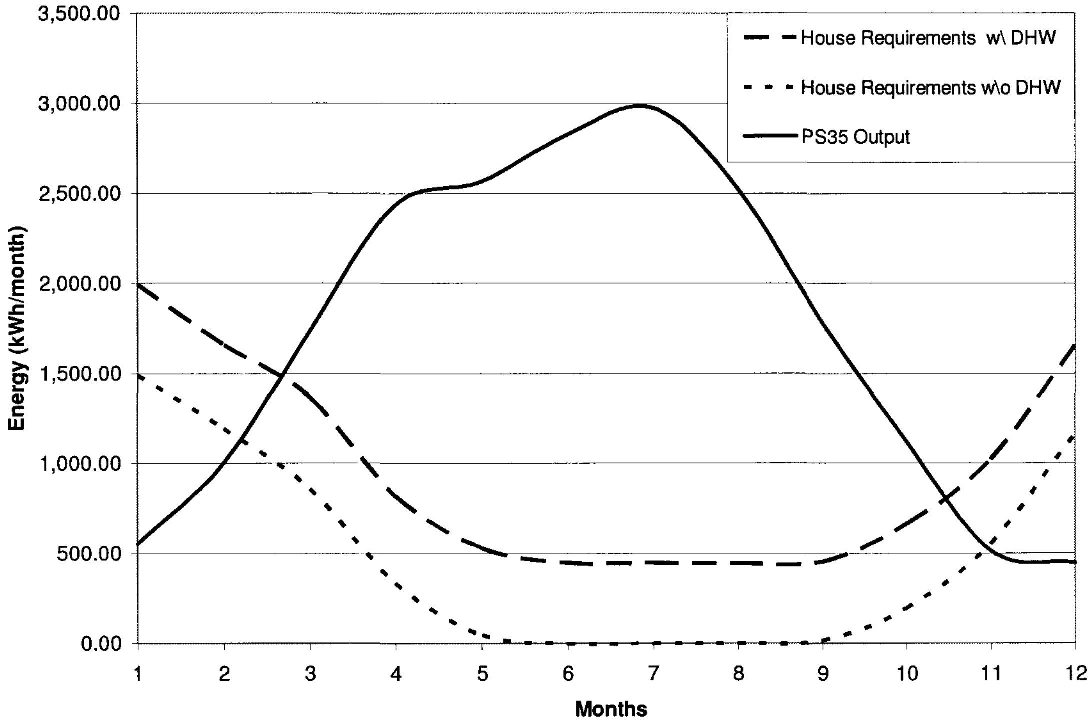

Figure 5.1: Monthly heating requirements for a typical Canadian home in (Montreal, Quèbec, Canada (with and without domestic hot water) and heating output for a solar collector PS-35 by, Menova Energy.

When the PS-35 output is higher then the house requirements, all the heating needs are being met by the thermal collector and there is an excess of heat. When the PS-35 output is below the house requirement, auxiliary heating is needed. As it can be seen in Figure 5.1 and was confirmed during discussions with our industry partners, a thermal collector with short term storage can provide a maximum of 70% of a typical home's heating needs. Other sources in the solar heating industry claim this number is closer to 50% for flat plate solar collectors. Therefore, the home requires a long term storage system to store the excess heat from the summer and use it during the winter to make up the missing 30-50% heating requirements.

Based on the HOT2000 simulations, including space and domestic hot water heating, and the performance of the PS-35, a typical Canadian home would require approximately 4000 kWh of long term storage as calculated in Appendix 2. Even with the lowest recorded storage efficiency of 30% from Chapter 2, there is enough excess heat during the summer to regenerate the long term storage and store enough energy for the winter. Using the average performance of 250 kWh/m^3 for the adsorbent system from Chapter 3, approximately 16 m^3 of adsorbent would be required to store 4000 kWh. It represents a volume of 2.5m x 2.5m x 2.5m dimensions. Although this large volume appears to be a setback, it is much smaller than what would be required by other thermal energy storage systems as illustrated in Figure 5.2. It compares the adsorption thermal energy storage system with the current sensible storage methods being used in the solar heating industry. The before last column represents an adsorption thermal energy storage system filled with modified hybrid adsorbent which has been regenerated with heat from solar collectors with a maximum temperature of 100°C. The resulting performance of the system is 150 kWh/m^3 as seen in Chapter 2. The last column represents a similar adsorption thermal energy storage system that has been regenerated with solar collectors that can achieve 250°C. The resulting performance is 250 kWh/m^3 as seen in Chapter 2. The other four columns represent sensible storage methods discussed in Chapter 1 and there energy densities are listed.

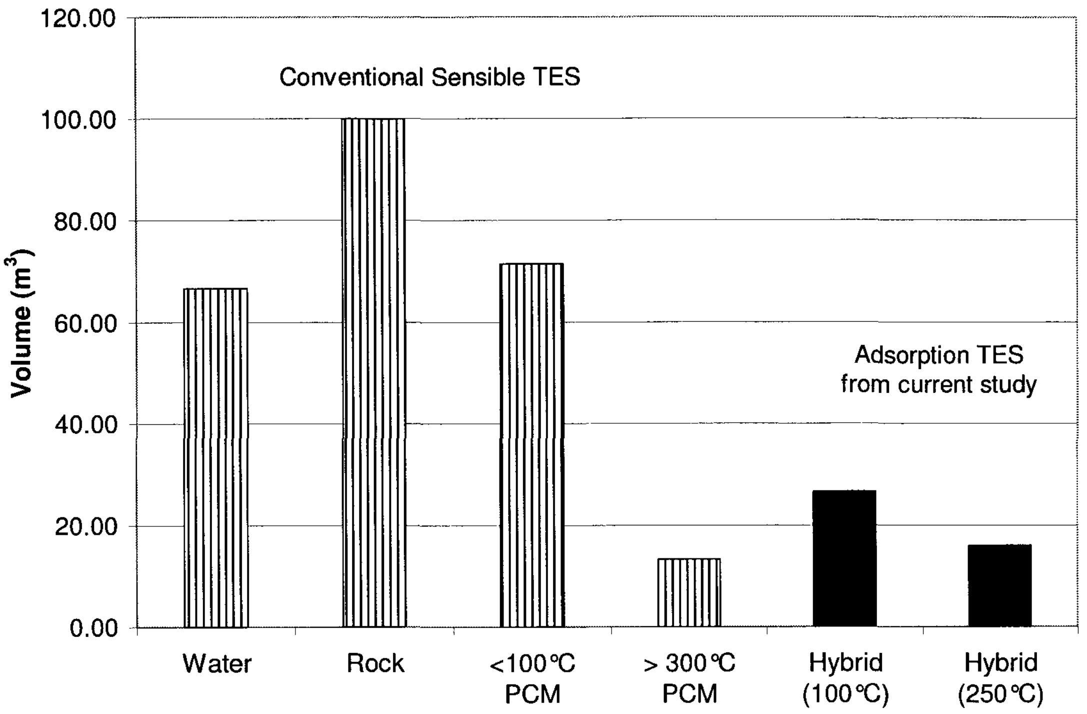

Figure 5.2: Comparison of volume required to store 4000 kWh of thermal energy using various thermal energy storage systems. Water (60 kWh/m^3) [32], Rock (40 kWh/m^3) [32], <100°C PCM (56 kWh/m^3) [1], >300°C PCM (300 kWh/m^3) [11]. Compared with hybrid from current study: Hybrid adsorbent regenerated at 100°C (150 kWh/m^3), Hybrid adsorbent regenerated at 250°C (250 kWh/m^3)

The other sensible thermal energy storage methods all have lower energy densities and therefore would require much larger volume than an adsorption TES from the present study. The only material that could compare would be phase change materials (PCM) with an operating temperature above 300°C but, as discussed previously, these would not be feasible in residential applications. It is also important to note, that even if these sensible heating volumes were feasible, the heat would not be able to last long enough to be utilized during the winter months when it is necessary, rendering the storage useless. Currently, water tanks and concrete are the most wide-spread thermal storage methods in

Canada. The largest state-of-the-art system is found in Alberta where a huge concrete storage system provide only 90% of the space heating needs to a community of 52 homes [7]. If an adsorption TES were used in its place, the storage would required approximately ¼ of the volume.

On the other hand, it is important to note that the long term thermal energy storage is always complemented by a small short term storage system that stores and supplies thermal energy continually. This system is required as it is the hub of energy distribution for the home and it can not be replaced by the long term storage system since there would be no use in storing heat in a long term system when it is required immediately. As a result, we must keep in mind that an extra 1000 gallons of volume (3.75m^3) required for the short term storage must also be added to the overall calculations [16].

Volume is more troublesome when adsorption thermal energy storage is compared to conventional heating by natural gas or electricity. These methods are on demand and require no storage since the fuel is delivered directly to the home, into the baseboard or furnace. The total operating volume of a furnace ranges between of 5-10 m^3 [22] and baseboard heaters are almost negligible. Matching this volume with an adsorption system would require 800 kWh/m^3 of energy density which is a considerable challenge. Most experts in the field agree that an energy density around 500 kWh/m^3, around 8-10 times that of the water tanks currently being used, is required to make long term thermal energy competitive in today's market.

Market research into the price of adsorbents has been performed and is summarized in Table 5.1. The first price was obtained from the distributor, Rio Tinto Alcan, and is their estimate for producing the adsorbent we have been using in bulk [28]. Other price quotes for a similar adsorbent were obtained from other manufacturers around the world for bulk orders of 100 000 tonnes /year. A copy of the communications used to obtain this information is included in Appendix 7.

Table 5.1: Price quotes for producing adsorbent from various adsorbent manufacturers around the world.

Rio Tinto Alcan	8-14 Mesh	-	3 $CDN /kg
Sorbead India	2-4 mm beads	2.40 $US/lbs FOB T.O.	5.29 $ CDN / kg
Zeochem	8-12 mesh	2.05 $Us / lbs FOB, Louisville KY	4.52 $ CDN/kg
UOP	MOLSIV 1/8"	1.86 $US/lbs	4.10 $ CDN / kg
Grace	8-12 Mesh	1.72 $US/lbs	3.79 $ CDN / kg
Grace	Pure zeolite powder	4.10 $US/lbs	9.04 $ CDN / kg

Considering the price that has been provided by our industry partner and the bulk density of the adsorbent which was determined in our laboratory to be 800 kg/m^3, the total price for a 16m^3 adsorbent bed would be around **$38 000**.

Solar collector and solar heating manufacturers would likely be the target market for this type of technology as long term storage would make solar heating available year round which would make their product more reliable and increase their sales. The following scenarios outline market research that was performed with some local solar collector and solar heating manufacturers in order to determine the value of long term storage to their company.

- Menova Energy: The goal is to obtain a heating solution that could be incorporated into their existing product so that the total system would have payback period of 5 years. Based on a natural gas price of 0.05$/kWh and the existing price for their system, the maximum value/cost they would attribute to a long term thermal energy storage system is **$5 000.** [26]
- Quadra Solar: The goal is to provide a reliable solar heating solution. Based on the life cycle analysis for their system (15 years), the projected increases in the conventional heating systems and what the solar market can bare, the maximum value/cost they would attribute to a long term thermal energy storage system is **$10 000**. [27]
- Technology Venture Challenge Business Plan Competition (Appendix 4): The goal is to evaluate the market from the customer and end users point of view. Based on the money saved compared to conventional heating systems and their operation, the government renewable energy incentive programs and the value of year round solar heating, the maximum value/cost for a long term thermal energy storage unit is **$6 500.**

When the market research is compared to the current system scenario, it is clear that the technology is not economically competitive. A more comprehensive study of conventional heating price increases, government incentive programs and area specific market research could be performed, but it is unlikely to bridge the $30,000 gap that exist between the current system and what the solar heating industry can bare.

In order to become economically feasible and compete in the current market either the price of the adsorbent needs to be reduced or the energy density of the adsorbent must be improved. The amount of energy being stored per home can also affect the feasibility as well as the payback period. Under the assumption that the adsorption thermal energy storage system could save a home approx $600 a year over conventional heating by storing and providing 40% of the homes heating needs (see Chapter 1), Figure 5.3, Figure 5.4 and Figure 5.5 illustrate the break even points of various scenarios by varying the price of the adsorbent, the energy density of the adsorbent and the amount of energy that needs to be stored to provide 40% of the homes heating needs in winter.

