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Abstract

As the worldwide energy demand continues to increase, scientists and engineers are faced with the increasingly difficult task of meeting these needs. Currently, the major energy sources, consisting of oil, coal, and natural gas, are non-renewable, contribute to climate change, and are rapidly depleting. Renewable technology research has become a major focus to provide energy alternatives which are environmentally-friendly and economically competitive to sustain the future worldwide needs. Thermal energy storage using adsorption is a promising technology which can provide energy for heating and cooling applications using solar and waste heat sources. The current work aims to improve adsorption systems to provide higher energy outputs and therefore, more economical systems. New adsorbents and operating conditions were tested with the goal of storing the available energy more efficiently. A model was also developed to gain a better understanding of the adsorption system to improve this developing technology.
Sommaire

Comme la demande énergétique mondiale continue d’augmenter, les scientifiques et ingénieurs sont confrontés à la tâche difficile de répondre à ces besoins. Présentement, les sources d’énergies principales, comprenant l’huile, le charbon et le gaz naturel, sont non renouvelables, contribuent au changement climatique, et diminuent rapidement. La recherche de technologie renouvelable est devenue un objectif majeur afin d’obtenir des alternatives énergétiques pour soutenir les besoins futurs. Le stockage d’énergie thermique par adsorption est une technologie qui peut fournir de l’énergie pour le chauffage et le refroidissement utilisant des sources de chaleur solaire et résiduale. Ce travail vise à améliorer les systèmes d'adsorption actuels pour augmenter leurs sorties d’énergie et obtenir des systèmes plus économiques. Des nouveaux adsorbants et conditions opératoires ont été testés pour emmagasiner l’énergie disponible de façon plus efficace. Un modèle a également été développé pour acquérir une meilleure compréhension du système d'adsorption pour améliorer cette technologie en développement.
Statement of Contribution of Collaborators

I hereby certify that I am the author of this thesis. The experimental work, the data analysis and the writing of articles was completed under the supervision of Dr. F. Handan Tezel at the University of Ottawa.

Chapters 2, 3 and 4 were completed and written entirely by me, with editorial comments from Dr. Tezel. Chapter 2 was prepared for submission as a review article to the Renewable & Sustainable Energy Reviews Journal. Chapter 4 is a journal article that was submitted to the Journal of Energy Storage.

Chapter 5 was completed in collaboration with Patrice Amyot, an undergraduate student, who assisted in the model development in MATLAB. The parametric study, analysis, and writing of this article was completed by me, with editorial comments from Patrice and Dr. Tezel. This paper was submitted to the Industrial & Engineering Chemistry Research Journal.

Appendix A is an article submitted to the Renewable Energy Journal. The first author of this work is Daniel Dicaire, who completed the experimental sections and writing of the first manuscript in partial fulfillment of his M.A.Sc. degree. My contributions to this work included expanding on the literature review, correcting and improving the data analysis, and submission of the paper to the journal. I am second author for this paper and therefore, it is provided in Appendix A.
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Chapter 1 - Introduction

1.1 General Background

According to the International Energy Agency, the total worldwide energy requirements have been steadily increasing throughout the past decades due to population growth and increased quality of life. Approximately 80% of the energy used is obtained from oil, coal, and natural gas, all of which are non-renewable and are rapidly depleting [1]. These fuel sources release significant greenhouse gas emissions, including carbon dioxide, carbon monoxide, sulphur oxides, nitrogen oxides, and particulate matter, which pollute the environment and have been shown to contribute to climate change [2]. As a result, much research and development has been dedicated to developing new technologies that are renewable, environmentally-friendly, and economically competitive to sustain the future energy needs. Renewable technologies are favourable as they can naturally replenish themselves and have the potential to provide energy security for future generations. Currently, renewable technologies account for approximately 19% of the global energy consumption from sources including biomass, hydroelectricity, wind, solar and geothermal [3]. These renewable sources have successfully been used to provide significant amounts of energy, demonstrating their achieved potential. With continued development, renewable technologies will become much more significant contributors of energy sources in the future.

One of the leading renewable technologies is energy storage from solar sources, which harnesses energy when it is available to store for later use. Energy storage is important because it allows for the correction between the supply and demand of intermittent energy supplies. There are many benefits of storing energy which include avoided costs due to the reduction of reliance on fossil fuels, increased revenue from the utilisation of available energy, reduced environmental emissions, and achieved energy security [4-6]. The storage of energy allows for its use to redistribute current energy systems for more efficient operations [7].

There are many technologies both existing and under development for energy storage applications. The current thesis examines thermal energy storage technology whereby energy is
captured and released in the form of heat. The sources under investigation for thermal inputs include solar heat and waste heat. One of the main challenges for the use of thermal energy is its high fluctuations in availability [8]. Therefore, capturing the energy efficiently when it is available is essential for the success of the storage technology. The current work investigates adsorption, a thermo-chemical process used to charge, store and discharge thermal energy. Thermo-chemical systems are desirable as they have high energy densities and therefore, can have smaller volumes, making them suitable for many applications [9]. Also, thermo-chemical systems store the available energy in the form of a chemical potential, therefore, it does not degrade over time, making this technology suitable for long-term storage [10].

1.2 Adsorption Technology for Thermal Energy Storage

Adsorption technology involves the binding of a fluid, the adsorbate, on the surface of a solid or porous material, the adsorbent. This process uses an exothermic adsorption step to release the energy, and an endothermic desorption (regeneration) step to store the energy. The major benefits of adsorption systems for thermal energy storage include their high energy densities, negligible heat losses, and continuous cyclic operation [11]. During regeneration, heat is provided to the system and stored in the adsorbent material, which represents the charging of the system. During adsorption, the adsorbate is contacted with the adsorbent to release the energy stored in the material. Adsorbent materials are porous in nature and thus have high surface areas with many adsorption sites to store large amounts of heat. Research is ongoing to determine the best adsorbent materials for energy storage which provide high heats of adsorption, high energy densities, high adsorbent capacities, low regeneration temperatures, and low environmental impacts.

Currently, the best adsorbents provide energy densities ranging from 226-309 kWh/m$^3$ using zeolite 13X and activated alumina hybrids with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition [11]. These materials include impregnated adsorbents and adsorbents with alkaline additions, which provide an
increased driving force for adsorption. These high energy densities were achieved using energy intensive conditions and air containing 100% humidity which place large energy constraints on the process. Research is ongoing to determine suitable adsorbent materials, favourable operating conditions, and accurate models to describe the thermal energy storage process.

1.3 Thesis Objectives

The purpose of this thesis is to further the research in the area of thermal energy storage using adsorption to contribute to the understanding of the current systems. To accomplish this, the specific goals for the work are as follows:

- Conduct a literature review of the previous work completed in this field for submission as a review article.
- Synthesize a new anhydrous magnesium carbonate that contains desirable adsorption properties which include a high water adsorption capacity and a low regeneration temperature.
- Test the synthesized adsorbent in the thermal energy storage system to evaluate its adsorption performance.
- Screen various adsorbents for their ability to store thermal energy and test these selected adsorbents at less energy intensive conditions, which include reduced regeneration temperatures and reduced relative humidity environments.
- Develop a mechanistic model in MATLAB describing the material and energy balances within the adsorption system and validate the model using experimental data.
- Use the developed model to conduct a parametric study to analyze the effect of varying parameters and their impact on the overall thermal energy storage system.
1.4 Thesis Structure

Chapter 2 of the current work is a review article entitled “A review of energy storage technologies with a focus on adsorption thermal energy storage processes for heating applications” which was submitted to the Renewable & Sustainable Energy Reviews Journal in July 2015. This article provides a review of the lab-scale work done in this field and presents a table summarizing the energy densities achieved to date for adsorption energy storage systems, the first compilation of this kind. It also presents the pilot-scale applications of this technology. This chapter serves as a general introduction to the thesis work.

Chapter 3 presents the synthesis of an anhydrous magnesium carbonate and its use for thermal energy storage applications. This chapter describes the synthesis procedure, characterization, and testing of the synthesized adsorbent. The novelty of this study includes the use of anhydrous magnesium carbonate for thermal energy storage systems.

Chapter 4 is a paper entitled “Adsorbent Screening for Low Relative Humidity Environments for Thermal Energy Storage of Solar and Waste Heat” which was submitted to the Journal of Energy Storage in December 2015. This paper presents the study of various adsorbents at low ambient humidity environments to assess their performance at these operating conditions in comparison to traditional energy intensive conditions. The selected adsorbents were tested for varying operating conditions to obtain thermal systems with higher energy efficiencies which require a reduced energy input.

Chapter 5 is a paper entitled “Adsorption Prediction and Modeling of Thermal Energy Storage Systems: A Parametric Study” which was submitted to the Industrial & Engineering Chemistry Research Journal in December 2015. This article presents the development of a mechanistic model that describes the material and energy balances in the adsorption system. The model was validated using experimental data and was used to conduct a parametric study. This unique study provides an understanding of the adsorption parameters and their effect on thermal energy storage performance.
Chapter 6 summarizes all of the main findings and contains general conclusions from all of the work completed. It also contains recommendations of future work.

Appendix A contains an article entitled “Improvements to Adsorption Thermal Energy Storage Systems using Hydrated Salt Impregnation” which was submitted to the Renewable Energy Journal in July 2015. This work describes the use of adsorbents impregnated with salt hydrates for thermal energy storage systems. Using lithium chloride, an energy density of 309 kWh/m$^3$ was achieved, currently, the highest value reported in the literature.

Appendix B contains the calculations used for the thermal energy storage system.
1.5 References


Chapter 2 - A Review of Energy Storage Technologies with a focus on Adsorption Thermal Energy Storage Processes for Heating Applications

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Abstract
With depleting reserves of traditional fuels, there is a worldwide demand for alternative energy solutions. One of the most promising developing technologies is energy storage, as it provides the benefit of capturing available energy for use at a later time. This paper gives an overview of the numerous forms of energy storage technologies under investigation and development, with a focus on thermal energy storage through adsorption. The current materials tested for adsorption energy storage capabilities are presented together with their corresponding performances. Furthermore, the demonstrative projects and systems that currently use this technology are presented. Although thermal energy storage using adsorption processes is not currently economically viable, with continued material development and system optimization, this technology has the potential to become competitive in the near future.

Submitted to the Renewable & Sustainable Energy Reviews Journal
2.1 Introduction

The worldwide energy requirement has more than doubled from 1970 to the present according to the International Energy Agency [1]. The increased energy use is attributed to many factors including population growth and increased prosperity. Over 80% of the energy used is derived from natural gas, oil, and coal [2]. Consequently, the worldwide carbon emissions have also more than doubled since 1970, which pollute the environment and contribute to global warming. Furthermore, these fuel sources are non-renewable and are continuously being depleted. Natural Resources Canada predicts that heating during the winter will become more challenging if fossil fuel prices rise in the future, which is likely to occur due to their depletion [3].

In order to reduce the use of natural gas, oil and coal, and thus reduce their environmental impact, renewable energy sources are being investigated. Renewable energy sources have recently been developed to a point where they have the potential and capability to significantly impact current technology [4]. These resources have the ability to naturally replenish themselves, and, if extracted at a reasonable price, could provide the energy required to sustain the worldwide energy needs [5]. Renewable energy sources include wind power, hydropower, solar, biomass, biofuel, and geothermal energy [1]. These sources of energy are sustainable as they can be relied on in the future, and their use could present a significant reduction of the current environmental and social impacts of traditional fuels [5]. Although this area of research has been pursued for decades, the recent emphasis placed on its importance has resulted in its prevalence. Currently, approximately 17% of the total global energy is derived from renewable sources [5]. The main contributors include biomass and hydro, however, wind and solar energy are expanding and with continued research and development, will have a more significant contribution [5].

With the current state of the environment and the continuous energy requirements, renewable energies are a promising solution for a safe and environmentally compatible energy supply. The main challenge remains in developing technologies that can efficiently make use of the available renewable energy sources. One of the leading areas of interest is energy storage, as it allows for the correction between the supply and demand of available energy. This paper
presents an overview of the energy storage technologies under investigation with a focus on adsorption processes for thermal energy storage. The materials under development, as well as the pilot-scale operations are presented to evaluate their capabilities and performances for energy storage.

2.2 Energy Storage Technologies

The ability to use many renewable energy sources, such as solar energy, is strongly dependent on the efficiency of the storage process. As a result, the energy storage processes are the main focus for the implementation of many renewable sources [6]. Storage is required to capture the energy when it is available to use at a later time. In order for energy storage technologies to be applicable, economically competitive, and reliable, systems and materials need to be developed to ensure that renewable energy sources reach their full potential [7].

Energy storage is a promising renewable energy solution that can contribute to the societal need for efficient and environmentally safe energy for many applications including building heating and cooling, and utility applications [4]. The benefits of energy storage systems include [4, 8]:

- reduced energy costs
- redistributed energy
- reduced initial and maintenance costs
- conservation of fossil fuels
- improved energy security
- reduced environmental emissions.

There are a variety of energy storage technologies that exist including mechanical, chemical, electrostatic, magnetic, biological, and thermal. Energy storage can be divided into two categories, short-term storage and long-term storage, depending on the length of the storage period [9]. Energy storage technologies not only benefit the environment through the reduction
in greenhouse gas emissions, they can also provide significant monetary savings [10]. The following sections give an overview of the main types of energy storage technologies under investigation, with a focus on thermal energy storage.

2.2.1 Mechanical Energy Storage

Mechanical energy storage systems typically operate by converting electricity into various forms of energy [4]. However, these systems generally have a significant energy penalty of up to 50% due to system inefficiencies. Hydrostorage is a simple mechanical energy storage system that operates based on the demand requirements. When the demand for energy is low, such as during the night, the water is pumped upward from a river to a reservoir to be released when the energy demand is high, such as during the day [11]. When the water is released from the reservoir, it drives turbines and thus produces electricity. Although hydrostorage is a proven technology, there are many developments being explored to overcome some of its limitations which include reserve size restrictions, landscape impacts and efficiency losses [11].

Compressed-air storage is another form of mechanical energy storage where air is compressed when the energy demand is low and stored in a large reservoir which could be either naturally occurring or man-made [8]. When the energy is required, the air is released from the reservoir and drives a gas turbine generator [4]. This technology is not currently used in many applications due to several limitations which include; difficulty in obtaining appropriate geographical location, non-independence of the system that requires gas turbine plants for effective operation, hazardous nature of compressed gas reservoirs, and environmental concerns [8].

Flywheels are another type of mechanical energy storage system. They use electric energy as an input and store energy in kinetic form [12]. When the stored energy is required, the kinetic energy is converted into electricity. Flywheels are typically operated in vacuum to reduce the effect of drag force [12]. They are used in many applications and are continuously being developed in order to make them suitable at a larger scale.
2.2.2 Chemical Energy Storage

The storage of energy through reversible chemical reactions is a developing research area whereby the energy is stored in chemical form [4]. In chemical energy storage, energy is absorbed and released when chemical compounds react. The most common application of chemical energy storage is in batteries, as a large amount of energy can be stored in a relatively small volume [13]. Batteries are referred to as electrochemical systems since the reaction in the battery is caused by electrical energy [4]. Batteries have been developed to the point where they can now provide significant capabilities, such as the lithium-ion batteries used in electric cars [14]. These types of batteries have largely improved performances and are now being incorporated into electric and hybrid vehicles. However, in comparison to other energy storage methods, batteries have slow power delivery and thus their use is not always appropriate [13].

Electricity is used in conjunction with chemicals for other applications such as for the production of hydrogen through the electrolysis of water. Energy can also be stored in various types of fuels, which when combusted, release their energy. This type of energy storage requires the production of the fuel itself, and the amount of energy available is dependent on the chemical composition of the material combusted. Another form of chemical energy storage that has been investigated is the storage of the energy available from direct sunlight through photochemical processes [15]. Attempts have been made to utilize the photosynthesis technique, which is used naturally by plants, to store energy. However, it has been difficult to replicate this energy storage mechanism due to the materials and steps involved, which result in significant losses [15]. Chemical energy storage systems are continuously being investigated to increase efficiencies and meet the energy requirements.

2.2.3 Electrostatic Energy Storage

Electrostatic energy storage through electrical medium has been accomplished using capacitor and supercapacitor energy storage technologies [8]. These systems operate on the principle that energy has the ability to be stored in the form of electric charges between two
metal or conductive plates that are separated by an insulating or dielectric medium through an applied voltage [8]. The storage capability of the system, therefore, depends on the size of the plates, their distance of separation, and the material selection [8]. It is important to consider not only the amount of energy that is available from the electrostatic storage, but also the quality of that energy, the voltage at which it is available [16]. Capacitors and similar devices may be more useful to smooth out short-term variations in electrical energy flows rather than for bulk energy storage applications [15]. Although research on the applications of these systems is ongoing, the high costs and low energy densities available from this technology presents major limitations.

2.2.4 Magnetic Energy Storage

Magnetic energy storage is an emerging technology whereby energy is stored in a magnetic field. The developments in magnetic energy storage include material advancements for the utilization of superconducting materials, which at low temperatures, have minimal electrical resistance [4]. The reduction of electrical resistance allows large currents to be transferred with minimal losses [4]. The amount of energy that can be stored in magnetic form is dependent on the intensity of the magnetic field and the permeability of the material [16]. There are several significant advantages of magnetic energy storage systems including practically no heat losses, and rapid discharging times [15]. However, the energy densities available from this technology are not yet comparable to the amounts achieved through chemical batteries [14]. Research in this area is ongoing to determine the suitability and economic feasibility of magnetic energy storage systems.

2.2.5 Biological Energy Storage

Biological energy storage has also been investigated through the breakdown of glucose by enzymes. The energy released from this breakdown process can be stored in a bio-battery storage system [8]. In this application, glucose is the energy source and therefore, the capacity
of the system depends on the glucose source provided. Common glucose sources include old papers, soda, living organisms, or natural sugar [8]. The material is converted using enzymes to produce protons and electrons, thereby producing electricity [8]. Lee et al. investigated the energy-storage mechanism of flavins, an organic compound produced in the mitochondria and chloroplasts, which have large energies stored in their chemical bonds. They found that modifications of the flavin molecule can improve its energy storage performance and could perform functions analogous to that of current batteries [17]. The research performed by Lee et al. has confirmed that natural living systems provide an opportunity to design sustainable energy storage processes. This type of battery development has received increasing interest and although it presents some limitations, has the potential to be applicable in many areas with further development.

2.2.6 Thermal Energy Storage

Thermal energy storage will be the main focus for energy storage technologies in this review article. Thermal energy storage has been extensively investigated as an environmentally-friendly technology. The storage of thermal energy is mainly required due to the inconsistency between the available energy supply and demand. A thermal energy storage system would store the intermittent energy when it is available to be used when it is needed. Solar energy is an example of an intermittent energy source where availability varies depending on the time of day and season. Therefore, the solar energy could be captured and stored during the daytime and in the summer months to be used during the nighttime and the winter months. The high fluctuations in the availability of solar energy present a major challenge for systems to store and use this resource effectively [6]. This process should be accomplished with little thermal energy loss and high extraction efficiency of the stored energy [4]. The investigations of thermal energy storage use the energy available as heat, as opposed to converting it to electricity.

Long-term heat storage is one of the main challenges for effective use of the energy available year round [18]. The three main types of thermal energy storage systems are sensible heat, latent heat, and thermo-chemical. All thermal energy storage systems have the same basic principles.
The excess energy is stored in a system for use at a later time. The main variations in the thermal energy storage systems are the scale and the storage method used [4]. The capacity of the system varies depending on the amount of time that the energy requires storage. Figure 2-1 provided by Dincer and Rosen [4] gives the three basic steps required for thermal energy storage systems; charging, storing, and discharging. The three steps presented in Figure 2-1 are repeated in a cyclic process as the energy supply and demand vary. $Q_1$ represents heat loss to the surroundings, which can occur in any of the three steps. The applications of this technology include space heating, hot water heating, and cooling [4]. The selection of a suitable thermal energy storage system depends on many factors including [19]:

- storage duration
- economics
- supply and demand temperature requirements
- storage capacity
- heat losses
- available space.

![Figure 2-1: Basic principle of thermal energy storage systems [4].](image)
The two most extensively studied types of thermal energy storage are sensible heat and latent heat. Both types are promising for energy storage and are at an advanced stage of development, whereas thermo-chemical storage systems are at the initial stages of development. However, both latent heat and sensible heat systems lose thermal energy over time to the surroundings and therefore, are not currently suitable for storing thermal energy on a long-term basis [20]. The various types of thermal energy storage systems will be discussed individually, with an emphasis placed on thermo-chemical energy storage systems.

### 2.2.6.1 Sensible Energy Storage

In sensible heat storage systems, the thermal energy is stored through temperature changes in a material. The feasibility of this storage method depends strongly on the mass, heat capacity, material stability, material cost, temperature differential, and system insulation [21, 22]. The main applications of sensible heat storage are divided into two categories: liquid media and solid media. Liquid media includes hot water storage, oil based fluids, and molten salts, whereas solid media includes metals and rock filled storage [7, 23]. In sensible energy systems, the storage is accomplished using various methods including boreholes, aquifers, and cavern storages [2].

