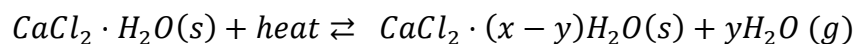


## CHAPTER 2

### LITERATURE REVIEW

**M. Gaeini (2018)** studied that thermochemical heat storage in salt hydrates is a promising method to improve the solar fraction in the built environment. The major concern at that stage is liquefaction followed by washing out of active material and agglomeration into large chunks of salt, thus deteriorating the diffusive properties of the porous salt hydrate structure. In his work, specific attention is given to the methods to stabilize a sample salt hydrate. Attempts have been made to stabilize calcium chloride by impregnation in expanded natural graphite and vermiculite, and by microencapsulation with ethyl cellulose. The effect of these stabilization methods on the performance of the material, such as kinetics and energy density, has investigated. Characterization of the materials is carried out with combined Thermo-Gravitation Analysis (TGA) and Differential Scanning Calorimetry (DSC) methods and microscopic observation, in order to evaluate the improvements on the basis of three subjects: reaction kinetics, heat storage density and stability

Calcium chloride is found to be one of the promising salt hydrates for thermochemical heat storage for common building applications. A reversible chemical gas-solid reaction can be employed that involves  $\text{CaCl}_2$ , according to the de/re-hydration reaction of



The interest for calcium chloride has been triggered by: easy availability and subsequently low price, high capacity for water uptake and energy storage density, relatively better chemical stability than other salt hydrates, low

corrosiveness and non toxicity. Furthermore, the material dehydrates at low temperature (below 100 °C), which makes it suitable for the applications.

The energy storage density is studied for the four calcium chloride based materials. The energy release for each sample during hydration from anhydrous to hexahydrous state was studied. The simultaneous thermal analysis method allows the estimation of the energy per mole of calcium chloride and per mole of absorbed water. Microencapsulated calcium chloride showed high multicyclic stability, compared with pure and impregnated materials, that liquefy upon hydration under the given conditions. Microencapsulated material remains stable over multiple cycles and shows the fastest kinetics. The only disadvantage of the encapsulation methodology used in paper is the resulting low energy storage density.

**Ard-Jan de Jong (2016)** observed that long-term and compact storage of solar energy is crucial for the eventual transition to a 100% renewable energy economy. For that, thermochemical materials provided a promising solution. The compactness of a long-term storage system was determined by the thermochemical reaction, operating conditions, and system implementation with the necessary additional system components. Within the prototype project a thermochemical storage system is being demonstrated using evacuated, closed thermochemical storage modules containing  $\text{Na}_2\text{S}$  as active material.

A significant part of energy to be stored is for space heating and domestic hot water for buildings. Daily storage can be arranged by mature boiler technology, but seasonal storage for at least half a year will require considerably lower heat losses. Besides, seasonal heat storage will usually imply storing very large amounts of heat, so that heat storage should be compact, with high storage density. Energy storage by using solar heat (e.g. at 60-140°C) to reverse chemical reactions is an attractive solution, as the reaction products can be stored virtually loss-free.

Thermochemical storage offers the potential of loss-free storage with a heat storage density higher than water. The first lab results of the prototype used in this project showed that a storage density of  $0.14\text{GJ/m}^3$  was achieved and they observed that it can expect to reach  $0.18\text{GJ/m}^3$  for coming field tests. In this paper identified and analyzed several possible improvements and show that by mere optimization of the prototype fixed-bed reactor concept using  $\text{Na}_2\text{S}$ , a heat storage density of approximately  $1\text{GJ/m}^3$  can already be achieved.

**Michael Graham(2016)** studied that thermal energy storage has many important applications, and is most efficiently achieved by latent heat storage using phase change materials (PCMs). Salt hydrates have advantages such as high energy storage density, high latent heat and incombustibility. However, they suffer from drawbacks such as incongruent melting and corrosion of metallic container materials. By encapsulating them in a polymer shell, problems can be eliminated. Here we demonstrate a simple method to nanoencapsulate magnesium nitrate hexhydrate, employing an in situ mini emulsion polymerisation with ethyl-2- cyanoacrylate as monomer. Using sonication to prepare mini emulsions improved the synthesis by reducing the amount of surfactant required as stabiliser. Thermal properties were analysed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Fourier transform infrared spectroscopy (FTIR) was employed to prove the presence of salt hydrate within the nanocapsules. Results showed the capsules are 100-200nm in size, have salt hydrate located in the core and are stable over at least 100 thermal cycles with only a 3% reduction in latent heat. Supercooling is also drastically reduced

DSC results demonstrated for the first time high thermal stability of the nanoencapsulated salt hydrates, which remained unchanged after 100 thermal cycles with a latent heat of  $83.2\text{Jg}^{-1}$ . Chemical and macroscale stability of the nanoencapsulated salt hydrates were also proven by FTIR and visual observations after heating/cooling cycles. The thermal properties of the nanocapsules are a

great improvement over the bulk  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , which loses its structural integrity and chemical composition after only 5 cycles.