Figure 5.3, Figure 5.4 and Figure 5.5 show payback periods of 5 years, 10 years and 15 years respectively which represent different suggested payback targets from various companies. Typically, small technology companies with paradigm shifting products require small payback periods of 5 years in order to ensure adoption of their product while larger companies that are more established and don't require instant returns can consider payback periods equal to the life of their product. Typical Canadian homes would require 4000 kWh of storage but other storage sizes from 3000 to 7000 kWh have been included in the legend for different sized homes or for other requirements like district heating purposes. As the values for energy density on the x-axis increase, the system becomes more and more compact and therefore the price per kilogram of material to break even can increase while keeping the same payback period which is why there is an increasing trend in each of these figures. However, if it is possible to decrease the price of the adsorbent by finding better manufacturers or buying large bulk quantities, the energy density or performance of the material could be reduced as it costs less to make. Regardless, if we look at the target energy density of 500 kWh/m^3 with the most optimistic payback period of 15 years, the maximum price of the adsorbent is 1.5$ which is half of the current estimated cost. It is also important to note that these payback periods are just for the adsorbent material and do not factor in the cost of the development, construction and installation of the entire adsorption thermal storage system.

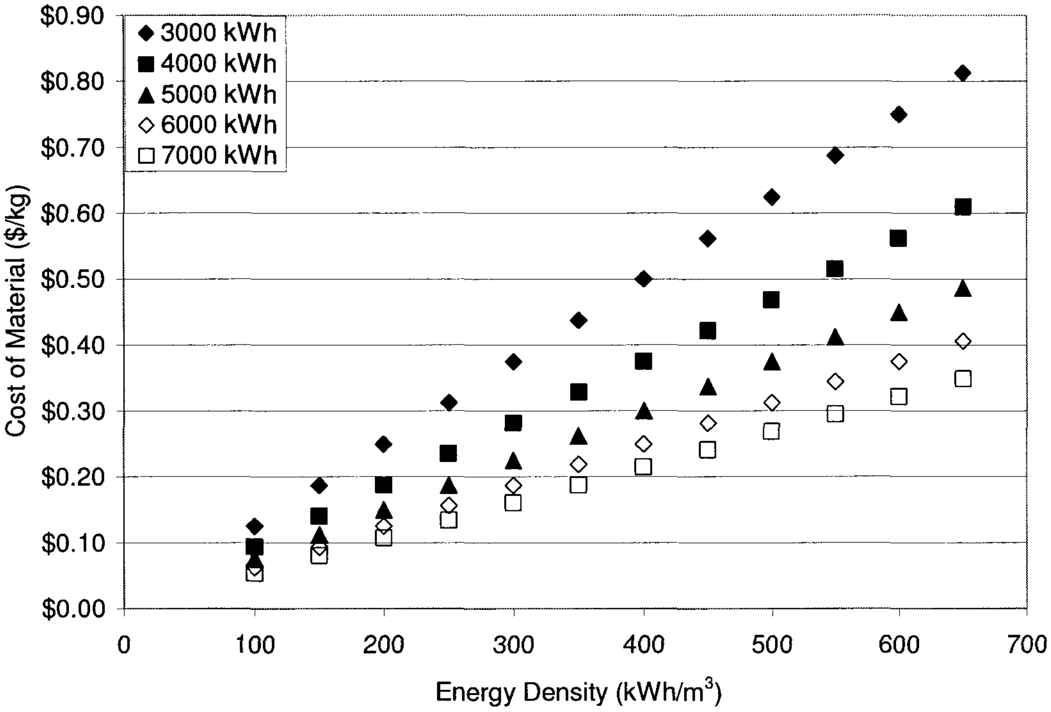

Figure 5.3: Required Energy Density and Material Cost for 5 Year Payback Period (Capital investment of $3,000) for various storage capacities (Storage = 40% of yearly heating requirements, Material 800kg/m^3)

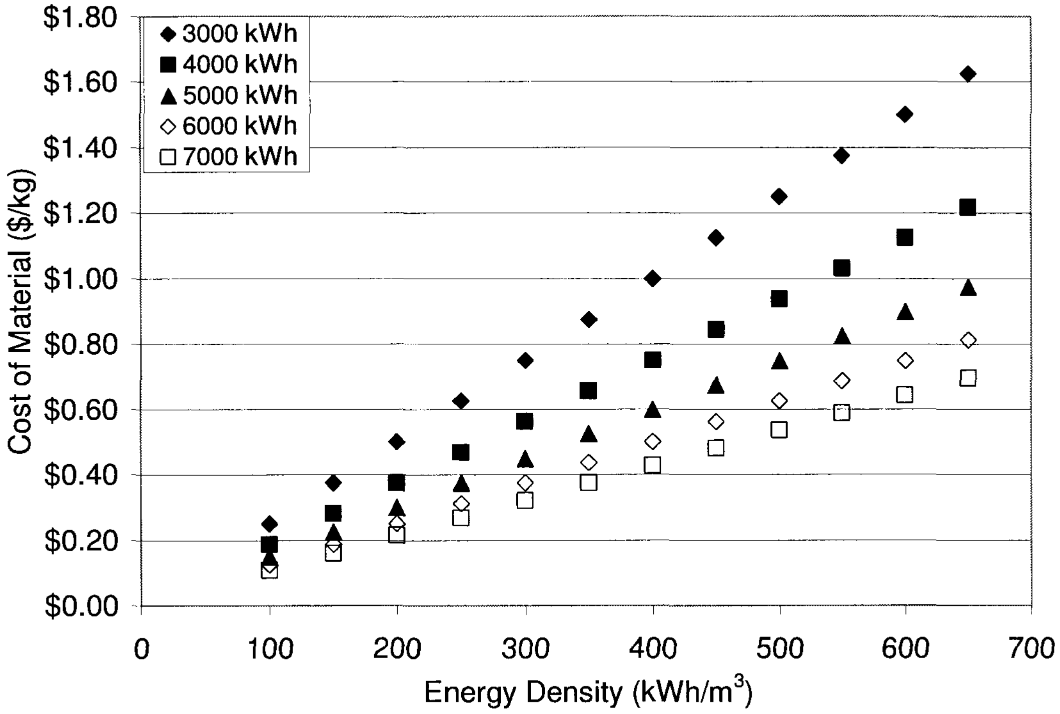

Figure 5.4: Required Energy Density and Material Cost for 10 Year Payback Period (Capital investment of $6,000) for various storage capacities (Storage = 40% of yearly heating requirements, Material 800kg/m^3)

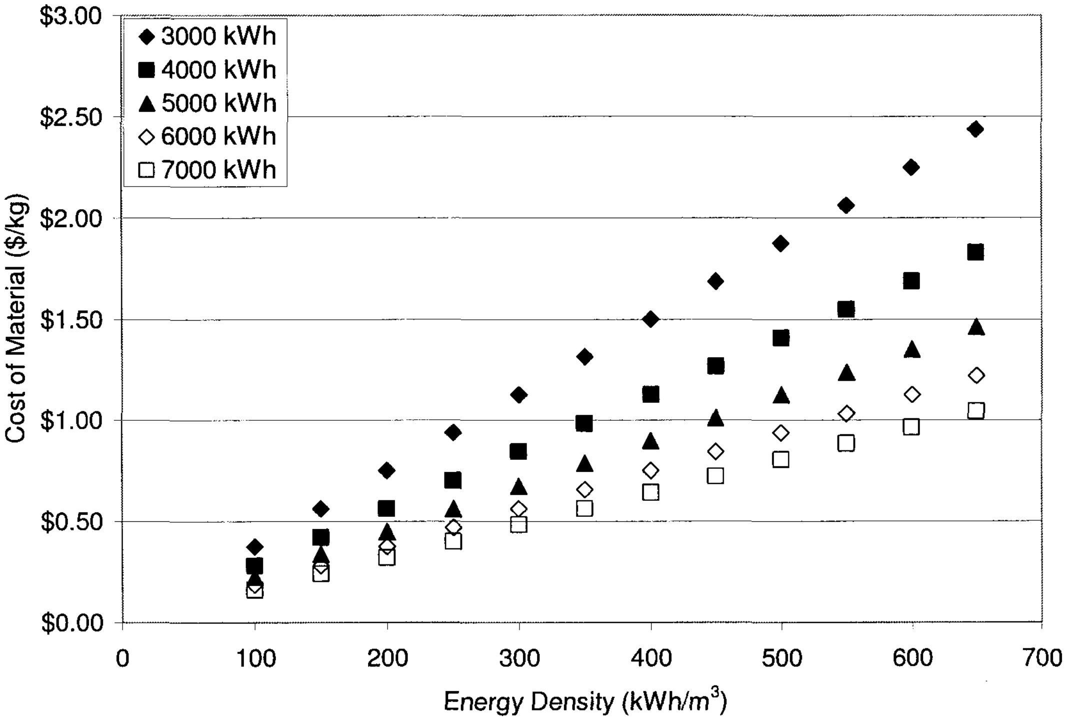

Figure 5.5: Required Energy Density and Material Cost for 15 Year Payback Period (Capital investment of $9,000) for various storage capacities (Storage = 40% of yearly heating requirements, Material 800kg/m3)

5.2 Apartment Building Seasonal Storage Scenario

In this scenario, the installation of 5 and a half PS-35 power spars on a 10 storey building in Montreal, Québec in considered. The heating requirements for the building have been simulated by EE4, large building simulation software by Natural Resources Canada [18]. Figure 5.6 displays the buildings heating requirements and the power spars heating output through out the year. Appendix 3 contains all data and calculations for this scenario.

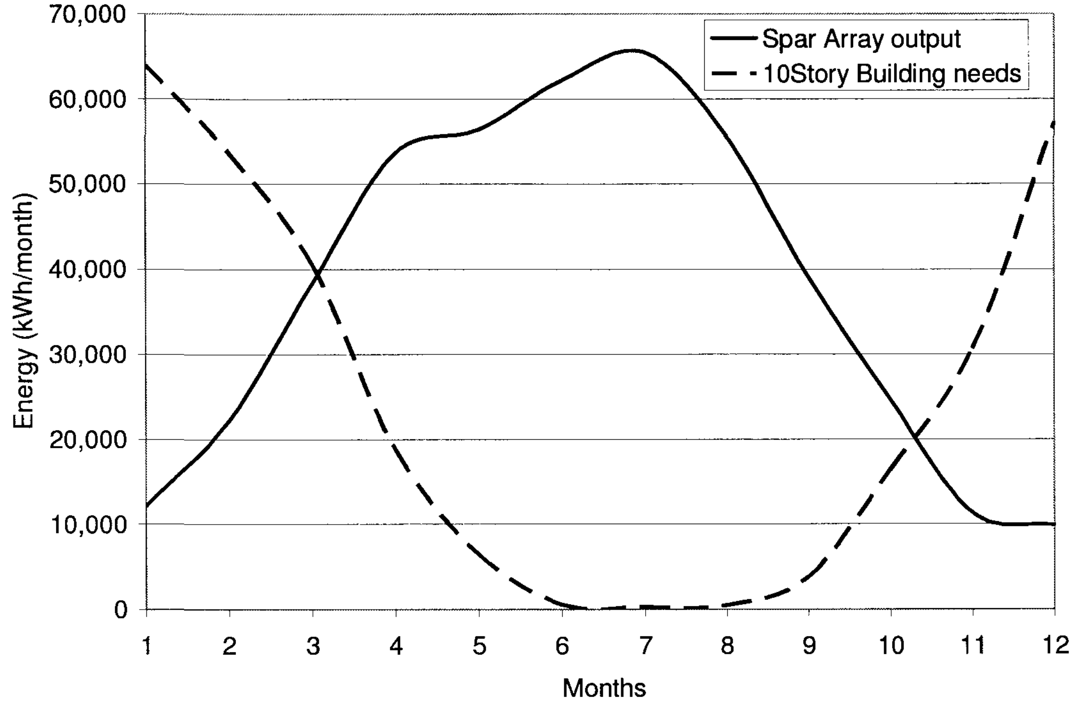

Figure 5.6: Monthly space heating requirements for a 10 Storey building modeled through EE4 and the heating output from 5.5 PS-35 power spars from Menova

In this scenario, direct heating from the PS-35 provides 50% of the buildings heating requirements which means that the other 50% must come from the storage system, approximately 150 000 kWh of storage on a yearly basis. The excess summer heat is 300 000 kWh, double the required storage, which, as was seen in Chapter 2, would only be enough to fully regenerate the system at 100°C because it has the highest efficiency (around 50%). The resulting energy density would be 150 kWh/m^3. If the system were regenerated at 250°C, which has an efficiency of 30%, it would require 500 000 kWh for complete regeneration which is more then the excess available from the panels. At this energy density, the size of adsorbent bed necessary is 1034 m^3, roughly the same size as 4 typical single family homes. The bed cost would be in the range of $2 million. Needless to say that similar conclusions to the residential scenario can be drawn. The bed is very large but better than other storage options and is entirely cost prohibitive at this point.