Thermal energy storage technologies using sensible heat have been developed for a wide variety of applications. One of the most common types of thermal energy storage systems is hot water storage, as this technology is now used in most modern homes for domestic hot water storage [24]. Also, many thermal storage systems have been built using gravel for sensible energy systems [24]. Some materials, such as metals and graphite, have high diffusivities and thus are best suited for quick charging and discharging of energy rather than long-term storage [25]. Other materials such as bricks and stones take longer to heat and cool and thus would be better suited for applications that do not require a fast energy response.
Sensible storage technologies are generally low in cost and are one of the current most popular thermal energy storage technologies [21, 26]. The storage density is equal to the product of the mass, the specific heat of the material and the temperature change [19, 20]. However, these storage systems provide very low energy densities, between 10-50 kWh/m³ [21]. Some of the main disadvantages of low energy densities include the need for large storage volumes, as well as large storage containers [27]. Sensible heat storage systems also have significant heat losses to the surroundings during storage as a result of a temperature gradient [9]. Due to the sensitivity of the efficiency of the storage process, sensible energy storage systems are not the most effective technology for storing thermal energy.

2.2.6.2 Latent Energy Storage

In latent heat storage systems, heat is released or absorbed through changing the phase of a material at a constant temperature. The material takes up energy and melts when the temperature is raised above its melting point. For energy storage applications, the phase change typically occurs between liquid and solid states rather than with liquid and vapour states, as the liquid-solid systems require less volume change [24]. The storage of energy is possible due to the high enthalpy change that accompanies the phase change. Latent energy systems are typically composed of three parts: a heat storage material that undergoes phase change, a heat exchanging surface, and a container that encloses the material [26].

There are many known types of phase change materials that can be used for heat storage which have the ability to store 5-14 times more heat than sensible heat materials, and thus require smaller volumes [20]. Phase change materials are often selected based on their heats of fusion, and the temperature at which their phase change occurs [24]. The latent heat of fusion is defined as the amount of energy per unit mass that must be removed from a liquid to become a solid, which is the same amount of energy that can be applied to change the same solid to a liquid [24]. Some common phase change materials include ice, paraffin waxes, salts, fatty acids, and metals [24, 27]. Phase change materials can have very high energy densities depending on
their chemical structure and the temperature at which they are used. In 2004, the Energy Research Centre of the Netherlands (ECN) studied approximately ninety potential materials for energy storage. They determined that magnesium sulphate heptahydrate (MgSO$_4$·7H$_2$O) was one of the most promising materials for the seasonal storage of solar energy as it can provide a theoretical energy density of 778 kWh/m$^3$ [28]. The most common type of latent thermal storage system in use is ice storage systems, as water is an excellent thermal storage medium and has a high latent heat of fusion [24]. Another family of materials that has received much attention is salt hydrates. Salt hydrates have high densities and high latent heats, although they are highly unstable [24].

However, many of the phase change materials are better suited for steam production as opposed to space heating applications since they are used at high temperatures [7, 29]. There are several difficulties that arise from the use of phase change materials including; difficulty maintaining the material within the system, chemical instability, uncertainty regarding long-term thermal behaviour, reduced storage capacity from dilution effect, and increased costs [4, 7]. Further research and development remains to be done to obtain reliable and effective phase change materials.

### 2.2.6.3 Thermo-Chemical Energy Storage

An emerging technology which can overcome the barriers present in latent and sensible heat storage is thermo-chemical energy storage systems. These include thermo-chemical reactions and sorption processes, both of which obtain energy through a thermal supply. In thermo-chemical reactions, energy is stored through a reversible reaction and recovered when the reaction is reversed [19]. A study conducted by the ECN determined that the reversible chemical reaction of iron oxide and water to produce iron hydroxide (Fe(OH)$_2$) was theoretically a promising reaction for the seasonal storage of solar heat as it generated an energy density of 611 kWh/m$^3$ [28]. Although chemical reactions can provide high energy densities, they often require a catalyst to release the heat and control the reaction, and thus are not always desirable [24]. Sorption storage systems include both adsorption and absorption and are also considered.
to be thermo-chemical storage technologies as they are based on chemical processes [19]. Absorption is the phenomenon that occurs when a liquid or gas enters another material and is taken up by its volume. In storage applications, absorption usually involves a gas entering a liquid [20]. Contrarily, adsorption involves the binding of a gas or liquid on the surface of a solid or porous material.

Many thermo-chemical storage systems have higher energy densities than other thermal energy storage technologies which allow large amounts of energy to be stored in smaller volumes, making it more suitable for residential applications as shown in Figure 2-2. Also, the energy in the thermo-chemical systems is stored as a chemical potential, therefore, it does not degrade over time, making it an appropriate technology for long-term storage [21, 31]. Thermo-chemical energy can theoretically be stored indefinitely at near ambient temperature which makes this technology particularly attractive. High energy densities can be obtained from the reactions of various materials, including salts and salt hydrates, although these processes are not the focus of the current article. The focus will be placed on adsorption technologies for thermal energy storage.

![Figure 2-2: Comparison of volumes required for storing the annual energy needed for an energy-efficient house (1800 kWh) [30].](image-url)
2.2.6.3.1 Adsorption

Adsorption systems, unlike latent or sensible storage systems, require no thermal insulation for storage as the energy is stored through a chemical potential [32]. Adsorption involves the binding of a fluid on the surface of a porous or solid material, which uses an endothermic desorption (regeneration) process to store the energy, and an exothermic adsorption process to release the energy. Adsorption processes have high energy densities, negligible heat losses, and can be operated in a continuous cycle to store thermal energy. Adsorption operates on the principle that a gas or vapour (adsorbate) is captured by a solid or porous material (adsorbent) and binds to its surface during the adsorption step. Once the adsorbent is saturated with the adsorbate, and thus no more gas or vapour can bind to its surface, the adsorbent material must be regenerated. Desorption (regeneration) is the process of removing the bound gas or vapour from the surface to return the adsorbent to a state where it can repeat the adsorption process in a cyclic manner. Theoretically, a given amount of heat can be stored in an adsorbent material and later the exact same amount of heat can be extracted, without any loss [33]. Figure 2-3 presents the main principle of the adsorption and desorption (regeneration) steps of an adsorption process. When the adsorbent is being regenerated, heat is provided to the system, which represents the charging step. This thermal energy can be provided by either waste heat sources or solar energy to avoid the depletion of natural resources and environmental pollution. When the adsorbate binds to the adsorbent during the adsorption step, heat is released through this exothermic process which can be used for various applications, such as space heating.
The adsorption processes can be classified into two categories; physisorption and chemisorption. Physisorption is mainly a result of van der Waals forces acting between the adsorbate and the adsorbent [10]. Chemisorption involves chemical bonds from valence forces which are more difficult to break, and sometimes irreversible [10]. The research that has been conducted related to thermal energy storage, specifically using physisorption systems rather than chemisorption systems, will be further discussed in the current work.

Because adsorbents are porous materials with high surface areas, they have the ability to store large amounts of heat [33]. The heat released during the adsorption step is referred to as the heat of adsorption. The adsorption step represents the discharging of the system, as the energy from the exothermic adsorption process is released to a given source. There are many factors that affect the behaviour of the adsorbent bed, which include thermal and adsorption properties of the materials, bed geometry, particle size, and flowrate [34]. Some of these parameters are controlled during an experiment and some are characteristic of the materials used in the system.

Much efforts have been put forth to determine suitable adsorbent materials for thermal energy storage applications. The characteristics of an ideal adsorbent include [8, 19, 35, 36]:

- high energy density
- high energy efficiency
high heat of adsorption
- high adsorbent capacity
- high affinity between adsorbent and adsorbate
- high heat transfer rate in the system during adsorption
- low temperature of desorption
- low toxicity and low environmental impact of materials
- non-corrosive materials
- high stability of material and system.

It is ideal to have an adsorbent containing all of the aforementioned characteristics, however, the perfect adsorbent has yet to be developed. Research is ongoing to determine suitable materials and systems that meet the requirements of an adsorption thermal energy storage system. The laboratory-scale research that has been performed on adsorption thermal energy storage systems, as well as the pilot-scale operations will be presented and discussed.

2.2.6.3.2 Laboratory-Scale Research on Adsorption Thermal Energy Storage

Much effort has been put forth worldwide to investigate various adsorbents, adsorbates, and working pairs, to obtain the most desirable and efficient adsorption system. There are a variety of available adsorbents which include activated carbon, silica gel, synthetic zeolites, natural zeolites, and activated alumina, which can be combined with a variety of adsorbates including carbon dioxide, water, ammonia, and hydrocarbons. The heat released from the adsorption process is dependent on the adsorbate/adsorbent interactions which involve polarity, pore size, molecular size, surface area, presence of cations, pressure, and temperature [37]. It is therefore not surprising that much work has been done to better understand these parameters. There are significant differences in the literature between the theoretical energy densities and those actually obtained through experiments due to many factors which could include energy losses (hysteresis, heat losses to surroundings), space losses (geometry, volume changes), and
inefficiencies [38]. The most promising adsorbents investigated, as well as the resulting energy densities obtained will be discussed for a wide range of materials.

A laboratory-scale open loop adsorption energy storage system has been built by Dicaire and Tezel [37] at the University of Ottawa to study various adsorbent materials, system conditions, and storage capabilities. Using this system, they conducted a series of experiments to observe the dependency of the energy storage capability on the regeneration conditions including temperature, flowrate, and humidity. It was determined that the maximum energy density can be achieved when operating at 100% relative humidity for the adsorbents that Dicaire and Tezel tested. They also determined the importance of the system insulation on obtaining an accurate energy density measurement to minimize the heat losses to the surroundings during the charging and discharging of energy. Moreover, they found that the energy density of a material increases as the regeneration temperature increases up to a certain value, which is different for each unique adsorbent. The regeneration step is charging the system with energy while removing the water that is bound to the adsorbent. Therefore, by studying the regeneration temperature for various adsorbents, the optimal energy density can be achieved. Dicaire and Tezel [29] also tested various adsorbents using water as an adsorbate to determine the most suitable material for energy storage. They determined that a hybrid adsorbent of activated alumina and zeolite 13X (AA/13X) gave the highest energy density of 200 kWh/m$^3$ [29].

Ugur [21], investigated various hybrid absorbents using water as the adsorbate with the goal of obtaining higher energy densities. Combinations of activated alumina with zeolites and alkaline additions were tested with varying amounts of each component to determine the best composite materials. It was found that as the alkaline addition increases, the water affinity, the water adsorption capacity, and the energy density increase. Since zeolites have higher water adsorption capacities than aluminas, and aluminas have higher heats of water adsorption, the optimal combination of both materials can result in a desirable adsorbent for this application. Ugur reported an energy density of 226 kWh/m$^3$ using an adsorbent composed of activated alumina with a high amount of alkaline addition [21].
Gantenbein et al. [39] constructed an adsorption system to optimize various operating parameters. They also studied the mass transfer zones of the adsorbent bed to properly characterize its behaviour. Their system consisted of an adsorption column packed with zeolite 13X pellets using water as the adsorbate and they achieved an energy density of 106 kWh/m³ [39]. Shigeishi et al. [27] conducted experiments on various adsorbents including charcoal, activated alumina, silica gel and zeolites, to determine their suitability for solar energy storage using water as the adsorbate [27]. They concluded that zeolites are the preferred storage material due to their high energy density capacity. However, their comparative study provided estimates of energy densities based on adsorptive capacities and assumed temperature rises of 50°C [27].

SPF Switzerland (Institute for Solar Technology) conducted experiments on a solid closed adsorption storage system [40]. They tested zeolite 13X with water as the adsorbate, and obtained an energy density of 180 kWh/m³ for the material [41]. Dawoud et al. [42] also performed experiments using zeolite 13X and water and obtained an energy density of 85.5 kWh/m³. Although the experiments by SPF Switzerland and Dawoud et al. used the same adsorbate/adsorbent working pair, the energy densities reported are significantly different due to the operating parameters used in the system. These results show the importance of reporting the operating conditions and system parameters together with the energy density value obtained as energy density is not a state function of the adsorbent, it must be defined with the corresponding operating conditions. Janchen and Stach [43] studied the applicability of chabazite type SAPO (SAPO-34), dealuminated faujasite type zeolite NaY 7, and mesostructured aluminosilicate (MCM-41) using water as the adsorbate in comparison to conventional adsorbents. However after testing the various synthesized adsorbents, the highest energy density reported by Janchen and Stach was achieved by a conventional zeolite NaX adsorbent.

Another group of adsorbent materials includes composite materials which are made of porous materials impregnated with salt hydrates. These composite materials offer several advantages which include low desorption temperatures, low prices, and simple production methods [44]. Posern and Kaps [44] studied the effect of salt impregnation in porous materials and concluded that the presence of the salt results in a higher water uptake rate and capacity.
The higher heat released from this process results in a higher temperature lift which is particularly important for heating applications [44]. They concluded that the optimal ratio of salt and porous material need to be determined, as well as the combination of different types of salts for impregnation.

Dicaire et al. [45] studied the effect of salt impregnation on energy density. The selected adsorbent was a zeolite 13X and activated alumina hybrid impregnated with magnesium sulphate, magnesium chloride, and lithium chloride using water as the adsorbate. The results obtained indicate that on average, the impregnated adsorbent had an energy density increase of 25% compared to the unmodified adsorbent. The highest performing impregnated adsorbent was impregnated with lithium chloride and gave an energy density of 309 kWh/m³, which represents a 50% increase over the unmodified adsorbent [45]. This laboratory-scale experiment reports the highest energy density achieved experimentally in the literature. Although these salt impregnated adsorbents have increased energy densities, the salt present in the material was unstable and thus unreliable for repeated energy storage applications.

Janchen et al. [46] studied the behaviour of ion exchanged zeolites and mesoporous materials, impregnated with hygroscopic salts using water as the adsorbate. They determined that the adsorption capacities and the heats of adsorption of the zeolites were increased through ion exchange with ions of different sizes and charges. They also observed much lower temperature lifts for the mesoporous materials than for the zeolites, which are microporous [46]. Aristov et al. [47] also studied composite materials for water adsorption applications including composites of hydroscopic salts and porous matrices with open pores. These materials possess intermediate behaviour between the salt and the porous material and thus their water adsorption properties can be controlled by combining various amounts of each component in the adsorbent. As a result, the behaviour of the composite can be altered by changing the porous structure of the matrix (varying the components) or by changing the chemical nature of the impregnated salt [47]. They tested composites of mesoporous and microporous silica gel with calcium chloride and lithium bromide salts and experimentally determined that salt impregnated matrices have a much higher water uptake than pure silica gel. It was also found that almost all
of the moisture can be removed during regeneration at relatively low temperatures of 110 to 120°C, which makes this composite material attractive for energy storage applications.

Hongois et al. [48] investigated a composite adsorbent of zeolite 13X impregnated with magnesium sulphate for long-term thermal energy storage using water as the adsorbate. They were able to obtain an energy density of 166 kWh/m³ using this composite adsorbent which they refer to as ZM15 (15 wt% MgSO₄ with zeolite) which gives an increase of 27% in energy density in comparison to a pure zeolite. Zhu et al. and Wu et al. synthesized silica gel impregnated with 30% calcium chloride and obtained a maximum and stable energy density of 228 kWh/m³ for water adsorption [49, 50]. They confirmed that the addition of the salt significantly increases the amount of water adsorption and therefore provides a greater potential for thermal energy storage.

Many adsorption kinetic studies have been performed, including those by Ovoshchnikov et al [51], Tokarev et al. [52, 53], and Aristov et al. [54], to identify the effect of the salt on the composite materials. The investigation conducted by Ovoshchnikov et al. [51] focused on the acceleration effect of the calcium chloride salt present in the pores of the silica gel composite material. They determined that an increased rate of water transport in the pores results from the salt addition [51]. They also predicted that the reason for the increased rate of water transport is due to the increased driving force for the diffusion of the adsorbate through the salt.

The optimizations and material studies discussed were compiled and the energy densities reported are summarized in Table 2-1 based on the results of the literature search conducted. This table presents the materials used for water adsorption processes including the adsorbent, the reported energy densities in decreasing order, and the corresponding reference where the information was obtained. Energy densities in the range of 86-309 kWh/m³ have been reported for various adsorbent/adsorbate pairs as shown in Table 2-1. The highest energy density, 309 kWh/m³, was obtained by Dicaire et al. [45] for a hybrid adsorbent of zeolite 13X and activated alumina impregnated with lithium chloride. Other adsorbent/salt pairs also reported high energy densities as shown in Table 2-1, and thus the composite material of adsorbent and salt is promising for energy storage. However, research remains to be done to improve the stability of
the salt addition to the adsorbent material for repeated consistent long-term applications. High energy densities have also been reported for hybrid materials and materials containing component additions. These stable and complex adsorbents have the potential to store large amounts of energy for repeated cyclic applications. To date, the most successful adsorbents reported in literature for energy storage are zeolite 13X and activated alumina hybrids with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition.

Table 2-1: Summary of energy densities for water adsorption reported for various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Reported Energy Density (kWh/m³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid of zeolite 13X and AA impregnated with LiCl</td>
<td>309</td>
<td>Dicaire et al., 2015 [45]</td>
</tr>
<tr>
<td>Silica gel impregnated with CaCl₂</td>
<td>228</td>
<td>Zhu et al., 2006 [49]</td>
</tr>
<tr>
<td>Activated alumina with high alkaline addition</td>
<td>226</td>
<td>Uğur, 2013 [21]</td>
</tr>
<tr>
<td>AA/13X (activated alumina and zeolite 13X hybrid)</td>
<td>200</td>
<td>Dicaire and Tezel, 2013 [29]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>180</td>
<td>Bales, 2008 [41]</td>
</tr>
<tr>
<td>AS/CaCl₂ (Impregnated aluminosilicate)</td>
<td>172</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite 13X + MgSO₄ (Impregnation)</td>
<td>166</td>
<td>Hongois et al., 2011 [48]</td>
</tr>
<tr>
<td>Zeolite 4A</td>
<td>160</td>
<td>Bales, 2008 [41]</td>
</tr>
<tr>
<td>Zeolite LiX</td>
<td>160</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>154</td>
<td>Dicaire and Tezel, 2013 [29]</td>
</tr>
<tr>
<td>Zeolite Na LSX</td>
<td>147</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>MgNaX (impregnated zeolite)</td>
<td>128</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>124</td>
<td>Hauer, 2002 [55]</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>123</td>
<td>AEE INTEC [35]</td>
</tr>
<tr>
<td>CaNaA-60 (zeolite)</td>
<td>116</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite NaX</td>
<td>110</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>106</td>
<td>Gantenbein et al., 2001 [39]</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>94</td>
<td>Janchen et al., 2004 [46]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>86</td>
<td>Dawoud et al., 2007 [42]</td>
</tr>
</tbody>
</table>

Recently, there have been international programs put forth to develop the technology and determine the feasibility of long-term energy storage. Adsorption has been one of the principle technologies investigated through these programs. The advancements in adsorption technology have focused both on material development as well as on prototype development. These programs include HYDES (high energy density sorption heat storage for solar space heating) from 1998 to 2001, MODESTORE (modular high energy density heat storage) from 2003 to 2006, Task 32 (advanced storage concepts for solar and low energy buildings), and Task 42 (development of advanced materials and systems for compact storage of thermal energy) by the
IEA from 2009-2012 [18, 20]. The adsorption heating applications that were developed through these programs, as well as other adsorption heating applications will be further discussed.

**2.2.6.3.3 Pilot-Scale Operations using Adsorption Thermal Energy Storage for Heating Applications**

Although thermal energy storage technology using adsorption has a wide range of applications, the two most feasible ones include the seasonal storage of solar energy for residential and commercial applications, and excess thermal energy storage in power plants [21]. The Institute of Thermodynamics and Thermal Engineering (ITW) at the University of Stuttgart in Germany has been involved in the development of an adsorption energy storage system using zeolite 4A as an adsorbent through the Monosorp project [40]. A schematic diagram of the system is presented in Figure 2-4. This system was designed to be very simple and flexible compared to other existing systems. The regeneration of the adsorbent is accomplished using hot air from a solar collector at a temperature of 180 to 190 °C which removes the water from the zeolite and thus charges the system by storing the provided energy until it is needed [40]. An energy density of 160 kWh/m³ has been reported for this system [41]. The energy obtained from the adsorption process is then used for heating. The high regeneration temperature required demonstrates the current limitations of this system in a large-scale application.
Another open adsorption system has been developed in 1997-1998 by the ZAE Bayern Center for Applied Energy Research in Germany and provides energy to the district heating facility [18]. Although this system is not specifically meant for long-term energy storage, it helps the district heating network meet its heating demands. During the winter, the system provides heating to a school building and during the summer, it provides cooling to a jazz club [18]. During the adsorption step, the system is independent of the district heating network and provides heating to the school building. The adsorption is accomplished using zeolite 13X and water, and an energy density of 124 kWh/m³ can be achieved in this system, which is 86% of the theoretical energy density [18]. Figure 2-5 presents the schematic representation of the system used for heating. The regeneration of the adsorbent, i.e. the charging of the system, is done during the night when the thermal demand is low. When the thermal demand is high during the day, the stored heat is discharged to the building through the adsorption process. The air enters the
adsorption column between 25 and 30 °C and exits the column at approximately 65 °C [18]. The significant temperature lift allows the heat to be transferred to the heating system of the school. The energy density of this system is close to the theoretical value and demonstrates the potential energy utilization that can be achieved with adsorption heating systems.

