9-5-2017

Evaluation of heat available from calcium chloride desiccant hydration reaction for domestic heating in San Francisco, CA

Michael Giglio
Santa Clara University, mgiglio@scu.edu

Recommended Citation

Giglio, Michael, "Evaluation of heat available from calcium chloride desiccant hydration reaction for domestic heating in San Francisco, CA" (2017). *Mechanical Engineering Master's Theses*. 14.
http://scholarcommons.scu.edu/mech_mstr/14

Santa Clara University

Department of Mechanical Engineering

September 5th, 2017

I HEARBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Michael Giglio

ENTITLED

EVALUATION OF HEAT AVAILABLE FROM CALCIUM CHLORIDE DESICCANT HYDRATION REACTION FOR DOMESTIC HEATING IN SAN FRANCISCO, CA

BE ACCEPTED IN PARTIAL FULFILLMENTS OF THE REQUIREMENTS FOR THE DEGREE

OF

MASTER IN SCIENCE OF MECHANICAL ENGINEERING

HOHYUN LEE, PhD, THESIS ADVISOR

Robert A. Marks

ROBERT MARKS, PhD, THESIS READER

DRAZEN FABRIS, PhD. CHAIRMAN OF DEPT.

EVALUATION OF HEAT AVAILABLE FROM CALCIUM CHLORIDE DESICCANT HYDRATION REACTION FOR DOMESTIC HEATING IN SAN FRANCISCO, CA

BY

MICHAEL GIGLIO

MASTER OF SCIENCE THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE
IN MECHANICAL ENGINEERING IN THE SCHOOL OF ENGINEERING
SANTA CLARA UNIVERSITY, 2017

SANTA CLARA, CALIFORNIA, USA

Acknowledgments

I would like to thank my advisor Dr. Hohyun Lee for his excellent guidance and support. I learned a lot about technical writing and thermal energy storage from working with him.

I would also like to thank Dr. Robert Marks as the second reader of this thesis. I am very grateful for his participation and feedback.

I would like to extend an additional thank you to Joseph Singer, Tom Watson, and Chenli Wang for their support and feedback during this experience as well.

Finally, I want to thank my family and friends for always supporting me throughout my education.

Abstract

Thermochemical energy storage has the potential to support the use of solar thermal energy collection in ways that traditional thermal energy storage, like sensible and latent heat storage, have fallen short. Thermochemical energy storage has been shown to have higher storage capacities than sensible and latent storage for dehumidifying applications and does not require insulation like sensible and latent heating do. Sensible heating is focused on maintaining an increased temperature of a storage medium while latent heat storage is focused on maintaining a phase of the storage material. Both sensible and latent heat storage have been shown to have lower storage capacities for the purposes of air cooling when compared to thermochemical energy storage, which allows for the conversion of heat energy to thermochemical energy. Liquid desiccants utilize heat in an endothermic reaction to concentrate the solution and create chemical bonds, resulting in a chemical potential that can later be released as heat with the addition of water or used to absorb water vapor with heat as the by product. Due to the fact that the energy is stored as a chemical potential, heat loss is minimal and insulation is not needed to store the majority of invested energy as much as other energy storage methods. However, current liquid desiccant energy storage systems focus on the dehumidification and cooling properties of desiccant materials and such systems face problems with desiccant carryover, corrosion, and are often expensive. This paper looks at using calcium chloride as a desiccant material to reduce costs, and examines the use of liquid desiccants for heating rather than cooling purposes. A test heat exchanger was built to evaluate the feasibility of heat extraction upon water addition and compare it to the theoretical prediction. A basic shell and tube heat exchanger was constructed, using copper piping, a plastic bin, a peristaltic pump and flexible hosing. The results from this experiment show the feasibility of a basic heat exchanger to extract significant heat from this reaction. The experiments done in this investigation reveal that a storage capacity of 19 kWh/m^3 can be expected for the best-case scenario of a dilution reaction between 100% concentrated calcium chloride and water to a 20% solution.

Table of Contents

List of Figures

List of Tables

NOMENCLATURE

A	Area, $[m^2]$
β	Thermal Expansion Coefficient
C_p	Specific Heat Capacity, $[J/kg \cdot K]$
D	Diameter, $[m]$
d	Discount Rate, [%]
FV	Future Value, [$]
g	Acceleration due to gravity, $[m/s^2]$
Gr	Grashof Number, [-]
h_c	Heat Transfer Coefficient of Cold Fluid, $[W/m^2K]$
h_f	Enthalpy of Formation, $[kJ/kg]$
h_h	Heat Transfer Coefficient of Hot Fluid, $[W/m^2K]$
h_T	Sensible Enthalpy, $[kJ/kg]$
k	Thermal Conductivity $[W/(m\text{-}K)]$
$LCOE$	Levelized Cost of Energy, $[\$/kWh]$
m	Mass, $[kg]$
$\dot{m}$	Mass Flowrate, $[kg/s]$
M_{Sol}	Molar Mass of Solution, $[mol]$

Nu_D	Nusselt Number with respect to Diameter,[-]
Pr	Prandtl Number, [-]
PV	Present Value, [$]
q	Rate of Heat Transfer, [kW]
Q_{rxn}	Heat of Reaction, [kJ]
Ra_D	Raleigh Number, [-]
Re_D	Reynolds Number, [-]
ROI	Return on Investment, [-]
T	Temperature, [°C]
t	Time, [years], [s]
U	Overall Heat Transfer Coefficient, [W/m^2K]
ν	Kinematic Viscosity, [m^2/s]

1 Introduction

1.1 Background

Energy usage in the United States is no longer a luxury but rather an essential part of the modern residential lifestyle. Heating, air-conditioning, and electrical appliance usage, all contribute to the demand for energy in the residential sector. The sources for energy production vary by climate and geography throughout the United States, however, energy derived from fossil fuels currently constitutes for approximately 75% of all residential energy consumption throughout the country [1]. The high demand for energy and the reliance on fossil fuels is contributing to the rise in global temperatures due to the release of carbon dioxide from the combustion of these fuels [2].

Domestic space and water heating, while decreasing in recent years in proportion of energy usage in the home, still reflects a majority (59.2%) of residential energy use in the United States [3]. Natural gas and electricity are the primary energy sources for domestic heating with just over 60% of electrical sources derived from fossil fuels [1], [4]. To put this in perspective, an average reduction in domestic heating by 10%, would correspond to a decrease of approximately 20 million metric tonnes of carbon dioxide. Since this reduction in domestic heating corresponds to a less than 1% reduction in total CO_2 production across the country, it becomes necessary to find a solution to drastically reduce the amount of domestic heating from fossil fuels to make a significant reduction in carbon output. These percentage reductions are based on national averages and would change based on a location, income, and climate within different regions across the country. Domestic space and water heating presents a sector of energy use that has yet to make a serious transition to clean and renewable sources.

Solar thermal energy provides a clean, renewable, and ample source of heat energy. While domestic heating systems can be tied to residential solar thermal systems, collected solar energy is often misaligned with domestic heating demand. Thus the full potential of heating from solar thermal systems is often not utilized. San Francisco, a city which currently derives the majority of its domestic heating from natural gas [5], provides an example of a city that has room to reduce its dependence on fossil fuels. If the domestic heating demand is compared with peak solar collection times for San Francisco, the misaligned relationship is clear. Figure 1 below shows the misalignment between the timing of average hourly solar energy available and the average hourly demand for domestic heating in San Francisco, California. The graph shows a normalized amount of solar radiation and heating demand to highlight the misalignment of the heating supply vs. the heating demand. San Francisco was originally selected as a city of interest for this investigation for its low humidity levels. This characteristic would provide an ideal environment for charging the desiccant since less energy would be required to vaporize the water from the solution to the ambient environment. This perspective was changed over the course of this investigation as the benefits of a closed system became more apparent and the advantage of having low humidity levels less advantageous.

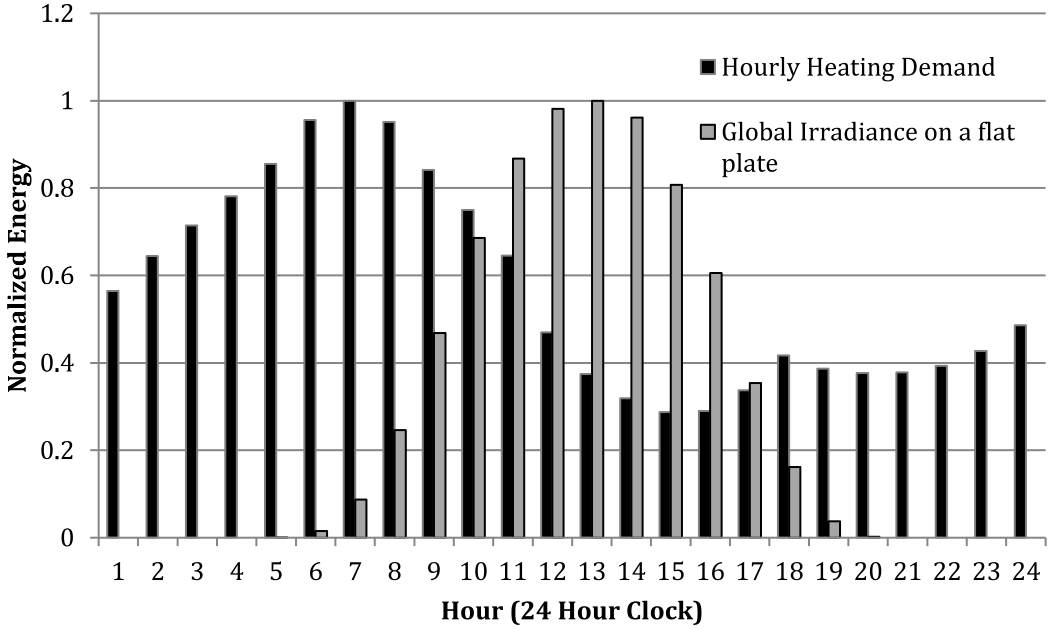

Figure 1: Average hourly consumption of natural gas for a single residential consumer in San Francisco for a Typical Meteorological Year [5]; and average hourly normal and diffuse solar radiation on a horizontal plate for San Francisco for a Typical Meteorological Year (TMY) [6]. Demand and solar supply are normalized by their respective maximum hourly values.

Figure 1 reveals that the peak amount of solar radiation available for collection occurs approximately 6 hours after the peak demand for domestic heating. Thus, solar thermal collection systems would only fully meet heating demands between the hours of 10 am and 5 pm, which are the hours of lowest heating demand. Thermal Energy Storage (TES) can be used to distribute collected thermal energy throughout the day and better align heating supply with demand. During times of low heating demand, excess solar radiation collected can be stored and then extracted at times when demand is high but solar radiation is low.

TES solutions have traditionally been focused on storing energy via sensible heating or latent heating. Sensible heat storage involves raising the temperature of the storage medium. Sensible heating has a relatively low storage capacity among TES methods, typically around 0.2 GJ/m^3 or 55 kWh/m^3 [7]. Latent heat storage involves the storage of energy by means of a phase change. Latent heat storage typically has energy storage capacities higher than sensible storage methods due to the high enthalpy change associated with a phase change in combination with a relatively high, although lower than some sensible storage materials like water, specific heat capacity [7]. Latent heat storage can be applied for phase change temperatures ranging up to the hundreds of degrees Celsius, but for domestic heating it is focused on temperatures closer to those experienced in the home, ranging between 20–80 ° C. Latent heat storage capacity for domestic heating typically ranges between 0.3-0.5 $\mathrm{GJ/m^3}$($\sim$80–140 $\mathrm{kWh/m^3}$) [7]. Both latent and sensible heat storage require insulation to maintain the temperature or phase of the storage medium, which adds an additional space requirement on top of the required volume of storage medium as dictated by the storage capacity of the material.

An alternative method of storing heat is by means of thermochemical energy storage (TCES), which involves the storing of heat via a reversible association/dissociation reaction between two substances. As explained by Abedin et al. [7], TCES can be visualized by three stages. The charging stage, which constitutes the investment of heat into an endothermic reaction, is comparable to other TES methods except the heat energy is used to separate (or concentrate) the storage medium rather than raise the temperature (sensible heating) or induce a change in phase (latent heating). The storage stage of TCES is accomplished by maintaining the separation of the TCES storage materials. This process accrues minimal losses (only from the cooling of the materials after charging) and requires no thermal insulation to maintain the separation of materials. This stage makes TCES advantageous for storing energy for longer periods of time since the stored energy will be maintained so long as the materials are kept separate. The final stage is the discharging stage, where the reverse reaction of the charging stage occurs. This reaction involves the recombination of the storage materials in an exothermic reaction allowing for the recovery of the stored energy.

Sorption processes, which include both adsorption and absorption, involve chemical reactions during the exchange of thermal energy and are thus included under the category of thermochemical energy storage. Adsorption is the adhesion of a fluid to a surface (solid or liquid) on a molecular level, while absorption involves the dissolving of a fluid in a liquid or solid to create a solution. Both adsorption and absorption are examples of the charging stage of TCES and both processes have respective desorption processes that represent the discharging stage of TCES.

Adsorption and absorption processes have been used in the past for their dehumidifying properties and their ability to remove contaminants from fluids. Adsorbent materials, such as zeolites and silica gels, have been used in solid desiccant wheels to remove water vapor from process air in air-conditioning applications with varied levels of success [8], [9]. Such systems expose desiccant wheels to incoming process air with high humidity and high temperatures. The desiccant wheel absorbs the water vapor from the air reducing the temperature. Simultaneously, an external heat source applies heat to the other side of the wheel away from the incoming process air to recharge the desiccant and expel the water that was previously absorbed. The wheel rotates continuously as incoming air is dehumidified and the absorbed moisture is expelled back to the environment on the other side of the wheel. Optimization of desiccant wheel materials and operating conditions are still being investigated. The Fraunhofer Institute claims to have developed a zeolite TCES system for heating purposes that has a storage capacity of up to 180 kWh/m^3, depending on the regeneration temperatures [10]. The institute is quick to say, however, that this zeolite based TCES system is relatively expensive.