5.3 Portable Heat Distribution System

The portable heat distribution system is designed to alleviate the two biggest problems with the adsorbent storage system; space required to install an on-site bed and the capital cost of the system. In this scenario, a large solar farm is built on the outskirts of a city or town. It uses concentrating solar collectors to collect solar radiation at high temperatures. This energy is used to regenerate modular sized beds of 2-4m^3 which have an energy density of 250 kWh/m^3. Similar to a propane tank system, these beds are then delivered to a residence where they are connected to a special unit that replaces the typical furnace. All the homes heating needs are provided from the portable beds. Every two weeks, the solar heating utility company comes to remove the spent beds and replace them with fresh ones. The burden of space is reduced by having replaceable modular units and the burden of capital cost of bore by the utility company. The home owners only pay for the energy they use, not the system cost. Table 5.2 outlines the monthly requirements for the portable heat system.

Table 5.2: Monthly energy requirements for portable heat distribution system (see Appendix 2)

Month	Space Heating + DHW (kWh)	Volume for Monthly Heating Requirement (m^3)	# of $2m^3$ modules required
Jan	1994.36	7.98	3.99
Feb	1656.26	6.63	3.31
Mar	1367.16	5.47	2.73
Apr	817.53	3.27	1.64
May	528.10	2.11	1.06
Jun	447.63	1.79	0.90
Jul	448.02	1.79	0.90
Aug	443.93	1.78	0.89
Sep	453.93	1.82	0.91
Oct	661.70	2.65	1.32
Nov	1021.39	4.09	2.04
Dec	1662.48	6.65	3.32

The heating requirements through out the year in Canada are not constant. The winter requires much more heating than the summer; while January might require 4 modules, one module could last all of June and July.

Although this scenario solves the problems encountered by the end user, there are a few things to consider. Several pieces of infrastructure, like transport trucks, the utility company, the home heating system, need to be added to the capital and operating costs. There would be very large storage requirements for the containers which mainly be regenerated in summer and used during winter. As well, the cost or heating value of the gasoline required to distribute the modules could be higher than the value of the heat it is delivering depending on the distance of the delivery, the fuel cost and the energy density of the system. Furthermore, it is not logical for a renewable energy technology to require or be supported by fossil fuel consumption.

Another use of the solar farm might be to use the concentrating solar collectors to produce steam to generate electricity and then use the current electrical infrastructure to distribute the electricity which could be used for heating. This could still be considered solar heating. In this scenario, the adsorption thermal energy storage system would have great value as a long term storage system for the excess heat collected which could be stored from the summer and released during the winter to produce steam to generate electricity, as will be discussed in the following scenario.

5.4 Thermal Energy Storage for Electricity Generation

Concentrating solar collectors can reach temperatures between 200-400°C which is enough to produce steam for electricity production. They are a great source of energy in areas with high amounts of constant solar radiation, like deserts or countries near the equator. However, their output still varies based on different times of day and seasons. Short term storage systems, like molten salts, are used as storage but suffer from the problems outlined in Chapter 1.

Adsorption thermal energy storage could be very useful in making this energy source more reliable. Excess heat from day to day or between seasons could be stored when it is not necessary and released during times of lower solar radiation like rainy days or the winter. This would not only utilise wasted thermal energy but make the entire power plant more reliable and more feasible. Adsorption TES could also increase the efficiency of the system by re-using the heat from spent steam. Wasted steam from power plants is vented around 200°C. This heat source could be used to regenerate adsorbent beds for thermal storage. When necessary, the energy could be released and used to drive a Hydrocarbon Rankine Cycle that uses hydrocarbons as the working fluid for electricity generation since its temperature would not be sufficient for steam generation.

6 Conclusions, Contributions and Future Work

6.1 Contributions and Conclusions

Adsorption can be used for long term thermal energy storage. The prototype system developed at the University of Ottawa is one of a kind in Canada. This lab scale high throughput open system for water adsorption is capable of determining energy density and characterizing regeneration simply and quickly which is ideal for screening adsorbents. The adsorbent screening performed through literature surveys and experiments identified the Activated Alumina / Zeolite 13X hybrid as the best adsorbent for long term thermal energy storage. This is the first work to analyze the adsorbent AA13X as an adsorption thermal energy storage material and characterize its properties. The regeneration temperature characterization performed in Chapter 2 establishes a very useful procedure that will be required in the development of adsorption thermal energy storage systems. The model suggested in Chapter 2 helps predict the performance of an adsorbent system based on its maximum performance and the regeneration temperature available. This model, which can likely be applied to other systems as demonstrated using the natural zeolite, is crucial to designing large scale adsorption thermal storage system and predicting performance based on the available quality of heat. The thermal storage efficiency from Chapter 2 is a new concept in adsorption thermal energy storage which establishes the amount of energy required for various regeneration levels which will also be useful in system design.

Remarkably, the adsorption thermal energy storage system using AA13X developed in this work has the highest reported energy density in literature so far at 200 kWh/m^3. The theories about salt impregnations to improve energy density proved to be fruitful. The salt impregnations in Chapter 3 have not only increased the previously highest reported energy density to 300 kWh/m^3, it has also confirmed a new method of adsorbent modification which could produce thermochemical heat storage materials with energy densities high enough to make long term thermal energy storage more economically and practically feasible. Although adsorbent impregnation has been performed before for various applications and salt hydration has been suggested as a method of energy storage, this study is the first to impregnate adsorbents with hydrated salts to improve their energy density and is the first to report successful results.

Defining parameters for building the eventual full storage system and exploring application scenarios was also an integral part of this study. Examining the energy flows through within the system helped identify some key parameters that must be taken into consideration in the design to ensure a positive energy return. The efficiency definitions in Chapter 4 have established the necessary guidelines for building adsorption thermal energy storage systems that have a positive energy rate of return and established criteria for it to be compared with other thermal storage system. The limitations of adsorption discussion identified some paramount items concerning the energy source of the water vaporization that must be incorporated into the adsorption thermal energy storage design. The useful energy discussion is also a key concept to bridging the gap between theoretical potential and practical applications.

Finally, various implementation scenarios of adsorption thermal energy storage system have been discussed and seeded for future research. The practical application of these systems has been investigated and determined to be feasible. However, the economic analysis performed in Chapter 5 has identified the key barriers to commercialization of this technology.

6.2 Future Work

The model developed for adsorbent performance as a function of regeneration temperature in Chapter 2 is very basic. However, it would be a very useful tool for designing adsorption thermal energy storage systems as it is necessary to know how the adsorbent will perform depending on the regeneration heat source. In order to build a more rigorous model, more adsorbents will need to be characterized in a similar fashion and methods of estimating the coefficients and maximum performance from basic adsorbent properties will need to be developed. The correlation between evaporative energy and energy released during adsorption should be investigated further. The first step would be to compare the energy released from the adsorption of other adsorbate gases with their enthalpy of evaporation for the amount of adsorbate adsorbed. It would also require performing these experiments on various adsorbent to verify that the correlation stands in all cases.

There is still much work to be done in the development of a full adsorption thermal energy storage system. The energy density of the storage material must be improved at least another 2 folds and the cost must be cut by half. Salt impregnations seemed to be a promising concept but it will be necessary to identify other more energetic reactions to impregnate or impregnating the salts into highly porous materials. There are still various combinations to be explored. Finally, the current system is useful for screening and high throughput experiments, but it is imperative that a larger scale system be developed in order to test the performance of the system at a more realistic level.

6.3 Acknowledgements

I would like to thank my industry partner, Menova Energy Inc, for helping me understand solar thermal collectors and supplying me with useful data. I would like to thank Rio Tinto Alcan for supplying me with the adsorbent used in this study. I would like to thank Natural Resources Canada for developing and making available the software used for the building simulations of this study. I would like to thank Dr. Tezel for her supervision and guidance. I would like to thank the shop staff of the Chemical and Biological Engineering Department of the University of Ottawa for helping me build the prototypes locked in my head. I would like to thank Shannon Lyrette for helping me elaborate a feasibility scenario. Finally I would like to thank Danielle, my loving girlfriend, for all of her support and encouragement.

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7.1 Nomenclature

Adsorbent Capacity : mass of water adsorbed per mass of adsorbent (kg water/kg adsorbent)
Adsorption Energy : Total amount of energy used during adsorption experiment (kJ)
Cp : Heat Capacity (kJ/kg*°C)
Column Volume : Volume of the adsorbent column (m^3)
D : diameter (m)
d(Energy Released) : amount of energy released over a certain period of time (kJ)
dMass of Air :Mass of air that has passed through the system over a period of time (kg)
$d(Mass\ H_2O\ Adsorbed)$: Mass of water adsorbed by the adsorbent over a period of time (kg)
EDehumidification : Energy used for dehumidification (kJ)
EFlow : Energy used by flow of air through system (kJ)
EHumidification : Energy used for humidification (kJ)
Energy Density : kWh/m^3
Energy Inputted : Amount of thermal energy that must be supplied to the adsorbent bed for regeneration (kJ)
Energy Released : Total amount of energy released during an adsorption experiment (kJ)
e: Roughness factor inside a pipe
f : friction factor
L : length (m)
m : Mass (kg)
$\dot{m}$: massic flow rate (kg/s)
g : gravitational constant, 9.81 m/s^2
P : Pressure (Pa)
Q : thermal energy (kWh of J)
Regeneration Energy : Total energy used during the regeneration experiment (kJ)
RH : Relative Humidity (%)
Re : Reynolds Number
T : Temperature (°K or °C)
t : time (sec)
Total Energy Released : Total amount of energy released during an entire experiment (kJ)
Total Flow Rate : Flow rate of air through the system (l/min)
$Total\ H_2O\ Adsorbed$: Total amount of water adsorbed onto the adsorbent during the experiment (kg)
u : Internal Energy (kJ/kg)
v : velocity (m/s)
$v_{\sup erficial}$: Superficial velocity (m/s)
W_s : Work done by the shaft (J)

y : height (m)

Greek Letters

ΔH_{ads} : Heat of Adsorption (kJ/mol)
ΔP : Pressure Difference (Pa)
ΔT : Temperature Difference (°C)
ε : bed porosity
μ : viscosity (kg/sec*m)
η : Thermal Efficiency
ρ : density (kg/m^3)
γ : Loading of water in air (kg of water / kg of dry air)

7.2 Abbreviations

AA13X: Hybrid adsorbent which is a mix of Activated Alumina and Zeolite 13X

ATES: Aquifer Thermal Energy Storage

BET: Method of estimate surface area of porous materials

BTES: Borehole Thermal Energy Storage

CECA: Name of a company that produce zeolite 13X

DHW: Domestic Hot Water

L/D: Length over Diameter ratio

LHS: Latent Heat Storage

MW$_{th}$: Megawatts of thermal energy

NLR: Non Linear Regression

η: Thermal Efficiency

OD: Outside diameter

PCM: Phase Change Material

RH: Relative Humidity

SCFM: Standard Cubic Feet per Minute

SHS: Sensible Heat Storage

SS: Stainless Steel

TES: Thermal Energy Storage

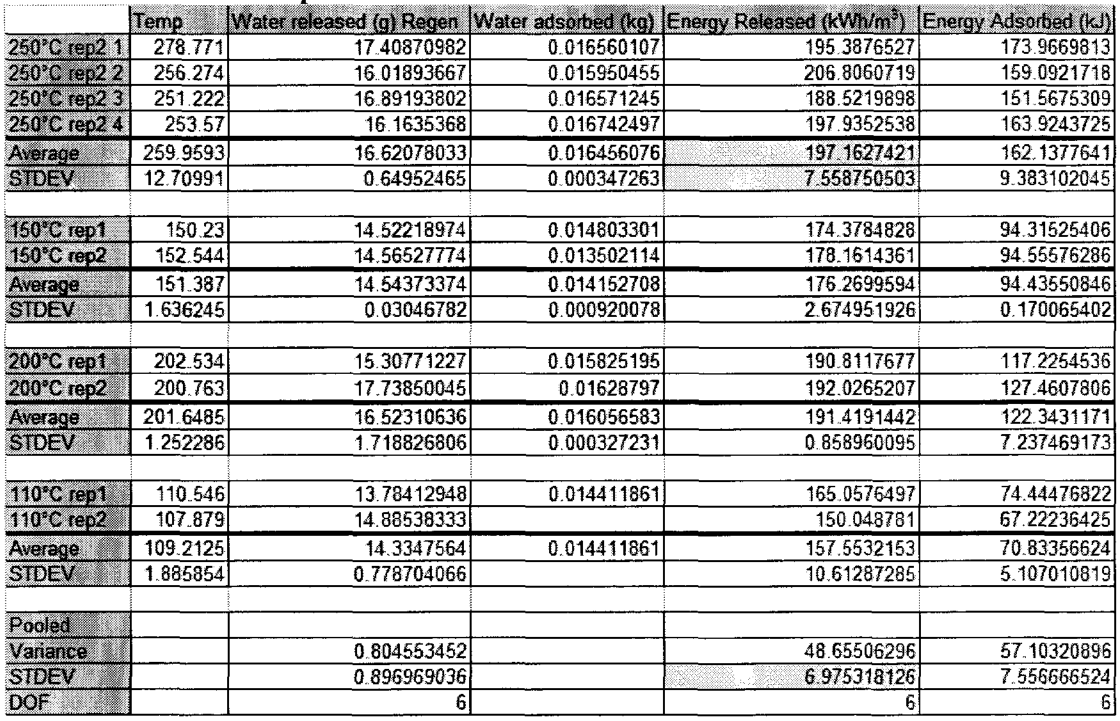
THS: Thermochemical Heat Storage

8 Appendices

Appendix 1: Statistical Analysis for Regeneration, Adsorption and Cycling

Table A.1. 1 outlines all of the duplicates runs that were performed during project in order to determine standard deviations and means for the metrics of the system like the amount of water released, the amount of water adsorbed, the energy density and the amount of energy adsorbed. All of the duplicate runs from different temperatures were then pooled to give an overall standard deviation for the system. Sometimes, statistics for the overall system is used; sometimes the statistics for specific temperature runs are used. The most pertinent test statistics are highlighted. All equations and statistical constant were taken from [*R. A. Johnson, Miller & Freund's Probability and Statistics for Engineers, Pearson Prentice Hall, 7th Edition, Upper Saddle River, New Jersey, 2005*]