![Diagram of adsorption energy storage system](image)

**Figure 2-5**: Adsorption energy storage system used for school heating in Germany [18].

The ZAE Bayern and Bosch Siemens Hausgerate in Germany have also implemented an adsorption heating system in a dishwasher application. The goal of the system was to reduce the energy load of the heating processes which occur at approximately 50°C for the heated washing step and at approximately 60°C for the drying step [56]. The second heating step can be eliminated and the dishes can be dried using the hot dry air from the adsorption process. The humid air in the dishwasher from the washing process is passed to the adsorption column which therefore allows for discharging of the energy from the system to dry the dishes. This coupled dishwasher system with adsorption technology in Germany has reported a 23% reduction in energy demand compared to a regular dishwasher [56]. This process demonstrates the ability of adsorption technology to be integrated into ordinary processes to store and use energy more efficiently.

A MODESTORE prototype was first developed by AEE INTEC in Austria which provides space heating for a single-family home. The system schematic is presented in Figure 2-6. The closed adsorption system uses silica gel as the adsorbent, water as the adsorbate, and solar
energy for regeneration. This pilot system was installed on a building in Austria to monitor its performance [57]. The water that is removed during the charging of the system is condensed and stored within the closed system but separately from the adsorption column. During the adsorption step, the water is evaporated and sent to the adsorption column to allow the stored heat to be released. The experimental results of this system were 20% less than theoretical energy density predictions for the system, although energy densities of up to 123 kWh/m³ for silica gel were obtained experimentally [35].

![Diagram of adsorption system](image)

Figure 2-6: Schematic representation of the closed adsorption system developed by AEE INTEC for space heating for a single-family home [57].

Therefore, through MODESTORE, a second-generation prototype was developed. However, due to the limitations of the working pair and the system itself, an energy density of approximately 50 kWh/m³ has been reported for this system which is significantly less compared to other adsorption storage units and only 25% of the theoretical energy storage density for the material [58]. They recommend that this type of technology is more suitable for long-term energy storage [58]. However, this project demonstrated that adsorption is technically feasible in a live test as the system was functional under real operating conditions [40].
2.3 Conclusion

Although adsorption processes for thermal energy storage have many benefits and applications, its present status remains in material characterization, laboratory-scale prototypes and pilot-scale operations. The most successful adsorbents reported in the literature for energy storage are zeolite 13X and activated alumina hybrids with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition which provide energy densities ranging from 226–309 kWh/m$^3$ for water adsorption. The future work of adsorption technologies for thermal energy storage includes the optimization of adsorbent sizes and adsorption columns to obtain constant outputs, as well as the optimization of temperatures during the charging and discharging processes. Material development is also required to screen for more suitable options which may include composite materials and materials with salt impregnations. Work also remains to be done to ensure the stability of the adsorbent material and to design systems to meet the desired application. Further investigation is also needed for developing systems with a stable usable energy output. Although thermal energy storage through adsorption has been proven to be technically feasible, it has yet to be proven economically viable. An extensive economic analysis is required to ensure the feasibility of this promising technology. Through material development to produce adsorbents with higher energy densities, energy storage technology is moving towards implementation with significant socio-economic benefits. Adsorption energy storage systems can be a competitive technology in the near future with the continuation of material development and system optimization.
2.4 Abbreviations

AEE INTEC - Institute for Sustainable Technologies

ECN – Energy Research Centre of the Netherlands

HYDES – High Energy Density Sorption Heat Storage for Solar Space Heating

IEA – International Energy Agency

ITW – Institute of Thermodynamics and Thermal Engineering

MODESTORE – Modular High Energy Density Heat Storage

SPF Switzerland – Institute for Solar Technology, Switzerland

2.5 Acknowledgements

The authors are grateful for the funding provided by Natural Resources Canada, and the National Sciences and Engineering Research Council of Canada (NSERC). The authors would also like to acknowledge the Department of Chemical and Biological Engineering at the University of Ottawa.
2.6 References


Chapter 3 – The Use of Anhydrous Magnesium Carbonate Adsorbent for Thermal Energy Storage Systems

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Abstract
Thermal energy storage using adsorption is a promising technology that can be used to store energy to satisfy the worldwide needs. An important aspect of this developing technology is material development, which is ongoing to identify suitable materials with high heats of adsorption and high adsorption capacities. This work describes the synthesis of a promising adsorbent, an anhydrous magnesium carbonate material, for use in a thermal energy storage system, a novel application of this material. The procedure for the synthesis of the material was optimized to obtain the desired product. The synthesized anhydrous magnesium carbonate was then tested for its thermal energy storage performance. When tested in comparison with other adsorbents, the synthesized material outperformed the traditional materials and reported the highest energy density. The material was tested at varying relative humidities to determine its suitability as an adsorbent for thermal energy storage. However, with repeated trials, the performance of the material decreased significantly, which is undesirable for energy storage applications.
3.1 Introduction

Adsorption systems have been investigated for thermal energy storage applications and their effectiveness has been demonstrated through the implementation of lab-scale systems, pilot plants, and functioning operating systems. The main challenge for thermal energy storage through adsorption is with the adsorbent material itself. There are many desirable chemical and physical properties of adsorbents for this particular application and there has yet to be a single material that meets all of the competing requirements. Currently, the materials that reported the highest energy densities include zeolite 13X and activated alumina hybrids with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition [1]. These materials provided energy densities of 226-309 kWh/m$^3$, the largest values reported in the literature. The current study investigates a new adsorbent material for thermal energy storage systems with the goal of improving current energy densities of this developing technology.

A recent study reports the synthesis of a novel template-free, ultra-adsorbing, high surface area carbon nanostructure. According to Forsgren et al., this adsorbent has an adsorption capacity 50% greater than that of zeolite Y at low relative humidities, and can be thermally regenerated below 100°C [2]. In the literature, this material has been used for a drug solubility application to improve the adsorption of these drugs in the human body. The current study investigates a novel application of this anhydrous magnesium carbonate material for thermal energy storage systems. If this adsorbent has the ability to adsorb large amounts of water as claimed, it has the potential to be used in thermal energy storage systems with low relative humidity environments to generate energy. Lower relative humidities reduce the amount of energy needed to vaporize water, and thus render the overall process more economically viable.

In this study, the synthesis procedure for this anhydrous magnesium carbonate material was investigated, conducted, and optimized to obtain the desired adsorbent for implementation in thermal energy storage systems. The material was then tested in a thermal energy storage system to determine its thermal energy storage ability with repeated cycles.
3.2 Adsorbent Synthesis Methodology

The proposed adsorbent was synthesized at the University of Ottawa. The procedure for the material synthesis was systematically optimized to obtain the desired product. The details of the synthesis and the resulting adsorbent obtained are further discussed as well as the material characterization completed.

3.2.1 Anhydrous Magnesium Carbonate Synthesis

The anhydrous magnesium carbonate material was originally synthesized according to the procedure described by Forsgren et al. [2] which included the four steps shown in Figure 3-1. However, following this procedure, the desired product was not obtained as many parameters of the reaction and system were not clearly stated in the original article [2] and therefore, needed to be determined experimentally. A study, performed by Frykstrand et al., defined additional specifications required for the synthesis procedure. This study specified the required MgO reactant purity to be $\geq 99\%$ to avoid the formation of undesired products [3]. The authors also included a calcination step in the synthesis procedure which required that the final powder be calcinated at 250°C to remove residual organic contaminants which act as pore barriers and thus reduce the material performance [3]. The initial drying step was also reduced from 3 days to 2 days in the revised procedure. In another study conducted by Zhang et al., anhydrous magnesium carbonate was successfully synthesized on a larger scale at slightly different conditions for a drug solubility application [4]. They also stated that after heating above 350°C, the carbonate decomposes into MgO and CO$_2$ [4]. Stromme et al. published a patent that clarifies that the gel formation step may not entirely form a gel, and that there may be both a solid and a liquid phase present [5]. A final study published by Pochard et al. investigated the water interaction properties of anhydrous magnesium carbonate; however, the authors did not provide the details of their synthesis procedure [6].
Figure 3-1: Synthesis route proposed by Forsgren et al. [2].

Table 3-1 provides a list of the parameters that were inconsistent or unclear from the various published synthesis routes. These parameters were systematically varied to attempt to obtain the desired material. Originally, it was desired to synthesize the material by scaling up the process. However, this system required large amounts of reactants and the effect of the reaction scale-up was unknown. Therefore, the process was scaled-down to a single batch size with the goal of replicating the synthesis experiment accurately compared to the original article [2]. The published synthesis routes specified that the reaction should be placed under 3 bar (gauge) CO$_2$ pressure, however, it did not provide information on the air removal from the reaction vessel. It was desired to remove the air content to avoid undesirable side-reactions. A CO$_2$ purge was introduced prior to the high temperature and high pressure step to eliminate air components from the reactor. The duration of the air purge was varied to ensure that the majority of the reactor volume contained only CO$_2$. 
Table 3-1: Reaction parameters for the optimization of the anhydrous magnesium carbonate synthesis.

<table>
<thead>
<tr>
<th>Item #</th>
<th>Parameter</th>
<th>Variation</th>
<th>Optimized Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Amounts of reactants</td>
<td>4g MgO &amp; 60mL CH$_3$OH – 170g MgO &amp; 2.5L CH$_3$OH</td>
<td>4g MgO &amp; 60mL CH$_3$OH</td>
</tr>
<tr>
<td>2</td>
<td>Duration of air purge</td>
<td>10-40 minutes</td>
<td>30 minutes</td>
</tr>
<tr>
<td>3</td>
<td>Reaction time</td>
<td>2.5-4 hours</td>
<td>4 hours</td>
</tr>
<tr>
<td>4</td>
<td>Time for gel formation</td>
<td>3-4 days</td>
<td>4 days</td>
</tr>
<tr>
<td>5</td>
<td>Duration of drying step</td>
<td>2-3 days</td>
<td>2 days</td>
</tr>
<tr>
<td>6</td>
<td>Calcination step</td>
<td>Include/not include</td>
<td>Include</td>
</tr>
<tr>
<td>7</td>
<td>Purity of MgO</td>
<td>98% - &gt;99%</td>
<td>≥ 99%</td>
</tr>
<tr>
<td>8</td>
<td>Reactor Size</td>
<td>Variable</td>
<td>4 cm diameter, 10 cm length</td>
</tr>
</tbody>
</table>

In this study, the reaction times at the elevated pressure and temperature were varied from 2.5 to 4 hours based on the different times used in the published work. The settling time was also varied with the objective of obtaining a gel phase product. The gel formation time, the period during which the reactor contents settle over several days (in Figure 3-1, this gel formation refers to the steps from bottle 2 to bottle 4), was optimized in the present study, to obtain the largest amount of gel. The drying time was also optimized to allow the gel to solidify and collapse into a white powder. In subsequent publications in the literature, a calcination step was added to the procedure to remove residual organic contaminants. In this study, the synthesis route was performed both with and without the calcination step, however, it was determined that the inclusion of the calcination step was beneficial in the synthesis procedure to obtain a product with higher purity. The purity of the MgO reactant was varied to minimize the presence of additional components which interfere with the desired synthesis route. Finally, the reactor size was varied to determine the reactor dimensions for optimal reaction mixing and product conversion. Figure 3-2 shows two of the reactors tested which were fabricated at the University of Ottawa. It was determined that a reactor with a height of 10 cm and an internal diameter of 4 cm provided the optimal dimensions for the given system.
After systematically varying the parameters in Table 3-1, the following optimized synthesis route was used to obtain the desired product:

1. Four grams of magnesium oxide ($\geq 99\%$ purity) and 60 mL of methanol (99.9% purity) were placed in a glass reactor with a stirring magnet. The glass reactor was fabricated using a glass container with a fitted metal lid. The container was pressure tested to ensure it could accommodate the high pressure required for the synthesis of the material. The combined reactants were placed behind a shield for safety precautions.

2. The reactor was connected to a carbon dioxide cylinder and the CO$_2$ was allowed to flow through the reactor for 30 minutes to purge the reactor of its air content.
3. Once the purge was completed, the reactor was sealed, the stirring was commenced. The temperature was raised to 50°C using a hot plate and the reactor was brought to 4 bar CO\(_2\) pressure. The reactor was kept at these conditions for 4 hours.

4. After 4 hours at 50°C and 4 bar CO\(_2\), the hot plate and the stirring were turned off and the solution was allowed to cool to room temperature. The pressure was lowered to 2 bar CO\(_2\) and left for 4 days to allow the gel formation to occur.

5. After the 4 days, the CO\(_2\) pressure was removed and the gel was separated from the remaining liquid. Both phases were allowed to solidify and dry in an oven separately at 70°C for 2 days.

6. The calcination of both phases was done by placing the contents in a furnace at room temperature and increasing the furnace temperature at a ramping rate of 15°C/min. The contents were kept at 250°C for 6 hours.

7. The products were stored separately in a desiccator to avoid the adsorption of moisture from air.

This optimized synthesis route is depicted in Figure 3-3. The appearance of the bottom gel phase closely matched the desired product described by Forsgren et al. [2] Figure 3-4 gives pictures of the products of the two phases after calcination. After calcination, the top liquid phase formed a brittle crystalline product, as can be seen from Figure 3-4A. The bottom gel phase solidified into dense white agglomerates as seen in Figure 3-4B. Both phases were characterized for material identification.

![Figure 3-3: Reaction pathway optimized for the synthesis of anhydrous magnesium carbonate.](image-url)
3.2.2 Adsorbent Characterization

X-ray photoelectron spectroscopy (XPS) was performed in order to confirm the structure of the synthesized material. The material was characterized in the mass spectroscopy lab in the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa by Dr. Sander Mommers. Two samples were analyzed: the bottom gel phase which was in the form of a white powder-like material, and the top liquid phase which was in the form of a yellow-colored crystal.

Forsgren et al., used XPS to confirm that MgCO$_3$ was present and that it was anhydrous in nature. Figure 3-5 represents the XPS peaks that were obtained by Forsgren et al. [2]. They determined that the peaks obtained at 52.1 eV and 533.5 eV from Figure 3-5 confirm the MgCO$_3$ structure of the material. They also determined that the shoulder from Figure 3-5 at 531.0 eV is indicative of residual MgO in the material. It should be noted that the dashed lines in Figure 3-5 were generated using an XPS software and were not actual measured peaks. Forsgren et al. [2] also determined from the XPS analysis that there was no crystal water present in the material.
In this study, XPS analysis was conducted in order to confirm the composition in comparison with the values reported. The gel phase was analyzed and the magnesium and oxygen peaks are presented in Figure 3-6. These peaks are very clear and indicative of a combination of MgCO$_3$ and residual MgO, as was expected and consistent with results of Forsgren et al. [2]. The Mg$_{2p}$ peak obtained is close to the 52.1 eV peak reported by Forsgren et al. [2], however, it appears to peak at a slightly lower value of approximately 51 eV. According to the NIST XPS database, MgO has a Mg$_{2p}$ peak at 51.0 eV, which explains why the peak is slightly lower [7]. The NIST XPS database also provides the O$_{1s}$ peak of MgO to be 532.10 eV, which is applicable to the peak obtained and explains why it is observed at a slightly lower value, due to the presence of unreacted MgO [7].
The most important confirmation that was obtained from the XPS analysis was the atomic concentration of the material. Table 3-2 presents the analysis obtained for the gel phase. As can be seen from this analysis, the material contains a slightly higher amount of magnesium than carbon. If the material was entirely MgCO$_3$, the magnesium and carbon atomic concentration would be equal as they are in a 1:1 atomic ratio in MgCO$_3$. However, the slightly higher concentration of magnesium is consistent with the presence of unreacted MgO, which would contribute to both the magnesium and oxygen concentrations. Similarly, if the material was entirely MgCO$_3$, the atomic concentration of oxygen would be three times the concentration of carbon and magnesium as there are three oxygen molecules per one molecule of each magnesium and carbon. The concentration of oxygen obtained was slightly higher than three times the amount, which is again consistent with the presence of unreacted MgO. There is also
a small amount (less than 1%) of chlorine present which could have been introduced through the impurities of the reactants or contamination. Therefore, the atomic concentration percentage is strongly indicative of a high degree of MgCO$_3$ with residual MgO present.

Table 3- 2: Atomic concentration obtained through XPS analysis for the gel phase.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>68.58</td>
</tr>
<tr>
<td>Mg</td>
<td>18.47</td>
</tr>
<tr>
<td>Cl</td>
<td>0.54</td>
</tr>
<tr>
<td>C</td>
<td>12.42</td>
</tr>
</tbody>
</table>

The above analysis was also performed for the top liquid phase material in order to determine if the phases were similar or different. The results obtained showed that the two phases are different in chemical composition and that the gel phase is more consistent with the desired material. The O$_{1s}$ and Mg$_{2p}$ peaks are presented in Figure 3-7 for the liquid phase. By comparing the two O$_{1s}$ peaks obtained, it can be seen that the one obtained for the liquid phase has more noise and thus has a higher amount of impurities. However, this peak occurs at the same binding energy as that for the gel phase and thus is indicative of the presence of MgCO$_3$ and residual MgO. The Mg$_{2p}$ peak obtained is present at a slightly higher binding energy than that obtained for the gel phase. The peak has a significant shoulder at the high side which is indicative of electron interactions with another component in the material. This indicated that the liquid phase has other undesired components, which may include reaction intermediates. This is confirmed by the atomic concentration percentage which is further away from the desired concentrations.
Table 3-3 presents the atomic concentrations for the liquid phase. The concentrations obtained show that there is not enough carbon present for the material to be MgCO$_3$ as there is more than double the amount of magnesium present compared to carbon which does not represent the 1:1 atomic ratio of Mg:C in MgCO$_3$. These atomic concentrations could indicate the presence of a higher amount of MgO than MgCO$_3$ or the presence of an intermediate in the reaction synthesis pathway. The atomic concentration analysis confirms that the liquid phase is not the desired product of anhydrous MgCO$_3$ and that the gel phase matches more closely the desired product. Due to the poor regenerability of the anhydrous magnesium carbonate as an energy storage material, which will be further discussed in the results, further characterisation was not performed.
Table 3-3: Atomic concentration obtained through XPS analysis for the liquid phase.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>70.65</td>
</tr>
<tr>
<td>Mg</td>
<td>20.52</td>
</tr>
<tr>
<td>Cl</td>
<td>0.39</td>
</tr>
<tr>
<td>C</td>
<td>8.44</td>
</tr>
</tbody>
</table>

3.3 Materials and Methods for Energy Storage Application

The synthesized adsorbent was tested for its thermal energy storage capabilities using the experimental energy storage system at the University of Ottawa. The adsorption column is made of a stainless steel tube with a length of 0.0794 m and an internal diameter of 0.0111 m, giving a total volume of $7.698 \times 10^{-6} \text{ m}^3$. A schematic of the system that was built for testing the performance of thermal energy storage is provided in Figure 3-8. The system input consists of a dry air supply from the building that is filtered to remove impurities. The air can enter the system through two pathways, the dry pathway or the wet pathway. The dry pathway is used during regeneration experiments to remove the adsorbed water and impurities from the adsorbent. The dry air is passed through an in-line heater that is adjusted to the desired temperature using a voltage controller. The heater is a 200 W AHP-5051 electric insulated heater. Once the air passes through the adsorption column, which is packed with the adsorbent material, it is sent through a cooling coil to a hygrometer, which measures the outlet relative humidity. The cooling coil is used to ensure that the hygrometer is reading relative humidity values consistently at room temperature. The hygrometer is a humidity and temperature probe transmitter, HX-15. The air flowrates are determined using a precision wet test meter which is attached to the outlet of the system. Once the outlet relative humidity of the air is stable and approximately zero, the regeneration is complete and the heater is turned off. Dry air is passed through the column to allow the system to cool to room temperature.
Figure 3-8: Thermal energy storage experimental set-up.
During the adsorption experiments, valves V-4 and V-5 are closed to isolate the column, and valves V-6 and V-7 are opened to allow the air stream to pass through the bypass. This allows for the inlet conditions to reach a steady and desired value before exposing it to the adsorbent material. The air is sent to a humidifier where it is humidified using a sparger and two ultra-sonic fog generators. The air is then passed to a water trap where excess water droplets are removed from the stream. The humidified air can be combined with dry air using both rotameters R-1 and R-2 to obtain the desired level of humidity. Once the desired inlet conditions are achieved, valves V-6 and V-7 are closed while valves V-4 and V-5 are simultaneously opened to allow the humidified air to pass through the adsorption column. The exothermic adsorption experiment is complete when the column temperature returns to room temperature and the outlet relative humidity is stable and equal to the inlet conditions. This indicates that the adsorbent is saturated. The system is attached to a Labview data acquisition software that records the temperatures at the column inlet, the column outlet and the column wall through thermocouples T-1, T-2, and T-3, as well as the relative humidity at the outlet through the hygrometer. The adsorption column is insulated to ensure that minimal heat loss occurs during the experiment.