Absorption processes tend to relate to liquid thermochemical reactions, but can also refer to solids. Liquid absorption processes include the combination of a solute and solvent in an exothermic process to create a solution. The solution can then be regenerated (charging stage) by supplying heat to the solution and inducing an endothermic reaction to concentrate the solute and expel the solvent from the solution.

There are many thermochemical materials that can undergo absorption/desorption reactions, each of which varies significantly with respect energy storage capacity, regeneration temperature, toxicity, cost, corrosiveness, reaction temperature, equilibrium vapor pressure, as well as heat transfer and flow properties. Of the properties mentioned, energy storage capacity and regeneration/reaction temperature may be the most important properties with respect to a material's ability to store thermal energy for a residential building. At the same time, toxicity, corrosiveness, and cost may be the most important properties when considering design and application of a TCES system. Many inorganic compounds and salts, such as magnesium sulfate, lithium chloride, iron carbonate exhibit strong thermochemical energy storage properties. Abedin et al. [7] give a comparison for a some of these thermochemical materials and report storage capacities between 0.5 and 3 GJ/m^3(140-830 kWh/m^3) and regeneration temperatures between 20 and 200 °C. This wide range of thermochemical properties allows for the selection of an absorption material for varying conditions. The following table, which was reformatted from the Abedin et al. text, summarizes some of the distinctions between thermal energy storage methods.

Table 1: Thermal energy storage method comparison. Information taken from Abedin et al. [7]

Performance Parameter	Type of Thermal Energy Storage		
	Sensible TES	Latent TES	Chemical TES (Sorption and Thermochemical)
Temperature Range	Up to: 110 °C (water tanks) 50 °C (aquifers and ground storage) 400 °C (concrete)	20-40 °C (paraffins) 30-80 °C (salt hydrates)	20-200 °C
Storage Density	0.2 GJ/m^3 (for typical water tanks)	0.3-0.5 GJ/m^3	0.5-3 GJ/m^3

One class of thermochemical absorption materials can be described as liquid desiccants. A desiccant is a substance that tends to induce a state of dryness in its vicinity, exhibiting hygroscopic properties. Such desiccants include lithium chloride, lithium bromide, calcium chloride. These salts act as the solute of the absorption process while water, either in vapor or liquid phase, acts as the solute. The driving force of the hygroscopic tendency of liquid desiccants is the low equilibrium vapor pressure of the solution, which varies by substance. A crystalized salt desiccant will naturally absorb water until the water vapor pressure is reduced to the pressure in equilibrium with the dissolved salt solution. In other words, water vapor pressure increases with decreasing concentration and, while practically unattainable in liquid form, the lowest vapor pressure for a given desiccant solution would occur at 100% concentration. It should be restated that desiccants will absorb water in the vapor or liquid phase, which allows for a wide range of applications for the stored energy in liquid or solid desiccants.

Similar to adsorption based dehumidification, absorption processes utilizing liquid desiccants have been applied to removing water vapor from process air and provide cooling for air-conditioning purposes. Such systems utilize an external heat source to concentrate the desiccant material, so that it can remove water vapor from the process air, which then dilutes the desiccant before it is introduced to the external heat source again. A solar driven liquid desiccant cooling system has been developed in Singapore by L-DCS and shown to provide a storage capacity of 183 kWh/m^3, while a similar system has been developed by ZAE Bayern that utilizes a lithium chloride solution and district heating to provide 12 kW of cooling and a storage density of 150 kWh/m^3 [11].

Andrew Lowenstein discusses the challenges of desiccant based cooling systems in his *Review of Liquid Desiccant Technology for HVAC Applications [12]*. Lowenstein describes that certain aspects of the heat and mass transfer systems in liquid desiccant cooling systems need to be improved to overcome challenges with current systems. Corrosion of the heat exchange surfaces as well as desiccant carryover, which describes a scenario when desiccant droplets are unintentionally introduced into the process air, are challenges that current research on heat and mass transfer systems are hoping to overcome. Desiccant carryover can be a problem for people within the spaces that are being cooled since desiccants possess varying levels of toxicity. This presents a safety issue for consumers and must be eliminated for desiccant based energy storage systems to be accepted by the public. This paper reveals that improvements in this hardware are focused on using plastic or plastic coated heat exchange surfaces to reduce corrosion and developing systems that utilize low flow desiccant and low flow process air systems to reduce carryover. This review makes note of the fact that fully closed/contained desiccant systems are less susceptible to corrosion given that there is less interaction between the corrosive desiccant and oxygen in the air. Although there are signs of success in reducing these challenges, this review concludes that there is still more research to be done to eliminate desiccant carryover and corrosion, and to select an appropriate, cost sensitive, desiccant.

The most common desiccant material used in liquid desiccant cooling systems has been lithium chloride. This has been an obvious choice given that it has a lower equilibrium vapor pressure at the same concentrations than other desiccant materials [13]. That being said, lithium chloride is by far one of the most expensive desiccant materials. Lithium chloride has been cited as five to twenty times more expensive than calcium chloride, a desiccant with similar but lower vapor pressure properties than lithium chloride [12],[14]. Calcium chloride has not been used as frequently in liquid desiccant cooling systems because it does not possess as strong dehumidifying properties as lithium chloride due to higher vapor pressures at the same concentrations (Table 2). This also leads to lower energy storage capacities, which again makes calcium chloride less attractive than lithium chloride.

Table 2: Comparison between Lithium and Calcium Chloride. Vapor pressures taken from Abedin et al., [7] and Sahlot et al., [15].Note that the vapor pressure is listed as relative to the vapor pressure of water at the same temperature. Prices ranges taken from online suppliers.

Desiccant	Cost	Relative Vapor Pressure at 40% Concentration and 45°C [-]
Lithium Chloride	\$1-100/kg	0.10
Lithium Bromide	\$1-100/kg	0.26
Calcium Chloride	\$0.1-1/kg	0.30

Lowenstein describes that Ertas et al. gives evidence for the benefit of combining mixtures of calcium chloride and lithium chloride in *Properties of a new liquid desiccant solution—lithium chloride and calcium chloride mixtures*. The experiments in this report reveal that a 50/50 mixture of calcium and lithium chloride in water solution would indeed reduce the cost of the desiccant material and reduce the equilibrium vapor pressure of the mixture closer to that of a pure lithium chloride and water solution. Lowenstein goes on to say that further that a complete design study of a liquid desiccant air conditioner using the 50/50 mixture would be need to determine if this would be an “attractive alternative.”

Given that three of the challenges, identified by Lowenstein, that face liquid desiccant energy storage are the cost of the desiccant material, the fact that salts tend to corrode the heat and mass transfer surfaces of the storage system, and that desiccant carryover must be reduced, calcium chloride will be investigated as a TCES material for domestic heating purposes. Calcium chloride offers a much more cost-effective alternative to other desiccant materials, especially lithium chloride, while focusing on heating reduces the need for the desiccant to be in contact with any process air, reducing the potential for corrosion and for desiccant carryover. That being said, calcium chloride needs to be evaluated for its exothermic potential and for its storage capacity to determine if it would be appropriate as a thermal storage medium for use in residential heating. Calcium chloride is known to have higher vapor pressures than other desiccant materials, making it a less effective dehumidifier, but the exothermic properties of this liquid desiccant could change the perspective of calcium chloride as a thermochemical energy storage medium.

This paper will provide a theoretical presentation of the exothermic potential of calcium chloride and will discuss the construction of a heat exchanger that was used to empirically evaluate the heating potential from a calcium chloride hydration reaction. The results from the experiments with this heat exchanger will be discussed and analyzed with respect to heating demands for the city of San Francisco.

1.2 Concept Desiccant Storage System for Domestic Heating

This investigation focuses on the discharge stage of a conceptual desiccant based heat storage system. This stage corresponds with the diluting of the desiccant with water and the release of heat from the exothermic reaction. The further understanding of this stage of the storage cycle will help determine the storage capacity of calcium chloride with respect to domestic heating. This will allow for the direct comparison between other storage methods that could be used for domestic heating. Other parts of such a storage system, including hardware required for the charging stage and potential control systems would need to be evaluated to show feasibility, but this first assessment will help determine if calcium chloride based thermal energy storage will be a viable option that exhibits high storage capacities for heating.

A conceptual thermochemical storage system for heating can be visualized in Figure 2. The storage system would include a method of collecting heat (likely solar thermal collectors), a heat exchanger to transfer the heat collected to the desiccant during the charging stage, and another heat exchanger to extract the stored heat for the home (upon the addition of water in the discharge stage). As the desiccant is heated by the solar thermal system, water would be evaporated to a separate storage tank. This storage tank would be kept isolated from the desiccant during the storage period to maintain the chemical potential in the charged desiccant. Water from the second tank would then be allowed to dilute the desiccant to release heat as demand increased. As stated previously, this thesis will focus on the discharge stage, which will help determine the amount of heat available after the storage period. The dashed box outlines the heat exchanger associated with this stage in Figure 2.

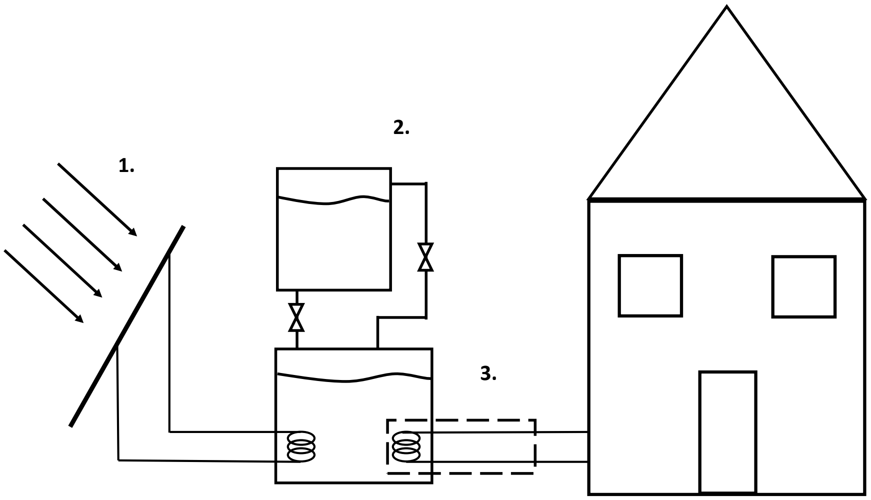

Figure 2: Solar driven thermochemical energy storage concept for domestic heating. 1-Solar Thermal Collector, 2-Concept storage system with water tank (above) and desiccant storage tank below, 3-Heat exchanger for the extraction of heat after storage.

This heat exchanger was intended to be an experimental tool to get a more realistic approximation of the exothermic potential of a calcium chloride hydration reaction. The results from the experiments run in this investigation were used to make an economic evaluation of such a desiccant storage/heating system. This understanding of the heating and economic potential of such a system was intended to provide a foundation for the use of calcium chloride as a heating source so that future investigations could determine if indeed desiccant carryover and corrosion could be reduced.

The system constructed for this thesis did not attempt to solve the challenges associated with desiccant corrosion and carryover, and it was not intended to be a potential product or solution that could be directly applied in a home setting. Rather, the heat exchanger was built to answer a more basic question, which had not been concluded in the research for this paper: can a calcium chloride storage system provide a significant amount of domestic heating, and if so, how persuasive are the economic considerations?

The heat exchanger was designed to contain the desiccant hydration reaction in a plastic bin, insulated by a Styrofoam casing. This would act as the shell portion of the heat exchanger, while the working fluid (water) was pumped through the heat exchange tubing, made of quarter inch copper piping, to extract the heat from the reaction. The fluid was pumped from a large reservoir through the heat exchange system using a peristaltic pump that supplied 1-2 grams/s of flow. The inlet and outlet temperatures were measured using submerged thermocouples to determine the overall amount of energy that was transferred. A schematic of the system and the actual hardware will be discussed further in more detail in Chapter 3.

Chapter 2 will discuss the theoretical predictions associated with amount of heat available from a calcium chloride reaction and will also present a method for sizing the experimental heat exchanger that will be used in this investigation. Chapter 3 will discuss the heat exchanger hardware in more detail and will discuss the experiments that were conducted. Chapter 4 will discuss the results from these experiments, while chapter 5 will provide an analysis of the results and bring in an economic perspective of using calcium chloride as a storage medium for heating purposes.

2 Theoretical Predictions

This investigation is focused on the discharge stage of a calcium chloride ($CaCl_2$) and water absorption reaction. The goal of this thesis is to determine how much heat could be extracted given a known amount of desiccant and to use this information to present a case for solar thermal heating with thermochemical energy storage for San Francisco, CA.

This section will include evaluations of the maximum heat of dissolution of a desiccant and water reaction from a thermodynamic perspective as well as an analysis to determine an appropriate sized heat exchanger to empirically verify the amount of heat available from such a desiccant and water reaction. The heat of dissolution is based on the heat of formation of the chemical compounds while the heat exchanger sizing employs the log mean temperature difference method for heat exchanger length. This section will also take a brief look into the rate of reaction given the resources available.

2.1 Thermodynamics of Dissolution (Exergy Calculation)

For the purpose of this paper, a few calculations were conducted to theoretically predict the amount of heat transfer available from the desiccant reaction and thus to appropriately design a test heat exchanger given the calculated amount of heat. This section will detail the predictions of the heat available from the discharge portion of the energy storage cycle.