Salt hydrate PCMs with long lifetimes are important for future energy storage applications, due to their high heat capacity and cost effectiveness compared to commonly used paraffin wax PCMs. Efficient energy storage has the potential to greatly reduce global energy demand, providing a sustainable future

**Lin Liang (2017)** studied that a new cold storage phase change material eutectic hydrate salt ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} - \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was prepared, modified, and tested. The modification was performed by adding a nucleating agent and thickener. The physical properties such as viscosity, surface tension, cold storage characteristics, supercooling, and the stability during freeze-thaw cycles were studied. Results showed that the use of nucleating agents, such as sodium tetraborate, sodium fluoride, and nanoparticles, are effective. The solidification temperature and latent heat of these materials which was added with 0, 3, and 5 wt% thickeners were  $-11.9$ ,  $-10.6$ , and  $-14.8^\circ \text{C}$  and 127.2, 118.6, 82.56 J/g, respectively. Adding a nucleating agent can effectively improve the nucleation rate and nucleation stability. Furthermore, increasing viscosity has a positive impact on the solidification rate, supercooling, and the stability during freeze-thaw cycles.

**Luca Scapino (2017)** studied that sorption heat storage has the potential to store large amounts of thermal energy from renewables and other distributed energy sources. This article provides an overview on the recent advancements on long-term sorption heat storage at material- and prototype- scales. The focus is on applications requiring heat within a temperature range of  $30\text{--}150^\circ\text{C}$  such as space heating, domestic hot water production, and some industrial processes.

Thermal energy storage is an attractive storage category because in principle it can be more economical than other technologies, it has a wide range of storage possibilities with storage periods ranging from minutes to months, and finally

because thermal energy dominates the final energy use in sectors such as industry or household .Thermal energy storage can be divided into three main categories according to how energy is stored: sensible heat (e.g. water tanks, underground storage) latent heat (e.g. ice, phase change materials) , and sorption heat storage

Currently, composite materials are investigated because they have the potential to overcome the disadvantages of pure salt hydrates by increasing their hydrothermal stability. This is done by mixing or impregnating salt hydrates with highly porous host matrices or powders. However, problems in heat and mass transport still can arise due to the reduction of empty pores, possible deliquescence and leakage of the salt from the composite, and degradation. To this regard, further research is needed to overcome these problems and to understand extensively the kinetics of a composite material, which does not follow a typical behavior of a salt hydrate nor of an adsorbent. Various prototype reactors and systems were developed by the scientific community to study the performances of sorption materials at macro-scale. Open and closed solid sorption systems have been analyzed and compared. Among the reviewed prototypes, mostly systems based on zeolites were able to achieve temperatures suitable for space heating or DHW production. For these systems, relatively high desorption temperatures were required, unachievable, for example, by conventional solar thermal collectors.

**Dongdong Li (2018)** studied on the development of a multi-temperature thermodynamically consistent model for salt lake brine systems. Under the comprehensive thermodynamic framework proposed in his previous work, the thermodynamic and phase equilibria properties of the sulfate binary systems (i.e.,  $\text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ ,  $\text{MgSO}_4 + \text{H}_2\text{O}$  and  $\text{CaSO}_4 + \text{H}_2\text{O}$ ) were simulated using the Pitzer-Simonson Clegg (PSC) model. Various type of thermodynamic properties (i.e., water activity, osmotic coefficient, mean ionic activity coefficient, enthalpy of dilution and solution, relative apparent molar enthalpy, heat capacity of aqueous phase and solid phases) were collected and

fitted to the model equations. The thermodynamic properties of these systems can be well reproduced or predicted using the obtained model parameters.

**Farzad Deyhimi (2009)** studied the use of Pitzer, PSC as well as an extended PSC ion-interaction approaches for modelling the non-ideal behavior of the ternary HCl + water + 1- propanol systems. These modelling purposes were achieved based on the experimental potentiometric data of a galvanic cell containing a pH glass membrane and Ag/AgCl electrodes. The measurements were performed over the HCl electrolyte molality ranging from 0.01 up to 4.5 mol kg<sup>-1</sup> system with different alcohol percent mass fractions (x% = 10, 20, 30, 40 and 50%), at 298.15 ± 0.05 K

Pitzer semi-empirical virial coefficient approach has been remarkably successful in modeling the thermodynamic properties of aqueous electrolyte solutions. Although this approach proved to be also a valuable method for correlation and prediction of thermodynamic properties of electrolytes in mixed solvent media, there is still only a limited number of reported studies concerning its application for modeling such systems. Pitzer and Simonson (PS) developed a newer model as well that is applicable over the entire concentration range for the investigation of mixtures containing ions of symmetrical charge type. Both experimental potentiometric data along with the related model parameters associated with Pitzer, PSC, and an extended PSC approaches concerning the investigation of the ternary HCl + 1- PrOH + water electrolyte system, are for the first time reported in his work.