### 3.4 Results and Discussion

The synthesized material was tested for its energy storage capabilities in comparison to traditional adsorbents to evaluate its performance. The adsorbents that were used for comparison included silica gel, activated alumina with alkaline addition, zeolite NaY, hydrogen mordenite, sodium mordenite, and zeolite 3A. The identical experimental procedure was performed for each adsorbent in the energy storage system using a flowrate of 24 LPM, a relative humidity of 15 % at the inlet of the column, and a regeneration temperature of 150°C. Each adsorbent was crushed to 20 x 50 mesh size (0.297 mm-0.85 mm) for the adsorption column used. The resulting energy densities of the adsorption experiments were calculated based on the total energy released per column volume (kWh/m³) as shown in Appendix B. The energy densities obtained for the various adsorbents are shown in Figure 3-9 in decreasing order. This figure shows that the synthesized anhydrous magnesium carbonate generated an energy density of
37.3 kWh/m$^3$, which is the highest of all of the leading adsorbents tested at 15% relative humidity.

![Energy densities for various adsorbents at 24 LPM and 15% relative humidity.](image)

At a low relative humidity environment of 15%, the anhydrous magnesium carbonate’s thermal energy storage performance surpasses that of activated alumina with alkaline addition, one of the adsorbents with the highest reported energy densities in the literature. Figure 3-10 presents the temperature lift observed at the outlet of the column during the adsorption experiment of the synthesized adsorbent at 15% relative humidity and 24 LPM. The energy density is dependent on the magnitude and the duration of the temperature lift which determines the amount of useable energy that is released from the material for a given set of operating conditions. The temperature lift generated in Figure 3-10 was obtained using a very low relative humidity and a small adsorption column. Increasing both the relative humidity and the column size would result in higher temperature lifts observed and thus higher energy densities [8, 9].
Figure 3-10: Column inlet and outlet temperature as a function of time for MgCO$_3$ at 15% relative humidity and 24 LPM.

The adsorption experiments were repeated for relative humidities in the order of 20, 30, 40, and 55% at 24 LPM using the same adsorbent by performing regeneration at 150°C between trials. The breakthrough curves obtained are presented in Figure 3-11 as the ratio of the outlet relative humidity to the inlet relative humidity as a function of time at the outlet of the column. As the inlet relative humidity increases, the column outlet relative humidity reaches the inlet value more quickly, indicating column saturation. The higher the water content of the inlet stream, the higher will be the driving force for adsorption, and thus the faster saturation is achieved.
An ideal adsorbent for thermal energy storage would have a high heat of adsorption, thus producing a high energy density, as well as a high adsorption capacity. The amount of water adsorbed by the anhydrous magnesium carbonate was analyzed as a function of relative humidity and is presented in Figure 3-12. As can be seen from this figure, as the relative humidity increases, the synthesized adsorbent is able to uptake more water due to the equilibrium established between the adsorbent and the surrounding fluid. An adsorbent that is in contact with a fluid of a given composition for a sufficiently long time will reach equilibrium [10]. This is indicative of a desirable adsorbent as increasing amounts of water uptake can result in higher amounts of energy released depending on the heat of adsorption observed.
Figure 3-12: Adsorption capacity for a column volume of $7.698 \times 10^{-6}$ m$^3$ as a function of relative humidity for anhydrous MgCO$_3$ at 24 LPM.

The energy densities were determined for the various relative humidities and are shown in Figure 3-13. Although the energy densities from Figure 3-13 are indicating an overall increasing trend as the relative humidity increases, these increases are not as large as expected. Also, from 15% to 20%, the energy density is seen to decrease slightly, which is not typical of adsorbent behaviour. However, since the same adsorbent sample was reused for consecutive trials, the decrease in energy density may be attributed to adsorbent degradation during regeneration, as further explained in the following paragraph.
Figure 3-13: Energy density as a function of relative humidity at the inlet of the column for MgCO$_3$ at 24 LPM.

To confirm the adsorbent degradation, identical trials were performed consecutively using the same regeneration temperature and operating conditions to see if the adsorbent was able to produce consistent energy outputs. The resulting energy densities are presented in Figure 3-14 which demonstrate the material’s deterioration with repeated trials. This is due to changes occurring on the adsorbent either from the adsorption process or from the thermal regeneration process. The adsorbent may be decreasing in performance due to several factors, which could include deactivation and irreversible adsorption. The adsorbent may be deactivated during regeneration as exposure to both high temperature and high humidity can cause irreversible breakdown of the adsorbent structure. Partial pore closure can also occur, which reduces the pore availability. The water may also be chemically adsorbed to the surface of the adsorbent, rather than physically adsorbed due to the unreacted MgO or other intermediate products. Chemically adsorbed water can be extremely difficult to remove from the adsorbent surface, even impossible. The changes in the adsorbent performance with repeated runs seen in Figure 3-14 explains the behaviour in Figure 3-13. The results obtained in Figure 3-13 were conducted starting with 15% relative humidity in increasing order of relative humidity. The dip obtained in
Figure 3-13 going from 15% relative humidity to 20% relative humidity could be explained by the deterioration of the adsorbent due to regeneration. At further increases in relative humidity, the increase in adsorption driving force more than compensates for the deterioration of the adsorbent, resulting in a slight increase in energy density as relative humidity increases. The increasing energy density values obtained at higher relative humidities would likely be even larger if fresh adsorbent was used for each trial. The regeneration temperature was increased to 210°C to attempt to further regenerate the adsorbent, however, no improvements were observed. A study performed by Dicaire and Tezel confirmed that increasing the regeneration temperature above 200°C results in limited improvement in energy density [8]. For energy storage applications, regenerability of the adsorbent is essential as the material must be able to undergo repeated adsorption and desorption runs. Therefore, although the synthesized material was able to produce the highest energy density of the adsorbents tested, it is not suitable for thermal energy storage applications based on the analysis conducted, as it is not reusable for repeated adsorption experiments.

Figure 3-14: Energy density for consecutive trials of MgCO₃ adsorption at 24 LPM and 15% relative humidity.
3.5 Conclusions

An anhydrous magnesium carbonate adsorbent was successfully synthesized using an optimized procedure. The resulting adsorbent was tested for its energy storage ability in an adsorption energy storage system. The material successfully generated the highest energy density of 37.3 kWh/m$^3$ in comparison with traditional adsorbents including silica gel, activated alumina with alkaline addition, zeolite NaY, hydrogen mordenite, sodium mordenite, and zeolite 3A at 15% relative humidity. The synthesized adsorbent was then tested at varying relative humidities of 15, 20, 30, 40, and 55% for energy density and adsorption capacity. Both the energy density and the adsorption capacity had an overall increasing trend as the relative humidity increased. However, with repeated trials, the observed energy densities decreased significantly due to changes on the adsorbent. This degradation in adsorbent performance with repeated experiments is undesirable for thermal energy storage applications as the material would need replacing after each run, which is not efficient or cost-effective. Therefore, although the anhydrous magnesium carbonate material produced a desirable energy output at low humidity environments, it is not suitable for adsorption energy storage applications.
3.6 References


Chapter 4 – Adsorbent Screening for Low Relative Humidity Environments for Thermal Energy Storage of Solar and Waste Heat

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F. Handan Tezel, University of Ottawa

Abstract

The current study investigates the use of various adsorbents for thermal energy storage systems using adsorption processes for low regeneration temperatures and ambient humidity environments. These operating conditions require less intensive energy inputs and thus help move the technology towards economic feasibility. The adsorbents tested included zeolites (zeolite 3A, zeolite NaY, Na mordenite, and H mordenite), silica gel and activated alumina with 20% alkaline addition using water as the adsorbate. It was found that the zeolites tested were not suitable for thermal energy storage at low humidity environments as they provided short temperature outputs, low energy densities, low adsorption capacities, and rapid breakthrough curves. Silica gel and activated alumina with alkaline addition were determined to be the most suitable with silica gel having superior performance. At a low relative humidity of 55%, silica gel achieved an energy density of 135 kWh/m³ and the activated alumina with alkaline addition gave an energy density of 128 kWh/m³. This study demonstrates that significant energy outputs can be achieved using low ambient humidity environments which require reduced energy inputs to the process.

Submitted to the Journal of Energy Storage
4.1 Introduction

As traditional methods of obtaining energy are evolving, new and innovative technologies are being investigated as potential energy sources. Among the developing technologies is thermal energy storage (TES). TES involves storing energy from sources such as solar or waste heat, and using the energy for applications including space heating. This expanding technology is promising as it utilizes energy that would otherwise be wasted, for common operations that would otherwise use alternative energy sources. Energy storage is essential for the efficient use of solar and waste heat as it allows for the energy to be captured from these intermittent sources when it is available. The captured energy, which is stored in the form of a chemical potential and thus does not degrade over time, can then be used at a later time when needed for a desired application.

There are several storage mechanisms that are currently under investigation for thermal applications including adsorption. Adsorption is a chemical process that involves the binding of a fluid adsorbate on the surface of a solid or porous material, the adsorbent [1]. The binding of the adsorbate occurs on active sites of the adsorbent and is accompanied by the release of energy [2]. The amount of energy that is released from a given adsorption site is quantified by the heat of adsorption and the adsorption capacity. The heat of adsorption determines how much energy accompanies the binding of the adsorbate to an adsorption site. The adsorption capacity indicates the quantity of adsorbate that will undergo adsorption and thus bind to the material. For TES, it is desirable to use materials with both high heats of adsorption and high adsorption capacities to obtain systems with high energy densities. Energy density characterizes the energy storage performance as it describes the amount of energy released per unit volume of the system, which gives a normalized measurement of the system output.

Common materials used for adsorption processes include zeolites, activated alumina, silica gel, and activated carbon [3, 4]. Water is a common adsorbate used in conjunction with energy storage adsorbents and is obtained through a humidification process. The criteria for a desirable adsorbent for TES include high adsorption capacity, high heat of adsorption, high energy density, and low regeneration temperature and duration [5]. The best materials currently
reported in the literature include zeolite 13X and activated alumina hybrids with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition which provide energy densities ranging from 226-309 kWh/m³ for water adsorption [6-9]. However, energy density is not a state function, it must be defined together with certain operating conditions to be relevant. Most research conducted has focused on obtaining high energy density values, which almost always utilizes extreme conditions that render the process non-viable. Systems that use humid air with 100% relative humidity as the adsorbate and high regeneration temperatures are expending a large amount of energy in order to obtain a variable amount of energy in return. There is limited information in the literature regarding low regeneration temperatures and low relative humidity environments.

Therefore, the current study is aimed at testing various adsorbents for TES applications using low ambient relative humidities between 15% and 55%. These humidities are present in the outdoor air and vary throughout the seasons of the year and geographical location. If the ambient humid air could be used to generate energy without the need to spend energy for additional humidification, a large amount of energy would be saved. The regeneration is also performed at a lower temperature of 150°C to reduce the energy requirements. Reducing the regeneration temperature and using air with ambient humidity would result in minimal energy being inputted to the adsorption system, which at high energy densities, moves the process towards economic feasibility. The materials that were tested for their TES performance include zeolite 3A, silica gel, zeolite NaY, Na mordenite, H mordenite, and activated alumina with 20% alkaline addition (AA20A). These adsorbents were tested at varying ambient humidities in a TES system to determine their suitability for energy storage.

4.2 Materials and Methods

The adsorbents were tested in a TES system built at the University of Ottawa to assess their performance. Each experimental run consisted of two steps, a regeneration step and an adsorption step. The regeneration step liberates the adsorption sites and charges the material
with energy. The adsorption step is the exothermic process that releases the stored energy.
Experiments were performed at consistent regeneration temperatures and flowrates with varying relative humidities from 15% to 55% to test the TES outputs of low relative humidity environments. Fresh adsorbent samples were used for each trial to eliminate the potential effect of performance decline with repeated adsorbent use. A detailed description of the experimental set-up, as well as the experimental procedure is provided.

4.2.1 Experimental Set-Up

The experimental set-up used is similar to that used by Dicaire and Tezel, and Ugur with several modifications [8, 10, 11]. A schematic of the system is provided in Figure 4-1. The air supplied from the building contains little to no humidity and is passed through a filter to remove any residual impurities. The air can then pass to one of the two pathways; the dry pathway or the wet pathway. The dry pathway can be isolated and used for regeneration. It contains a 200 W AHP-5051 electric insulated heater from Omega, (Laval, Canada) that is adjusted using a voltage controller to obtain a desired temperature output. During adsorption, the wet pathway is used to humidify the air to a desired relative humidity. The air enters a humidifier where it is passed through a sparger and placed in contact with two ultrasonic fog generators that add moisture to the air. In practical applications, humid ambient air can be used directly for adsorption. The humidifier air is then sent to a water trap to remove excess water droplets before entering the adsorption column. The relative humidity can be controlled by varying the flowrate through the wet pathway, by reducing the number of fog generators used, or by combining the humidified air from the wet pathway with dry air from the dry pathway. Rotameters R-1 and R-2 control the air flowrate through either pathway, and a wet-test precision meter is used to accurately determine the resulting flowrate. The adsorption column is equipped with thermocouples T-1, T-2, and T-3, which are placed at the inlet, outlet, and middle of the column and connected to Labview data acquisition software for recording.
Figure 4-1: Thermal energy storage laboratory experimental set-up for determining adsorbent performance.
The adsorption column used for TES testing at low humidity environments is a stainless steel tube retrofitted for the given application. The adsorption column has a length of 0.0794 m and an internal diameter of 0.0111 m, resulting in a total volume of $7.698 \times 10^{-6}$ m$^3$. Insulation is placed around the column during experiments to minimize heat losses. The adsorption system also contains a by-pass route, which can be used to achieve steady state conditions for the feed before exposing it to the adsorption column. The by-pass route is made of $\frac{3}{8}''$ stainless steel piping. The air flow can either be directed through the column or through the by-pass using valves V-4 and V-5, or valves V-6 and V-7, respectively. The air exiting the adsorption column or by-pass is then passed through a cooling coil which is submerged in a cooling bath to cool the air to approximately 23°C to ensure that the relative humidity output is recorded at a consistent temperature. The air is then sent to the hygrometer container which contains a HX-15 humidity and temperature probe transmitter which is connected to the data acquisition software.

### 4.2.2 Experimental Procedure

The adsorbents tested included zeolite 3A, silica gel, zeolite NaY, Na mordenite, H mordenite, and AA20A, which were each crushed to a mesh size of 20 X 50 (0.297-0.85 mm). For a given experiment, the adsorption column was tightly packed with an adsorbent and a screen with a pore size of 0.043 mm was placed at both ends of the column to isolate the adsorbent material in the column and prevent it from being entrained in the system. After packing the column, it was connected to the system and covered with insulation. The experimental procedure included both the regeneration and the adsorption steps. The regeneration experiment was performed first whereby the air was passed through the in-line heater and heated to 200°C. The regeneration required less than one hour, after which, the relative humidity of the air leaving the column was measured to be zero, indicating that no moisture remained in the adsorbent. The heater was then turned off and room temperature dry air was allowed to pass through the column to cool its contents.
The exothermic adsorption process was then performed. Valves V-4 and V-5 were closed to isolate the column and allow the air to flow through the by-pass to achieve steady state for a given relative humidity. Rotameters R-1 and R-2 were used to combine air from the wet pathway with air from the dry pathway to obtain air with the desired relative humidity ranging from 15% to 55%. Once a constant humidity was achieved, the column valves V-4 and V-5 were opened, and the by-pass valves V-6 and V-7 were closed to commence the adsorption experiment. Throughout the experiment the temperatures and humidities were recorded using Labview. Once the inlet and outlet temperatures were equal, and the outlet relative humidity was constant and equal to the inlet relative humidity, the adsorption process was complete.

4.3 Results and Discussion

The regeneration and adsorption experiments were conducted for the different adsorbents at a range of relative humidities. Regeneration was first performed and is used to restore the adsorbent’s capacity by liberating its active adsorption sites [3]. A sufficiently high regeneration temperature is required to ensure full regeneration of the adsorbent, without using excess energy. In real applications of this technology, the regeneration energy would be supplied from either waste heat, or from a concentrating solar power collector, which can provide temperatures up to 1000°C [12]. Adsorption operations used in real applications will require cyclic processes which include both the regeneration and adsorption step while reusing the same adsorbent. As a result, the cost and efficiency of regeneration are extremely important in establishing the overall feasibility of the TES process [3]. Typically in literature, temperatures up to 1000°C are used for regeneration which require large energy inputs and jeopardize the process feasibility [13].

Therefore, the current study performed regeneration at a lower temperature of 150°C to improve the viability. Figures 4-2 and 4-3 present the results of a typical regeneration experiment which include the changes in the system temperatures, and the changes in the column outlet relative humidity, respectively. Figure 4-2 shows that the column is exposed to air at 200°C for
the regeneration experiment and as a result, the column outlet gradually increases from room temperature to a constant value of approximately 150°C, which is considered the regeneration temperature. This steady outlet temperature is the maximum that can be achieved for the given system with an input of 200°C due to heat losses, which are more significant at high temperatures, such as during regeneration. Initially, for approximately the first 5 minutes, there is a small plateau, as seen in Figure 4-2. This plateau is observed as the heat input is being used to desorb the water present in the adsorbent pores, which also accounts for the increase in the outlet relative humidity observed in Figure 4-3 during the same time period [12]. Once the maximum relative humidity is reached, it gradually decreases to zero, thus indicating that the material is not performing any further desorption. Consequently, when the energy is not being used to desorb water, it is used to heat the material, as seen in Figure 4-2. After approximately 40 minutes, there is no further changes in relative humidity nor in temperature, thus the material is considered regenerated. Therefore, the current TES system can be regenerated at lower temperatures than those reported in the literature. The favorable time requirement and energy input are promising for TES systems and were used for the aforementioned adsorbents to test their resulting performances.

Figure 4-2: Typical regeneration run temperature as a function of time for the column inlet, column outlet, and hygrometer, using AA20A.
A set of optimization experiments were performed to determine the best flowrate for the given column dimensions and particle size. AA20A adsorbent was used for the analysis and a fresh sample was used for each run. Experiments were performed at a consistent regeneration temperature of 150°C and with air at 40% relative humidity with varying flowrates from 10 LPM to 30 LPM to observe the resulting effect. It was found that the maximum energy density occurs at a flowrate of 24 LPM, which is consistent with the results obtained by Ugur [8]. Flowrates lower than 24 LPM have longer residence times in the column to allow for adsorption to occur, however longer residence times result in increased heat dissipations, which reduce the energy density of the system [10]. Higher flowrates have less energy losses, however, the reduced contact time provides less opportunity for adsorption and results in reduced energy densities. As a result, there is an optimal flowrate for a given system at which the highest energy density can be extracted. Therefore, a consistent flowrate of 24 LPM was used for all subsequent experiments to obtain the best energy performance in order to isolate the effect of relative humidity. The resulting energy densities were determined based on the amount of energy released during the adsorption process. The observed temperature lifts, as well as the column breakthrough experiments were analyzed to determine a suitable adsorbent for TES.
The zeolite 3A, silica gel, zeolite NaY, Na mordenite, H mordenite, and AA20A adsorbents were each tested at relative humidities of 15%, 20%, 30%, 40% and 55%, using fresh adsorbent for each experiment. These adsorbents include a range of common materials used for adsorption applications. Each adsorbent was prepared and tested using the described procedure. Figure 4-4 presents the column outlet temperatures as a function of time at varying relative humidities for each adsorbent tested. This figure shows the range of temperature outputs that can be achieved based on the adsorbent selected for TES. It was observed that increasing the relative humidity increases the observed temperature lift. This is expected as increasing the relative humidity increases the driving force for adsorption due to an increase in the concentration of water in the gas phase. That in turn increases the capacity for adsorption which increases the temperature lift.

The amount of energy that is released from the adsorption process is dependent on the heat of adsorption which is characteristic of the interactions between the working fluid-solid pair, polarity, pore size, molecule size, surface area, and the presence of cations [11]. Therefore, the nature of the adsorbent and its properties are primarily responsible for the large variations observed in Figure 4-4 between the tested adsorbents. The zeolite and mordenite adsorbents show similar behaviour and produce short temperature peaks. This corresponds to a short energy releasing spurt, followed by the adsorbent returning quickly to room temperature.
Contrarily, silica gel and AA20A are seen to have comparable temperature lifts with broad peaks, which slowly decrease back to room temperature. These temperature outputs persist for
a longer duration, representing a larger release of energy. The temperature lifts observed are directly related to the amount of energy released, which depends on the overall adsorption process. For the adsorption process to occur, the water molecules must reach an active site of the porous adsorbent. For a high degree of adsorption, it is desired to have a large number of pores, thus allowing for many sites for adsorption [3]. However, the adsorbate molecules must diffuse into the pores to reach an adsorption site to release energy. The diffusion of the adsorbate into the pores depends on the structure of the adsorbent, the combination of the adsorbent-adsorbate pair, and the adsorption conditions, such as temperature and concentration [3]. Thus, all of these factors, which are different for each adsorbent tested, result in the highly variable temperature output graphs obtained.