The chemical equation for the discharge portion of a storage cycle between calcium chloride and water can be seen in equation 1. This equation reveals that with the addition of water, the ionic compound “calcium chloride” disassociates into calcium and chloride ions. Knowing the reactants and products allows for the calculation of the enthalpy of the reaction as will be discussed.

$$CaCl_2(s) \rightarrow Ca^{+}(aq) + 2Cl^{-}(aq) \qquad (1)$$

The theoretical heat available from the desiccant reaction can be determined by calculating the enthalpy of formation of the reaction. The enthalpy of formation for this reaction is sometimes referred to as the enthalpy of dissolution, due to the disassociation of the calcium and chloride ions into the solvent, water. The enthalpy of dissolution is calculated by finding the difference between the enthalpies of formation of the products and the enthalpy of formation of the reactants.

$$Q_{rxn} = \sum_{prod} h_f - \sum_{React} h_f \qquad (2)$$

If we refer to equation (1) in the previous section, we see that we the enthalpy of dissolution can be calculated as follows. Applying equation (2) to the chemical reaction in (1), we have:

$$Q_{rxn} = \left(h_{f,Ca^{2+}} + 2h_{f,Ca^{-}}\right)_{Prod} + (h_{T_f} - h_{T_i})M_{Sol} - (h_{f,CaCl_2})_{React} \qquad (3)$$

One can see, equation (3) also includes enthalpy terms associated with the temperature of the solution at both the initial and final stages of the reaction. All of the enthalpy terms associated with the formation of either one of the reactants or the products are known tabulated values and can thus be used in equation (3). The sensible enthalpy increase during the reaction is calculated by integrating the specific heat of the solution with respect to temperature.

$$h(T) = \int_0^T C_{p,sol} dT \qquad (4)$$

The specific heat of the calcium chloride solution, $C_{p,sol}$, varies with temperature and concentration, but will be approximated as constant for this initial understanding of the available heat of dissolution (2.93 $[\frac{kJ}{kg-K}]$).

Finally, the molar mass of the final solution, M_{Sol}, must be determined. This can be done by taking a weighted average (with respect to mass concentration) of the molar masses of both components in the solution; water (75% by mass) and calcium chloride (25%).

If we assume a perfectly insulated reaction and the initial temperature of the solution to be 25 °C we can allow the final temperature of the function to vary, and plot the enthalpy of dissolution as a function of the final temperature as seen in the following figure.

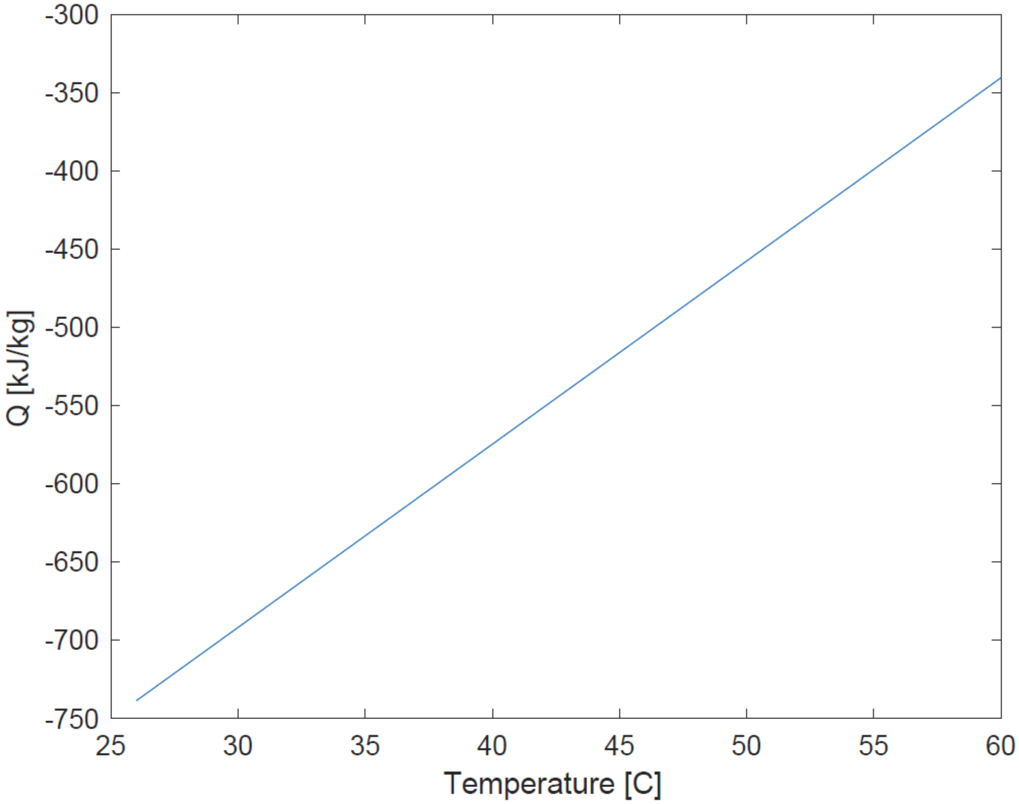

Figure 3: Heat available from desiccant reaction as a function of the final temperature of the products of the reaction.

The linear trend of the figure above is somewhat obvious; nonetheless, it provides useful information regarding the amount of heat available from the reaction. It can be seen that the total exergy of the reaction, which describes the maximum energy available and occurs when the final temperature of the solution is equal to the initial temperature, is roughly -740 kJ/kg of desiccant. This energy per mass of desiccant can be better compared when converted to reflect the storage capacity of the total system, 50 kWh/m^3. This storage capacity reflects the added water required to dilute the desiccant during the reaction. The negative sign from the exergy calculation indicates that the heat is being released during the exothermic reaction.

Using this exergetic calculation as a baseline comparison and a design parameter, the heat exchanger used to extract heat from the stored desiccant, as discussed in the conceptual storage system, can be sized and modeled. This analysis will provide the basis for the physical construction of the heat exchanger used for the experiments in this thesis.

2.2 Heat Exchanger Sizing

Prior to building the heat exchanger, a study was carried out to determine appropriate sizing of the heat exchanger. This included calculating the length of a heat exchanger based on an expected average heat transfer rate from the reaction.

The process of determining the appropriate sizing of the heat exchanger employed the use of the Log Mean Temperature Difference (LMTD) method for heat exchangers [16]. In short, this method uses a logarithmic mean of the temperatures of both the inlet and outlet condition of the working fluid (water in this case) in conjunction with the temperature of the reacting calcium chloride and water solution, to determine an appropriate length of heat transfer surface. The governing equation for this method is the following.

$$q = UA\Delta T_{lm} \qquad (5)$$

Where q is the rate of heat transfer occurring in the heat exchanger, U is the overall heat transfer coefficient, A is the heat transfer surface area, and ΔT_{lm} is the logarithmic mean of the difference in temperatures.

$$\Delta T_{lm} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2/\Delta T_1)} \qquad (6)$$

Where,

$$\Delta T_1 = T_f - T_{in} \qquad (7)$$

$$\Delta T_2 = T_f - T_{out} \qquad (8)$$

Equations 7 and 8 are applicable for the case where the final temperature of the products, T_f, is constant. While this is not physically the case for this experiment, since the temperature of the products increases as the reaction occurs, an assumption was made to use a constant temperature that reflected the actual final temperature of the reaction products. This assumption was made to simplify this process and to allow for the calculation of heat exchanger lengths at higher outlet temperatures of the working fluid, which will always be lower than the final temperature of the solution.

Knowing an estimate of the rise in temperature of the desiccant solution during the reaction as calculated previously, and verified experimentally as discussed in the next section, we can begin to determine some appropriate parameters to solve equation (5) for the heat transfer surface area, which can then be used with the geometry of the pipe to determine the length. First, the temperature rise of the reaction can be used to determine the amount of heat available for extraction by the following equation.

$$\dot{q}_{rxn} = \frac{mC_{p,sol}(T_f - T_i)}{t} \qquad (9)$$

Where m is the mass of solution, $C_{p,sol}$ is the specific heat of the solution, the temperature difference is based on the initial and final temperatures of the reaction, and t is the time for the reaction to occur. For the purposes of this investigation, the time for the reaction to occur was approximated using experimental data and will be explained in the next chapter.

Taking the rate of heat transfer as calculated by equation (9) another overall energy balance can be employed to determine the outlet temperature of the working fluid. This must be done, however, by assuming a mass flowrate, or for the purposes of investigating an appropriate magnitude, a range of flowrates. We can then calculate the exit temperature of the working fluid using equation (10).

$$\dot{q}_{rxn} = \dot{m}C_p(T_{out} - T_{in}) \qquad (10)$$

At this point, all temperatures of the heat exchange process can be determined and thus the logarithmic mean can be taken as using equations 6 through 8.

At this point, all the temperatures of interest are known, an estimate for the mass flowrate of the working fluid is known and the overall heat transfer coefficient U can be determined using equation (11).

$$U = \frac{1}{\frac{1}{h_c} + \frac{1}{h_h} + R''_f + R''_c} \qquad (11)$$

Equation (11) includes the heat transfer coefficients of the reaction fluid, which is labeled with a subscript h, and the working fluid, which is labeled with a subscript of c. Each of the heat transfer coefficients must be determined using a Nusselt number correlation appropriate to the fluid conditions for internal flow and the reaction reservoir. For the purpose of this calculation, the Nusselt number correlation for the working fluid was taken to be that of an internal flow which depended on the Reynolds number of the flow. When the flow was deemed to be laminar, the Nusselt number correlation used was a constant 3.66, which is descriptive of laminar flows with uniform surface temperatures [16]. This simplifying assumption was used to describe the overall temperature of the reaction as being uniform throughout the solution even though, in reality, the solution temperature varies spatially with respect to the physical and thermal diffusion of the desiccant and heat in the solution. This assumption is a definite limitation of this analysis. While it is known that this exchange surface was not going to be of uniform temperature with respect to the length of the surface, it was also known that the heat flux along the length of the heat exchange surface was not uniform. Given that the heat exchanger surface was to be coiled, which would allow for the desiccant to be distributed in the shell in a more localized fashion, and that the solution was to be of enough volume to fully submerge the coil, the spatial difference from one side of the heat exchange surface to the other could be reduced to 15-20 cm in the longest direction. Thus, an approximation of constant temperature along the surface seemed more appropriate than a constant heat flux along the length of the heat exchanger. Additionally, the introduction of the water to the reaction was by pouring from above the heat exchange coils and desiccant materials which caused some initial mixing and distribution of material and heat as the reaction started. Thus, the main source of difference in temperature along the heat exchanger surface would be due to the inconsistent amount of heat transfer between the solution and the working fluid as the working fluid heated up.

It would be possible to derive new heat exchanger relations to accommodate a changing surface temperature along the length of the coils, but for the purposes of this first assessment, a constant surface temperature assumption was made to simplify these initial calculations.

When the working fluid in the heat exchanger was deemed turbulent (over the course of varying the flowrate) the Nusselt number correlation was taken to be

$$Nu_D = \frac{(f/8)(Re_D - 1000)Pr}{1+12.7(f/8)^{1/2}(Pr^{2/3}-1)} \qquad (12)$$

where,

$$f = (0.790 * \ln(\mathrm{Re_D}) - 1.64)^{-2} \qquad (13)$$

which is appropriate for fully developed turbulent flows with Reynolds number between 3,000 and 5 x 10^6 and Prandtl numbers between 0.5 and 2,000, [16].

Additionally, a fouling factor and thermal resistance due to conduction were included for the calculation of the overall heat transfer coefficient U. Fouling factors take into account an accumulation of unintended material on the heat transfer surface creating a deposited layer that inhibits the transfer of heat. A fouling factor of 0.0005 $[m^2K/W]$was used for the diluted calcium chloride solution and is included as R_f'' in Equation 11, [17]. The thermal resistance due to conduction through the copper heat transfer surface was included as well and is written as R_c'' in Equation 11. This conductive resistance is calculated as follows for a cylindrical pipe:

$$R_c'' = \frac{\ln(D_o/D_i)}{2\pi kL} \qquad (14)$$

Where the subscripts “o” and “i” refer to the inner and outer diameters of the piping, k is the thermal conductivity of copper and L is the length of heat exchanger pipe. Since the length of the heat exchanger is unknown at this point, a guess for the length was used to determine the order of magnitude of the thermal resistance due to conduction. Then, once the final heat exchanger length was determined, the thermal resistance was updated with the calculated length. This calculation determined that the thermal resistance due to conduction was 0.00027 $[m^2K/W]$ for a length of one meter, which was less than the thermal resistance due to fouling.

The reaction solution on the other hand, was, for the sake of simplicity, assumed to not experience any forced movement and thus any convective element would be the result of natural convection. This scenario required a Nusselt number correlation of the following form [16].

$$Nu = \left\{0.060 + \frac{0.387 * {Ra_D}^{1/6}}{\left[1+(0.559/\mathrm{Pr})^{9/16}\right]^{8/27}}\right\}^2 \qquad (15)$$

Where the Rayleigh number, Ra_D is defined as the Grashof number *Gr* multiplied by the Prandtl number *Pr*. The Grashof number can be found using the following relation:

$$Gr = \frac{g\beta(T_f - T_{in})D^3}{\nu^2} \qquad (16)$$

Noting that g is the acceleration due to gravity, β is the volumetric expansivity, and ν is the kinematic viscosity of the fluid. For reasons that will be identified later, the diameter (D) of the pipe system was taken to be ¼" to reflect the piping that was available for this experiment.

At this point, all the quantities in equation (5) can be determined and the length of the heat transfer surface can be calculated.