Table A.1. 1: Outline of duplicate runs



	Temp	Water released (g) Regen	Water adsorbed (kg)	Energy Released (kWh/m^3)	Energy Adsorbed (kJ)
250°C rep2 1	278.771	17.40870982	0.016560107	195.3876527	173.9669813
250°C rep2 2	256.274	16.01893667	0.015950455	206.8060719	159.0921718
250°C rep2 3	251.222	16.89193802	0.016571245	188.5219898	151.5675309
250°C rep2 4	253.57	16.1635368	0.016742497	197.9352538	163.9243725
Average	259.9593	16.62078033	0.016456076	197.1627421	162.1377641
STDEV	12.70991	0.64952465	0.000347263	7.558750503	9.383102045
150°C rep1	150.23	14.52218974	0.014803301	174.3784828	94.31525406
150°C rep2	152.544	14.56527774	0.013502114	178.1614361	94.55576286
Average	151.387	14.54373374	0.014152708	176.2699594	94.43550846
STDEV	1.636245	0.03046782	0.000920078	2.674951926	0.170065402
200°C rep1	202.534	15.30771227	0.015825195	190.8117677	117.2254536
200°C rep2	200.763	17.73850045	0.01628797	192.0265207	127.4607806
Average	201.6485	16.52310636	0.016056583	191.4191442	122.3431171
STDEV	1.252286	1.718826806	0.000327231	0.858960095	7.237469173
110°C rep1	110.546	13.78412948	0.014411861	165.0576497	74.44476822
110°C rep2	107.879	14.88538333		150.048781	67.22236425
Average	109.2125	14.3347564	0.014411861	157.5532153	70.83356624
STDEV	1.885854	0.778704066		10.61287285	5.107010819
Pooled					
Variance		0.804553452		48.65506296	57.10320896
STDEV		0.896969036		6.975318126	7.556666524
DOF		6		6	6

Does cycling the adsorbent significantly affect the energy density?

Table A.1. 2: Data from cycling experiments

Run Code	Flowrate (l/min)	Energy Out (kJ)	Energy Density (kWh/m^3)	Run #
repeats1	24.20	44.95	198.94	1
repeats2	24.55	43.39	192.05	2
repeats3	24.43	42.35	187.45	3
repeats4	24.40	42.47	187.96	4
repeats5	24.44	44.73	197.97	5
Regen3	24.30	43.85	194.08	10
Repeats2 1	24.62	44.15	195.39	14
Repeats2 2	24.40	46.72	206.81	15
Repeats2 3	24.41	42.59	188.52	16
0.45Regen1	24.45	45.11	199.64	22
Repeats2 4	24.48	44.72	197.94	23
0.15Regen1	24.48	43.53	192.69	28
0.45Regen6	24.56	45.13	199.74	29
0.15REgen6	24.51	43.21	191.26	34
Average			195.03	
STD			5.50	

Are the 250°C Repeat mean and the Cycling mean the same at a 5% significance level?

$$H_o : u_1 = u_2$$

$$H_1 : u_1 \neq u_2$$

$$Z_o = \frac{\overline{Y}_1 - \overline{Y}_2}{\sqrt{\left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2} \right)}} = \frac{Mean\ D}{Variance\ D}$$

$$Z_{\alpha/2} = 1.96$$

We reject the null hypothesis if $Z_o < -Z_{\alpha/2}$ or $Z_o > Z_{\alpha/2}$.

	Values	# of Runs
Mean1 (Repeats at 250°C) (kWh/m^3)	197.1627	4
Mean2 (Cycling) (kWh/m3)	195.0304	17
STD1(Repeats at 250°C) (kWh/m3)	7.558751	4
STD2 (Cycling) (kWh/m3)	5.504135	17

Variance D	4.008212
Mean D	2.132301
Z_0	0.531983

Since Z_0 is between -1.96 and 1.96, we do not reject the null hypothesis and conclude that there is no statistical significant difference between the two means at a 5% level of significance.

Are the 250°C Repeat variance and the Cycling variance the same at a 5% significance level?

$$H_o : \frac{\sigma_1^2}{\sigma_2^3} = 1$$

$$H_1 : \frac{\sigma_1^2}{\sigma_2^3} \rhd 1$$

$$F_o = \frac{s_1^2}{s_2^2}$$

$$F_{\alpha/2, v_1, v_2}, \ where\ v_1 = n_1 - 1, v_2 = n_2 - 1$$

Reject the null hypothesis if $F_o > F_{\alpha/2,v_1,v_2} = 3.2$.

	Values	# of Runs	DOF
STD1(Repeats at 250°C) (kWh/m3)	7.558751	4	
STD2 (Cycling) (kWh/m3)	5.504135	17	

F_o	1.885914
F5, 3, 16	3.2

Since F_o is smaller then $F_{\alpha/2,v_1,v_2}$, we do not reject the null hypothesis and conclude that there is no statistically significance difference between the two means at a 5% level.

Are the Overall variance and the Cycling variance the same at a 5% significance level?

$$H_o : \frac{\sigma_1^2}{\sigma_2^3} = 1$$

$$H_1 : \frac{\sigma_1^2}{\sigma_2^3} \rhd 1$$

$$F_o = \frac{s_1^2}{s_2^2}$$

$$F_{\alpha/2, v_1, v_2}, \ where\ v_1 = n_1 - 1, v_2 = n_2 - 1$$

Reject the null hypothesis if $F_o > F_{\alpha/2,v_1,v_2} = 2.85$.

	Values	# of Runs	DOF
STD2 (Cycling) (kWh/m3)	5.504135	17	
STD (Overall Pooled) (kWh/m3)	6.975318		6

Fo	1.606016
F5,5,16	2.85

Since F_o is smaller then $F_{\alpha/2,v_1,v_2}$, we do not reject the null hypothesis and conclude that there is no statistically significance difference between the two means at a 5% level.

Does the flow rate used for adsorption runs significantly affect the energy density?

Table A.1. 3: Data from adsorption flow rate experiments

Run Code	Flowrate (l/min)	Energy Out	Energy Density (kwh/m^3)
New Column8	32	43.95775567	194.55844
NewColumn 14	24.48	46.04802992	203.8100611
New Column 15	16.27	43.37391002	191.9743204
repeats1	24.2	44.94827761	198.942522
repeats2	24.55	43.39127268	192.0511681
repeats5	24.44	44.72774726	197.9664475
repeats7	8.17	43.64109187	193.1568759
Regen3	24.3	43.84861047	194.0753599
Repeats2 1	24.62	44.14510467	195.3876527
Repeats2 2	24.4	46.72493663	206.8060719
0.45Regen1	24.45	45.105448	199.6381632
Repeats2 4	24.48	44.72069948	197.9352538
0.15Regen1	24.48	43.53467189	192.6858576
0.45Regen6	24.56	45.12896607	199.7422549
0.15REgen6	24.51	43.21222509	191.2586977
adsflow2	16.27	43.49162811	192.4953445
adsflow3	28.64	45.36040186	200.7665972
adsflow4	10.78	46.52682213	205.9292108
adsflow8	24.36	45.08032415	199.5269642
Average			197.3003823
STD			4.79980264

Are the 250°C Repeat mean and the Adsorption flow rate mean the same at a 5% significance level?

$H_o : u_1 = u_2$

$H_1 : u_1 \neq u_2$

$$Z_o = \frac{\bar{Y}_1 - \bar{Y}_2}{\sqrt{\left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}\right)}} = \frac{Mean\ D}{Variance\ D}$$

$Z_{\alpha/2} = 1.96$

We reject the null hypothesis if $Z_o < -Z_{\alpha/2}$ or $Z_o > Z_{\alpha/2}$.

	Value	# of Runs
Mean1 (Repeats at 250°C) (kWh/m^3)	197.1627	4
Mean2 (Adsorption) (kWh/m3)	197.3004	19
STD1(Repeats at 250°C) (kWh/m3)	7.558751	4
STD2 (Adsorption) (kWh/m3)	4.799803	19

Variance D	3.936522
Mean D	0.13764
Z	0.034965

Since Z_o is between -1.96 and 1.96, we do not reject the null hypothesis and conclude that there is no statistical significant difference between the two means at a 5% level of significance.

Are the 250°C Repeat variance and the Cycling variance the same at a 5% significance level?

$$H_o : \frac{\sigma_1^2}{\sigma_2^3} = 1$$

$$H_1 : \frac{\sigma_1^2}{\sigma_2^3} \rhd 1$$

$$F_o = \frac{s_1^2}{s_2^2}$$

$$F_{\alpha/2, v_1, v_2}, \; where \; v_1 = n_1 - 1, v_2 = n_2 - 1$$

Reject the null hypothesis if $F_o > F_{\alpha/2, v_1, v_2} = 3.16$.

	Value	# of Runs
STD1(Repeats at 250℃) (kWh/m3)	7.558751	4
STD2 (Adsorption) (kWh/m3)	4.799803	19

Fo	2.480009
F5, 3, 18	3.16

Since F_o is smaller then $F_{\alpha/2, v_1, v_2}$, we do not reject the null hypothesis and conclude that there is no statistically significance difference between the two means at a 5% level.

Are the Overall variance and the Cycling variance the same at a 5% significance level?

$$H_o : \frac{\sigma_1^2}{\sigma_2^3} = 1$$

$$H_1 : \frac{\sigma_1^2}{\sigma_2^3} \rhd 1$$

$$F_o = \frac{s_1^2}{s_2^2}$$

$F_{\alpha/2,v_1,v_2}$, *where* $v_1 = n_1 - 1, v_2 = n_2 - 1$

Reject the null hypothesis if $F_o > F_{\alpha/2,v_1,v_2} = 2.77$.

	Value	# of Runs	DOF
STD2 (Adsorption) (kWh/m3)	4.799803	19	
STD (Overall Pooled) (kWh/m3)	6.975318		6

Fo	2.111939
F5,5,18	2.77

Since F_o is smaller then $F_{\alpha/2,v_1,v_2}$, we do not reject the null hypothesis and conclude that there is no statistically significance difference between the two means at a 5% level.