Figure 4-5 presents the corresponding breakthrough curves at varying relative humidities for each adsorbent which corresponds to the ratio of column outlet relative humidity to the column inlet relative humidity as a function of time. The inlet relative humidity was taken to be the final steady state value that was achieved at the column outlet at the end of the adsorption process. The breakthrough curves of the zeolites and mordenites are characterized by steep curves which quickly stabilize, indicating that the outlet relative humidity has reached the inlet value. These adsorbents essentially transition from being completely regenerated to fully saturated in several minutes, demonstrating that their ability to adsorb water is lower than the other adsorbents tested. However, the breakthrough curves of silica gel and AA20A are broader and require a longer time to achieve saturation.
Figure 4-5: Breakthrough curves for the ratio of outlet relative humidity to inlet relative humidity as a function of time for the different relative humidities tested for each adsorbent.

A desirable breakthrough curve is one in which the concentration is zero for a significant period of time, indicating that the adsorbate is undergoing complete adsorption. Once the adsorbent is close to saturation, the adsorbate will begin to reach the outlet of the column. It is desired at this point to have a steep increase in the breakthrough curve, indicating a transition...
from zero humidity at the outlet to full saturation. This transition indicates that the column is operating efficiently, with effective use of the mass transfer zone. The mass transfer zone is the region where mass is transferred from the fluid to the solid adsorbent. It is desired for adsorbents to have a narrow mass transfer zone which moves throughout the column length as saturation at each section is achieved. As seen from the general trends in Figure 4-5, as the relative humidity is decreased, the breakthrough time increased. The increased time required is due to the lower concentration of adsorbate in the fluid phase, which provides a lower driving force and requires a longer time to breakthrough from the adsorption column.

The temperature lifts in Figure 4-4 are used to determine the resulting energy densities, which are directly related to the areas under the temperature output curves as shown in Appendix B. Thus, the energy density is dependent on both the temperature lift and the duration. Figure 4-6 presents the calculated energy densities for the adsorbents at varying relative humidities which correspond to the temperature lifts reported in Figure 4-4. It was observed that as the relative humidity increases, the resulting energy density increases overall due to the increased driving force for the adsorption process. As can be seen from Figure 4-6, the highest energy densities at each relative humidity tested were achieved using silica gel. Through the analysis of the temperature lifts of silica gel from Figure 4-4, it is evident that this adsorbent has superior water adsorption performance. Although its temperature lift is comparable to those of the other adsorbents tested, the duration of the temperature lift far surpasses that of the other adsorbents, which results in a longer energy output and thus a higher amount of overall energy released. Although zeolite 3A has the highest temperature lift of 37°C, the duration of the temperature output is minimal and as a result, a low energy density is produced, as seen in Figure 4-6.
The effect of the cation present on the mordenite zeolites was also investigated. H mordenite and Na mordenite are a type of zeolite mineral composed of aluminosilicate structures [14]. They differ by the cation present, which can result in significantly different adsorption outcomes, as seen in Figure 4-6. The energy density of H mordenite is consistently higher than that of Na mordenite for all conditions tested. Both cations have a charge of +1 and therefore, have a comparable effect in terms of the overall charge of the structure. However, each cation produces a different ionic distribution in the zeolitic channels, which affects the accessibility of adsorption sites to the adsorbate [15]. Changing the cation present changes the pore size and thus affects the adsorption dynamics. At low-pressure ranges, which corresponds to low relative humidities, H mordenite has a higher adsorption capacity than Na mordenite for various adsorbates, as confirmed by the energy density outputs as well as the amounts of water adsorbed, which is related to the adsorption capacity. The amount of water adsorbed was calculated based on the difference in the inlet humidity and the outlet humidity, as shown in Appendix B and given in Figure 4-7 for the different adsorbents studied. Varying adsorption capacities have been observed in the literature for different cations [16]. Kawamura et al., determined that at low-pressure ranges, the adsorption capacity increases with decreasing
atomic number of the exchanged cation [16]. The cations have significantly different ionic radii of 0.012 Å for hydrogen, and 1.02 Å for sodium [17]. Therefore, these variations in ion size result in different pore sizes in the mordenite adsorbent and affect the overall adsorbent performance.

Figure 4- 7: Amount of water adsorbed for the tested adsorbents at varying relative humidities in the column volume.

Zeolite 3A, zeolite NaY, Na mordenite, and H mordenite are not ideal for use in TES systems due to their temperature outputs, energy densities, and breakthrough curves. These four adsorbents, produced similar output temperature lift curves whereby a short peak is observed when the column is initially in contact with the adsorbate, followed by a rapid decrease in temperature output. This is indicative of adsorbents with low adsorption capacities for the corresponding adsorbate. Since adsorption is an equilibrium process, the higher the concentration of water in the gas stream (the higher the relative humidity), the higher the amount adsorbed, as seen in Figure 4-7, due to the increased driving force [10]. Figure 4-7 shows that zeolite 3A, zeolite NaY, Na mordenite, and H mordenite adsorb the lowest mass of water due to their low adsorption capacities. These adsorbents also achieve saturation rapidly, as shown in Figure 4-5. This indicates that the adsorbents, which are freshly regenerated, achieves
their maximum water saturation very quickly, which is directly related to their low water capacity. The available adsorption sites are rapidly filled and thus the column outlet relative humidity reached the inlet humidity, indicating that no further adsorption was occurring. Therefore, due to their short temperature outputs, low energy densities, low adsorption capacities, and rapid breakthrough curves, the zeolite and mordenite adsorbents tested are not suitable for TES systems at low relative humidity environments.

Conversely, silica gel and AA20A adsorbents show promising TES behaviour at low relative humidity environments. These two adsorbents have high temperature lifts and durations, seen in Figure 4-4, with silica gel having the best performance among the adsorbents studied. The large areas under the resulting temperature output curves account for the large energy densities observed for both silica gel and AA20A seen in Figure 4-6. Silica gel achieves the highest energy density of the adsorbents tested of 135 kWh/m³ at a relative humidity of 55%. The AA20A achieves an energy density of 128 kWh/m³ at the same relative humidity of 55%. These energy densities are comparable to typical energy densities reported in the literature, and were achieved using lower regeneration temperatures and low relative humidity environments.

The breakthrough curves in Figure 4-5 demonstrate the superior performance of silica gel for TES systems. The total time to reach saturation for both silica gel and AA20A are approximately the same, however, the performance during this time is significantly different. The outlet relative humidity for silica gel is zero for a period of time while the entire adsorbate inputed to the system is being adsorbed by the material. During this time, there is no adsorbate leaving the system, which is desirable for adsorption systems. This type of behaviour is indicative of an efficient mass transfer zone. As the entrance of the column becomes saturated, the adsorption front and mass transfer zone move through the column until the outlet is reached. Once the adsorbate reaches the column outlet, the breakthrough curve has a steep slope and quickly reaches saturation. This behaviour represents a desirable S-shaped breakthrough curve whereby the adsorbent is operating efficiently. The work performed by Dieng and Wang confirms that silica gel and water adsorption systems provide promising outputs for utilizing low temperature energy in many applications [18].
Contrarily, the breakthrough curve for AA20A is a constant broad and slow increase in concentration, indicating inefficiency. For AA20A, the breakthrough curves do not begin at zero. When the regenerated column is exposed to the adsorbate, there is immediately water detected at the outlet, which represents a wide mass transfer zone. The material is not able to adsorb all of the inputed adsorbate as efficiently as silica gel, indicating more resistance to mass transfer. Upon contact with the fluid, there is adsorbate detected at the column outlet, and thus adsorption occurs gradually throughout the entire column. Since AA20A cannot fully capture the adsorbate, and since its breakthrough curve does not exhibit desirable steep S-shape behaviour, it is considered to be inferior to silica gel for TES at low relative humidity environments.

In order to determine the effect of the relative humidity and regeneration temperature on the adsorbent performance, experiments were conducted for the two best TES adsorbents, silica gel and AA20A, at regeneration temperatures of 210°C and relative humidities of approximately 100%. By performing adsorption experiments at the highest possible relative humidity and with an increased regeneration temperature, an analysis can be made to determine whether the increased energy expended for regeneration and humidification provide sufficient energy outputs to justify the additional energy input. The experiments were performed using a consistent flowrate of 24 LPM, a relative humidity of 100%, and a regeneration temperature of 210°C. A comparison of the results obtained for both silica gel and AA20A at 15%, 55%, and 100% is presented in Figure 4-8. It should be noted that the energy densities obtained for 15% and 55% relative humidities were obtained using a regeneration temperature of 150°C and the energy density for 100% relative humidity was obtained using a regeneration temperature of 210°C. An energy density of 138 kWh/m³ was obtained for silica gel at 100% relative humidity, compared to 135 kWh/m³ at a relative humidity of 55%. This presents a marginal increase of only 3 kWh/m³ for the large increase in energy input. For AA20A, an energy density of 168 kWh/m³ was obtained at 100% relative humidity and a regeneration temperature of 210°C, in comparison to 128 kWh/m³, which was achieved using a relative humidity of 55% and a regeneration temperature of 150°C. This results in an increase of 40 kWh/m³ for AA20A at the expense of the additional energy inputs. These results show that the additional energy expended for increased
humidification and regeneration temperature provide only marginal increases in the system output and therefore, are not recommended.

Figure 4-8: Energy densities of silica gel and AA20A for varying relative humidities.

4.4 Conclusion

With the increasing need for alternative energy solutions, energy storage technologies are being investigated. Thermal energy storage technologies using adsorption processes have received much research and development to better understand the chemical process and how it can be used to extract available energy. The current study focused on using adsorption for TES under practical conditions to reduce the energy input requirements and move towards feasibility. The adsorbent materials were regenerated at a low temperature of 150°C to reduce the energy requirement of the regeneration process. The adsorbent was fully regenerated in less than one hour. The adsorption was then performed using waster as the adsorbate, at low relative humidity.
environments to eliminate the need for additional humidification. Zeolite 3A, silica gel, zeolite NaY, Na mordenite, H mordenite, and activated alumina with 20% alkaline addition (AA20A) were used for the current study to assess their performance in TES systems. An optimization study was performed to determine the best flowrate for the given column dimensions, which was found to be 24 LPM. The adsorbents were tested at a constant flowrate of 24 LPM with relative humidities varying from 15% to 55%. It was found that the best adsorbent for TES at the conditions tested was silica gel, which at a relative humidity of 55%, provided an energy density of 135 kWh/m³. AA20A was also determined to be a suitable adsorbent for TES applications, however, its performance was found to be inferior to that of silica gel. The zeolites tested were not found to be suitable due to their minimal temperature outputs, low energy densities, and low water adsorption capacities. Silica gel provided high energy densities, desirable breakthrough curves, significant temperature outputs, and high adsorption capacities, demonstrating its superior performance for TES among the adsorbents studied. Both silica gel and AA20A were then tested at higher relative humidities and regeneration temperatures, and resulted in only marginal increases in energy output. The results of this study demonstrate that high energy outputs can be achieved without the need for large energy inputs for TES systems.
4.5 References


Chapter 5 – Adsorption Prediction and Modeling of Thermal Energy Storage Systems: A Parametric Study

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Abstract
As worldwide energy needs continue to rise, it is becoming increasingly difficult to meet these strenuous demands. Traditional energy sources are rapidly depleting, polluting the environment, and contributing to climate change. As a result, much effort has been dedicated to developing renewable technologies that can sustain the global energy needs to provide energy security. Among these technologies is thermal energy storage, a promising process that allows for the storage of energy from intermittent sources to correct for the variable supply and demand. The current work investigates adsorption technology for thermal energy storage through the development of a mechanistic model, which describes the material and energy transfers in the system. The mechanistic model was used to conduct a parametric study which examines the effect of column dimension, particle diameter, adsorbent activation energy, flowrate, column void fraction, and adsorbent heat of adsorption on the thermal energy storage system performance. It was found that an optimal column length to column diameter ratio of 1.4, a column diameter to particle diameter ratio of 14.7, a flowrate of 24 LPM, and a void fraction of 0.4 gave the best thermal energy performance for a column volume of 6.276x10⁻⁵ m³. Also, a low activation energy and a high heat of adsorption represent the best adsorption parameters for optimal temperature outputs, breakthrough behaviour, and energy densities.

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5.1 Introduction

Energy storage systems are gaining much attention and development as traditional methods of obtaining energy are no longer prevalent. With decreasing reserves of fossil fuels worldwide, alternative energy systems are being investigated as solutions to the continuously increasing energy demand. Renewable sources are promising for energy applications as they have the ability to naturally replenish themselves and the potential to sustain the worldwide energy needs [1]. An important renewable energy source is solar energy. Although solar energy provided is intermittent, it can be utilized to its full potential if stored during high availability periods to be used as needed afterwards. Thus, energy storage allows for the correction between the supply and demand of available energy for redistribution as desired. There are many types of energy storage technologies that currently exist including mechanical, chemical, electrostatic, magnetic, biological, and thermal.

The current study investigates thermal energy storage for applications including space heating. The specific process investigated for thermal energy storage is adsorption. Adsorption energy storage systems are attractive as they require much less thermal insulation due to the energy being stored in the form of a chemical potential, and the systems can store the energy for long periods of time, as long as the adsorbate and adsorbent are kept separate [2, 3]. These systems are also favourable as they are simple in nature, contain minimal moving parts, and are environmentally friendly [4]. Adsorption involves the binding of a fluid on the surface of a solid or porous material known as the adsorbent. An endothermic desorption (regeneration) process is used to store the energy and charge the system, and an exothermic adsorption process is employed to release the energy and discharge the system. Adsorption energy storage systems are promising as they provide high energy densities, negligible heat losses, and can operate in a continuous cycle to store thermal energy [1]. Although adsorption thermal energy storage systems have many benefits, their present status is in material development, laboratory-scale prototypes, and pilot-scale applications. Adsorption has been previously investigated by others for thermal energy storage applications [3, 5-8]. Models have also been developed by others to study numerous adsorption parameters, which has led to a better understanding of adsorption...
systems [2, 4, 9, 10]. The current study includes a unique parametric study of the effect of varying adsorption parameters on the overall energy density and thermal output to better understand their effect on energy storage.

This study investigates the potential of adsorption energy storage systems using the adsorption of moisture from air for a wide range of scales, conditions, and properties. This analysis is accomplished through the development of a mechanistic model to evaluate the system performance. The model was created using material and energy balances, and validated using experimental data. The validated model was then used to perform a parametric study that predicts the behaviour and capability of adsorption systems using a variety of conditions in order to assess the feasibility of the process. The parametric study includes the analysis of adsorption column dimension, particle diameter, adsorbent activation energy, system flowrate, adsorption column void fraction, and adsorbent heat of adsorption.

5.2 Materials and Methods

The laboratory experiments were performed with the objective of validating the mechanistic model. Experiments were performed at a range of flowrates, relative humidities and temperatures to ensure that the model correctly predicts the system behaviour regardless of operating conditions. A detailed description of the experimental set-up, as well as the experimental procedure is provided. The experimental set-up is similar to the system used by Dicaire and Tezel [6, 11].

5.2.1 Experimental Set-Up

A schematic of the system that was built and used to study the performance of thermal energy storage is provided in Figure 5-1. Dry air with little to no humidity is supplied by the building and fed through a filter to remove impurities. The filtered air can either pass through the dry pathway, or the wet pathway, based on the valve positioning. Rotameters R-1 and R-2
are used to control the flowrate of air through the respective pathways. When humid air is desired, the air flows through the wet path to a humidifier, where a sparger and two ultrasonic fog generators add moisture to the air. The moist air then passes to a water trap where condensed water droplets are removed to prevent liquid water from entering the system. The humidity of the air can be controlled by adjusting the air flowrate, the number of ultrasonic humidifiers operating, and by combing the humid air with dry air provided through the dry pathway. If dry air is desired, valve V-3 is closed and the air is not humidified. An inline heater can be used to heat the dry inlet air for regeneration of the adsorption column. The heater is a 200 W AHP-5051 electric insulated heater from Omega in Laval, Canada, and is attached to a voltage controller to adjust the desired temperature. Thermocouples T-1, T-2, and T-3 are installed at the inlet, center, and outlet of the adsorption column respectively. Table 5-1 presents the properties of the adsorption column used to validate the model.

Table 5-1: Characteristics of the adsorption column used for thermal energy storage model validation.

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<th>Parameter</th>
<th>Value</th>
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<td>Internal diameter (m)</td>
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</tr>
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</tr>
<tr>
<td>Density of column walls (kg m⁻³)</td>
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</tr>
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</table>
Figure 5-1: Thermal energy storage system set-up.
The adsorption column was well insulated to ensure that minimal heat is lost during the experiment. The column contains a by-pass route made of ¼” stainless steel piping. The direction of air flow through either the column or the piping can be controlled using valves V-4, V-5, V-6, and V-7. The air exiting the column or by-pass is then sent to a cooling coil to cool the air to approximately 23°C to ensure that the hygrometer is reading values at a consistent temperature. The cooled air is then sent to the hygrometer where the relative humidity and temperature are recorded. The hygrometer is a humidity and temperature probe transmitter HX-15 purchased from Omega in Laval, Canada. The rotameters are calibrated using a precision wet test meter located at the exit of the system to ensure correct flow rates are recorded. The experimental set-up is connected to Labview data acquisition system to record and store the data for the temperature readings from the thermocouples as well as the information from the hygrometer at different times.

5.2.2 Experimental Procedure

The experimental procedure can be divided into two parts; the regeneration experiment and the adsorption experiment. The endothermic regeneration experiment was performed first. The adsorbent was supplied with energy from the heater using dry air to both liberate the pore sites and charge the adsorbent with energy. Each experimental run was performed with fresh adsorbent. The adsorbent used to validate the model was a hybrid adsorbent of activated alumina and zeolite 13X (AA13X). The adsorbent’s properties are presented in Table 5-2. The adsorption column was tightly packed with the adsorbent and a mesh was placed at each end of the column to isolate the adsorption process and prevent the material from being entrained by the flowing air. The humidification pathway was closed and dry air was heated to 250°C and passed through the column. The regeneration step was complete when the relative humidity of the air leaving the column was zero, and thus no moisture remained in the column. The heater was then turned off and air continued to pass through the column to allow the column to cool to room temperature.
Table 5-2: Properties of the AA13X adsorbent used for model validation.

<table>
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</thead>
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</tr>
<tr>
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</tr>
<tr>
<td>Heat capacity of solid (J kg(^{-1}) K(^{-1}))</td>
<td>836.8</td>
</tr>
<tr>
<td>Pellet density (kg m(^{-3}))</td>
<td>2,000</td>
</tr>
<tr>
<td>Heat of water adsorption (J mol(^{-1}))</td>
<td>54,000</td>
</tr>
</tbody>
</table>

The exothermic adsorption experiment was then performed as the second part of the experimental procedure. Valves V-4 and V-5 were closed to isolate the column. The air was sent through the bypass until the steady desired flowrate and relative humidity were achieved. The humid air from the wet path was combined with dry air to obtain the desired relative humidity ranging from 15% to 100%. Once stable conditions were achieved, the air was passed through the column and the bypass was closed to begin the adsorption experiment. Adsorption is an exothermic process and thus the temperature and relative humidity changes were recorded as a function of time at the exit of the column. The adsorption process was complete when the inlet and outlet column temperatures were equivalent and the outlet relative humidity was equal to the inlet relative humidity, indicating that the adsorbent was saturated.

5.3 Modeling

Modeling of adsorption phenomenon has been previously performed by others using various models and simulators [4, 12-14]. The modeling for the current adsorption study was performed using MATLAB software. The modeling describes both material and energy balances including: material balance in the bulk phase of the column, material balance in the pellet, energy balance in the column, and energy balance around the column wall. There were several assumptions made using this model which include:

- constant void fraction throughout the column
- constant void fraction in the pellets
- perfectly spherical adsorbent particles
negligible pressure drop through the column
only water is adsorbed from the inlet humid air mixture
no radial changes in concentration or temperature in the column or column wall
constant superficial gas velocity
instantaneous adsorption on pellet surface.