For a typical rise in temperature of the desiccant reaction, the outlet temperature of the working fluid can be determined along with an appropriate length of the heat exchanger. This will, however, require the assumption of a mass flowrate as previously mentioned. Due to the fact that the goal is to increase the temperature of the working fluid, smaller flowrates in the range of 0.001 – 0.011 kg/s were used in conjunction with quarter inch piping to ensure the working fluid was in contact with the hot reaction for as long as possible. This size of piping was chosen based on the piping that was available in the lab. It was the smaller size of piping available which would reduce the over all area of the heat transfer surface which would allow for higher outlet temperatures to be reached given a fixed rate of heat transfer. Faster flowrates approach turbulent flow regimes and are more effective at transferring heat, but have less time in contact with the hot reservoir. Figure 4a shows the calculated length of the heat exchanger as a function of flowrate based on a fixed rate of heat transfer from the reaction. The relationship is a manipulation of Equation 5, where the flowrate has influence on both overall heat transfer coefficient, *U,* and the log mean temperature difference. The equation can be seen below.

$$L = q/(U\pi\Delta T_{lm}) \qquad (17)$$

It can be seen that the required length decreases with increasing flowrate and a steep drop off occurs with a transition to a turbulent flow at a flowrate of 0.011 kg/s. The known heat transfer rate is an average based on a 70 °C temperature rise and an average reaction time for the change in concentration of the desiccant. Despite the drop in heat exchanger length with the introduction of a turbulent flow, it can be seen in Figure 4b that the heat exchanger outlet temperature is also lowered with the addition of the turbulent flow. This is expected since the faster moving fluid would have less time in contact with the hot surface of the heat exchanger. This relationship between outlet temperature and flowrate can be arrived at from Equation (10) as follows.

$$T_{out} = \frac{q_{rxn}}{(\dot{m}c_p)} + T_{in} \qquad (18)$$

The steep drop in heat exchanger length between the last two flowrates is a reflection of the different Nusselt Number correlation used for turbulent flow, which is descriptive of the added convective element in turbulent flows allowing for more effective heat transfer. Figures 4 a and b reveal that although turbulent flows may be more effective at transferring heat, the fluid passes through the heat exchanger more quickly and does not allow enough time for the fluid to have any significant temperature rise. This theoretical prediction shows that for a flowrate of 2 g/s and a length of just about two meters, one could expect an outlet temperature of about 50 °C. It is important to reiterate that this calculation is performed under the assumption that the rate of heat transfer is constant and that all the heat from the desiccant reaction transfers to the working fluid with no losses.

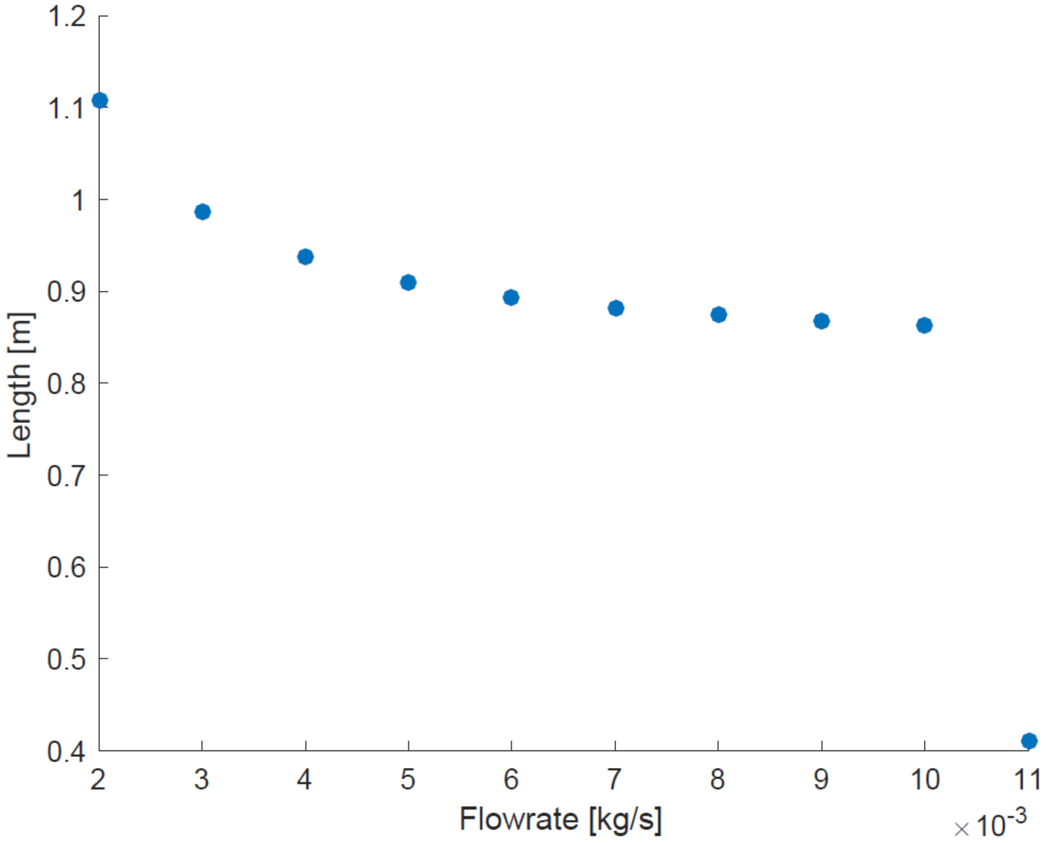

Figure 4a: Required heat exchanger length to fully extract heat from a fixed rate of heat transfer as a function of flowrate.

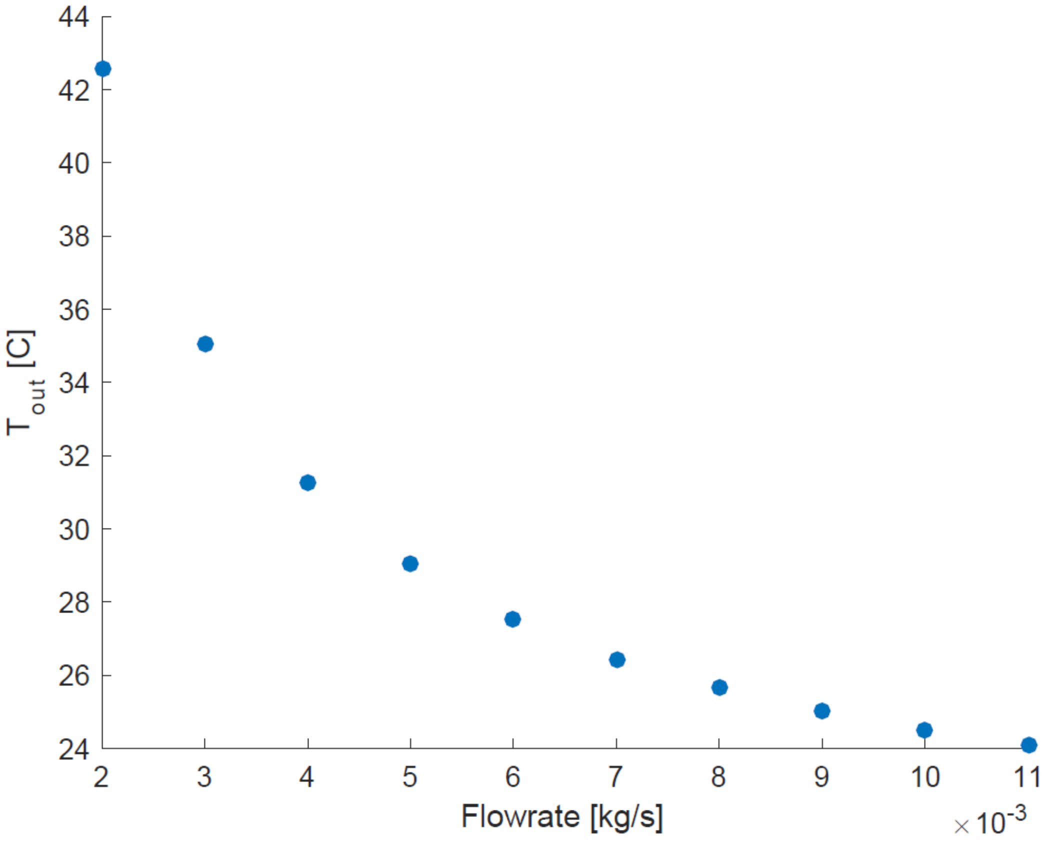

Figure 5b: Expected temperature rise from the fixed rate of heat transfer as a function of flowrate.

Given the theoretical calculations in this section, there are some key conclusions. One, the maximum exergy of a calcium chloride reaction with water is approximately 750 kJ/kg. Any heat extracted or measured from the following experiments should be less than this value. Second, a laminar flow along with a longer length of heat exchange surface would provide the right conditions for a maximum temperature increase between inlet and outlet. An appropriate flowrate for a test system is projected to be on the order of 0.002 kg/s to produce a 18 °C increase in temperature, while an appropriate length of heat exchanger is in the range of 1 meter. This is an idealized case where a constant average power is assumed for the entire reaction and heat is not lost from the system.

3 Experiments

This section details the experiments that were performed for this thesis. The experiments were performed to verify the amount of heat available from the calcium chloride and water absorption reaction and provide insight to some of the problems that might be faced for future construction of thermochemical energy storage systems.

The first experiment focuses on the reaction itself and how much heat is released based on the change in temperature of the reaction inside a test beaker. The second part of this section details the construction of the heat exchanger that was used to determine the heat available and potential energy storage capacity from a system that was more representative of a heat storage system. The results from the heat exchanger experiment will be discussed in Section 4.

3.1 Temperature Increase from Desiccant Reaction

To verify the theoretical calculations and explore the challenges associated with extracting heat from a liquid desiccant solution, two basic physical experiments were performed. The first experiment was conducted to confirm the amount of heat available from an isolated reaction. The second experiment included the construction of an experimental heat exchanger to confirm the amount of heat available from the desiccant reaction when being extracted for the purposes of domestic water heating. As was the focus with the calculations, the experiments carried out on behalf of this thesis pertained only to the discharge/absorption portion of the storage cycle.

To begin, two different reactions were conducted for changes in solution concentration between 100% desiccant and either 20% or 25% solution of desiccant and water. For the rest of the paper it will help to think of the discharge portion of the storage cycle in two stages; the concentrated stage, when the solution has the most chemical potential, and the diluted stage, when the solution achieves its lowest chemical potential and loses its ability to provide useful heat. Table 3 shows both the concentrated and diluted concentrations of the solution as well as the increase in temperature of the reaction. The heat available from the temperature increase can also be seen in the table for each of the reactions. The reaction was held in a 500 ml beaker and the temperature was measured using a K-type thermocouple connected through a National Instruments data acquisition tool.

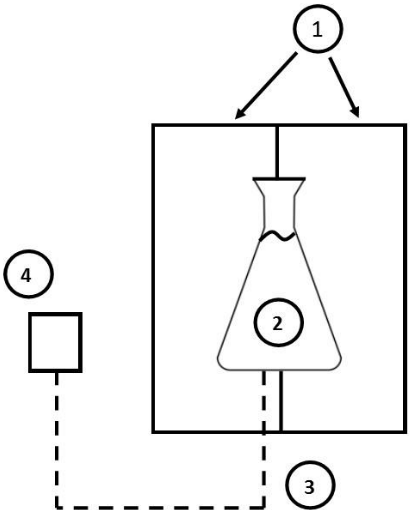

Figure 6: Beaker experiment schematic with styrofoam casing (1), desiccant reaction in beaker (2), thermocouple (3), data acquisition tool cDAQ NI 9171 (4)

First the beaker was placed in a form-fitting casing of Styrofoam insulation and filled with the appropriate amount of desiccant. The corresponding mass of water was then measured separately and then poured into the beaker containing the calcium chloride. As mentioned, a k-type thermocouple was attached to the bottom of the beaker inside the insulation to monitor the rise in temperature during the reaction.

Table 3: Heat released during the hydration of calcium chloride in water for diluted concentrations of 20 and 25% desiccant.

Change in Concentration	Mass of Desiccant	Mass of Water	Temperature Rise	Experimental Storage Capacity
[%]	[kg]	[kg]	[°C]	[kWh/m^3]
100 - 25	0.1	0.3	63.25	29.0
100 - 20	0.1	0.4	63.17	27.9

The heat released was calculated by multiplying the specific heat of a 50% calcium chloride solution (~2.1 kJ/kg-K), the total mass of the solution and the temperature difference measured. This product was then divided by the mass of the desiccant to normalize the heat energy per kilogram of desiccant.

3.2 Rate of Reaction

The rate of reaction is important to this investigation to determine the power available during the desiccant reaction. This evaluation of the power is necessary for the heat exchanger sizing predictions discussed in Chapter 2. This process was conducted slightly out of order as presented in this report, in that the an average power was determined from this initial beaker experiment and used in the heat exchanger calculations from the previous section.

The rate of reaction of a chemical reaction depends on two factors, the order of the reaction and the rate constant. The order of a reaction can be determined through experimental analysis [18]. Determining the order of a reaction requires the knowledge of the concentration of the reaction at different times, which can be done by experimental analysis. An example of a first order rate law for a reactant A can be seen in Equation 19, where k is the rate constant. Higher order rate laws would simply have the concentration of A raised to a higher power.

$$Rate = k[A]^1 \qquad (19)$$

Since the ultimate goal is to determine the time for the entire reaction to occur, the integrated form of the rate law, Equation 20, could be used which allows for the calculation of k, the rate constant.

$$ln\frac{[A]_t}{[A]_0} = -kt \qquad (20)$$

The limiting factor with using either the rate law or the integrated form of the rate law is that the concentrations must be known at two specific times during the reaction. Again, determining the concentrations can only be done experimentally by running the reaction and monitoring either the concentrations of the reactants or the volume change of the solution. This can be done, but requires precise equipment that can perform either polarimetry, chemical spectroscopy or pressure measurements (for the case of gaseous reactants only) [18]. Unfortunately these tools were not available for this experiment. Instead, an approximation of the average rate of reaction was determined and used in the calculations for the heat exchanger design.

The temperature rise data from the test beaker experiment in Section 3.1 was used to determine the average power mentioned above. Temperature was measured for this reaction every 0.5 seconds using the data acquisition tool. It was assumed for the purposes of this experiment that all the solid desiccant material had reacted with the water at the point of maximum temperature rise. Once the temperature reading reached its maximum during the reaction, it was assumed that the heat loss through the beaker and insulation became dominant and the heat generation from the reaction was no longer considered significant. A time delay should be expected for natural convection to occur within the solution and for conduction to occur through the glass to the thermocouple. To account for this expected time delay, the time selected corresponded to 90% that associated with the maximum temperature rise. This test reaction was between a 100% concentrated granulated solid (100 g) to 25% concentrated solution. Dividing the amount of desiccant reacting (75 g) by the molar mass of calcium chloride (110.98 g/mol) the number of moles reacting during this experiment can be determined. The number of moles can then be divided by the amount of time for the reaction to occur to generate an average rate of reaction, in units of moles per second, to be 4.3 x 10^{-3} [mol/s].