Nomenclature:

F_o = F-distribution test statistic

$F_{\alpha/2,v_1,v_2}$ =F-distribution table value

H_o = null hypothesis

H_1 = alternative hypothesis

n = number of point in the data set

σ = real variance of a data set

s = calculated standard deviation

u = real mean of a data set

v = degrees of freedom

$\overline{Y}$ = calculated mean of data set

Z_o = normal distribution test statistic

$Z_{\alpha/2}$ = normal distribution table value

Appendix 2: HOT2000 Report, PS-35 Power Spar output data and residential energy balance calculations

HOT2000
Natural Resources CANADA
Version 10.31

File: Montreal Wizard House.HSE
Application Type: General

User Weather File:

Weather Data for ,

Builder Code:

Data Entry by:
Date of entry: 6/20/2008
Company:

Client name: ,
Street address:

City: **Region:** ontario
Postal code: **Telephone:**

GENERAL HOUSE CHARACTERISTICS

House type: Single Detached
Number of storeys: Two storeys
Plan shape: Rectangular
Front orientation: South
Year House Built: 2002
Wall colour: Default **Absorptivity:** 0.40
Roof colour: Medium brown **Absorptivity:** 0.84
Soil Condition: Normal conductivity (dry sand, loam, clay)
Water Table Level: Normal (7-10m/23-33ft)

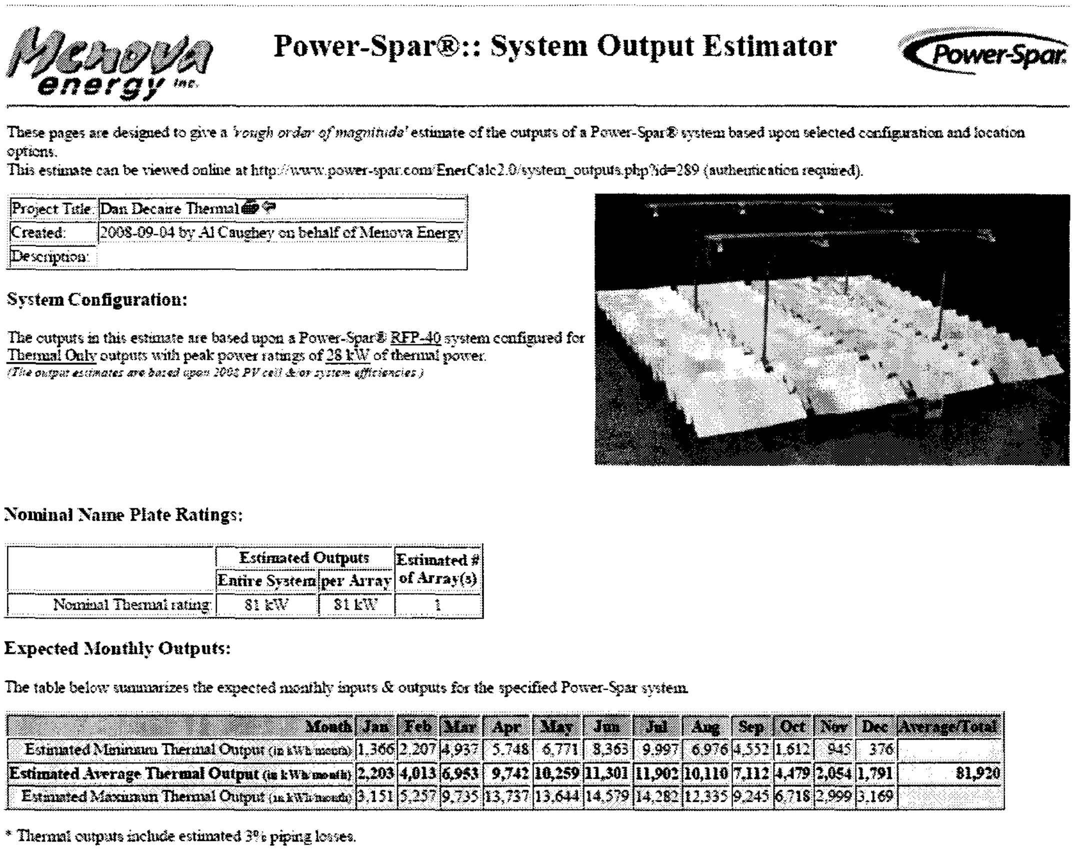
House Thermal Mass Level: (A) Light, wood frame

Effective mass fraction 1.000

Occupants : 2 Adults for 50.0% of the time
2 Children for 50.0% of the time
0 Infants for 0.0% of the time

MONTHLY ESTIMATED ENERGY CONSUMPTION BY DEVICE (MJ)

	Space Heating		DHW Heating		Lights &	HRV &	Air
Month	Primary	Secondary	Primary	Secondary	Appliances	FANS	Conditioner
Jan	5351.2	0.0	1828.7	0.0	2678.4	0.0	0.0
Feb	4293.0	0.0	1669.7	0.0	2419.2	0.0	0.0
Mar	3082.2	0.0	1839.7	0.0	2678.4	0.0	0.0
Apr	1200.9	0.0	1742.3	0.0	2592.0	0.0	0.0
May	166.1	0.0	1735.1	0.0	2678.4	0.0	0.0
Jun	2.2	0.0	1609.3	0.0	2592.0	0.0	0.0
Jul	0.0	0.0	1612.9	0.0	2678.4	0.0	0.0
Aug	0.0	0.0	1598.2	0.0	2678.4	0.0	0.0
Sep	61.6	0.0	1572.6	0.0	2592.0	0.0	0.0
Oct	705.6	0.0	1676.6	0.0	2678.4	0.0	0.0
Nov	1997.2	0.0	1679.9	0.0	2592.0	0.0	0.0
Dec	4196.3	0.0	1788.8	0.0	2678.4	0.0	0.0
Ann	21056.3	0.0	20353.6	0.0	31536.0	0.0	0.0



Power-Spar®:: System Output Estimator

These pages are designed to give a *'rough order of magnitude'* estimate of the outputs of a Power-Spar® system based upon selected configuration and location options.
This estimate can be viewed online at http://www.power-spar.com/EnerCalc2.0/system_outputs.php?id=289 (authentication required).

Project Title:	Dan Decarre Thermal
Created:	2008-09-04 by Al Caughey on behalf of Menova Energy
Description:	

System Configuration:

The outputs in this estimate are based upon a Power-Spar® RFP-40 system configured for Thermal Only outputs with peak power ratings of 28 kW of thermal power.
(The output estimates are based upon 2008 PV cell &/or system efficiencies.)

Nominal Name Plate Ratings:

	Estimated Outputs		Estimated # of Array(s)
	Entire System	per Array	
Nominal Thermal rating:	81 kW	81 kW	1

Expected Monthly Outputs:

The table below summarizes the expected monthly inputs & outputs for the specified Power-Spar system.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Average/Total
Estimated Minimum Thermal Output (in kWh/month)	1,366	2,207	4,937	5,748	6,771	8,363	9,997	6,976	4,552	1,612	945	376	
Estimated Average Thermal Output (in kWh/month)	**2,203**	**4,013**	**6,953**	**9,742**	**10,259**	**11,301**	**11,902**	**10,110**	**7,112**	**4,479**	**2,054**	**1,791**	**81,920**
Estimated Maximum Thermal Output (in kWh/month)	3,151	5,257	9,735	13,737	13,644	14,579	14,282	12,335	9,245	6,718	2,999	3,169	

* Thermal outputs include estimated 3% piping losses.

Table A.2. 1: Residential energy balance calculations

Month	Space Heating + DHW (kWh)	Only Space Heating (kWh)	Average Thermal Output (in kWh/month)	Excess Energy (kWh)	Missing Needs (kWh)
Jan	1,994.36	1,486.40	550.75	0.00	1,443.61
Feb	1,656.26	1,192.47	1,003.25	0.00	653.01
Mar	1,367.16	856.14	1,738.25	371.09	0.00
Apr	817.53	333.57	2,435.50	1,617.97	0.00
May	528.10	46.14	2,564.75	2,036.65	0.00
Jun	447.63	0.61	2,825.25	2,377.62	0.00
Jul	448.02	0.00	2,975.50	2,527.48	0.00
Aug	443.93	0.00	2,527.50	2,083.57	0.00
Sep	453.93	17.11	1,778.00	1,324.07	0.00
Oct	661.70	195.99	1,119.75	458.05	0.00
Nov	1,021.39	554.76	513.50	0.00	507.89
Dec	1,662.48	1,165.61	447.75	0.00	1,214.73
TOTAL	11,502.48	5,848.81	20,479.75	12,796.51	3,819.24

Table A.2. 2: System Parameters

Regeneration Temperature (℃)	250
Energy density (kWh/m^3)	250
Efficiency	0.3
Bed Size (m^3)	15.28
Energy Required (kWh)	12730.80
Density (kg/m^3)	800.00
Cost of adsorbent ($/kg)	3.00
Cost of Bed ($)	38400

Appendix 3: Report from EE4 software: Monthly heating requirements for 10 storey building

```
                                                      10 Storey Building MTL

                                                                          DOE-2.1Ec133   1/19/2009    13:25:49  LDL RUN  1
                                            Proposed                     Building Type
REPORT- LS-D BUILDING MONTHLY LOADS SUMMARY                                        WEATHER FILE- Montreal Que CWEC
---------------------------------------------------------------------------------------------------------------------------


      - - - - - - - - C O O L I N G - - - - - - - -    - - - - - - - - H E A T I N G - - - - - - - -    - - - E L E C - - -

                                            MAXIMUM                                             MAXIMUM        ELEC-    MAXIMUM
       COOLING    TIME   DRY-  WET-         COOLING       HEATING    TIME   DRY-  WET-          HEATING       TRICAL       ELEC
        ENERGY  OF MAX   BULB  BULB            LOAD        ENERGY  OF MAX   BULB  BULB             LOAD       ENERGY       LOAD
MONTH   (MBTU)  DY  HR   TEMP  TEMP       (KBTU/HR)        (MBTU)  DY  HR   TEMP  TEMP        (KBTU/HR)        (KWH)       (KW)


JAN    51.87485  3  15   32.F  28.F         421.567      -218.257  15   6  -18.F -18.F         -762.128       57436.    181.318

FEB    52.96482  8  15   35.F  31.F         497.005      -183.236   4   9  -12.F -13.F         -740.229       50520.    181.318

MAR    77.12418 28  16   40.F  33.F         586.167      -138.349   6   6   -1.F  -2.F         -531.636       55683.    181.318

APR   111.77605 13  15   58.F  47.F         713.659       -63.848   1   6   19.F  17.F         -429.135       53378.    181.318

MAY   186.82262 30  15   76.F  60.F         862.915       -22.013   7   5   33.F  29.F         -316.741       57436.    181.318

JUN   235.20972 28  15   79.F  62.F         911.159        -1.849  10   3   47.F  46.F          -97.149       53378.    181.318

JUL   276.62372 16  15   89.F  79.F         997.952        -1.022  30   5   47.F  46.F         -116.963       55683.    181.318

AUG   260.36197 16  15   82.F  68.F         968.622        -1.670  23   5   46.F  45.F          -85.534       57436.    181.318

SEP   187.81027  5  15   78.F  66.F         938.876       -13.089  23   6   38.F  36.F         -195.810       51625.    181.318

OCT   142.24585 11  15   73.F  60.F         895.548       -55.952  29   6   24.F  23.F         -382.104       57436.    181.318

NOV    79.15990  5  15   48.F  41.F         618.664      -104.643  27   6   14.F  13.F         -444.213       55131.    181.318

DEC    46.57395  6  16   37.F  34.F         406.962      -195.561  30   8    1.F   0.F         -595.267       53930.    181.318
      ---------                          ----------     ---------                           ----------      --------    -------

TOTAL  1708.548                                          -999.488                                           659070.

MAX                                         997.952                                         -762.128                  181.318
```

Table A.3. 1: Energy balance for PS-35 and 10 storey building simulation from EE4

			Building Requirements			
Month	Average Thermal Output (in kWh/month)	Array output (kWh/month)	(MBTU)	kWh	Summer Excess (kWh)	Winter Needs (kWh)
Jan	2,203	12,116.5	-218.257	63964.8191	0	51,848
Feb	4,013	22,071.5	-183.236	53701.1761	0	31,630
Mar	6,953	38,241.5	-138.349	40546.0936	0	2,305
Apr	9,742	53,581	-63.848	18712.0036	34,869	0
May	10,259	56,424.5	-22.013	6451.37412	49,973	0
Jun	11,301	62,155.5	-1.849	541.888464	61,614	0
Jul	11,902	65,461	-1.022	299.518664	65,161	0
Aug	10,110	55,605	-1.67	489.428737	55,116	0
Sep	7,112	39,116	-13.089	3836.00763	35,280	0
Oct	4,479	24,634.5	-55.952	16397.9142	8,237	0
Nov	2,054	11,297	-104.643	30667.8391	0	19,371
Dec	1,791	9,850.5	-195.561	57313.2774	0	47,463
Total	81,920	450,554.5		292921.341	310,249	152,616

Table A.3. 2: System Parameters

Number of Spars in Array	5.5
Storage Efficiency	0.5
Energy density (kwh/m^3)	150
Adsorbent density (kg/m^3)	800
Adsorbent Cost ($/kg)	3.00
Possible Energy Stored (kWh)	155,124.68
Bed Size (m^3)	1,034.16
Bed Cost($)	1,861,496.19

Appendix 4: TVC Business Plan Competition

The S.A.T.E.S.S. Business Plan

By:
Dan Dicaire
Full-Time M.A.Sc.

Presented for the TVC Competition

University of Ottawa
April 14th, 2009

Pitch

There is currently a large push towards renewable energy. SATESS Inc. is developing a hybrid material that can permanently store thermal energy from the sun and be combined with solar panels to provide 100% of a home's heating needs by storing heat from the summer and releasing it during the winter. SATESS will sell this material to solar heating suppliers and manufacturers to bridge the reliability gap with their product. The solar users will realize a 30% reduction in heating costs and SATESS will establish a leadership position in thermal storage for the multi-billion dollar solar heating industry.