These assumptions were relevant for the given system. The assumption of constant void fraction in the column and pellet is applicable as the pellets are of uniform size and tightly packed in the column. The pellets in question are nearly perfect spheres thus the assumption of sphericity is appropriate. The pressure drop throughout the column is minimal and thus can be neglected. The assumption of only water being adsorbed was relevant as the adsorbent readily adsorbs moisture over air. The assumption of no radial changes in concentration or temperature is justified for the given system as the superficial gas velocity is sufficiently high for axial flow to dominate any spatial variations. The assumption of constant superficial gas velocity is applicable as the moisture being adsorbed is a small component of the overall gas composition, and there is a negligible pressure gradient, therefore, the gas flowrate stays relatively constant. Finally, the assumption of instantaneous adsorption on the pellet surface is justified as the rate of water diffusion in the pellet and adsorption onto the solid phase is very high compared to the internal resistance to diffusion which allows the adsorbent to be modeled as spatially independent particles with respect to the radial space coordinate. The assumption of instantaneous adsorption on the pellet surface is known as the linear driving force (LDF) model and is further discussed below. The material and energy balances used to describe and model the system are presented in further detail.

5.3.1 Material Balance in the Bulk Phase of the Column

The mass balance in the bulk phase of the column is described by Eq. 1 [15].
\[ \varepsilon_c \frac{\partial c_g}{\partial t} = \varepsilon_c D_z \frac{\partial^2 c_g}{\partial z^2} - \varepsilon_c v_i \frac{\partial c_g}{\partial z} - \rho_p \frac{\partial q}{\partial t} \]  

(1)

The terms in Eq. 1 represent the material accumulation, the axial diffusion due to the concentration gradient, the convection due to flow, and the mass transfer due to adsorption respectively. The parameters in Eq.1 include the column void fraction \( \varepsilon_c \), the bulk gas concentration in the column \( c_g \), the axial dispersion coefficient \( D_z \), the interstitial gas velocity \( v_i \), the pellet density \( \rho_p \), and the rate of water adsorption \( \frac{\partial q}{\partial t} \). The axial dispersion coefficient was calculated using Eq.2, where \( D_m \) is the molecular diffusivity, \( Re_p \) is the Reynold’s number of the fluid over the particles (Eq. 3), and Sc is the Schmidt number (Eq. 4) [16].

\[ D_z = \frac{D_m}{\varepsilon_c} \left[ 20 + 0.5 \frac{Re_p}{Sc} \right] \]  

(2)

\[ Re_p = \frac{\rho_g v_i D_p}{\mu_g} \]  

(3)

\[ Sc = \frac{\mu_g}{\rho_g D_m} \]  

(4)

The corresponding initial and boundary conditions for the material balance in the bulk phase of the column include [15, 17]:

\[ \text{at } t = 0, c_g = 0, \text{ for all } z \]  

(5)

\[ \text{at } z = 0, c_g = c_{g\text{inlet}}, \text{ for all } t \]  

(6)

\[ \text{at } z = L, \frac{\partial c_g}{\partial z} = 0, \text{ for all } t \]  

(7)

The initial condition states that before the adsorption process, there is no water in the column or pellets, and therefore, the concentration of water everywhere in the column is 0. The boundary conditions state that at the inlet of the column, the gas stream has a constant water vapour concentration, which is valid for the feed, and that at the exit of the column, there is no
further changes in concentration with respect to distance, which was taken as an approximation for the current system.

5.3.2 Material Balance in the Pellet

The mass balance in the pellet accounts for the water adsorbed on the pellet pore surfaces which is represented by a water accumulation rate. The rate of accumulation is calculated based on the adsorption mass transfer rate coefficient \( k_{ads} \), the pellet density \( \rho_p \), and the difference between the water concentration of the gas stream in the bulk phase \( C_g \) and the equilibrium water concentration at the surface of the adsorbed phase \( C_{ge} \), represented by Eq. 8.

\[
\frac{\partial q}{\partial t} = \frac{k_{ads} \varepsilon \rho}{\rho_p} \left( C_g - C_{ge} \right)
\]

(8)

The mass transfer due to adsorption is described using the LDF model, which was first proposed by Gleuckauf and Coates in 1947, and is widely accepted for the analysis of adsorption kinetics [9, 10, 18-20]. The LDF model is favourable due to its simple, analytical, and physical consistency [21]. The adsorption mass transfer rate coefficient was calculated using Eq. 9 with the parameters summarized in Table 5-3 [18].

\[
k_{ads} = \frac{15D_{so} \exp \left( \frac{-E_a}{RT} \right)}{\rho_p^2}
\]

(9)

Table 5-3: Parameters used in the calculation of the adsorption mass transfer rate coefficient.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{so} ) (m² s⁻¹)</td>
<td>145</td>
</tr>
<tr>
<td>( E_a ) (J mol⁻¹)</td>
<td>45,800</td>
</tr>
</tbody>
</table>

Since the LDF model was used, it was implied that there were no spatial concentration considerations within the radial dimension of the spherical particles. Eq. 8 represents the LDF model also used in Eq. 1 to describe the adsorption mass transfer. Therefore, the mass of the
adsorbate that is being removed from the bulk phase is taken up by the pellet. The equilibrium water concentration was calculated using the Temperature-Dependent Toth isotherm, shown in Eq. 10 [22].

\[ q = \frac{aP_{H_2O}}{[1 + (bP_{H_2O})]^n} \]  \hspace{1cm} (10)

In Eq. 10, a, b, and n are Toth parameters calculated as a function of temperature using Eqs. 11-13 [22].

\[ a = a_0 \exp\left(\frac{E}{T}\right) \]  \hspace{1cm} (11)

\[ b = b_0 \exp\left(\frac{E}{T}\right) \]  \hspace{1cm} (12)

\[ n = n_0 + \left(\frac{c}{T}\right) \]  \hspace{1cm} (13)

Eqs. 10-13 include the partial pressure of water (\(P_{H_2O}\)), the gas temperature (T), as well as the fitted Toth parameters (\(a_0, b_0, E, n_0, c\)). The fitted parameters were obtained from experimental data from Wang and LeVan [22] and are presented in Table 5-4. The parameters were generated from experiments using water vapour adsorption on zeolite 13X.

Table 5-4: Temperature-dependent Toth isotherm parameters for water vapour adsorption on zeolite 13X obtained from Wang and LeVan [22].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0) (mol kg(^{-1}) kPa(^{-1}))</td>
<td>3.634 x 10(^{-6})</td>
</tr>
<tr>
<td>(b_0) (kPa(^{-1}))</td>
<td>2.408 x 10(^{-7})</td>
</tr>
<tr>
<td>(E) (K)</td>
<td>6.852 x 10(^3)</td>
</tr>
<tr>
<td>(n_0) (dimensionless)</td>
<td>0.3974</td>
</tr>
<tr>
<td>(c) (K)</td>
<td>-4.199</td>
</tr>
</tbody>
</table>
Eq. 10 was rearranged to solve for the equilibrium water vapour concentration at the surface of the adsorbed phase using the ideal gas law in Eq. 14, to obtain Eq. 15.

\[ P_{H_2O} = C_{ge}RT \]  

(14)

\[ C_{ge} = \frac{q}{\left((aRT)^n - (qbRT)^n\right)^{\frac{1}{n}}} \]  

(15)

The initial condition for the water mass balance in the pellet is given by Eq. 16 which shows that before the adsorption process, there is no water vapour adsorbed on the pellet surface anywhere in the column.

at \( t = 0 \), for all \( z \) and \( r \), \( q = 0 \)  

(16)

### 5.3.3 Energy Balance in the Column

The energy balance in the column is represented using Eq. 17 [23].

\[ \eta \frac{\partial T_g}{\partial t} = k \frac{\partial^2 T_g}{\partial z^2} - v_g \rho_g c_{pg} \frac{\partial T_g}{\partial z} - \frac{2h_{fd}}{r_c} \left(T_g - T_w\right) + \rho_f \Delta H_{ads} \frac{\partial q}{\partial t} \]  

(17)

The terms in Eq. 17 represent the energy accumulation, the axial heat conduction due to the temperature gradient, the convection through the column, the heat loss to the surrounding column, and the heat generation due to the heat of adsorption of the material, respectively. The parameters in Eq. 17 include the apparent thermal heat capacity of the heterogeneous system (\( \eta \)), the gas temperature (\( T_g \)), the thermal conductivity of the bulk gas (\( k \)), the density of the gas stream (\( \rho_g \)), the superficial gas velocity (\( v_g \)), the heat capacity of the gas stream (\( c_{pg} \)), the heat transfer coefficient in the bulk phase (\( h_{fd} \)), the column radius (\( r_c \)), the column wall temperature (\( T_w \)), and the heat of adsorption (\( \Delta H_{ads} \)). The apparent thermal heat capacity was needed since the 1-D LDF model was used, to account for the different layers of conductivity and density changes throughout the column. Thus, it was calculated using Eq. 18, which takes into account
both the heat capacity in the gas phase in the void fraction of the bulk phase ($\varepsilon_c$) as well as the heat capacity of the solid pellet ($\varepsilon_p$) [17].

$$\eta = \rho_g c_p \varepsilon_c + (1 - \varepsilon_c) \varepsilon_p + (1 - \varepsilon_c)(1 - \varepsilon_p) \rho_s c_p$$  

(18)

The heat transfer coefficient in the bulk phase was calculated using Eq. 19, where Nu is the Nusselt number in the column [16]. Given the confirmed laminar flow in the system, it was assumed that the condition of constant surface heat flux was applicable and therefore, a constant value of 4.36 was used for the Nusselt number in the column.

$$h_{\mu} = \frac{k_{Nu}}{D_c}$$  

(19)

The corresponding initial and boundary conditions for the energy balance in the column include [17]:

$$at \ t = 0, \ T_g = T_0$$  

(20)

$$at \ t = 0, \ q = 0$$  

(21)

$$at \ z = 0, \ T_g = T_0$$  

(22)

$$at \ z = L, \ \frac{\partial T_g}{\partial z} = 0$$  

(23)

The initial conditions state that the temperature of the gas stream is equal to the ambient room temperature before the adsorption process begins, and that initially, there is no water in the pellets. The boundary conditions include that at the inlet of the column, the gas temperature is equal to the ambient room temperature, and that at the exit of the column, there is no further changes in temperature with respect to distance.

### 5.3.4 Energy Balance around the Column Wall

The energy balance around the column wall is described by Eq. 24.
\[(r_o^2 - r_c^2) \rho_w c_{pw} \frac{dT_w}{dt} = 2r_c h_d (T_g - T_w) - 2r_o h_o (T_w - T_o) \] (24)

The terms in Eq. 24 represent the energy accumulation in the wall, the convection from the gas stream to the wall, and convection from the wall to the surrounding air respectively. The parameters in Eq. 24 include the outer radius of the column \(r_o\), the density of the column wall \(\rho_w\), the heat capacity of the column wall \(c_{pw}\), the temperature of the wall \(T_w\), the heat transfer coefficient outside the column \(h_o\), and the temperature outside the column \(T_o\). The heat transfer coefficient outside the column was calculated using Eq. 25 where \(k_A\) is the thermal conductivity of air, \(N u_A\) is the Nusselt number outside the column which is calculated using Eq. 26, and \(D_o\) is the column external diameter \([16]\).

\[h_o = \frac{k_A N u_A}{D_o} \] (25)

\[N u_A = \left[0.60 + \frac{0.387 (Ra)^{\frac{1}{5}}}{\left(1 + \left(\frac{0.559}{Pr}\right)^{9/16}\right)^{27}}\right]^2 \] (26)

In Eq. 26, \(Ra\) is the Rayleigh number and \(Pr\) is the Prandtl number \([16]\). The Rayleigh number was calculated using Eq. 27, where \(g\) is the acceleration due to gravity, \(\beta\) is the coefficient of thermal expansion, \(T_s\) is the surface temperature of the column, and \(\nu\) is the kinematic viscosity.

\[Ra = \frac{Pr \beta (T_s - T_g) D_c^3}{\nu^2} \] (27)

The corresponding initial condition is presented in Eq. 28.

\[at \ t = 0, \ T_w = T_0 \] (28)
The initial condition states that initially, the temperature of the wall is equal to the ambient room temperature.

5.4 Results and Discussion

The coupled material and energy balance equations were coded in MATLAB and solved for the given thermal energy storage system. For various sets of operating conditions, both laboratory experiments and model simulations were conducted to compare the results and validate the model. Once the model was validated, a parametric study was performed to observe the effect of varying parameters on the outlet concentration, the outlet temperature, the energy density and the energy released. Many parameters were evaluated including both system and material properties.

5.4.1 Model Validation

The model was validated using laboratory experiments at varying conditions for the AA13X adsorbent. The resulting experimental temperature and concentration values determined at the outlet of the column as a function of time were plotted together with the data generated using the model to perform model validation. Two of the resulting model validations are presented in Figures 5-2 and 5-3. In Figure 5-2, the results were obtained using an inlet flowrate of the bulk gas of 24 LPM, a relative humidity of 90%, and inlet gas temperature of 25°C. In Figure 5-3, the results were obtained using an inlet flowrate of the bulk gas of 28 LPM, a relative humidity of 80%, and inlet gas temperature of 25°C. The experimental adsorption column dimensions were used in the model simulation to perform the validation. As can be seen from the model validation results, the temperature lifts in Figures 5-2a and 5-3a generated using the model are very similar to the temperature lifts obtained experimentally. Both the peak and duration of the models line up with the experimental results well. A discrepancy is seen for the total time to return to room temperature as the model is seen to return to room temperature
more rapidly than the experimental data, which gradually returns to room temperature over a longer period of time. This discrepancy is the result of the assumption of instantaneous adsorption on the surface of the pellet for the model, which does not take into account the resistance of the water molecules reaching the pores of the adsorbent pellets. This increased resistance, which is very small but present nonetheless, results in the experimental column outlet temperature gradually decreasing to room temperature as opposed to quickly dropping as the adsorbent takes longer to reach saturation than the model accounts for. It should be noted that for the breakthrough curves, the modeling solution was highly unstable for the first few seconds and therefore, was excluded from the results presented.
Figure 5-2: Column outlet a) temperature and b) concentration as a function of time for comparison of experimental data and model prediction for a flowrate of 24 LPM, a relative humidity of 90%, and a column volume of \(6.276 \times 10^{-5} \text{ m}^3\).
As observed in Figures 5-2b and 5-3b, the outlet water concentration profiles of the model match the experimental data closely. The slopes of the concentration curves are very similar during the steep increase period. A discrepancy results when comparing the time to reach saturation. The concentration curves generated using the model predict more abrupt and quick adsorbent saturation compared to the experimental data which shows a more gradual and
sluggish time to reach saturation. This is again due to the assumption of instantaneous adsorption on the pellet surface for the model, which assumes that as soon as the water molecule reached the adsorbent, adsorption instantly occurs in the whole pellet. In reality, there is a resistance present and the water molecules must reach an active adsorption site within the pellet for adsorption to occur. Regardless, the assumption of instantaneous adsorption on the pellet surface does not present a significant variation between the model and the experimental data. Although a model is never going to predict actual behaviour with complete accuracy, the model obtained for the thermal energy storage system closely predicts the experimental behaviour. The current model gives the most accurate description of the system with the parameters that are known. Discrepancies result since the resistance in the pellet was not accounted for. This resistance was excluded from the model as its inclusion would require the estimation of unknown parameters through parameter fitting, which doesn’t provide any additional information to the model. Based on the similar results obtained from both the models and laboratory experiments, the model developed was considered validated and was further used for the parametric study.

5.4.2 Parametric Study

A parametric study was performed using the model to predict the behaviour of the thermal energy storage system for varying operating conditions and parameters. The results were compared to those predicted using the model at the laboratory-scale. The effects of the different parameters studied were observed by independently changing one parameter while keeping all other system parameters constant. The outputs observed included the temperature lift and duration, the outlet concentration profile, and the energy density. The energy density is determined based on the amount of energy released per unit volume. The amount of energy released is directly proportional to the area under the outlet temperature as a function of time curve. Eq. 29 presents the equation for the calculation of the energy density.

\[
EnergyDensity = \frac{TotalEnergy\ Released}{ColumnVolume} = \frac{\sum mC_p \Delta T}{ColumnVolume}
\]  

(29)
Therefore, the energy density is dependent on the mass of moist air (m), the heat capacity \(C_{pg}\), the change in temperature \(\Delta T\), and the column volume [24]. The parameters studied included column dimensions, particle diameter, adsorbent activation energy, system flowrate, column void fraction, and material heat of adsorption. The base case, described in Table 5-5, provides the standard values used for the parametric study variables. When one parameter was varied, all other parameters in the model were kept constant and equal to the values in Table 5-5, which are referred to as the base case values. The values in Table 5-5 were selected based on the tested experimental data and setup. Each parameter studied is further discussed in detail.

Table 5-5: Base case values used in the parametric study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length (m)</td>
<td>0.07</td>
</tr>
<tr>
<td>Column internal diameter (m)</td>
<td>0.0339</td>
</tr>
<tr>
<td>Column volume (m(^3))</td>
<td>6.276x10(^{-5})</td>
</tr>
<tr>
<td>Particle diameter (m)</td>
<td>0.0023</td>
</tr>
<tr>
<td>Flowrate (LPM)</td>
<td>24</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>80</td>
</tr>
<tr>
<td>Adsorbent activation energy (J mol(^{-1}))</td>
<td>45,500</td>
</tr>
<tr>
<td>Column void fraction (dimensionless)</td>
<td>0.39</td>
</tr>
<tr>
<td>Heat of adsorption (J mol(^{-1}))</td>
<td>52,000</td>
</tr>
</tbody>
</table>

5.4.2.1 Changing Column Dimensions

The column length and diameter were varied to observe the effect on the thermal energy storage performance. The column dimensions affect the energy loss to the surroundings, as well as the surface area and volume of the adsorption column, which play important roles in the overall energy storage system. The column diameter was varied from 0.01 m to 1 m while keeping all other parameters constant, including column length. The resulting column outlet temperatures are presented in Figure 5-4. This figure shows that as the column diameter is increased, the outlet temperature lift and duration increase to a certain point, resulting in more energy released. An increase in the amount of energy released is observed as the temperature
lift and duration increase. The increased energy released is the result of an increase in the amount of material present in the system through increasing the diameter while keeping the column length constant.

Figure 5-4: Column outlet temperature as a function of time for different column diameters.

In order to analyze the effect of the column diameter on the overall energy performance independently of the amount of material present, the energy density was used as a point of comparison for the different column diameters, as shown in Figure 5-5. The energy density is defined as the amount of energy released per unit volume of adsorbent, which provides a normalized measurement of the energy produced from the system. Figure 5-5 shows that once the column diameter is increased above 0.05 m for the base case length, the energy density drops significantly, resulting in less efficient energy outputs. Although the larger the diameter the more energy that is released, the adsorption column is not as efficient as the column begins to resemble a large disk that doesn’t provide optimal flow dispersion.
The effect of column volume was confirmed by changing the column length while keeping the diameter constant, as shown in Figure 5-6. This analysis also increases the amount of material present in the system and thus provides higher temperature lifts and durations, in a similar way that increasing the column diameter while keeping the column length constant does. Although this effect can partially be explained by the increase in the amount of material in the system, the effect of length and diameter play an important role in energy outputs.
When considering the column dimensions, it is important to look at the length to diameter ratio (L/D). For thermal energy storage systems, it is desirable to minimize the surface area to volume to reduce the heat losses to the surroundings for cylindrical systems [1]. However, this presents a trade-off between the temperature lift and duration, the means of obtaining the energy, and the L/D ratio. As seen in Figure 5-4, a large diameter (small L/D), gives a desirable temperature lift and duration for energy storage. However, Figure 5-5 shows that a much larger column diameter (small L/D) results in significantly lower energy densities and thus poor system performances. Therefore, it is desired to optimize the temperature lift and duration, as well as the energy density to obtain an L/D ratio that gives the best overall performance. A column diameter of 0.05 m gives an L/D ratio of 1.4, which gives a high energy density of approximately 118 kWh/m³, as shown in Figure 5-5, and a sufficient temperature lift and duration for energy storage applications shown in Figure 5-4. Thus, it was determined that the optimal L/D ratio for the current thermal energy storage system was 1.4 to provide both optimal temperature outputs and energy storage density. If a smaller diameter is used, sufficient temperature lift and duration are not achieved. If a larger diameter is used, the energy density significantly decreases. This analysis is relevant for the base case column length selected. It should be performed for the specific column length in question for TES adsorption design.
5.4.2.2 Changing Particle Diameter

Variations in the diameter of the adsorbent pellets were studied in order to observe the resulting effect on the energy outputs. The particle diameter was varied from 0.0005 m to 0.01 m for the base case column dimensions. According to Turton et al., it is best to have a column diameter to pellet diameter ratio ($D_C/D_P$) of greater than 15 to give an optimal performance [25]. This was tested for the given system using the mechanistic model for $D_C/D_P$ ranging from 3.4 to 67.8. For a fixed column diameter, changes in the pellet diameter not only affect the adsorption kinetics, they also affect the bed void fraction, as smaller particles generally result in an adsorption column with a lower void fraction. For the current study, a consistent base case column void fraction was used for the analysis of varying particle diameters. The adsorption column void fraction will later be examined in detail. According to the equations used to describe the system, the particle diameter is used to calculate the Reynold’s number in the column ($Re_p$), and the heat transfer coefficient in the column bulk phase ($h_{fd}$). The $Re_p$ is then used to calculate the axial dispersion coefficient ($D_z$) which is used in the material balance in the column bulk phase to describe the axial dispersion for the concentration gradient term. The $h_{fd}$ is then used in the energy balance in the column equation to determine the heat loss to the surroundings, as well as in the energy balance equation around the column wall to determine the convection from the bulk gas to the wall. Therefore, changes in the particle diameter affect many parameters of the system and studying its overall effect provides a better understanding of adsorption thermal energy storage system behaviour.