**Edilson C. Tavares (1999)** studied the solid-liquid equilibrium in aqueous multi-electrolyte systems using the quasiisothermic thermometric technique (QTT). The principle of the QTT is based on thermal effects associated with the phase transformations that occur in the system. In order to test the apparatus, salt solubility data at 298.15 K for the aqueous systems H<sub>2</sub>O+NaCl+KCl, H<sub>2</sub>O+NaCl+Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O+NiCl<sub>2</sub>+NiSO<sub>4</sub> are presented. The data obtained for the

three systems are in good agreement with the literature, including solid phase boundaries due to hydration. This agreement indicates the accuracy of the proposed method.

The QTT has been properly tested for the measurement of salt solubilities and solid phase transitions. The apparatus is simple construction and can be operated with the aid of the computer interface, giving accurate data. The burette should be monitored via interface and computer. The QTT has been applied for the measurement of new salt solubility and solid phase transition data for the system  $\text{NiCl}_2 + \text{NiSO}_4 + \text{H}_2\text{O}$  at 298.15 K.

**Huinan Wang (2020)** Vapor–liquid equilibrium (VLE) data and modeling for  $\text{LiBr} + \text{H}_2\text{O}$  and  $\text{LiBr} + \text{CaCl}_2 + \text{H}_2\text{O}$  are reported in this paper. This work focuses on the experimental determination of the boiling point of  $\text{LiBr} + \text{H}_2\text{O}$  and  $\text{LiBr} + \text{CaCl}_2 + \text{H}_2\text{O}$  solutions with vapor pressures between 6 and 101.3 kPa and the total molality of salt ranging from 0 to 21.05 mol kg<sup>-1</sup>. The procedures were carried out in a computer-controlled glass apparatus. The relationship between the boiling point and saturated vapor pressure is obtained, and Xu's model is used to correlate and predict the VLE. By correlation of the data (literature and experimental) for  $\text{LiBr} + \text{H}_2\text{O}$  and  $\text{LiBr} + \text{CaCl}_2 + \text{H}_2\text{O}$ , the parameters are obtained. e compared the results with the ElecNRTL model and Pitzer model. The parameters for the  $\text{LiBr} + \text{H}_2\text{O}$ ,  $\text{CaCl}_2 + \text{H}_2\text{O}$ , and  $\text{LiBr} + \text{CaCl}_2 + \text{H}_2\text{O}$  systems can be successfully used to calculate and predict the VLE data

**Christoph Rathgeber (2019)** In this work, the modified BET equations are extended in order to calculate solubility phase diagrams of concentrated salt solutions with relatively high water activities within the range of undersaturation. Predicting solubility phase diagrams of mixtures of salts and water is of interest in various application fields, e.g. in the process of extracting salts or salt hydrates from natural salt brines to develop working fluids in absorption refrigeration systems, or to develop phase change materials for thermal energy storage . As an

example, BET parameters of NaCl are determined and applied to calculate solubility phase diagrams of NaCl + H<sub>2</sub>O, NaCl + LiCl + H<sub>2</sub>O, and NaCl + CaCl<sub>2</sub> + H<sub>2</sub>O within the temperature range of around 250–500 K. In the ternary systems, the best agreement with solubility data from literature is obtained using constant BET parameters of NaCl and an additional temperature-dependent regular solution parameter to account for salt-salt interaction.

## **2.2 Various Models Available**

Various Thermodynamic models are studied from literature.

### **1-Debye–Hückel equation**

The Debye Hückel equation is a mathematical expression developed to explain certain properties of electrolyte solutions, or substances found in solutions in the form of charged particles (ions). The Debye Hückel equation accounts for the interactions between the different ions, which are the primary cause of differences between the properties of dilute electrolyte solutions and those of so-called ideal solutions.

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

1. Electrolytes completely dissociate into ions in solution
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M
3. Each ion is surrounded by ions of the opposite charge, on average

### **2- Davies equation**

Davies equation is useful at ionic strengths up to 0.5M, making it a better choice than the Debye-Huckel Model. It makes better calculation in concentrated solutions than Debye-Huckel Model. This equation was originally published in 1938. The calculation gets deviated from experiment for electrolytes that dissociate into ions with higher charges