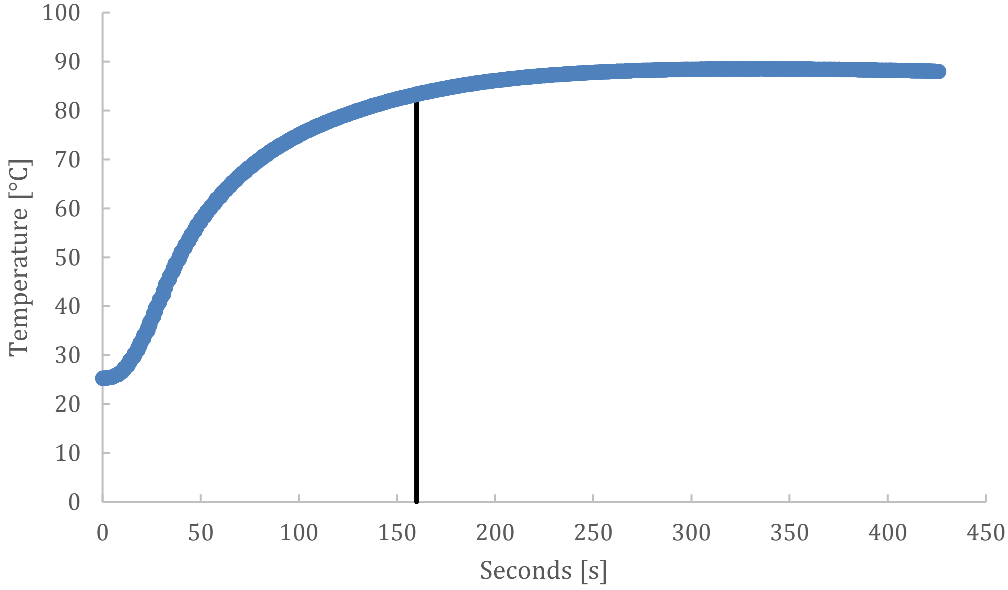

Figure 7: Time corresponding to 90% of the temperature rise for a reaction between 100 g of 100% calcium chloride and 300 g of water. This time is an estimate of the time for this reaction to occur.

Using the calculated rate of reaction, an overall estimate of the time for 1 kg of desiccant to react can be determined by dividing the mass of the desiccant by the molar mass of calcium chloride and then dividing by the reaction rate. Additional reaction time was also included to produce a low rate of heat transfer. This would ensure that the prediction for the heat exchanger length was of a manageable size with respect to the construction of this experiment. A low reaction time would increase the rate of heat transfer and could have pushed the prediction for the length of the heat exchanger to be difficulty small to build. Thus, for the purposes of sizing the heat exchanger in the previous section, a time of 2000 seconds was used as the time required for the desiccant reaction to occur starting with 1 kg of granulated desiccant material being diluted to 25% concentration.

3.3 Heat Exchanger Experiment

The second verification for heat extraction from a calcium chloride absorption process included the construction of a heat exchanger. This experiment was performed to give a realistic perspective of how much heating could be supplied to a domestic space heating or hot water system. Special focus was also given to determine some of the difficulties associated with heat extraction during the absorption reaction. The construction of the heat exchanger included the sizing of the piping, pump, heat exchanger surface, and insulation. The main driving criteria for the heat exchanger design stemmed from the need to maximize the outlet temperature, rather than the heat transfer from the reaction. Since the potential goal of such a storage system is to provide heating to domestic hot water systems or provide supplemental space heating, the useful amount of heat extraction corresponds to a large increase in temperature of the working fluid as opposed to using large flowrates to extract heat as quickly as possible, with little temperature rise. Thus, this goal of maximizing the outlet temperature required that the flowrate of the working fluid be very low.

Due to the experimental nature of this heat exchanger and the limited amount of space and materials, the heat exchanger was designed to be especially small, with the largest component, the insulation, taking up approximately 10 L of space and the shell (where the reaction was taking place) only occupying 5 L of space. In order to achieve the small flowrate for the system, a peristaltic pump was used for its low flowrate capabilities. A peristaltic pump, in comparison to a centrifugal pump, supplies liquid to a piping system by using a series of rollers to push or squeeze water through a flexible tube, rather than using an impellor to pressurize the liquid. The pump selected was capable of supplying a flowrate of 0.001 – 0.006 kg/s, which was sufficient for the application and consistent with the ideal flowrates determined in the theoretical calculations. The pump was powered by a 12 V DC power source.

The following figure is a line diagram of the heat exchanger test. The peristaltic pump labeled as “2” in the figure draws from a reservoir and provides the flow for the working fluid to pass through the heat exchange surface. The flow passes through a submerged thermocouple labeled as “3” to record the initial temperature. The flow then passes through the shell and tube heat exchanger “4” and returns to the reservoir after passing through a second submerged thermocouple measuring the final temperature after the transfer of heat. The reaction can be thought of as happening in the “box” labeled “4.” of this figure and is insulated except for the transfer of fluid through the copper piping. The dashed lines represent the electrical thermocouple lines that feed into a National Instruments thermocouple module (NI 9213) and is used in conjunction with a National Instruments data acquisition (cDAQ 9171) system. The read out from the DAQ is displayed through LabVIEW software.

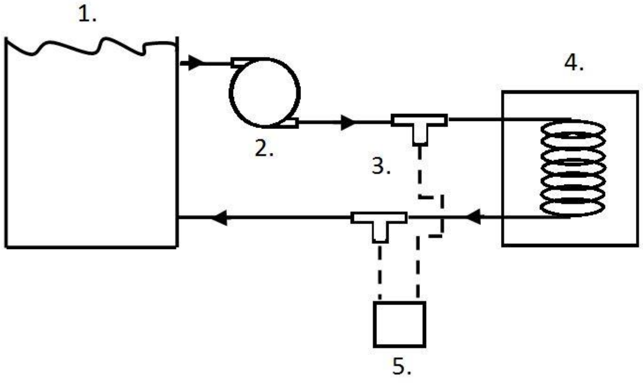

Figure 8: Line diagram for heat exchanger experiment. 1. Reservoir; 2. Peristaltic Pump; 3. Submerged Thermocouples; 4. Shell and tube heat exchanger; 5. Data Acquisition System (DAQ).

Figure 9 is a picture of the actual hardware used with the shell and tube heat exchanger on the left-hand side of the picture. This included the peristaltic pump, plastic reservoirs, copper piping and unions, thermocouples, plastic hosing, data acquisition tool, DC power source and Styrofoam insulation as seen in Figure 9.

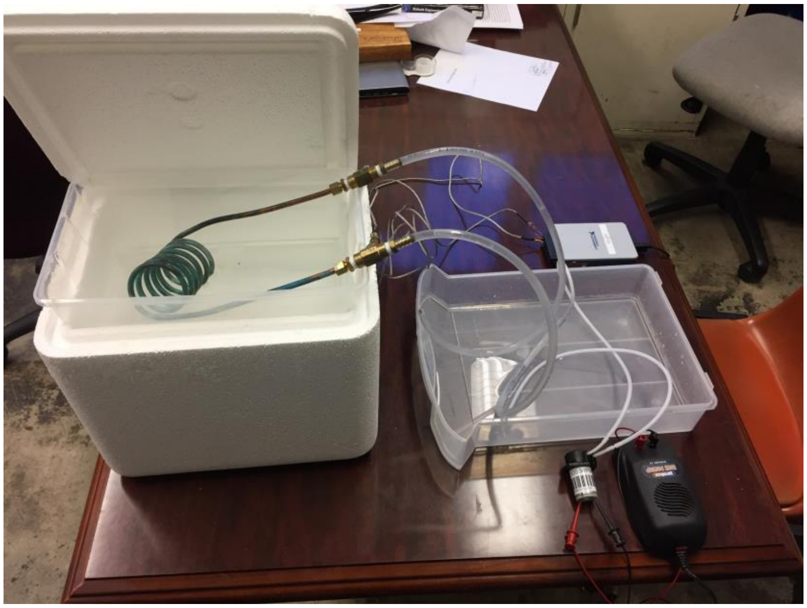

Figure 9: Experimental Heat Exchanger

Smaller diameter piping used for the heat transfer surface was selected to ensure the mean temperature of the working fluid would be closer to that of the hot reservoir, increasing the potential for a higher outlet temperature at smaller heat exchanger lengths. Thus, quarter inch copper piping was used as the heat transfer surface that was to be submerged in the "shell" portion of the heat exchanger and was cut at just over one meter in length with approximately eight turns. In-line with the copper piping and the pump, $3/8^{th}$ inch flexible hosing was used to complete the system. Additionally, the union that was used to connect the hosing and the copper piping at the beginning and end of the heat exchange surface included a port for a submerged thermocouple to measure the inlet and outlet temperature of the heat exchanger. The expected temperature rise for this heat exchanger design was approximately 25°C given an average rate of heat transfer of 210 W.

The desiccant reaction was to occur in the “shell” portion of the heat exchanger, which, for simplicity’s sake, consisted of a plastic bin insulated by a Styrofoam chest. It should be stated that this heat exchanger was not a traditional shell and tube heat exchanger, but rather consisted of a reservoir containing the kinematically stagnant desiccant reaction and a pipe acting as the heat transfer surface that was submerged in the reaction. This reservoir was large enough to accommodate approximately four liters of solution, which would provide enough depth to fully submerge the heat exchanger coils. Water was used as the working fluid for the heat exchanger and was supplied via a reservoir from a separate plastic bucket. The path of the heat exchanger fluid can be traced in the line diagram of Figure 8.

During the actual experiment, the shell portion of the heat exchanger was filled with the desired amount of desiccant material. The pump was then turned on while the DAQ system began recording inlet and outlet temperatures. Once the temperature difference was observed to be approximately zero, the corresponding amount of water (depending on the experiment) was added to the desiccant material and the top of the Styrofoam insulation was placed on top of the shell to isolate the reaction from any unwanted heat losses. The temperature difference of the working fluid was measured with respect to time and plotted using the LabVIEW software connected to the DAQ system.

3.4 Error Analysis

The data acquisition tool used in these experiments was a Compact Data Acquisition (cDAQ) tool made by National Instruments. Specifically, the tool was a USB supported cDAQ with model number 9171. A National Instruments thermocouple module (NI 9213) was used in conjunction with the cDAQ system. National Instruments claims a sensitivity between 0.02 and 2.8 °C for the NI 9213 module, depending on the mode and thermocouple being used. A K-type thermocouple was used for this experiment, which corresponds to about a potential 1°C measurement error at any given reading as described on the NI 9213 datasheet. For the beaker tests, this corresponds to a 1.5 kJ measurement error after combining the error from the difference in temperature using a root sum square and then multiplying it through the energy calculation. Since there were two thermocouples measuring the temperature difference at the same time for the heat exchanger experiment, the total error of the temperature difference measurement could be 2 °C at each measured time. This error, when propagated through each calculation of the power turns out to be 0.008 kJ. Although this seems small, if the same error is assumed for all the calculated instantaneous powers, the error would combine in a root sum square fashion when determining the total energy and correspond to 0.2 kJ.

4 Results

This section details the data that was collected from the experiments mentioned in the previous chapter and gives a quantitative measure of the energy that can be expected from a calcium chloride dissolution reaction. One set of test data is presented to show the amount of heat available, while other test data presented is used to provide insight to other aspects of extracting heat from the desiccant hydration reaction. Analysis of the results will be given in the Chapter 5.

4.1 Energy Extracted From Heat Exchanger

A few experiments were run using the heat exchanger. Each run consisted of diluting the desiccant from a starting concentration (between 45% and 100%) to a diluted state between 7% and 25% concentration by mass, depending on the test. The temperature difference between the inlet and outlet of the heat transfer surface was monitored and recorded. Table 4 gives a summary of the three major tests that were conducted. The first test was to determine a best-case scenario, in other words, to determine the most heat that could be extracted from a fully concentrated initial desiccant state. The second test was performed to verify the effect of adding a convective component in the reaction. The third test was to determine the amount of heat that could be extracted from a non-crystallized concentrated solution. For comparison, Table 3 can be referred to for the storage capacities of the test beaker experiments.

Table 4: Summary of heat exchanger test data.

Change in Concentration	Mass of Desiccant [g]	Maximum ΔT [°C]	Energy Extracted [kJ/kg]	Storage Capacity [kWh/m^3]
100% - 20%	750	25	288	19.0
100% - 7%	240	8.5	75	1.7
44% -20%	375	3.5	51	3.4

The first experiment was conducted to verify the amount of heat that could be extracted from the desiccant reaction. This experiment included the dilution of 750 g of solid desiccant pellets to a hydrated solution of 20% calcium chloride and 80% water. These solid 100% concentrated desiccant pellets were used as the initial state to evaluate the heat that could be extracted from the highest chemical potential state of the material. While this may not be a realistic starting state for an actual desiccant based thermal storage system, it provides a best-case scenario as a start. The desiccant was diluted using 3 L of water to reduce the solution to a 20% concentrated solution. This diluted concentration was based on the diluted conditions used in the desiccant based air conditioning systems as presented in Astrid Hublitz's *Efficient Energy Storage in Liquid Desiccant Cooling Systems [11]*. The total mass of the solution was chosen to ensure that the heat exchange coil would be fully submerged in order to allow for the most heat transfer. The following figure shows the results of the experiment.