The column outlet temperatures generated by varying the particle diameter are provided in Figure 5-7. This figure shows that as the adsorbent particle diameter is increased, the temperature lift decreases as the gas stream must diffuse through the particle to be adsorbed into the volume of the whole pellet. Increasing the particle diameter makes it more challenging for the water molecules to diffuse into the adsorption sites available within the larger pellets. The duration of the temperature lift is also broader as the particle diameter increases due to the increased time needed to release the energy stored in the material, producing a dispersed effect on the temperature. At large particle diameters, there is a negligible temperature rise and
adsorption is minimal due to extreme resistance to mass transfer. The water vapour can only be adsorbed at the surface of the pellets under these conditions, which is a very small fraction compared to the total volume of the pellet.

![Column outlet temperature as a function of time for varying particle diameters.](image)

**Figure 5-7:** Column outlet temperature as a function of time for varying particle diameters.

The breakthrough curve in Figure 5-8 shows that as the diameter of the particle is increased, the breakthrough time decreases as the pores are not readily accessible to the gas stream, which decreases storage performance. With small particle diameters, the gas can readily access the adsorption sites and therefore, the outlet concentration takes longer to breakthrough. This effect can also be explained by the resulting change in external mass transfer resistance with changing pellet diameters. As the particle size is decreased, the boundary layer through which the adsorbate must diffuse to reach the pellet surface is also decreased, thus decreasing the external particle resistance and allowing for better adsorption, which produces a later breakthrough, as seen in Figure 5-8 [26].
Figure 5-8: Column outlet gas concentration as a function of time for varying particle diameters.

Increasing the particle diameter also has a negative effect on the overall energy density, as shown in Figure 5-9. In the lower range of adsorbent particle diameters, up to 0.005 m, the energy density does not significantly change with increasing particle diameter. However, as the particle diameter is increased above 0.005 m, the energy density significantly decreases due to the difficulty of the adsorbate reaching the adsorption sites. These effects are not significant at low particle diameters, but as seen in Figure 5-9, are extremely significant at larger particle diameters.
Therefore, it was found that based on the temperature outputs, column breakthrough curves, and energy densities, the optimal particle diameter is 0.0023 m \((D_C/D_P = 14.7)\) for the given system as it provides a high energy density, an efficient breakthrough curve, and a sufficient temperature output. These findings of the optimal \(D_C/D_P = 14.7\) confirm the design guideline provided by Turton \textit{et al.} which state that a ratio of 15 is desired [25]. Lower particle diameters result in slightly lower energy densities and increased pressure drops. Higher particle diameters provide broadened breakthrough curves due to increased resistance to mass transfer and reduced temperature lifts, which are not favourable for thermal energy storage systems.

5.4.2.3 Changing Adsorbent Activation Energy

The adsorbent activation energy was varied to observe the resulting effect on the energy storage performance. The activation energy is used in Eq. 9 to determine the adsorption coefficient for adsorption in the LDF model, which strongly affects the adsorption process. Increasing the activation energy increases the energy barrier that must be overcome for
adsorption, which results in a decrease in the mass transfer coefficient, reducing the mass transfer capabilities.

Figure 5-10 presents the temperature lifts observed as a function of time for varying activation energies. This figure confirms that the lower the activation energy, the higher the adsorption mass transfer rate and therefore, the higher the observed temperature lift. With increasing activation energy, the mass transfer becomes more difficult, and the water adsorbate cannot reach the pores as easily. The temperature lift is decreased until the activation energy is so high, as is the case for \( \text{Ea} = 55,000 \text{ J mol}^{-1} \), that the mass transfer coefficient is sufficiently low that virtually no adsorption occurs, and the column temperature remains at room temperature, as seen in Figure 5-10.

![Figure 5-10](image_url)

Figure 5-10: Temperature lifts as a function of time for different adsorption activation energies. Activation energy is reported in J mol\(^{-1}\).

Figure 5-11 shows the outlet gas concentration as a function of time for different activation energies and confirms that when the activation energy is sufficiently high, no adsorption occurs and thus water breaks through the column immediately. This figure shows that for low activation energies, water is readily adsorbed in the adsorbent and the breakthrough of water happens at a later time. As the activation energy is increased, the breakthrough time decreases as the energy barrier for adsorption is higher, resulting in a more sluggish
breakthrough curve and an expanded mass transfer zone in the column. Therefore, it is desirable to have an adsorbent with the lowest possible activation energy, as this would indicate a minimal energy barrier which results in high rates of adsorption and later adsorbent breakthroughs for energy storage applications.

![Figure 5-11: Column outlet gas concentration as a function of time for varying adsorbent activation energies. Activation energy is reported in J mol⁻¹.](image)

5.4.2.4 Changing Flowrate

The column inlet stream flowrate was varied to observe its effect on the thermal energy storage system. This parameter has been experimentally studied previously by others [6, 27]. Both Dicaire and Tezel, and Ugur experimentally found that as the flowrate increased, the energy density, and thus the thermal energy storage performance, increased up to a certain point, beyond which the performance decreased. This is due to the adsorption residence time that is directly related to the flowrate. This effect was studied using the mechanistic model developed. Flowrates ranging from 8 LPM to 32 LPM were used and the resulting temperature lifts are presented in Figure 5-12. As can be seen from Figure 5-12, as the flowrate decreases, the temperature peak is broadened as it takes longer for the water molecules to produce a temperature effect at a reduced flowrate. It can also be seen that as the flowrate increases, the
temperature lift and duration are reduced, which is not desirable for thermal energy storage systems. This is due to the decrease in residence time that accompanies the increased flowrate and thus does not allow sufficient time for the adsorbate to bind to the material surface. With decreasing flowrate, the residence time is increased and the adsorbate has sufficient time to undergo adsorption, resulting in a higher effective temperature observed.

Figure 5-12: Column outlet temperature as a function of time for varying flowrates in the column.

However, lower flowrates result in lower energy densities, as shown in Figure 5-13, as reduced flowrate do not allow for optimal energy output from the adsorption column. The increased residence time resulting from a decreased flowrate also involved higher temperature losses to the surroundings and thus is a trade-off between energy density and temperature output. It can also be seen from Figure 5-13 that the energy density begins to plateau as the flowrate is increased above 24 LPM, due to the reduction in residence time in the adsorption column. Increasing the flowrate above 24 LPM for the current system dimensions results in minimal energy density improvements. This was confirmed by Ugur through experimental studies [27].
The column breakthrough was also obtained for varying gas flowrates and is presented in Figure 5-14. This figure shows that as the flowrate is decreased, the time to achieved breakthrough is significantly increased. This result was also observed during the laboratory experiments. Lower flowrates result in an increase in the time to achieve breakthrough as there is slower delivery of the adsorbate to the pellet pores. Lower flowrates also result in a breakthrough curve that is more sluggish. Increased flowrates produce a sharper breakthrough curve, which is more desirable for efficient mass transfer.

Figure 5-13: Energy densities for varying flowrates.
The breakthrough results shown in Figure 5-14 can also be justified by analyzing the boundary layer behaviour. When the fluid is flowing at low velocities over the pellet, the boundary that the adsorbate must diffuse through to reach the pellet is thick, thus increasing the time for adsorption to occur, as seen in Figure 5-14, and resulting in a small mass transfer coefficient [26]. At increased flowrates, the boundary layer is reduced, thus increasing the mass transfer rate and allowing for quicker adsorption [26]. Both increasing the flowrate, and reducing the particle diameter have a similar effect on the resulting boundary layer and allow for more effective column adsorption breakthrough curves [26]. Therefore, a faster flowrate corresponded to a quick column breakthrough, however, it also resulted in a reduced temperature output. As a result, a flowrate of approximately 24 LPM was determined to be the optimal as increasing the flowrate above this value results in limited improvements in the energy density at the cost of the temperature lift and duration.

Figure 5-14: Outlet gas concentration as a function of time for varying gas flowrates.
5.4.2.5 Changing Column Void Fraction

The column void fraction was changed to observe its effect on the thermal energy storage performance. The column void fraction is a measure of the amount of empty space in the adsorption column. Empty space allows the gas to move freely and reach the adsorbent pores. However, empty space also reduces the column performance as there is less material available for adsorption. The void fraction was varied from 0.1 to 0.95 to observe the resulting effect on the temperature outputs, column outlet concentrations, and energy densities. Figure 5-15 presents the temperature outputs obtained from the mechanistic model. This figure shows that as the void fraction is decreased, the temperature lift is decreased but the duration is increased. This could be useful for systems that require lower constant temperature outputs. The decreasing temperature lift with decreasing void fraction is due to the fact that for a low void fraction system, there is minimal space for the gas to travel and therefore, reaching the pore external surfaces is more challenging, producing a lower and steadier output. When the void fraction is high, for example when it is 0.95, the gas can easily pass through the adsorption column and can quickly reach the pore sites, adsorb to the surface, and produce a high and short temperature peak.
Figure 5-15: Column outlet temperature as a function of time for varying column void fractions.

However, increasing the void fraction reduces the amount of material present in the volume of the column. Therefore, although the temperature lift is increased, it is at the cost of the energy density, as seen in Figure 5-16. This figure shows that as the void fraction is increased, and thus there is more empty space in the adsorption column, the energy density is decreased. This is due to the reduction in the amount of material present per column volume. Less material for adsorption results in less energy produced. Therefore, although the temperature lift is increased, the amount of energy produced per unit volume is actually decreased.
The column breakthrough was also analyzed and is shown in Figure 5-17. The breakthrough curves in this figure show that as the void fraction is increased, the column breakthrough occurs at a later time than at low porosities. This is due to the increased amount of empty space which allows the adsorbate to reach the adsorbent pores and perform the adsorption process more readily. Low void fraction adsorption columns have more difficulty in reaching saturation and thus produce a breakthrough curve with a broader more gradual increase. In low void fraction systems, not only is there less empty space for the fluid to move through, there is an increased amount of material for the adsorbate to saturate, which accounts for the increased time required to reach saturation. The increase in the sluggish behaviour of the breakthrough curve with decreasing void fraction can also be attributed to the enlargement of the mass transfer zone. The mass transfer zone is defined as the place within the column where adsorption occurs. The width of the mass transfer zone is dependent on several factors including the adsorption isotherm, flowrate, mass transfer rate, and diffusion in the pores [15]. Thus, changing these parameters changes the mass transfer zone, which in turn alters the breakthrough behaviour. As the adsorbent at the entrance of the column becomes saturated, the mass transfer zone moves through the column until the exit achieves saturation [15]. However, with decreasing void fraction, the water cannot easily access the pores for adsorption at a given

Figure 5-16: Energy density as a function of column void fractions.
location and therefore, the fluid will proceed through the column where empty space is found. The mass transfer zone is therefore expanded due to the limited amount of free space available. An enlargement of the mass transfer zone is not favourable as the adsorbent is not utilizing a large portion of its capacity [15]. Thus, large mass transfer zones do not make efficient use of the adsorbent.

Figure 5-17: Column outlet gas concentration as a function of time for varying column void fractions.

Based on the temperature lift, energy density, and breakthrough analysis, it was determined that a void fraction of approximately 0.4 is optimal for thermal energy storage systems. This void fraction provides sufficiently high temperature lift and duration, energy density, and breakthrough behaviour. Columns with lower void fractions do not provide optimal temperature outputs and do not result in a sharp column breakthrough. Although higher void fraction columns produce greater temperature lifts and sharper breakthroughs, they result in lower overall energy densities, which are not favourable for energy storage.
5.4.2.6 Changing Heat of Adsorption

The heat of adsorption of the adsorbent material was also varied to observe the resulting effect on the thermal energy storage system. Adsorption is an exothermic process and therefore, the binding of the adsorbate on the surface of an adsorbent material operates on the principle of surface energy. Thus the adsorption process produces a heat of adsorption, which is the amount of energy that accompanies the adsorbate binding. For thermal energy storage, it is desirable to have materials with high heats of adsorption, as these materials can provide large amounts of energy and help move the process toward economic feasibility. Therefore, the heat of adsorption was varied between 20,000 J mol\(^{-1}\) and 110,000 J mol\(^{-1}\) to observe the effect on the temperature lift, energy density, and column breakthroughs. Figure 5-18 provides the resulting temperature lifts which shows that an increase in the heat of adsorption results in both a higher temperature lift and duration. The increased temperature output is a result of the increased amount of energy that is produced from water adsorption on a material with a higher heat of adsorption.

Figure 5-18: Column outlet temperature as a function of time for varying material heats of adsorption.
The breakthrough curves, shown in Figure 5-19, stay relatively constant, as the same amount of water is being adsorbed for the varying cases, the only difference is the amount of energy that is associated with the process. The breakthrough curves in Figure 5-19 stay relatively constant with changing heats of adsorption as all other parameters in the system are kept the same for the analysis.

![Figure 5-19: Column outlet gas concentration as a function of time for varying material heats of adsorption.](image)

The energy densities produced from the changing heats of adsorption were also calculated and are shown in Figure 5-20. The increase in the energy density of the system is linear with an increase in the material heat of adsorption. An increase in the energy density is produced because an increase in the heat of adsorption affects the energy balance in the column (Eq. 17), and results in a larger energy generation. Consequently, an increase in the heat of adsorption produces an increase in both temperature output and energy density. Therefore, the higher the heat of adsorption, the more overall energy that is produced from the system and the better the performance of the thermal energy storage process.
5.5 Conclusions

A mechanistic model was successfully developed for the simulation of thermal energy storage using adsorption. The model was built using material and energy balances including a material balance in the bulk phase of the column, a material balance in the pellet, an energy balance in the column, and an energy balance around the column wall. The model was validated using experimental data at varying conditions. The validated model was then used to perform a parametric study to observe the effect of changing parameters on the thermal energy storage performance.

The column dimensions were varied and it was found that an optimal L/D ratio of 1.4 provided sufficiently high output temperature lift and duration for energy storage applications. The particle diameter was studied to observe the effect of the column diameter to particle diameter ratio on the overall performance of the thermal energy storage system. It was found that for the given system, a particle size of 0.0023 m (Dc/Dp=14.7) provided the best thermal energy storage outputs. The adsorbent activation energy was studied to observe its effect on the adsorption process. It was found that it is desirable to have a low adsorbent activation energy to reduce the
energy barrier in order to obtain a high adsorption rate. The system flowrate was also varied and it was found that an optimal flowrate of 24 LPM provided a sufficient residence time for the adsorbate to reach the pores of the adsorbent and produced a desirable energy density. The adsorption column void fraction was then varied to determine the effect of the bed void fraction on energy storage. A void fraction of 0.4 was found to be optimal in order to produce sufficient temperature outputs and material energy densities. Finally, the heat of adsorption was studied and it was found that the highest possible heat of adsorption provided the largest amount of energy for the adsorption process, thus improving the performance of the thermal energy storage system.
## 5.6 Nomenclature

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<tr>
<th>Symbol</th>
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<th>Unit</th>
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5.7 References


Chapter 6 – Conclusions

6.1 General Conclusions

With continued development of renewable technologies, the worldwide energy demands will be sustained in future years. Thermal energy storage using adsorption is amongst these promising technologies which can provide reliable and environmentally-friendly energy supplies. Thermal energy storage allows for the use of energy sources that would otherwise be wasted, including solar and waste heat. The adsorption process allows for the correction between the supply and demand of these intermittent sources, for use when needed. The current study focused on expanding the knowledge related to this field to further the development of adsorption thermal energy storage technology. The areas investigated include material development, adsorbent performance testing, system parameter optimization, and mechanistic modeling.

A literature review was conducted to provide an overview of the various forms of energy storage technologies that are under development. The article focused on thermal energy storage using adsorption processes, and included a review of the leading materials used as well as the pilot-scale systems. The best adsorbents reported in the literature for adsorption thermal energy storage include zeolite 13X and activated alumina hybrid with lithium chloride salt impregnation, silica gel with calcium chloride impregnation, and activated alumina with alkaline addition, which provide energy densities from 226-309 kWh/m³ for water adsorption. These adsorbents, which include composite materials and materials with salt impregnation, are currently the most suitable adsorbents for this application. Additional research is required to ensure their stability in adsorption columns. The pilot-scale systems developed demonstrate the feasibility of this technology and the actual thermal outputs that can be achieved in real application. This research shows that although adsorption thermal energy storage is not yet economically viable, with continued development, this technology can become competitive and applicable in the near future.

For the investigation of new adsorbent materials to obtain better storage performances, an anhydrous magnesium carbonate was synthesized for used in the lab-scale thermal energy
storage system at the University of Ottawa. The novelty of this study resulted from the use of the anhydrous magnesium carbonate material as an adsorbent for thermal energy storage systems. The material was promising as it was reported to have an adsorption capacity larger than other adsorbents at low humidity environments, and to be thermally regenerated at temperatures below 100°C. The material synthesis procedure was systematically optimized to obtain the desired product with the limited details provided in the literature. The anhydrous magnesium carbonate was then tested in the adsorption system in comparison with other traditional adsorbents which included silica gel, activated alumina with alkaline addition, zeolite NaY, hydrogen mordenite, sodium mordenite, and zeolite 3A. At a relative humidity of 15%, the anhydrous magnesium carbonate provided the largest energy density of the adsorbents tested. The material was then tested at varying relative humidities of 20-55% to investigate its thermal performance and adsorption capacity. As the relative humidity increased, both the adsorption capacity and energy density had an overall increasing trend, as was expected. The synthesized material was also tested for its reusability by thermally regenerating the sample at 150°C between trials. It was found that with each new trial, the energy density of the material decreased significantly. The decline in performance is likely due to modifications of the adsorbent material, which can occur either during the regeneration step or the adsorption step. The decrease in performance observed with repeated trials is undesirable for adsorbents in thermal energy storage systems as the reusability of the material is an important factor in establishing the viability of the technology. Therefore, it was found that although the material produced significant energy outputs, it is not suitable for thermal energy storage applications.

A study was conducted to investigate the performance of various adsorbents at optimized system operating conditions. A major limitation of adsorption energy storage systems is their economics, as the energy outputs are not sufficient to render the process feasible. Current lab-scale systems in the literature use large energy inputs through high regeneration temperatures up to 1000°C, and high humidity environments up to 100% relative humidity, which require energy inputs for humidification. These conditions present significant monetary and energy requirements, which jeopardize the applicability of thermal energy storage systems. The current study explored a set of reduced energy intensive conditions to observe the effect on the energy
storage performance. The reduced conditions included a regeneration temperature of 150°C and low ambient humidity environments of 15-55% relative humidity. The adsorbents tested included zeolite 3A, silica gel, zeolite NaY, Na mordenite, H mordenite, and activated alumina with alkaline addition. An optimization study was done to determine the flowrate that gave the highest energy outputs for the adsorption column dimensions. A flowrate of 24 LPM was found to provide the highest energy density, and was therefore used for all adsorbent testing. The zeolites tested were not suitable for the adsorption system at low relative humidity environments due to their minimal temperature outputs, low energy densities, and poor water adsorption capacity. Both silica gel and activated alumina with alkaline addition were found to be suitable, with silica gel having a superior performance. At a relative humidity of 55%, silica gel provided an energy density of 135 kWh/m³ and activated alumina with alkaline addition provided an energy density of 128 kWh/m³. Silica gel performed better as it gave desirable breakthrough behaviour, significant temperature outputs, and high adsorption capacities. Both silica gel and activated alumina with alkaline addition were then tested at more energy intensive conditions to compare their performance. A regeneration temperature of 210°C and a relative humidity of 100% was used. Under these conditions, an energy density of 138 kWh/m³ was obtained for silica, which presents a minimal improvement. An energy density of 168 kWh/m³ was obtained for activated alumina with alkaline addition under these conditions, which presents a marginal increase in performance. The additional energy that was required for these intensive conditions was not recovered during the energy discharge and thus is not recommended. These results show that the additional energy inputs required for higher relative humidities and regeneration temperatures may not be necessary depending on the adsorbent used, and that high energy outputs can be obtained at reduced energy intensive conditions.