Opportunity and Application

The residential heating industry is seeing a change in social values towards renewable energy like solar heating. The prices of natural gas and electricity are constantly increasing and these outdated methods of heating produce Green House Gases and other emissions that are a growing concern for global warming and human health. As a result, there are several incentive programs and tax breaks helping renewable energy expand because it has great potential for growth and investment. There is a significant need for heating that produces no emissions and is environmentally friendly.

Solar heating's main issue is there are currently no long term thermal energy storage methods. Solar heating systems use sensible heat storage in hot water tanks or boreholes to supply the immediate heating needs of households for a maximum of 4 days. Thus, with typical Canadian solar irradiation, all commercial systems can supply at most 60-70% of the house's heating needs, requiring an additional secondary heating system to cover the 30-40% discrepancy, because the excess heat from the summer is sensibly stored and degrades with time [5]. There is an abundance of thermal energy available during the summer; as much as 3 times more than yearly heating requirements. Attempts at long term storage currently use modified short term storage which require large volume of materials like rocks, sand or water and copious amounts of insulation. Even state of the art systems, like the one found at Drake Landing in Alberta, can only provide 90% of the homes heating requirements [28]. As a result, solar heating suppliers don't provide long term thermal storage, which creates a large gap in their product and services.

SATESS Inc. is developing a high energy density material that can permanently store thermal energy and release it on demand. Using adsorption technology, heat is released when the material is exposed to water vapours; similar to the way heat is released during an exothermic reaction [5]. Once the heat is released, the water can be removed and the material can be recharged by exposing it to a heat source, like a solar panel, similar to an endothermic reaction. This long term thermal storage solution can store heat for an indefinite period of time, without degrading the heat, at ambient temperature [4]. It uses low grade heat and can be recharged repeatedly. Thermal energy storage in adsorbent beds has existed for several decades and has been proven in several systems, but the quest for a new adsorbent material with a higher energy density is ongoing. We can currently provide this long term thermal storage solution with our technology. Our lab scale tests have proven superior energy density to existing available materials and scheduled improvements will lead to a better, more compact system.

With this material, SATESS Inc. will provide solar heating suppliers with a thermal storage solution to provide 100% of a home's heating needs. It is combined with solar panels to provide solar heating year round by storing the excess energy collected during the summer, approximately 30-40% of the yearly heating needs, and releasing it during winter. The SATESS material circumvents the unpredictability of weather, making solar heating reliable. All the components are non-toxic and environmentally friendly. The SATESS material can currently achieve an energy density that is 4 times higher than water tanks--the most popular form of short term storage--and integrates well with existing solar heating and ventilation systems [10]. It can be installed in a brand new home or retrofitted into an old one. The reliability that SATESS brings will level the playing field for solar heating with conventional heating.

The SATESS will contribute to a healthier environment at a competitive price with conventional heating and users will benefit from additional financial savings due to government renewable incentives and tax credits, reducing their heating costs by up to 30%. The material will allow home-owners to be self-sufficient in terms of their thermal energy needs and will shield them from the unpredictable price increases of fossil fuels.

Market Analysis

Energy supply for space heating in Canada is a 15 billion dollar industry [8]. Over 80% of residential energy comes from electricity or natural gas; 60% of the energy used in Canadian residences is for space heating and 20% is hot water heating [15]. An average home owner in Ontario can expect to spend about $1140-1240 on space heating and about $400 on hot water heating every year [19].

The total installed capacity of solar thermal energy in Canada has grown to just under 600 $\text{MW}_{\text{thermal}}$ in 2006 [24]. There are 360-500 firms in Canada whose primary business is solar energy [11]. As of 2004, over 60% of those businesses were located in Ontario [11]. The solar heating industry in Canada has recently seen considerable growth and is projected to see accelerated growth going forward [9]. Also, Ontario is a leader in clean energy incentives; the Green Energy Act will soon guarantee 1500 MW of newly installed clean distributed energy by 2015, 3000 MW by 2025, and a 30% reduction in natural gas consumption by 2017 [31]. There are also millions of dollars in financial incentives from the provincial and federal government to develop renewable energy like the Ontario Solar Thermal Heating Incentive Program (up to $440\$/\text{m}^2$ panel installed [21]) or the Ontario Home Energy Savings Program (up to 10 000$ for retrofitting to address energy issues [20]).

At the end of 2008, there was an estimated 1000 solar roofs in Ontario. The Government of Ontario's Go Green initiative is aiming for 100 000 solar roofs, designed to supply hot water and space heating, within the next 11 years which represent only 3% of Ontario detached family homes (5000 by 2011, 60 000 by 2017) [18][2]. British Columbia has also announced their "100 000 solar roofs by 2020" initiative [22] and similar federal and provincial incentive programs and trends are developing for the rest of Canada's 11 million single detached homes [16]. Also, Europe is already a world leader in the renewable industry with 15.4 $\text{GW}_{\text{thermal}}$ [7] of installed solar heating and will continue to grow. It plans to have 20% of its energy from renewable sources by 2020 [25].

Our target market is solar heating manufacturers and suppliers (referred to as "the costumers") as they have a direct need for a long term thermal storage solution. Each of our costumers will likely have a different solar heating system with different specifications and operations; it would be very hard to produce storage containers for the hybrid material that suit everyone needs. And if we did design and produce the containers, we would outsource the production to an Original Equipment Manufacturer (OEM), something that most of our costumers do already for their own products. As a result, we will offer the SATESS material to the costumers for use in storage tanks that they design and produce. The material will be sold in units with enough capacity to store the 30% energy discrepancy to be matched with solar systems providing the other 70%. Therefore, one "unit" of SATESS material will correspond to the amount of material necessary to store 4000 kWh, which is approximately 30% of the heating needs of a typical home.

The cost of one unit of SATESS material to our costumers will be $4000. The cost of a solar heating system including an the extra long term storage tank but excluding the SATESS material is approximated at 11 000$ [1] [3] [12]. The total net cost of a year round solar heating system would be $15 000, where SATESS is providing 30% of the energy and makes up 30% of the cost. Our costumers sell these complete solar heating system at $21 000, for a gross profit of approximately 30%. Ultimately, the true pull will come from the home owners and home builders who will be purchasing this product to promote renewable energy, to save money, and make their home self-sufficient for their heating needs. Table 1 outlines the savings that end users purchasing from the solar heating suppliers will incur. The rebate from incentive programs may vary but an average value of 6000$ per system installed has been determined [20] [21] [6].

The main competition with solar heating for residential space and water heating is electricity and natural gas. Both of these sources are well established and fairly convenient. However, both sources release GHG or other emissions from combustion of fossil fuels or use nuclear fuel and are subject to constant price increases; up to 10% increase per year [14][23] in the future. There is also competing technology being developed for long term thermal energy storage, mainly in Europe where solar heating has a higher penetration. Some people are applying short term storage methods (water tanks, phase change material, thermocline) in large scale, heavily insulated systems, but this is expensive and requires large amounts of planning and space. Others are using exothermic reactions or molten salts to store heat but these systems operate at much higher temperatures than residential solar panels can produce and are good for electricity production. There is also a bank of research on absorbent thermal energy storage but as of yet, no commercialization has occurred.

Table 1: Cash Flows for End User

Total Cost of Ownership	Home w/t New Furnace	Retrofit w/ Existing Furnace	Solar Heating System
Capital	$7,000		$21,000
Rebate			-$6,000
Operating (annual)			
Fuel and Operation	$1,500	$1,500	$50
Maintenance	$100	$100	$200
15 Year TCO	$31,000	$24,000	$18,750
Annual Saving	$1,350	$1,350	
Payback period (years)	5.93	11.11	

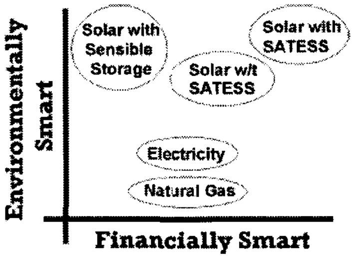


Figure 1: Position against the competition

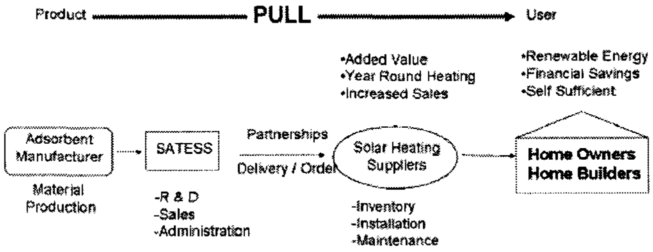


Figure 2: Business model diagram

Business Model, Validation and Execution

SATESS will pursue an OEM/direct sales business model as shown in Figure 2. Instead of trying to establish a processing facility, we will outsource the hybrid material production to an existing adsorbent manufacturer through the SATESS patent. SATESS Inc. will retain control of the research and development (R&D) as well as the sales and marketing. The SATESS material will be delivered to solar heating suppliers or manufacturers who will then use the material in their long term thermal storage tanks, which are separate entities from their short term storage tanks. This model not only allows the different partners to focus on their strengths but is also very conducive to large scale deployment through out the world as we will be able to partner with many different adsorbent manufacturers and solar heating suppliers. The solar heating suppliers will deal with installation and maintenance of the complete solar heating system and will benefit from the added value of making their product reliable year round as well as the increased sales that accompany it. We will reach our target market using direct sales, partnerships and presentations at clean energy conferences, like the Clean Technology Conference & Expo [27] or Effstock [29], solar heating conferences, like CanSIA's Solar Conference [26], and home shows, like the National Home Show [32].

Initially, the team will consist of Dan Dicaire (M.A.Sc. candidate), Rudy Jones (Ph.D. candidate) and Mohamed Hashi (M.A.Sc. candidate) of the Separation and Modeling of Adsorption for Research and Technology (SMART) group at the University of Ottawa where the project originated. These people have been following the project since its inception and they all have ample knowledge in adsorption technology and applications. At first, all will be working in together on reaching the project milestones, with Dan as acting CEO and CTO, but as the project matures, Dan, Rudy, and Mohamed respectively occupy the CTO, VP Engineering and VP of Marketing and Sales positions. After the first two years, we will need to expand the Sales and Marketing, R&D and administrative organizations as well as adding a CEO, Chief Financial Officer (CFO).

The first step will be to complete the experimental validation of the material that we are developing. This will produce the final recipe for the adsorbent as well as confirm operating parameters and energy density. This step is currently taking place at the University of Ottawa and will remain there to keep costs low and take advantage of the existing equipment and infrastructure. Current funding for the project is estimated to be enough for this step which should be concluded within 4 months. Afterwards, the company's focus will be to build a pilot scale system to confirm the results from the lab scale system and establish real life working conditions for the material. We have been working with a local solar heating supplier called Menova Energy who has manifested interest in applying the long term thermal storage technology. They will likely be our point of entry into the industry as well as the first customers for our material. We have also been in contact with the developers of the Drake Landing Solar community [28] as well as a research team in Germany working with ZAE Bayern [38] who has attempted large scale adsorbent storage system in the past. These contacts have aided and will continue to aid with technology scaling from the lab to real life application as well as understanding residential heating. The adsorbent manufacturer will likely be Alcan (Rio Tinto) in Kingston as the SMART group has had a long standing partnership with them. The expenses of establishing the pilot project and the salaries of those involved are estimated at $600 000. Obtaining a working pilot system of the SATESS material in a working solar heating system will take 8 months. We will also collect the necessary Hazardous Materials (HazMat) and Material Safety Data Sheet (MSDS) documentation for our costumers, which will be very simple as all materials are non-toxic and environmentally friendly.

Towards the beginning of the second year, the material will be ready for early adoption in 3 of Menova's systems. At the same time, we will be establishing our facility to do Marketing and Sales as well as R&D which should cost $250 000. Before the end of the second year, we will have proof of our materials performance in actual working situations which we will use to pursue more partnerships with other solar heating suppliers in Ontario. The expenses for the second year of operation are estimated at $500 000. The total investment required for the first two years of operation, during which no income is expected, is 1.4 million dollars.

The goal in the third year will be continue creating partnerships with the ultimate goal of partnering with a large solar heating supplier, such as Reliance Home Comfort, who has an established heating reputation with 1.4 million Ontario homes and a strong plan to proliferate solar heating through affordable financing [35]. Subsequently, we will pursue partnerships with National and international players like WSE Technologies [37] and EnerWorks [30].