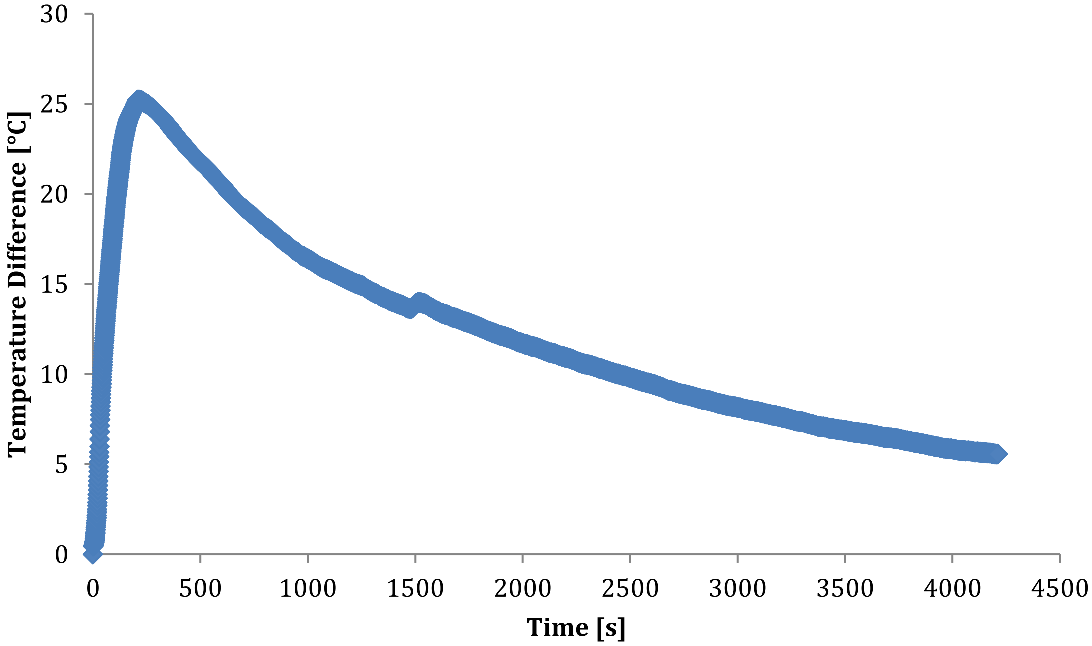

Figure 10: Experimental results from heat exchanger. Temperature difference between inlet and outlet for a 100% concentrated solution to a 20% concentrated solution.

The temperature difference in this experiment reached a maximum of just over 25 °C and sustained a temperature difference of at least 10 °C for approximately 41 minutes. The test was cut short after 1 hour once the temperature difference dropped to about 5 °C. Thus there is some heat from the reaction that was not accounted for in this data collection.

Knowing the difference in temperature as well as the mass flowrate for the system (determined to be 1 g/s from the experiment), and taking the specific heat of water to be 4.184 J/(kg-K), the power extracted by the heat exchanger can be calculated for every point using the following equation,

$$\dot{Q} = \dot{m}C_p(T_{in} - T_{out}) \qquad (21)$$

The temperature difference in equation (21) is the temperature that is plotted in Figure 10. Thus for each point in time, the corresponding rate of heat transfer can be determined by multiplying each point on the plot by the specific heat of water and the mass flowrate

The rate of heat transfer calculated using equation (21) could be numerically integrated over time to determine the total energy extracted from the system. This was done by calculating the area between 2 consecutive points and then taking the summation of the all the areas. For this data the total energy extracted was almost 216 kJ. Normalizing this energy extraction per kg of calcium chloride yields 288 kJ/kg. This corresponds to a storage capacity of 19 [kWh/m^3]. The inflection in this graph, at approximately 1500 seconds, occurred when part of the lid of the insulation was lifted. It is interesting to note that the temperature difference increased when opening a portion of the insulation, but this is believed to have happened because the thermocouple measuring the temperature at the inlet of the heat exchanger was located inside the insulation for this experiment and experienced a drop in temperature since it was closest to the point where the lid was opened. This showed that part of the design of the heat exchanger system was not ideal. The thermocouples measuring the inlet and outlet temperatures were inside the insulation for this test and thus were receiving heat from outside the copper piping in addition to reading the desired temperature of the internal fluid.

This result of 288 kJ/kg of heat energy extracted is about 75% of the energy used to determine the size of the heat exchanger and reached the same predicted temperature rise of 25 °C. It is important to remember that some of the energy of the reaction was not accounted for since the test was ended before the difference in temperature returned to zero. The test was ended in this way for scheduling and timing issues.

A second experiment was performed to determine the effect of added convection in the solution on the outlet temperature that could be achieved. The addition of the forced convection was to increase the rate of diffusion of the reaction. This was achieved by manually stirring the solution for approximately 10 seconds with a glass stir bar when the temperature difference started to level out. This experiment was conducted between an initial state of 240 g of 100% concentrated CaCl2 and was diluted to a 7% concentration with 3 kg of water. These proportions of the solution were limited by the amount of desiccant that was available at the time. The manual stirring can be seen in the data where the temperature difference looks to begin to settle and then sharply increases.

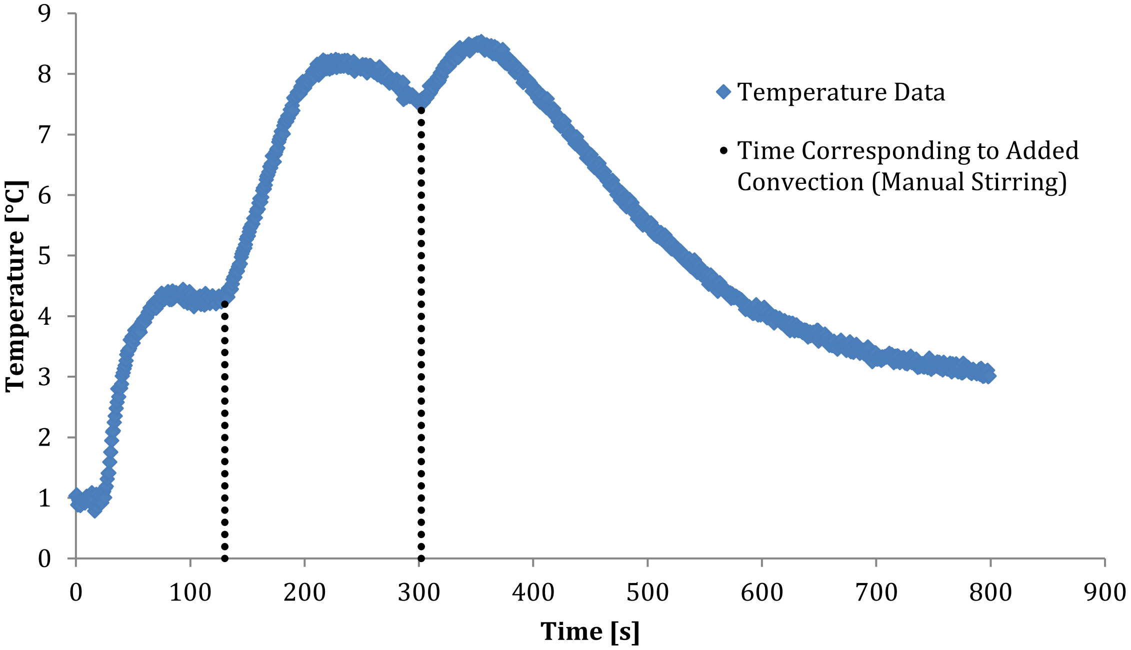

Figure 11: Experimental results from heat exchanger with manual stirring occurring at 130 s and 300 s. Temperature difference between inlet and outlet for a 100% concentrated solution to a 25% concentrated solution.

It is clear from this test that adding an element of forced convection in the reaction chamber increased the temperature difference of the heat exchanger. The forced convection allowed for the dispersal of concentrated regions of the solution to reduce the diffusion distance between concentrated and unconcentrated regions. This allowed desiccant material to react with water at a quicker rate which drove the temperature difference up as seen in the graph. By extension this also increased the instantaneous rate of heat transfer of the system. However the exact relation between convection and rate of heat transfer extracted was not determined and this paper does not attempt to define the exact relationship. This experiment accrued some higher losses, however, due to the fact that the lid of the insulation had to be opened multiple times. This undoubtedly led to the loss of heat through convection to the surrounding environment, which led to a lower total heat extracted per kilogram. In practice an internal stirring device, whether it be mechanical or flow induced, would likely be used, rather than a stir bar, to reduce unnecessary heat loss.

Another test was run between 44% initial concentration of calcium chloride and diluted to 20%. Starting with 375 g of desiccant and 475 g of water as the concentrated solution, an additional 1025 g of water was added to dilute the solution to 20%. This experiment was carried out to determine the amount of heat transfer available when reacting a solution without crystalized desiccant material (below 45%). The results from this experiment seen in Figure 12 below reveal a maximum temperature difference of just over 3.5 °C. This temperature increase corresponds to a storage capacity of about 3.4 [kWh/m^3]..

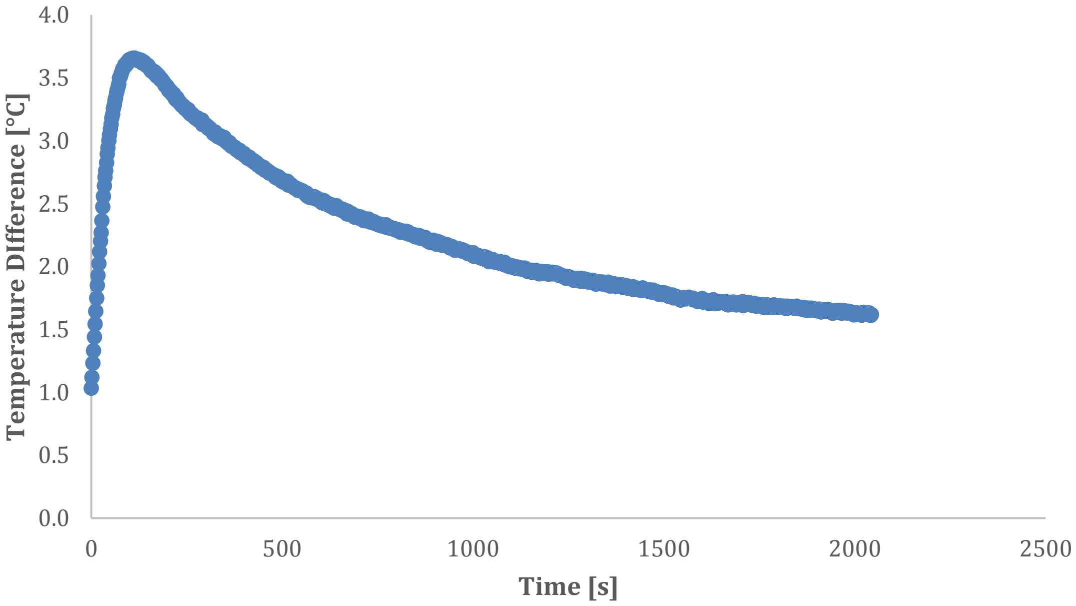

Figure 12: Temperature difference for a reaction between 44% concentrated solution and 20% diluted solution.

Unfortunately, the temperature data between 0 °C and 1°C was lost from this experiment. The LabVIEW software collecting the data auto adjusted the time axis to accommodate new data and in doing so deleted some of the initial data. This is why the temperature difference seems to start at 1°C rather than 0°C.

The next section will be focused on analyzing the results that were collected and discussed in this section. Using the amount of heat extracted as determined from the first set of data in this section, the next section will provide some analysis regarding how large a storage system might need to be to provide significant heating for homes in San Francisco. Additionally, a first analysis of the economic benefit of such a storage system will be conducted to determine the amount of savings associated with reducing consumption of natural gas. Economic tools such as return on investment and levelized cost of energy will be used to give some perspective on the savings associated with a basic thermal storage system.

5 Analysis

This section will focus on analyzing a few topics with respect to the results gathered above. It will look at the sizing expectations for a system that is able to provide heating at levels similar to that seen in the experiments described previously. This section will also discuss the economic considerations that this type of storage system would include and how it would compare to heating an average home in San Francisco with natural gas.

5.1 Sizing Requirements

The underlying question of this study has been to determine how much heat could be extracted from a reaction of calcium chloride and water. The first heat exchanger experiment reached a maximum temperature rise of 25 degrees with a storage capacity of 19 kWh/m^3.

Now, the question becomes, how significant is this amount of energy with respect to heating demands and how much storage material would be needed to fulfill the heating needs of a home in San Francisco. This section will also take a look at cost estimation and savings for the consumer.

To begin to evaluate the viability of desiccant thermal storage for heating, we must understand the demand for space and water heating. This analysis will look at the demands associated with an average domestic home in San Francisco, CA. An average daily heating load for a domestic home in San Francisco is approximately 50 kWh. This includes space heating as well as hot water heating. This amount of energy was determined by taking the sum of the demand data in Figure 1, prior to the normalization of the data.

As stated, the measured amount of heat from the first heat exchanger test was 19 kWh/m^3. This heat available was the amount extracted from a 100% concentrated desiccant solid, in the form of pellets, diluted to a concentration of 20% desiccant and water solution. This might be an unrealistic starting concentration for a fully reversible desiccant based storage system, but will provide a good assessment of an upper limit or best-case scenario. This is understood to be an oversimplification of the problem, but will provide a first understanding as to the viability of this energy storage technique and will hopefully motivate the further investigation of this subject.

Figure 13 gives a visual representation of the storage capacity by showing what percentage of heating demand a known volume of storage material can meet.

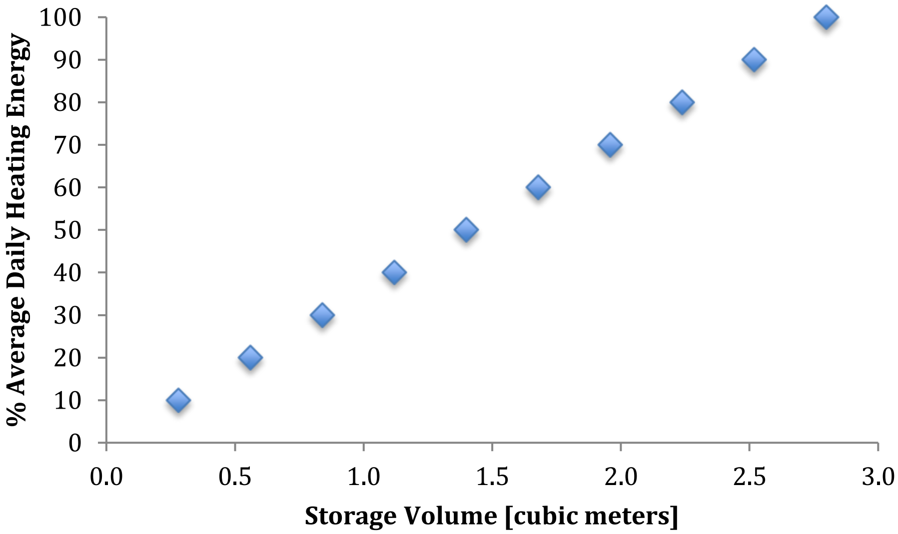

Figure 13: Percentage of daily heating demand met for varying amounts storage medium for an average home in San Francisco.