Finally, a mechanistic model was developed based on the material and energy balances in the adsorption system which included the material balance in the bulk phase, the material balance in the pellet, the energy balance in the column, and the energy balance around the column wall. The model developed was validated using experimental data at varying sets of operating conditions. The model was then used to conduct a parametric study, to observe the effect of varying parameters on the overall temperature outputs, energy densities, and
adsorption capacities. The parameters studied included the column dimensions, the adsorbent particle diameter, the adsorbent activation energy, the flowrate, the column void fraction, and the heat of adsorption. The column length and diameter were varied in the model and it was found that an optimal L/D ratio of 1.4 provided the best thermal output for energy storage systems. The effect of column diameter to particle diameter was investigated and it was found that a ratio of \( D_c/D_p = 14.7 \) gave the best thermal energy storage performance. Through investigation of the adsorbent activation energy, it was determined that the lowest possible value reduced the energy barrier and thus allowed for a high adsorption rate. Therefore, the lower the activation energy, the better the adsorption thermal energy storage performance. The effect of flowrate on thermal energy storage was studied and a value of 24 LPM was found to be the optimal flowrate for the current system dimensions, which is consistent with the results determined experimentally. This flowrate allows for sufficient residence time in the column for the adsorbate to reach the pore sites, and significant energy outputs. The adsorption column void fraction was also varied to observe its effect on the system performance. It was found that a void fraction of 0.4 was optimal for the delivery of the adsorbate to the adsorption sites to produce a substantial energy output. Finally, the heat of adsorption was investigated and it was found that the highest possible heat of adsorption provided the largest energy output from the adsorbent material, thus improving the thermal energy storage performance, as expected.

### 6.2 Recommendations

Additional work remains to be done for adsorption thermal energy storage systems to advance this promising technology for future implementation. Future areas of investigation include the development of new adsorbent materials with high energy densities, high temperature outputs, high adsorption capacities, and high heats of adsorption. The materials must also be reusable without a decline in performance between uses. Recommended adsorbents for future investigation include hybrids of silica gel and alkaline additions, silica gel with various salts impregnated, and activated alumina with various salts impregnated. Finally, the development of a pilot-scale system that could be used to assess the thermal energy storage
performance of suitable adsorbents at a large scale would allow for the testing and optimization of this technology.
APPENDICES
Appendix A – Improvements to Adsorption Thermal Energy Storage Systems using Hydrated Salt Impregnation

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Dominique Lefebvre, University of Ottawa
F. Handan Tezel, University of Ottawa

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 using water as the adsorbate. Magnesium sulphate, magnesium chloride and lithium chloride salts were chosen for their reaction properties and hygroscopic nature. The salts were impregnated into the hybrid adsorbent through submersion in a 37.5% wt. salt solution at 80°C for 24 hours and then dried in an oven at 250°C. Repeated adsorption/desorption cycles were performed on the impregnated adsorbents to determine their stability, performance and cycling behaviour. On average, the modified adsorbents had an increase of 25% in energy density compared to the unmodified adsorbent. The highest performing adsorbent recorded gave an energy density value of 309 kWh/m³, which represents a 50% increase over the performance of the unmodified adsorbent.

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1.0 Introduction: Organic Salts

Adsorption thermal energy storage systems have been present since the late 1970s [1]. During the oil crisis, these systems presented a promising technology that could lessen the dependency on foreign energy sources. Several promising adsorbent and adsorbate pairs were identified based on experimental lab-scale tests. The experiments were successful and several patents were filed on these types of systems [2-4]. However, as the oil crisis faded and fuel prices returned to normal levels, interest in adsorption thermal energy storage systems diminished before they were fully developed. Towards the 1990s, as the effects of global warming and the fear of depleting oil reserves set in, a new movement of renewable technologies was born. The concept of adsorption thermal energy storage was revisited and several institutes and associations began exploring combinations of adsorbent and adsorbate working pairs for a variety of applications. Much emphasis was placed on the screening of adsorbents to determine the best working pairs. Some of the highest previously reported energy density materials include silica gels, zeolites, activated aluminas, adsorbents with alkaline additions, and adsorbents with salt impregnation. Based on the experiments conducted, zeolite 13X and silica gel adsorbents using water as the adsorbate were identified as promising systems based on toxicity, availability and performance [5]. The next step in the technology development required prototype testing to store and extract the energy from the adsorbent beds and attempt to reach high energy densities, i.e. the thermal energy stored per volume of material or system volume, typically given in kWh/m$^3$. Although these systems worked, their energy densities per volume seldom surpassed 150 kWh/m$^3$ which made them too bulky for commercialization [6-10].

Attention was also placed on thermo-chemical materials and exothermic reactions as means of thermal energy storage, such as ammonia synthesis [11], boron [12] and inorganic oxides [13]. However, most reactions with pertinent energy densities require high temperatures in the range of 400-600°C to occur which could be applicable for high temperature steam production, but not useful for lower temperature heating applications. The hydration reaction of inorganic salts was suitable for lower temperature systems and thus gained interest. Using calorimeters and small powder samples, several salts were identified as having energy densities between 400-1500 kWh/m$^3$ which surpassed conventional adsorbent energy density values [14,
15]. Systems to exploit the energy density of salts are currently being developed with some difficulty. Salts require high surface areas for the hydration reaction and are usually in powdered form, causing large pressure drops in reactors. Additionally, some hydrates only release their maximum energy under 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 by supporting the salts on a porous material or lattice. However, any lattice that is not participating in the reaction is wasted space and makes the system more voluminous than required. This obstacle can be avoided by combining salts and adsorbents, two materials which released heat when combined with water, by impregnation which combines the benefits of both materials. This was observed by Aristov et al. [16] who studied composite materials of hygroscopic salts and porous matrices. They found that the resulting hybrid materials possessed intermediate behaviour between the salt and the porous matrix, which provided control of the water adsorption properties. Thus, 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 study explores the use of this combined salt hydrate and adsorbent system.

Impregnation is a simple method of modifying porous materials which typically involves 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 whereby an aqueous salt solution of varying concentration and temperature is produced [9, 14, 17-20]. 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 to the adsorbent. Some methods also include a calcination step to ensure that the salt is fixed to the adsorbent structure.
Much research has been performed using salt impregnated adsorbent hybrids. A large number of adsorbents have been used (silica gel, alumina, zeolites) in combination with various hygroscopic salts (CaCl$_2$, LiBr, MgCl$_2$, LiCl). These enhanced adsorbents are commonly referred to as selective water sorbents (SWSs). Zhu et al. [21], Daou et al. [22], and Ahm and Kim [23] prepared hybrid adsorbents of silica gel impregnated with CaCl$_2$ and studied the water adsorption properties of the material. They observed a much larger water uptake with the impregnated material. Zhu et al. obtained a high energy density of 228 kWh/m$^3$ for the impregnated CaCl$_2$ silica gel hybrid [21]. Aristov et al. [16] also tested hybrids of silica gel with CaCl$_2$ and LiBr salts and confirmed that the impregnated adsorbents have higher water uptake in comparison with the unmodified material. Janchen et al. [9] investigated the ion exchanged zeolites and mesoporous materials with hygroscopic salt impregnation and found that the adsorption capacities and the integral heats of adsorption were increased. This increase was observed as a result of the ion exchange with the adsorbent and salt hybrid. Janchen et al. [9] reported energy densities for aluminosilicate impregnated with CaCl$_2$ (172 kWh/m$^3$), and MgNaX impregnated zeolite (128 kWh/m$^3$). Hongois et al. [24] also investigated zeolites impregnated with MgSO$_4$ and attained energy densities of 166 kWh/m$^3$, a 27% increase in energy density in comparison with the pure zeolite. CaCl$_2$ is a commonly selected salt for use in adsorbent impregnation and investigative studies and was investigated by Ovoshchnikov et al. [25]. They confirmed that its presence results in an acceleration effect and determined that the salt addition provides increased water transport in the pores of the hybrid adsorbent due to the additional diffusion channel present.

Although calcium chloride is the most commonly investigated hygroscopic salt for adsorbent impregnation, the current work investigated magnesium sulphate, magnesium chloride, and lithium chloride salts to determine their effect on water adsorption. A hybrid adsorbent of activated alumina and zeolite 13X was impregnated with the respective salts and the resulting energy densities were determined for thermal energy storage applications.
2.0 Materials and Methods

The adsorbent to be impregnated was chosen after an extensive screening procedure in an earlier study [26]. The properties of the adsorbent are listed in Table 1. The chosen salts for impregnation were:

- Magnesium sulphate as it is identified in the literature as the most promising salt with a reported energy density of up to 777 kWh/m$^3$ [15, 27-30],
- Magnesium chloride as it is similar to magnesium sulphate and has 6 degrees of hydration (magnesium chloride hexahydrate) [14, 31],
- Lithium chloride as it has a hygroscopic nature [32].

Table 1: Adsorbent information.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Supplier</th>
<th>Product Name</th>
<th>Mesh size</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA /13X</td>
<td>Rio Tinto Alcan, Brockville, Ontario, Canada</td>
<td>ACTIGUARD 650PCAP</td>
<td>8x14</td>
</tr>
</tbody>
</table>

The salts were impregnated into the given adsorbent using the following procedure. 1.2 kg of salt was dissolved into 2 L of distilled water to produce a 37.5 wt% solution which is approximately the maximum concentration due to the salt solubility [33]. The solution was then heated to 80°C. 130 g of AA13X adsorbent was added to the solution and left to penetrate the pores 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. The weight changes observed for the produced adsorbent/salts are listed in Table 2.
Table 2: Initial and final data for salt impregnated hybrid adsorbents.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Initial adsorbent weight (g)</th>
<th>Final adsorbent weight (g)</th>
<th>Salt % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄</td>
<td>136.1</td>
<td>160.3</td>
<td>15.1</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>128.5</td>
<td>149.1</td>
<td>13.81</td>
</tr>
<tr>
<td>LiCl</td>
<td>129.7</td>
<td>150.5</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Once dried, adsorption and regeneration experiments were performed to determine the resulting energy densities using the same procedure and equipment as outlined in previous studies by Dicaire and Tezel [5]. Energy density, defined as the amount of thermal energy stored per volume of material, i.e. “material energy density”, was evaluated for the adsorbent/salt materials. The adsorption column was fabricated using 7 cm of 1.5” stainless steel tubing with a volume of 62.5 mL. Experiments were carried out in a controlled environment at 21°C and 101.3 kPa. During adsorption experiments, 100% relative humidity at 21°C (0.015 kg of water / kg of air) was fed to the column at 24 LPM by sparging the air through a chamber with an ultrasonic humidifier to create a moist environment. The air was then sent to a humidity trap where the excess condensed water was captured before the saturated air was sent to a hygrometer to measure its humidity content. For desorption experiments, 0% relative humidity air (0.00 kg of water / kg of air) was heated to 250°C and fed at 24 LPM to the column. In each desorption and adsorption run, sufficient time was given for equilibrium to be reached. The experiments ran for over 2.5 hours; adsorption runs reached equilibrium on average in 110 minutes, while desorption runs reached equilibrium on average in 120 minutes.

3.0 Results and Discussion

Each modified adsorbent was tested for 15 consecutive cycles where each cycle included one adsorption and one desorption step. The salts are extremely hygroscopic, and if left out in ambient humidity, will pull humidity from the air and form a liquid. Magnesium chloride and lithium chloride are often used as desiccants and dehumidification materials. The particular
properties of the salt hydrates were of concern as the impregnated adsorbents were being exposed to humidity as part of the adsorption 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 the 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. After the first experiment, the system was taken apart and cleaned. 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 1.

![Figure 1: Energy density for both the modified and unmodified adsorbents as a function of the number of cycles.](image-url)
As previously discussed [5], it is expected that the energy density that can be achieved by any adsorption material will be proportional to the amount of water adsorbed and the heat of adsorption of the material for that particular adsorbate. Therefore, an increase in the amount of water adsorbed results in an increase in the amount of energy released, and thus an increase in the energy density of the material.

Although the energy density values varied, the modified adsorbents showed a definite improvement over the unmodified adsorbent. Both modified adsorbents in Figure 1 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 unmodified adsorbent. The amount of water adsorbed during the experiments also increased by approximately the same percentage. The variations in the results obtained were also different than the original adsorbent. Not only were the standard deviation values doubled for magnesium sulphate and tripled for magnesium chloride, the variations oscillated before eventually tailing off to a more constant value. This type of oscillation has been previously recorded through other adsorbent studies. Storch et al. [34] performed a thorough analysis of adsorbent aging during hydrothermal cycling as well as the impact on the water uptake and energy density due to modification of the crystalline structure. Thus, it is not uncommon for the crystalline structure of an adsorbent to change with repeated experiments resulting in an increase or decrease of pore sizes and overall pore volume.

Another factor seen in typical adsorption columns is swelling and grinding of the adsorbent. The adsorption of water on an adsorbent causes it to swell, therefore, in a tightly packed column, this can result in grinding of the material as well as the production of fissures and erosion. Fissures are desirable as they increase the surface area of the adsorbent and thus can result in higher energy densities due to the new reaction sites exposed. However, excessive fissures and grinding causes erosion of the particles which then exit the column as fine dust. A combination of these factors, together with the addition of the impregnated hydrated salts is thought to be responsible for the variations in energy densities observed in Figure 1.
It was hypothesized that accounting for swelling of the particles and leaving empty space in the column could prevent variations. This theory was tested using the adsorbent impregnated with lithium chloride salt. The 62 mL column was filled with 51 mL of adsorbent and then 15 cycles of experiments were performed. The results obtained are displayed in Figure 2.

Lithium chloride had the best performance of the three salt impregnated materials tested. It reached a maximum performance above 309 kWh/m$^3$ and averaged 272 kWh/m$^3$ based on the adsorbent volume. The oscillation trend does not seem to be present although a large variation between runs is still evident with a standard deviation that is doubled that of the unmodified adsorbent. This performance is based on the adsorbent volume which was 51 mL. However, if the column volume is considered to include the void space required to produce these results, the performance would drop to 250 kWh/m$^3$, which is similar to the performance of the
other salts tested. Although it was not possible to quantify the swelling of the adsorbent and thus the actual working volume required, it was clear that more than 51 mL would be necessary. Therefore, a more representative energy density would be a value between the two data series reported in Figure 2.

![Figure 3: Comparison of energy density as a function of the number of cycles for all modified and unmodified adsorbents.](image)

Figure 3 displays the results of all three modified adsorbents impregnated with salts as well as the unmodified adsorbent for comparison. Lithium chloride gave the highest performance, followed by magnesium sulphate and then magnesium chloride. Since the variations in values were significant, a confidence interval was calculated using Equation 1 for the three modified adsorbents [35].

\[
\text{Limits} = \bar{X} \pm t_{\alpha/2, n-1} \frac{\text{Standard Deviation}}{\sqrt{\text{number of runs}}}, \text{ where } t_{\alpha/2, n-1} = 3.012
\]  

[1]
In Equation 1, $\bar{X}$ represents the sample mean, and $t_{\frac{\alpha}{2},n-1}$ represents the upper $\alpha/2\%$ point of the t-distribution with n-1 degrees of freedom. A confidence interval is a range of potential values to represent a reported value when there is a large amount of variations in the experimental reading. First, the average and standard deviation of the data set were calculated. Then, a range of potential other average values were 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.

Table 3: Statistical analysis of energy density for modified adsorbents.

<table>
<thead>
<tr>
<th></th>
<th>Energy Density Mean (kWh/m$^3$)</th>
<th>Standard Deviation (kWh/m$^3$)</th>
<th>Degrees of Freedom</th>
<th>Lower Limit (99%) (kWh/m$^3$)</th>
<th>Upper Limit (99%) (kWh/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO$_4$</td>
<td>249.99</td>
<td>13.74</td>
<td>13</td>
<td>238.92</td>
<td>261.04</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>234.93</td>
<td>21.97</td>
<td>13</td>
<td>217.24</td>
<td>252.61</td>
</tr>
<tr>
<td>LiCl</td>
<td>272.40</td>
<td>25.23</td>
<td>13</td>
<td>252.09</td>
<td>292.70</td>
</tr>
</tbody>
</table>

The lithium chloride impregnated adsorbent has the highest performance, 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 at approximately 252 kWh/m$^3$, therefore 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; the AA13X 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 both react with the salt and get adsorbed. It is possible that the salts were only achieving partial hydration. If each pore can accommodate a given amount of salt molecules and water molecules, 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 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 [36]. Although the presence of a salt will increase the driving force and add to the 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 part of the pore volume. To exploit the maximum potential of the salts, 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 well which means the adsorbent would act like a support and not participate in increasing the energy density.

4.0 Conclusion

Magnesium sulphate, magnesium chloride and lithium chloride salts have been successfully impregnated into the base AA13X adsorbent. The salt impregnations significantly improved the energy density of the adsorbent material but presented large variations in performance. Lithium chloride salt gave the highest performance of the three salt impregnated adsorbents tested, with a maximum recorded energy density of 309 kWh/m³. However, as the standard deviation for the performance of all hybrid adsorbents is sufficiently large, all salt impregnated adsorbents tested can be considered to have comparatively the same performance, with an energy density of approximately 252 kWh/m³. This suggests that the adsorbent pore size may be the limiting factor in exploiting the salt potential. Further work remains to be done to improve the salt hydrate behaviour as an impregnation material in adsorbents. Some of the observed aspects are inconsistent and undesirable, including variation in crystalline structure, change in pore size and distribution, material erosion, and material fissures. Regardless, the impregnated salt adsorbents represented a 25 % improvement on energy density over the base adsorbent. The high energy density values obtained surpass those previously reported in the literature for both conventional
adsorbents and salt impregnated adsorbents. Thus, with further development, salt impregnated adsorbents have the potential to provide a large amount of energy for a wide variety of applications.

5.0 Acknowledgements

The authors would like to thank the National Sciences and Engineering Research Council of Canada (NSERC), as well as the Ontario Centres of Excellence (OCE) for the funding provided for the research conducted. The authors would also like to thank their industrial partner Menova Energy Inc. for the data they supplied.
6.0 Works Cited


Appendix B – Thermal Energy Storage System Calculations

Humidity

The humidity was calculated using Eq. A1:

\[ H = \left( \frac{x}{100} \right) 0.0042 e^{0.0629T} \]  
(Eq. A1)

where \( H \) is the humidity [kg H\(_2\)O/ kg dry air], \( x \) is the relative humidity [%], and \( T \) is the temperature at which the relative humidity was recorded [°C]. Equation A1 is used to calculate both the column inlet and the column outlet relative humidity.

Partial Pressure of Water Vapour

The partial pressure of the water vapour in the stream was calculated using Eq. A2:

\[ p_{H_2O} = \frac{P 
\times H_{av}}{M_{H_2O} + M_{Air}} \]  
(Eq. A2)

where \( p_{H_2O} \) is the partial pressure of water in the mixture [Pa], \( P \) is the total pressure [Pa], \( M_{H_2O} \) and \( M_{Air} \) are the molecular weights of water and air, respectively [g/mol], and \( H_{av} \) is the average humidity at the inlet and outlet of the column [kg H\(_2\)O/kg dry air].

Density of Moist Air

The density of the moist air was calculated using Eq. A3:

\[ \rho_{MA} = \frac{P - 0.378p_{H_2O}}{287.1T_{av}} \]  
(Eq. A3)

where \( \rho_{MA} \) is the density of the moist air [kg/m\(^3\)], and \( T_{av} \) is the average temperature in the column [K].

Heat Capacity of Moist Air

The heat capacity of the moist air was calculated using Eq. A4:

\[ C_{p,MA} = C_{p,DA} + C_{p,H_2O}H \]  
(Eq. A4)

where \( C_{p,MA} \) is the heat capacity of the moist air [kJ/kg K], \( C_{p,DA} \) is the heat capacity of dry air [kJ/kg K], and \( C_{p,H_2O} \) is the heat capacity of water vapour.
Mass of Moist Air

The mass of moist air that flows through the system at a given point was calculated using Eq. A5:

\[ M_{MA,i} = \sum_{i=1}^{n} (t_i - t_{i-1}) \nu \rho_{MA,i} \]  

(Eq. A5)

where \( M_{MA,i} \) is the mass of moist air at a given point [kg], \( t_i - t_{i-1} \) is a step in time [min.], \( \nu \) is the volumetric flowrate [m\(^3\)/min.], and \( \rho_{MA,i} \) is the density of the moist air for a given time step.

Energy Released

The energy released was calculated using Eq. A6:

\[ E = \sum_{i=1}^{n} M_{MA,i} C_{p,MA} (T_{out} - T_{in}) \]  

(Eq. A6)

where \( E \) is the total energy released [kJ], and \( T_{out} - T_{in} \) is the temperature differential between the column outlet and inlet.

Energy Density

The energy density is calculated using Eq. A7:

\[ E.D. = \frac{E \cdot 1 \text{ kWh}}{V \cdot 3600 \text{ kJ}} \]  

(Eq. A7)

where E.D. is the energy density [kWh/m\(^3\)], and \( V \) is the column volume [m\(^3\)].

Amount of Water Adsorbed

The amount of water adsorbed in the adsorption column was calculated using Eq. A8:

\[ M_{H_2O,ADS} = \sum_{i=1}^{n} M_{DA} (H_{in} - H_{out})_i \]  

(Eq. A8)

where \( M_{H_2O,ADS} \) is the amount of water adsorbed [kg], \( M_{DA} \) is the mass of dry air [kg], and \( (H_{in} - H_{out})_i \) is the difference between the inlet and outlet relative humidity at a given point [kg H\(_2\)O/kg dry air].