A large barrier to overcome is the current monopoly that conventional heating companies have on the space heating industry. The entire infrastructure currently in place is designed to make money from natural gas and fossil fuels and is not easily removed. However, most of these companies are seeing the renewable energy shift and are looking to diversify into the renewable energy market as it grows and if they are made distribution partners, they could prove a great channel to market. Another barrier is public mis-information surrounding the reliability of renewable energies; most people don't believe solar heating can fulfill their heating requirements but we will prove to them that it is possible. There are also several inherent risks to developing this company. Federal and provincial incentive programs like the Green Energy Act could fail or be removed, which would have to be offset. The development of the hybrid material might not produce material with a considerably higher energy density or produce it at a higher cost than estimated. The material might perform better with certain solar panels, limiting the useful channels for our product, or perhaps, because of the economic down turn, few solar manufacturers and suppliers will want to invest time and resources into developing a long term storage module. There is also the threat of indirect competition from other adsorbent manufacturers or European research teams who can attempt to synthesize a material similar to SATESS.

Barriers and risks aside, there is a great promise of sustainability from SATESS. The SATESS hybrid material will be patented and we will continue to R & D to ensure we maintain ahead of the likely competition. Outside of Ontario, there are ample amounts of support in other provinces and countries to grow SATESS and by capturing even a small portion of those markets the business will be profitable. SATESS has industrial and commercial applications aside from the residential applications discussed here which could lead to expansion of the market for our product.

The initial investment funding for this project will be obtained from two sources. The first will be federal and provincial government incentive programs for the development of renewable energy, such as Sustainable Development Technology Canada [36], which is designed to help establish and grow clean tech businesses. There are also many resources and much funding available through Centers of Excellence and Commercialization of Research, such as the Center for the Commercialization of Research in Ottawa [33] or OCE proof of concept grants

[34]. It is estimated that approximately $500 000 of the initial investment can be obtained through these means. The balance of the funding will be obtained through private investments in return for value in the company. One unit of SATESS material will cost $2400 from the adsorbent manufacturer which will then be sold to the solar manufacturer or supplier for $4000; which represents a 40% margin. 10% of revenues are expended by sales and general administration and 10% goes to research and development, leaving a 20% profit margin for the company.

Figure 3 shows the revenues, expenses, and profits over the next the 10 years. Until 2015, the focus will be growing the business within Ontario because of the province's intention to grow renewable energy and its strong market (home builders: 30 000 new homes a year in Ontario [2]). We expect to sell a low number of units, fewer than 300 over 5 years which represent 3% of the planned solar homes to be developed in Ontario, as the technology will still be in the adoption phase. After 2015, large scale deployments will commence and sales will increase considerably. The business will expand to other regions promoting renewable energy, like British Columbia. We will also grow into Europe where there is larger solar heating penetration and even bigger incentive programs. These growth trends also follow the expected deployment of solar heating systems in Canada. Over all, we anticipate to sell approximately 15 000 SATESS material units in the next 10 years across Canada and Europe which represents less than 5% and less then 1% of their respective forecasted markets. With the outlined growth, pricing, and margins, the company is profitable by 2014 with revenues hitting $25M by 2020.

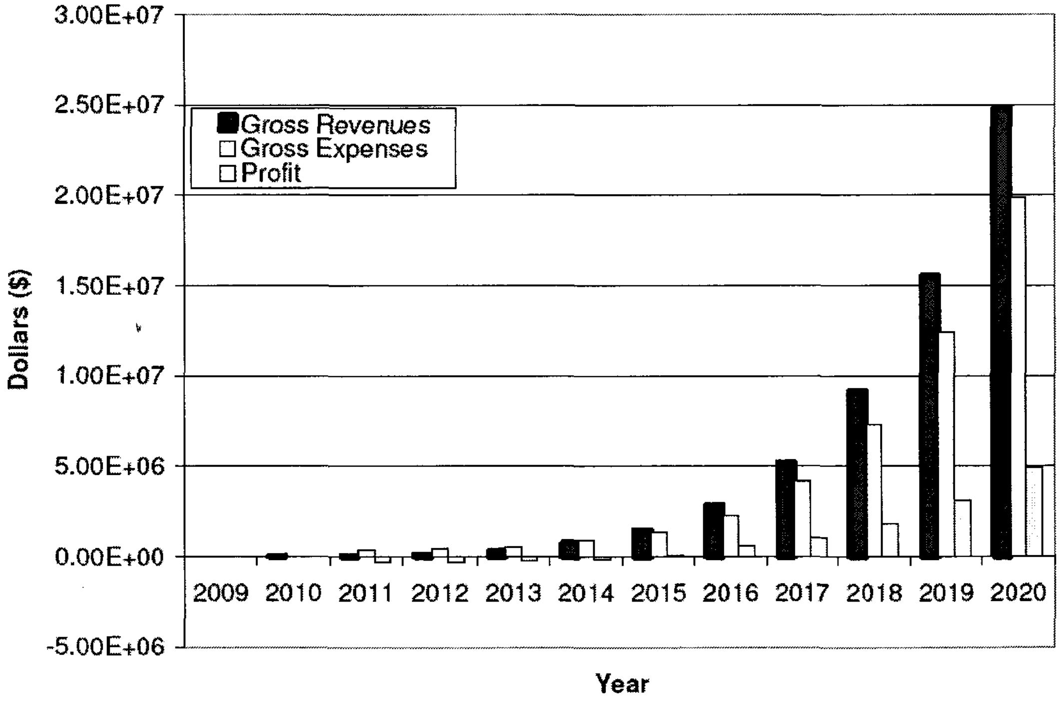


Figure 3: Cash Flows for SATESS Inc. of the next 10 years

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Appendix 5: Data Analysis and Equations

Assumptions and Data Analysis

The data acquisition system records the conditions in the system every 15 seconds by taking 1000 readings every second and calculation an average. The data collected is the relative humidity in the hygrometer and 5 temperatures; one at the inlet of the column (T1), one on the surface of the column under the insulation (T2), one at the outlet of the column (T3), one in the humidity trap (T4) and one at the Hygrometer (TH). These temperature and relative humidity data along with other pertinent information, like initial conditions and the flow rate, are converted into useful information using the following equations. The same equations are used for adsorption and desorption experiments and they represent mass and energy balances that have been adapted to the system.

Equation A.5.1, Equation A.5.2 and Equation A.5.3 are used to calculate the density, the humidity capacity and the heat capacity of the air, respectively. All three equations were obtained from or derived from information in [R.H. Perry, D.W. Green. Perry's Chemical Engineers' Handbook (7th Edition). (1997). McGraw-Hill. ISBN: 978-0-07-049841-9]

$$\rho_{air} = 360.77819 \cdot (T_{Kelvin})^{-1.00336} \tag{A.5. 1}$$

$$\gamma_{air} = 0.0044 \exp(0.0607^{T}) \tag{A.5. 2}$$

$$Cp_{air} = 1.005 + 1.88\gamma_{air} \tag{A.5. 3}$$

Equation A.5.4, Equation A.5.5 and Equation A.5.6 are used to calculate the mass of air flowing through the system, the mass of water adsorbed/desorbed and the amount of energy absorbed/released by the adsorbent every 15 seconds of the experiments (i.e. $t_n - t_{n-1} = 15\,\text{sec}$, where n is the index for the time for every 15 seconds).

$$dMass\ of\ Air = (t_n - t_{n-1}) * (Total\ Flow\ Rate) * \frac{1m^3}{1000l} * \rho_{air} \tag{A.5. 4}$$

$$d(Mass\ H_2O\ Adsorbed) = dMass\ of\ Air * (\frac{RH_{inlet}}{100}) * \gamma_{air} - dMass\ of\ Air * (\frac{RH_{outlet}}{100}) * \gamma_{air} \tag{A.5. 5}$$

$$d(Energy\ Released) = dMass\ of\ Air * (T_n - T_{n-1}) * Cp_{air} = Q = m * Cp_{air} * \Delta T \tag{A.5. 6}$$

The total amount of water adsorbed/desorbed and the total amount of energy released/absorbed during the entire experiment is calculated by Equation A.5.7 and Equation A.5.8.

$$Total\ Energy\ Released = \sum_{i=0}^{n} d(Energy\ Released)_n \tag{A.5. 7}$$

$$Total\ H_2O\ Adsorbed = \sum_{i=0}^{n} d(Mass\ H_2O\ Adsorbed) \tag{A.5. 8}$$

Overall system parameters like Heat of adsorption, adsorbent capacity for water and energy density are calculated by Equation A.5.9, Equation A.5.10 and Equation A.5.11.

$$\Delta H_{ads} = \frac{Total\ Energy\ Released}{(Total\ H_2O\ Adsorbed * \frac{1000g}{18g/mol})} \qquad \textbf{A.5. 9}$$

$$Adsorbent\ Capacity = \frac{Total\ H_2O\ Adsorbed}{m_{ads}} \qquad \textbf{A.5. 10}$$

$$Energy\ Density = \frac{Total\ Energy\ Released}{Column\ Volume} \qquad \textbf{A.5. 11}$$

Finally, the storage efficiency of the entire system is calculated by Equation A.5.12.

$$\eta = \frac{Energy\ Released_{(Adsorption)}}{Energy\ Inputted_{(Regeneration)}} \qquad \textbf{A.5. 12}$$

Appendix 6: Energy balance calculations for efficiency

The following tables outline the energy use calculations for different work done in the system during adsorption and desorption experiments. The compressor efficiency is assumed to be 70% for the air flow.

Table A.6. 1: 24 l/min Adsorption Run Energy Audit

Energy input from Flow of Air		
Flow rate (l/min)	24	l/min
Flow rate (m^3/s)	0.0004	m^3/s
Mass flow rate	0.00046	kg/s
Superficial velocity in column	0.442	m/s
Superficial velocity in tube	21.92	m/s
Experimentally measures pressure drop	17.43	kpa
Power required	10	W
Energy Used	72000	J
Energy input from Evaporation		
Amount of water that will be adsorbed into the adsorbent	16	g
Enthalpy of evaporation at 21.7°C	2450.2	kJ/kg
Power required to vaporize water	5.44489	W
Energy Used	39203.2	J
Total Required Energy	10	
Duration of the experiment	120	min
Total energy used	111203	J

Table A.6. 2: 24 l/min Desorption Run Energy Audit

Energy input from Flow of Air		
Flow rate (l/min)	24	l/min
Flow rate (m^3/s)	0.0004	m^3/s
Mass flow rate	0.000465	kg/s
Superficial velocity in column	0.442	m/s
Superficial velocity in tube	21.92	m/s
Experimentally measures pressure drop	17.43	kpa
Power required	10	W
Energy Used	54000	
Dehumidification		
Water vapour through the system (100% RH)	0.02	kgH2O/s
Starting Relative Humidity of air	50%	
Required Power	11.39705	W
Energy that needs to be removed from system	61544.07	J
Energy Input from Heating	29.62963	W
	160000	J
Total Extra Energy from flow and evap	51.02668	W
Duration of the experiment	90	min
Total energy used	275544.1	J

Table A.6. 3: 8 l/min Adsorption Run Energy Audit

Energy input from Flow of Air		
Flow rate (l/min)	10	l/min
Flow rate (m^3/s)	0.00017	m^3/s
Mass flow rate	0.00019	kg/s
Superficial velocity in column	0.442	m/s
Superficial velocity in tube	21.92	m/s
Experimentally measures pressure drop	5	kpa
Power required	1	W
Energy Used	15000	J
Energy input from Evaporation		
Amount of water that will be adsorbed into the adsorbent	16	g
Enthalpy of evaporation at 21.7oC	2450.2	kJ/kg
Power required to vaporize water	2.61355	W
Energy Used	39203.2	J
Total Required Energy	3.61355	
Duration of the experiment	250	min
Total energy used	54203.2	J

Table A.6. 4: 8 l/min Desorption Run Energy Audit

Energy input from Flow of Air		
Flow rate (l/min)	8	l/min
Flow rate (m^3/s)	0.000133	m^3/s
Mass flow rate	0.000155	kg/s
Superficial velocity in column	0.15	m/s
Superficial velocity in tube	7.3	m/s
Experimentally measures pressure drop	5	kpa
Power required	1	W
Energy Used	15000	J
Dehumidification		
Water vapour through the system (100% RH)	0.02	kgH2O/s
Starting relative Humidity of air	50%	
Required Power	3.799017	W
Energy that needs to be removed from system	56985.25	J
Energy Input from Heating	10.66667	W
	160000	J
Total Extra Energy from flow and evap	15.46568	W
Duration of the experiment	250	min
Total energy used	231985.3	J

Pressure Drop Calculations:

The following outlines pressure drop modelling for the adsorption thermal energy storage system built for this thesis [N. de Nevers, Fluid Mechanics for Chemical Engineers, Third Edition, McGraw Hill, New York, 2005, 632 pages].