For the purposes of the rest of this investigation we will look at the energy available from 1 cubic meter of storage space which would supply just about 40% of the daily heating load for an average home in San Francisco. This volume correlates to about 285 kg of calcium chloride. It should be reiterated that this sizing analysis assumes that the desiccant is not being regenerated at the same time that it is being used. Instead this estimated sizing is based on extracting the energy stored in a solid, granulated, desiccant by constantly diluting it down to a 20% concentrated solution over the course of a day. Again this is an oversimplification of a potential storage system, but it provides a first level of insight with regard to heating potential.

5.2 Cost of Heat Exchanger Materials

An estimate for the total cost of the heat exchanger can be made based on the materials that were used. This estimate will then be used to help determine an estimate for a larger system sized for domestic use.

The desiccant was the most expensive element of the experiment by far. Purchased at $100/kg from Sigma Aldrich, a chemical supplies distributor, the cost of the desiccant was the strongest contributor to the cost of the experiment. However to ensure the integrity of the material, especially for the scientific perspective sought after in this investigation, it was deemed appropriate to purchase pure desiccant material from a reliable source.

The other materials that were used are summarized in the following figure and total to approximately $150. This total takes into account only the amount of desiccant that was used for one experiment to generate one set of data.

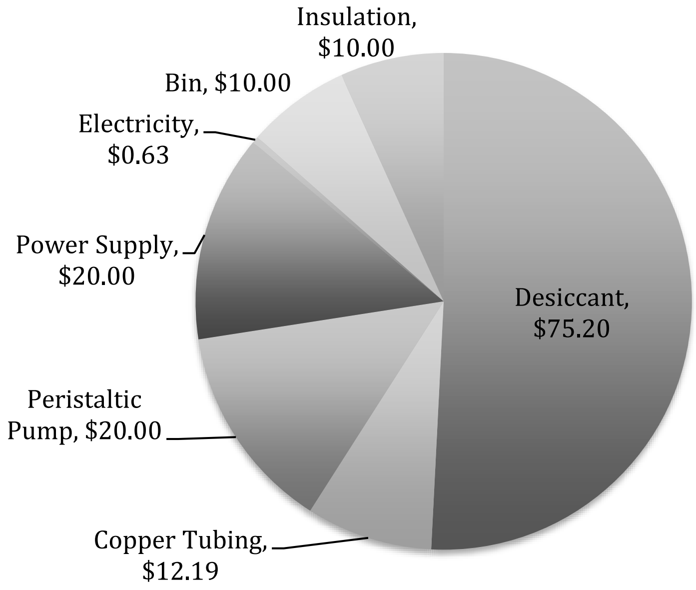

Figure 14: Cost distribution for a single heat exchanger experiment including materials.

The prices for the materials used in the construction of this heat exchanger will be used as a basis for an approximated cost for an actual storage system. The theorized storage system will be sized appropriately and the relative costs of the materials used will be applied to the larger system to achieve an estimate.

5.3 Savings From Reduction In Natural Gas Consumption

Continuing with the size and energy available as discussed in section 5.1, an economic analysis can be conducted while considering the cost of heating and the cost of storage materials. Natural gas, which is the primary heating fuel for homes in San Francisco, is at an all time low at the moment and is currently priced at $0.04/kWh. The desiccant material, on the other hand, can be fairly expensive as seen with the costs for the experiment discussed earlier, but it is a one-time purchase. The desiccant was purchased at a price of about $100/kg, which upon initial assessment proved to be too expensive to show a reasonable economic incentive for consumers. Thus, for the purposes of this analysis, it will be assumed that the desiccant can be purchased at a bulk price of about $10/kg. This price is based on a calcium chloride ice melt material that is available online at Factory Direct Chemicals (FDC) [19]. It should be noted that while some of the research discussed in Chapter 1 suggested that calcium chloride could be purchased at $0.48/kg, such a low price was not found from a chemical supplier. As stated in the experiment section, the desiccant used for the actual experiments in this thesis was purchased at the much higher price to ensure the purity of the substance. Considering simply the amount of savings due to the 40% reduction in natural gas fuel costs, such a desiccant based system would save approximately $328 per year by reducing the need for roughly 20 kWh per day from natural gas heating.

5.4 Return on Investment

Based on the costs associated with the experimental heat exchanger used in this investigation, a first approximation of the cost for a sufficiently large thermal storage system can be made. First, the increase in desiccant needed to provide the 20 kWh would be almost 380 times as much as the desiccant used in the experiment. If the material were purchased at the $100/kg price this would lead to a completely unreasonable cost of $28,500 for the desiccant material based on the price per kilogram that the experiment material was purchased at. Thus, it would be vital to purchase the desiccant material at a lower price. As mentioned in the previous section, there are some providers of ice melt chemicals, of which Calcium Chloride is one of their products, that offer the material at roughly $10 kg when purchased in bulk. This would make the 285 kg of desiccant $2,850. For the purposes of this analysis, it will be assumed that the desiccant can be purchased at the lower price mentioned above in order to evaluate a rate of return (ROI) and a Levilized Cost of Energy (LCOE).

Another increase in cost associated with the increase in size of the system would come from the increased heat exchange surface area. If the amount of copper tubing increased by the same amount as the desiccant, 380 times as much, and was purchased in bulk, the cost of the copper would come to approximately $775. We could similarly increase the size and cost of the shell of the heat exchanger, the pump, the insulation and other components to come up with a first estimate of the cost of such a system. For this investigation, we will assume a capital cost of $4000 for the discharge portion the storage system.

Similarly, if we include the costs of the hardware for another heat exchanger for the charging portion of the system, we would likely increase our total to $5,000. In addition, it becomes necessary to include the solar collection system that would be required to initially collect the thermal energy. In practice, solar thermal systems are sized according to meeting a certain amount of demand for summer and winter, but in this case we will only consider the solar panels necessary to collect enough energy to charge the desiccant. Note that this evaluation does not consider the temperatures required to fully concentrate the desiccant. The solar panels are sized based on the amount of energy that the desiccant is able to release during dilution, with an additional 70% efficiency considered. Taking the amount of energy available from 1 cubic meter of storage space (20 kWh) and using the average daily amount of solar radiation from Figure 1 (4.7 kWh/m^2), it can be concluded that 8 square meters of solar collectors would be required.

The cost of 1 square meter of a solar thermal collector seems to vary substantially with numbers between $400 -$1000 per square meter, [20]. Thus, 8 square meters of required solar collector area could very easily cost $8,000. Some references even cite prices closer to $1,500 per square meter, [21].

In total, this rough estimate of a simple solar collection and storage system would be approximately $13,000. An ROI assessment for this substantial cost, using Equations 20 and 21, reveals that even for a 75 year time span a consumer would not see their money made back if they made the investment for such a system. While this theorized storage system is quite expensive, the most inhibiting factor is the low cost of natural gas.

$$ROI = \frac{PV_{Savings} - PV_{Costs}}{PV_{Costs}} * 100 \qquad (22)$$

$$PV = FV/(1 + d)^t \qquad (23)$$

Equation (22) is the basic form of the ROI equation. When costs and savings are distributed over multiple years, each amount of money must be converted from its future value (FV) to a present value (PV) to be able to compare with current prices. When applying equation (22) to the costs and savings associated with this analysis one must take into account the yearly savings, which must be converted to a present value. Similarly, one must account for the cost of the system, which includes a one time capital cost of the system (already in present value form), and any yearly costs (which must be converted to a present value). The yearly costs assumed in this scenario would be for the electricity used for the pump and an estimated maintenance cost. These future costs as well as the future savings are all converted to a present value using equation (23).

Looking at equation (23), “d” is the discount rate and “t” is the number of years in the future. The discount rate describes the time value of money, which dictates that one dollar at present is more valuable than one dollar in the future. Discount rates fluctuate based on the perception of value of money and usually range between 2-6%. For example, the Google “Project Sunroof” website uses a discount rate of 4% to generate estimates for the savings associated with installing solar photovoltaic systems on residential buildings [22]. For the purposes of this analysis, a more conservative discount rate of 5% was used which assumes that the current perception of the time value of money is lower than that used by the “Project Sunroof” tool. If a smaller discount rate is used the ROI and LCOE calculations will prove to be more persuasive economically since savings in the future would be valued the same as savings in the present.

A more explicit version of the ROI calculation for an amount of years “n” can be seen below:

$$ROI = \frac{\sum_{t=1}^{n} PV_{savings\ in\ year\ "t"} - (PV_{Capital\ Cost} + \sum_{t=2}^{n} PV_{cost\ in\ year\ "t"})}{(PV_{Capital\ Cost} + \sum_{t=2}^{n} PV_{cost\ in\ year\ "t"})} * 100 \qquad (24)$$

If the cost of the storage system alone were being considered (~$5,000) an ROI evaluation would show a pay back period of 32 years for 1 cubic meters worth of storage space.

Similar to Figure 13, this calculation can be performed for varying volumes of storage space and plotted to reveal how the payback period varies. This relationship can be seen below in Figure 15.

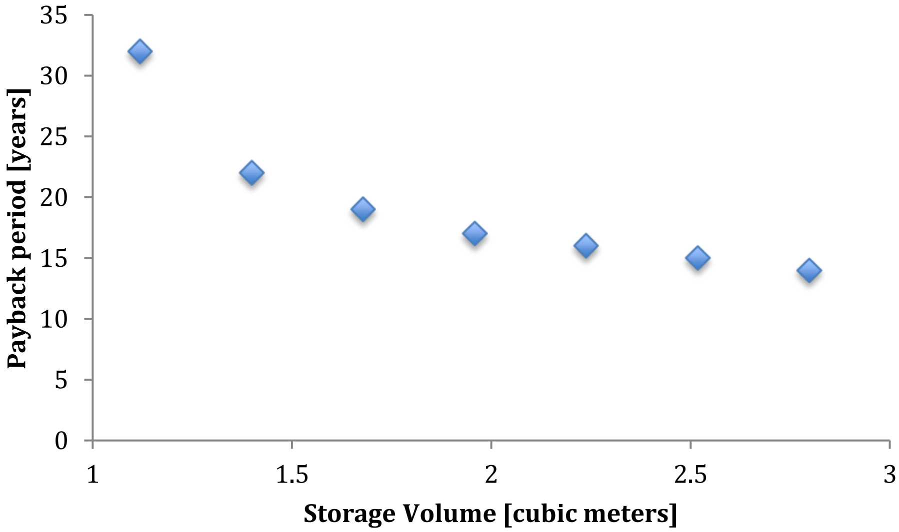

Figure 15: Expected payback period for varying volumes of storage medium (not considering cost of solar collectors). Payback periods, for volumes lower than 1 cubic meter, where omitted for taking too long to reveal a positive ROI.

Additionally, it is anticipated that the price of natural gas will change during the time that a desiccant based thermal energy storage system might be operating. And thus the yearly savings associated with reducing consumption of natural gas will change. According to an article posted on the Forbes website: “The Long Term

Outlook for Natural Gas," the price of natural gas is expected to either maintain at current levels or increase in the coming years [23]. This is good news for renewable heating sources that are currently finding it difficult to compete with the low cost of natural gas. Thus for the purposes of this analysis another conservative assumption was made and all savings associated with replacing heating from natural gas with heating from a desiccant thermal storage system are calculated assuming current prices.

5.5 Levelized Cost of Energy

Given the same capital costs, operating costs and annual heat available, a levelized cost of energy (LCOE) calculation can be performed to reveal a cost of \$0.86/kwh over a 32-year span. Again, this is considering the storage system only without the cost of solar collectors.

$$LCOE = \frac{\sum_{t=1}^{n} \frac{FV_{cost\ in\ year\ "t"}}{(1+d)^{t}}}{\sum_{t=1}^{n} \frac{E_{generated\ in\ year\ "t"}}{(1+d)^{t}}} \tag{25}$$

The levelized cost of energy is similar to the ROI calculation except it compares costs of the system to the amount of energy generated instead of comparing savings to the cost of the system, like the ROI. The variable "E" represents the energy generated in year "t". The LCOE equation above includes the conversion of both yearly costs and yearly energy generated into a present value form and thus the costs do need to be additionally modified to represent the present value.

Since there is no fuel to be purchased, the only yearly cost is for the small amount of electricity to run the low flow pump and any other maintenance costs.

Table 5: ROI and LCOE for a 32 year period. The 32^{nd} year would be the first year that a consumer transitioning from natural gas to stored thermal heating would experience a positive ROI value for 1 cubic meter of storage space.

Year	ROI [%]	LCOE [$/kWh]
1	-93	-
32	0.6	0.86

As seen in this table, which presents the ROI and LCOE values based on transitioning from heating with natural gas to heating from a thermochemical based energy storage system, it would take approximately 32 years for a consumer to see a positive return on investment. This would correlate to $0.86/kWh rate of heating over the same period. While the ROI value after the 32-year period is not very large, the consumer would know that they made their money back while reducing their reliance on fossil fuels. The LCOE was left blank for the first year because it is a tool that is supposed to be used over a number of years. That way the cost of energy can be seen over the lifetime of the project. The LCOE for the first year would be misleadingly large and thus it is left out of the table.

5.6 Limitations of Economic Analysis

It should be reiterated that this analysis is solely based on the theoretical amount of heat that can be extracted from a desiccant hydration reaction when the system has been fully charged by the start of each day. Additionally, no design has been done on a potential heat exchange system that could be integrated with a solar thermal system and existing hot water or space heating systems. It is also understood that the level of this economic analysis is very rough given the estimated costs of the parts and overly simple system. This initial simplified analysis (that uses best case assumptions for heat extraction) shows that the heating method investigated in this report is within reason to continue investigating for the replacement of natural gas heating. As the system becomes more complex, with the addition of hardware necessary for the recharging of the system, and as the heat available for extraction is limited by the maximum concentration of the desiccant solution (as dictated by other design considerations for such a system, like potential crystallization limits) the overall ROI will likely decrease and extend the expected pay back period.

At this point there is a persuasive argument to be made for further investigation into liquid desiccants as a decentralized domestic thermal energy storage medium for heating purposes. The results for the experiments show a level of heat extractable from a calcium chloride and water reaction to supplement some domestic heating and reduce consumption of natural gas. While there is a significant amount of desiccant required to supply such heating, one cubic meter of space would be sufficient to provide almost half of the daily heating demand of an average house in San Francisco. The economic assessment, however, presents a more challenging obstacle for this thermal energy storage method. All this being said, there is still much to learn about how such thermochemical energy storage systems might operate. The next section will summarize this thesis and provide final conclusions about the results determined from this investigation.

6 Conclusions

This final section will summarize and conclude the information presented in this thesis. The motivation and basis for this investigation will be revisited in addition to a restating of the methods used to reach the final conclusions. Finally, the results will be presented again and some thoughts will be given regarding future investigation on this subject.

The experiments performed for this thesis used solid, circular, calcium chloride pellets of about 1 mm in diameter. Thus, the volume of space that the pellets required when packed tightly was greater than the actual volume occupied by mass of the calcium chloride. Thus the required volume to hold 285 kg of desiccant and the associated amount of water would likely be slightly larger than 1 cubic meter. The pellets used in these experiments required an initial volume just over two times as large as the volume occupied by their mass. While the pellets do require more space, they allow for the reaction to occur more rapidly as the rate of diffusion will increase with the larger surface area of the desiccant that is in contact with the water. This means that higher temperatures are attainable during the reaction.

6.1 Thesis Summary

Climate change is occurring [2]. In order to combat this problem, states like California must continue its transition away from a fossil fuel based society and towards a renewable energy sourced society. Part of this movement will include the use of renewable energy sources that do not always produce peak energy at peak demand times. Energy from solar radiation will always be intermittent but will always be intermittently available with less green house gas emissions than fossil fuels. In order to maximize the potential of the solar resource, it becomes essential to store unused energy that has already been collected, for times when it is not otherwise available.

An ideal thermal energy storage system has yet to be determined for solar thermal applications. Sensible and latent heat storage have relatively low storage capacity and require large quantities of expensive insulation. Thermochemical energy storage has shown promise in air conditioning systems acting as a dehumidifying agent, however there are some challenges to overcome regarding corrosion of the heat and mass transfer systems, desiccant carryover, and then of course the selection of a cheap, non-toxic desiccant.

Calcium chloride presents a good option as a relatively inexpensive and non-toxic desiccant and when applied to heating, corrosion and carryover concerns might be reduced.

This thesis was focused on showing an initial assessment for the use of calcium chloride as a storage medium for thermal energy with the goal of extracting the energy as heat. Additionally this was done with a focus on decentralized domestic systems, appropriately sized for single home use. A theoretical assessment of the maximum amount of heat available in calcium chloride was performed to reveal an exergy of almost 750 kJ/kg which corresponds to 50 kWh/m^3.

To determine the actual amount of heat that could be extracted and used from this desiccant hydration reaction, a heat exchanger was sized and constructed to test how much heat could be physically extracted from a desiccant hydration reaction. This heat exchanger was constructed with domestic hot water heating in mind and offered a maximum storage capacity of 19 kWh/m^3, with a maximum temperature difference of 25 °C and a maximum rate of heat transfer of 105 W.

A first attempt at providing an economic perspective regarding the use of desiccant based thermal energy storage was conducted. This was done by determining an appropriate amount of desiccant material to supplement current domestic heating demands and determining the savings associated with the corresponding reduction in natural gas consumption. The costs associated with such a system were based on extrapolating the costs associated with the test heat exchanger that was built for the purposes of this thesis.

6.2 Conclusions Of This Investigation

There are a few key conclusions that can be drawn from this investigation. First, a conclusion which might be obvious, is that this investigation provides a very high-level, proof of concept analysis for whether calcium chloride based thermochemical energy storage can be an effective method of storing thermal energy for the extraction of heat. There are a lot of specifics with regard to how such a system might be built or operate that were not discussed in this investigation. The information concluded by this report does reveal an amount of heat that can be expected from such a desiccant reaction and how large a storage system would need to be, given the amount of heat available. Additionally, this report gives a first look at the savings that a homeowner in San Francisco might see from reducing their dependence on natural gas and electrical heating.

One of the main conclusions is that the heat exchanger used in this investigation revealed a heating storage capacity of 19 kWh/m^3. This, while it is an experimental result, is still an idealized case where the temperature difference is measured for close to a fully insulated reaction and for a scenario where the desiccant starts at 100% concentration. While starting from this concentration provides the most heat per amount of desiccant and by extension per volume, it introduces a potential obstacle for reversible cycles, namely, the crystallization of the desiccant. The regeneration half of the cycle would require the vaporization of the water from the desiccant solution, which would cause the crystallization of the desiccant if concentrations of 45% or higher are reached. The reactions in this experiment were performed using a granulated solid desiccant material, which allowed for faster diffusion rates of the solid in the solution than a single crystallized solid desiccant would.

With regard to heat extraction methods for this desiccant absorption reaction, it is likely that a more sophisticated heat exchanger would be necessary to maximize the heating potential. An ideal heat exchanger for this application would likely include fins or another method to increase the heat exchange surface, and a method to inject forced convection into the solution. The forced convection would increase the reaction rate and could be used to moderate the rate of heat transfer for the system depending on the temperature that is being demanded. Such a method could be a submersed fan or stirring rod, or a small water jet within the shell portion of the heat exchanger.

An additional analysis on how such a storage system would interact with a solar thermal collection system would also be beneficial. In practice, the solar thermal collection system could provide some level of heating during the middle of the day, but then provide the regeneration heat to the desiccant when there is excess solar collection. This relationship would require some sort of control system and may even reduce the storage volume since some of the heating demand could be met directly by the solar collection system without the need for storage.

All this being said, it would be hard to make an economic argument for using the heat from a desiccant hydration reaction as a means of supplementing natural gas based heating. Due to the low cost of natural gas, the time required to reach a positive ROI for such a system would likely be too long for many home owners even though a significant amount of energy could supplement daily heating needs (approximately 40% of daily needs as estimated by this report). This thesis concludes that after a period of 32 years a homeowner using such a system could save approximately $328 on heating per year. The real limiting factor for this analysis is the cost of the current heating source. If the price of residential natural gas were to approach the cost of residential electricity, namely $0.20/kWh, then customers could see a positive ROI much earlier. While the ROI would be quite small, residents could be assured that they would indeed be saving money and lowering their carbon footprint.

6.3 Thoughts Moving Forward

This investigation concludes that using a calcium chloride storage medium for heating purposes could provide supplemental heat energy and could be beneficial in maximizing the output of solar thermal systems. Assuming that a solar thermal system can be used to effectively recharge the desiccant solution, heat can be extracted from the material when needed. That being said, the storage capacities determined from this investigation are quite low in comparison to sensible and latent storage. However, a follow up investigation on the benefits of the extended storage time with thermochemical energy storage in comparison to the higher storage capacities with traditional thermal energy storage would be beneficial.

The charging of the desiccant storage system would also need to be investigated and verified to show the true value of such a storage system. Without knowing how effective an average solar thermal array could be at concentrating the desiccant material, it is hard to say exactly how well a desiccant based storage system could support domestic solar hot water systems.

Additionally, a more focused investigation on discharging the stored energy, such as developing a more effective heat exchanger that can regulate the reaction through the use of forced convection and/or controlled release of the reactants, would be beneficial. This would help to better understand the speed at which heating could be supplied from a desiccant reaction given an initial demand. The heat from this type of storage would likely be best utilized as a base level of heating for a home while the desired temperature from the consumer can be met by supplemental heating from natural gas. This type of system would help to give a more realistic estimate of the power and baseline amount of heating as well as the costs associated with such a storage system. This would provide valuable insight as to whether this type of energy storage could be economically feasible and technically compatible with existing heating hardware. Determining the appropriate level of baseline heating using a more sophisticated heat exchanger system would be a beneficial next step as well.

Given the results of this investigation there is some promise for the use of desiccant based heating but this thesis does not reveal that there is a strong economic argument for such a system at the moment. It is the hope of this investigation that further experimentation with regard to investing and extracting heat from desiccant reactions is pursued. Given that natural gas prices are expected to increase in the coming years, there will likely be a more favorable economic environment for a fully functioning, reversible thermochemical storage system

Bibliography

[1] US Energy Information Administration, 1973-2017, "Residential Energy Consumption Survey - Total Energy Data Browser."

[2] NASA, 2017, "Global Climate Change *Vital Signs of the Planet*," https://climate.nasa.gov/evidence/.

[3] US Energy Information Administration, 2013, "Heating and cooling no longer majority of U.S. home energy use."

[4] US Energy Information Administration, 2017, "U.S. households' heating equipment choices are diverse and cary by climate region."

[5] US Department of Energy, 2014, "Open Data Catalog - San Francisco, CA Heating Data.."

[6] 2010, "National Solar Radiation Data Base," http://rredc.nrel.gov/solar/old_data/nsrdb/1991-2010/.

[7] Abedin, A. H., and Rosen, M. A., 2011, "A Critical Review of Thermochemical Energy Storage Systems," The Open Renewable Energy Journal.

[8] Goodarzia, G., Thirukonda, N., Heidari, S., and Akbarzadeh, A., 2016, "Performance Evaluation of Solid Desiccant Wheel Regenerated by Waste Heat or Renewable Energy," 1st International Conference on Energy and Power, Science Direct, RMIT University, Melbourne, Australia.

[9] White, S. D., Goldsorthy, M., Reece, R., Spillman, T., Gorur, A., and Lee, D.-Y., 2011, "Characterization of Desiccant Wheels with Alternative Materials at Low Regeneration Temperatures," International Journal of Refrigeration, 34(8).

[10] Fraunhofer Institute, 2014, "Sorption Energy Storage and Conversion for Cooling and Heating."

[11] Hublitz, A., 2008, "Efficient Energy Storage in
Liquid Desiccant Cooling Systems,"Dissertation, Technical University of Munich.

[12] Lowenstein PhD, A., 2008, "Review of Liquid Desiccant Technology for HVAC Applications," HVAC&R Research, 14(6).

[13] Conde-Petit, M. R., 2014, "Aqueous Solutions of Lithium and Calcium Chlorides: - Property Formulations for use in Air conditioning Equipment Design," Zurich, Switzerland.

[14] Sigma Aldrich, 2017, "Anhydrous Calcium Chloride and Lithium Chloride," http://www.sigmaaldrich.com/catalog/search?term=calcium+chloride&interface=All&N=0&mode=match%20partialmax⟨=en&region=US&focus=product, http://www.sigmaaldrich.com/catalog/search?term=lithium+chloride&interface=All&N=0&mode=match%20partialmax⟨=en&region=US&focus=product.

[15] Sahlot, M., and Riffat, S. B., 2015, "Desiccant cooling systems: a review,"Department of Architecture and Built Environment, University of Nottingham,Nottingham NG7 2RD, UK.

[16] Bergman, T. L., Lavine, A. S., Incropera, F. P., and Dewitt, D. P., 2011, Introduction to Heat Transfer, John Wiley and Sons, Inc.

[17] Corporation, C., 1967, "Centrifugal Refrigeration Machines."

[18] Tro, N. J., 2011, Chemistry, A Molecular Approach, Prentice Hall, New Jersey.

[19] Chemicals, F. D., 2017, "Products - Calcium Chloride Pellets," https://www.factorydirectchemicals.com/.

[20] Taylor, R., 2006, "Solar Thermal Technology and Applications," NREL.

[21] Cassard, H., Denholm, P., and Ong, S., 2011, "Break-Even Cost for Residential Solar Water Heating in the United States," NREL.

[22] Google, 2015, "Project Sunroof," https://www.google.com/get/sunroof#p=0.

[23] Rapier, R., 2016, "The Long Term Outlook on Natural Gas," https://www.forbes.com/sites/rrapier/2016/10/31/the-long-term-outlook-for-natural-gas/#7a7313c857a4.

Appendix A: Summary of Values in Calculations

A.1 Exergy Calculation

$h_{f,Ca^{2+}} = -543\ kJ/mol$
$2h_{f,Cl^-} = -167.4\ kJ/mol$
$M_{Sol} = 0.04125\ kg/mol$
$h_{f,CaCl_2} = -795.8\ kJ/mol$
$C_{p,sol} = 2.93\ kJ/(kg-K)$

A.2 Heat Exchanger Sizing

$T_f = 70°C$
$T_{in} = 20°C$
$C_p = 4.184\ kJ/(kg-K)$
$C_{p,sol} = 2.01\ kJ/(kg-K)$
$t = 1500\ s$
$m = 3.75\ kg$
$R_f'' = 0.0005\ m^2 * K/W$
$Pr = 4.885$
$D = 0.00635\ m$
$D_o = 0.00635\ m$
$D_i = 0.00476\ m$
$k = 401\ W/(m-K)$
$\beta = 0.000214\ 1/K$
$\nu = 0.475 * 10^{-6}\ m^2/s$
$g = 9.81\ (kg * m)/s^2$

A.3 Experimental Rate of Heat Transfer

$\dot{m} = 0.001\ kg/s$
$C_p = 4.182\ kJ/(kg-K)$

A.4 ROI and LCOE Calculation

$d = 0.05$
$E = 7300\ kWh$