$$\mathrm{Re}_{pipe} = \frac{D \cdot v \cdot \rho}{\mu} \qquad \text{A.6. 1}$$

$$\mathrm{Re}_{porous\,media} = \frac{D_{particle} \cdot v_{fluid} \cdot \rho}{\mu(1-\varepsilon)} \qquad \text{A.6. 2}$$

$$f = 0.001375 \cdot \left[1 + \left(20{,}000\frac{\varepsilon}{D} + \frac{10^6}{\mathrm{Re}}\right)^{1/3}\right] \qquad \text{A.6. 3}$$

$$\Delta P = \frac{L}{D}\rho\left(4 \cdot f \cdot \frac{v^2}{2}\right) \qquad \text{A.6. 4}$$

Table A.6. 5: System Characteristics

	24 l/min (1/4" tube)	8 l/min (1/4" tube)	24 l/min (1/2" tube)
Diameter (m)	4.50E-03	4.50E-03	8.99E-03
Velocity (m/s)	21.92	7.3	4.6
Density (kg/m^3)	1.20	1.20	1.20
Viscossity (kg/s*m)	1.83E-05	1.83E-05	1.83E-05
Roughness "e" (in)	6.00E-05	6.00E-05	6.00E-05
Reynolds Number	6.49E+03	2.16E+03	2.73E+03
f (friction factor)	8.85E-03	1.21E-02	1.12E-02
Tube length (m)	5.60	5.60	5.60

Table A.6. 6: Fitting L/D Equivalent for friction factors

Fitting	# of Fittings	L/D Equivalent	Total L/D
Tee	3	20	60
Cross	1	20	20
Check Valve	2	110	220
90 elbow	8	20	160
45 elbow	1	15	15
Union	20	2	40
Total Fitting L/D			515

Table A.6. 7: Pressure Drop from fittings and Tubing Calculations

	24 l/min (1/4" tube)	8 l/min (1/4" tube)	24 l/min (1/2" tube)
Tube L/D	1,245.16	1,245.16	622.58
Total Fitting L/D	515.00	515.00	1,155.00
Total L/D	1,760.16	1,760.16	1,777.58
Pressure Drop (Pa)	18,026.17	2,723.76	1,018.82

Table A.6. 8: Pressure Drop from Packed Bed Calculations

	24 l/min (1/4" tube)	8 l/min (1/4" tube)	24 l/min (1/2" tube)
Internal diameter (m)	3.39E-02	3.39E-02	3.39E-02
Length (m)	0.07	0.07	0.07
superficial velocity (m/s)	0.45	0.15	0.45
Density (kg/m^3)	1.204	1.204	1.204
Viscossity (kg/s*m)	1.83E-05	1.83E-05	1.83E-05
e (in)	6.00E-05	6.00E-05	6.00E-05
Particle diameter (m)	1.00E-03	1.00E-03	1.00E-03
Porosity	0.1	0.1	0.1
Reynolds for Bed	32.95	10.98	32.95
f	7	11.5	7
dP (Pa)	7.05	1.29	7.05

Appendix 7: Prices from Adsorbent research

Email communication from SorbeadIndia:

Hi Dan,

These requirements are based on tomorrow need.

Pleased to Quote as you shall be buying for 220,000 lbs per grade [100 MT]

Molecular Sieves 13X beads 2-4mm $2.20 per Lbs FOB Toronto [Price valid till Nov 2007]

Molecular Sieves 13X beads 2-4mm $2.40 per Lbs FOB Toronto [Price valid from Nov 2007 -Aug 2008]

Silica Gel Beads 2-5mm $1.50 per Lbs FOB Toronto
[Price valid till Nov 2007]
Silica Gel Beads 2-5mm $1.75 per Lbs FOB Toronto
[Price valid from Nov 2007 -Aug 2008]

Please Note:
All custom clearance charges & Insurance, shall be Bourne by you. Delivery -Within 10-12 weeks from order confirmation for full quantities. Payment- 40% advance balance against 100% Irrevocable LC at sight terms.

Please do let me know your comment & please do not hesitate to ask for anything.

Thank you for the email, Please see the price for the two products you would like to use for your trials.
SILICA GEL CLEAR BEADS 2-4 mm
STANDARD PACK: 35 LBS PAIL
PRICE : $ 139.00/PAIL.

MOLECULAR SIEVES 13 X BEADS 2-4mm
STANDARD PACK: 25 KG DRUMS(55 LBS)
PRICE: $ 220.00/DRUM

SHIPPING EXTRA
TAXES AS APPLICABLE
PAYMENT TERMS: CREDIT CARD /CHEQUE

Please advice

Thanks
anita

Email communication from Grace

Gentlemen, I can provide the pricing for the 13X easily as this is a standard product. The silica gel is a made to order product thus I need to confirm pricing with our Product Manager who is currently on Holidays.

Hans and I spoke again and we wish to reiterate our concerns that the system would be able to achieve cooling 30°C. Our history shows the limit to generally be in the 50-60°C range. I am not sure that I am explaining this as fully or as eloquently as Herr Hoefer could.

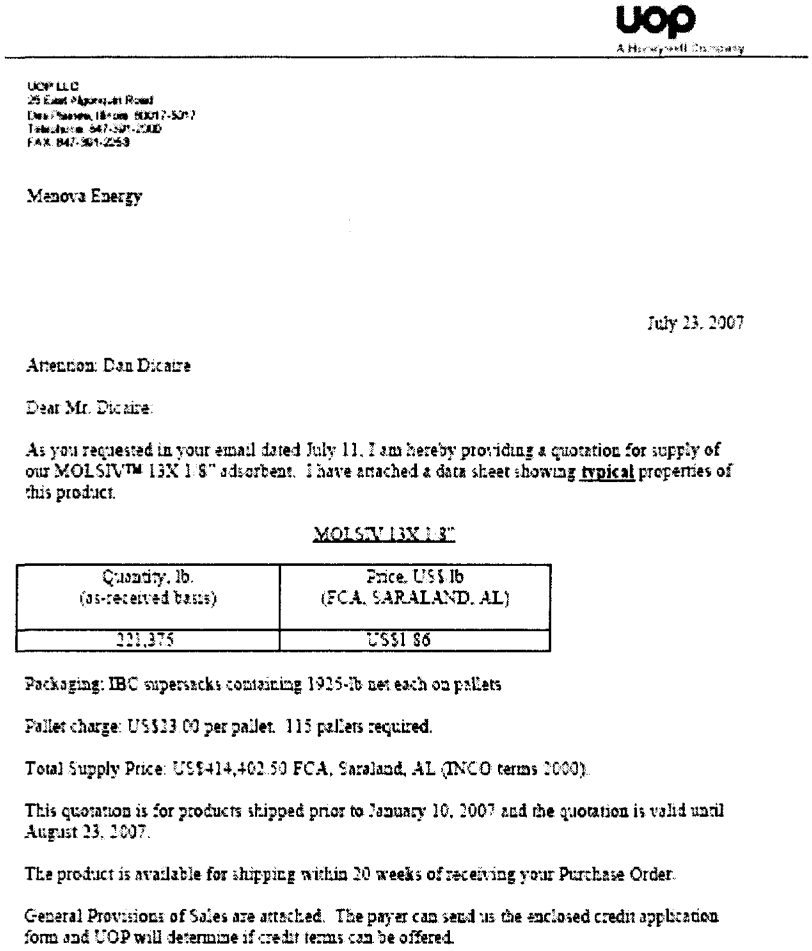
Regarding the 13X: For a 100 ton (short or metric!) release pricing would be

Sylobead® 544HP (nominal 8x12 mesh) or ca. 2.3 mm average bead size : $US1.72 per lb., FOB Elkridge (Baltimore, MD) packaged in 1,800 lb. supersacks.
Sylosiv® A10 powder (pure) zeolite : $US4.10 per lb., FOB Elkridge (Baltimore, MD) packaged in 15 kg bags.

These items may be dutiable upon importation to Canada. These prices are valid until 15th OCT 2007. A price increase may be possible after that date.

I hope to have the response on Gel pricing early next. Kind regards, John McNichol

Quote from UOP



UOP
A Honeywell Company

UOP LLC
25 East Algonquin Road
Des Plaines, Illinois 60017-5017
Telephone 847-391-2000
FAX 847-391-2253

Menova Energy

July 23, 2007

Attention: Dan Dicaire

Dear Mr. Dicaire:

As you requested in your email dated July 11, I am hereby providing a quotation for supply of our MOLSIV™ 13X 1/8" adsorbent. I have attached a data sheet showing **typical** properties of this product.

MOLSIV 13X 1/8"

Quantity, lb. (as-received basis)	Price, US$/lb (FCA, SARALAND, AL)
221,375	US$1.86

Packaging: IBC supersacks containing 1925-lb net each on pallets

Pallet charge: US$23.00 per pallet. 115 pallets required.

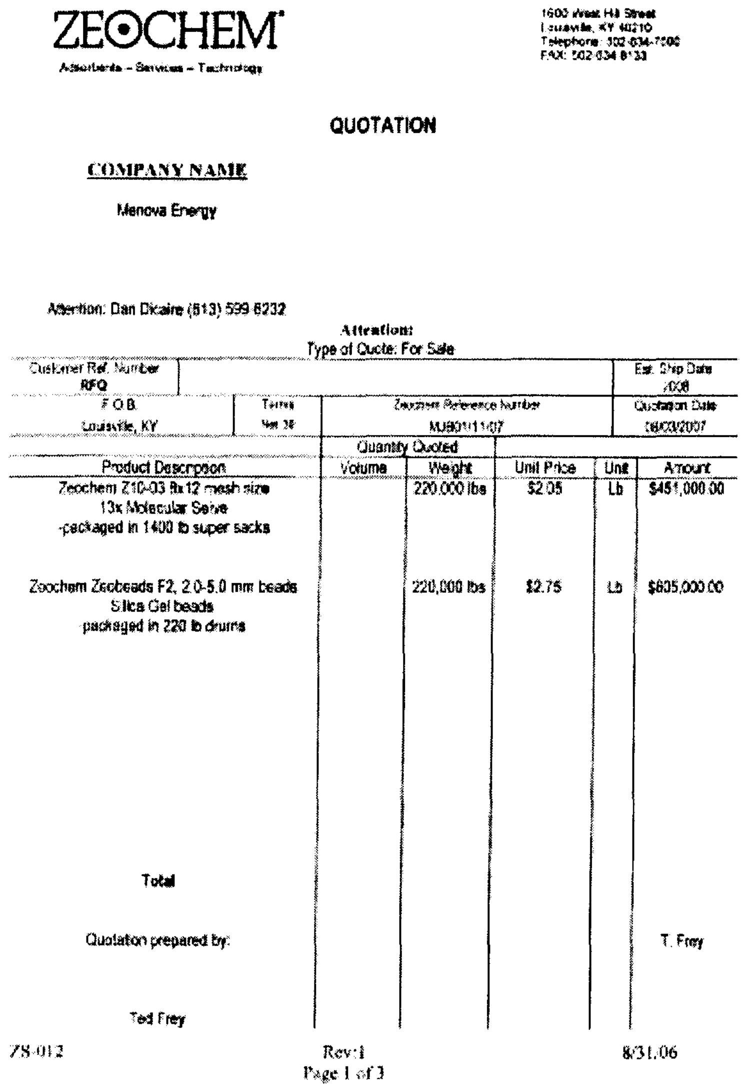
Total Supply Price: US$414,402.50 FCA, Saraland, AL (INCO terms 2000).

This quotation is for products shipped prior to January 10, 2007 and the quotation is valid until August 23, 2007.

The product is available for shipping within 20 weeks of receiving your Purchase Order.

General Provisions of Sales are attached. The payer can send us the enclosed credit application form and UOP will determine if credit terms can be offered.

Quote from Zeochem



ZEOCHEM®
Adsorbents – Services – Technology

1600 West Hill Street
Louisville, KY 40210
Telephone: 502-634-7600
FAX: 502-634-8133

QUOTATION

COMPANY NAME

Menova Energy

Attention: Dan Dicaire (613) 599 6232

Attention:
Type of Quote: For Sale

Customer Ref. Number RFQ			Est. Ship Date 2008
F.O.B. Louisville, KY	Terms Net 30	Zeochem Reference Number MJB0111107	Quotation Date 08/03/2007

Product Description	Quantity Quoted Volume	Quantity Quoted Weight	Unit Price	Unit	Amount
Zeochem Z10-03 8x12 mesh size 13x Molecular Seive -packaged in 1400 lb super sacks		220,000 lbs	$2.05	Lb	$451,000.00
Zeochem Zeobeads F2, 2.0-5.0 mm beads Silica Gel beads packaged in 220 lb drums		220,000 lbs	$2.75	Lb	$605,000.00
Total					
Quotation prepared by:					T. Frey
Ted Frey					

ZS-012 Rev:1 8/31/06
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