

Stability analysis of Calcium chloride hexahydrate inorganic phase change material

Hamza AYZAZ^{a*}, José LARA CRUZ^a, Jorge SALGADO-BECEIRO^b, Magnus ROTAN^b, Ragnhild SÆTERLI^b, Fride VULLUM-BRUER^b, Alexis SEVAULT^b and Jean-Pierre BEDECARRATS^a

^a Université de Pau et des Pays de l'Adour, E2S UPPA, LaTEP, Laboratoire de Thermique, Énergétique et Procédés, 64000 Pau, France

^b SINTEF Energy Research, Postboks 4761 Torgarden, 7465 Trondheim, Norway.

*(Corresponding author: hamza.ayaz@univ-pau.fr)

Abstract

Calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is a potential thermal battery material with a primary issue of phase segregation which is more pronounced with time and temperature. This study is performed to prepare $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM from dry CaCl_2 and investigate its thermal stability (impact of temperature on thermal properties variation and phase segregation). In addition, a commercial product was analyzed to compare the results of the prepared sample. The result shows that the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sample thermal properties did not vary much, and a small phase segregation seems to be observed.

Keywords: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ preparation; Thermal energy storage; Inorganic phase change material; Stability analysis

1. Introduction

Phase change materials (solid to liquid) used for thermal energy storage, offer a lot of potential applications. Thermal energy storage systems are designed to mitigate the supply and demand difference of thermal energy and augment the performance of conventional systems. Depending on their chemical structure, phase change materials (PCMs) are classified as organic and inorganic. The reported data in the open literature shows that inorganic PCMs must have high thermal conductivity, high phase change enthalpy, a non-flammable nature, and are cheap [1]. Considering the qualitative properties, the selection of PCMs for any application includes the phase change equilibrium temperature, the amount of energy stored during phase transition, and the stability of the PCM. Furthermore, certain materials with pertinent thermal characteristics are not very stable over time. These PCMs' ability to store energy is negatively impacted by prolonged exposure to the temperature or by solidification and melting thermal cycles.

Salt hydrates PCM are mixtures of dry salt and water molecules mixed in a very specific composition. The main issue linked with these PCMs is phase segregation which has a direct influence on the thermal properties of the PCMs. The salt hydrate is formed by performing a stoichiometric balance for the mixture of salt and water molecules where the water molecules are trapped in the crystal lattice of the salt that is associated by an ion-dipole or hydrogen bond with the salt. A salt hydrate becomes an interesting PCM candidate when its ratio of salt to water molecules provides a mixture with constant phase change temperature during the melting process. During the melting process, the water molecules are released and mixed in the solvent

where the salt ions are dissolved. The water molecules are loosely bonded, and the stoichiometric balance of the salt hydrate mixture significantly depends on the aqueous interaction between salt and water. During the phase transition, we can observe some phase segregation in a salt hydrate due to poor aqueous interaction between molecules and density difference between water and the other phases formed (either pure salt or most frequently salty solutions). This can be due to the influence of the temperature or the phase transition. Different studies reported the stability investigation of salt hydrates PCM. Stephen [2] performed a cyclic stability test of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ salt hydrate PCM also known as Glauber salt. Two samples were prepared one without thickeners and in the second sample $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and Attapulgite Clay were added as thickeners. The results showed that the phase change enthalpy of the Glauber salt without thickener declines from 238 J/g to 63 J/g after 20-40 thermal cycles whereas for the thickened sample the value dropped to 105 J/g after 200 thermal cycles. El-Sebaai et al. [3] investigated cyclic stability of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ PCM and the result showed that for the first cycle the phase change temperature ($T_{m(\text{onset})}$) and phase change enthalpy (ΔH_m) were 111.5 °C and 155.1 J/g, and it varied to 124.1 °C and 85 J/g after 500 thermal cycles. Tyagi and Buddhi [4] performed cyclic stability test of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM which is widely utilized in the building sector. The result presented has $T_{m(\text{onset})}$ of 23.2 °C and ΔH_m of 125.4 J/g after 1000 thermal cycles. The thermal properties after 1000 thermal cycles were the same as after the first thermal cycle. Guo et al. [5] investigated thermal properties of calcium chloride hexahydrate with 1.2% of strontium chloride. The result shows $T_{m(\text{onset})}$ and ΔH_m were 28.7 °C and 193.4 J/g. The thermal properties of the sample were examined for 30 thermal cycles that show a decrease of 0.2% in the phase change temperature and 2.7% in the phase change enthalpy. Thakkar J et al. [6] studied the impact of nucleating agent and stabilizer for calcium chloride hexahydrate PCM. The results show $T_{m(\text{onset})}$ of 25.2 °C and ΔH_m of 172 J/g for pure PCM without adding any nucleating agent or stabilizer. After 15 thermal cycles the $T_{m(\text{onset})}$ was 25.1 °C and ΔH_m was 145 J/g. Whereas with the nucleating agent and stabilizer, no significant change was noticed in the thermal properties after 15 thermal cycles. The previous results show that the long term thermal stability of the salt hydrate was investigated with accelerated cycling whereas no result shows the impact of the temperature.

The issue with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ salt hydrate PCM is its phase segregation. In our study, samples with significant phase segregation are reformed by adjusting the phase equilibrium without adding any thickeners. After the preparation of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (reformed from an old sample of the salt hydrate), the thermal properties were compared with the commercial product available by Sigma Aldrich. Another aspect that is addressed in the study is the influence of the temperature on the phase segregation. Whereas in the open literature, the long-term stability of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is only performed with accelerated thermal cycling, and no results are found for the impact of thermal stress. The thermal stress experiment is performed for the reformed product and the commercially available PCM. The objective of this study is to prepare a stable salt hydrate from the old sample, compare its thermal properties to a commercial product, and investigate the long term stability when it is subjected to a temperature above its melting temperature. The old sample was procured 11 years ago from Sigma Aldrich and stored at ambient conditions where it has experienced temperature above its melting point, difference in the atmospheric pressure, and humidity which has probably triggered the phase segregation for this product. The results will be helpful for researchers who want to reform a $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ old sample and design a thermal energy storage system with it.

2. Materials and research methodology

The calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is an inorganic salt hydrate PCM that is prepared from dry salt CaCl_2 and water. In this study, two $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ products were utilized. The first sample was reformed from old $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (a product procured 11 years ago from Sigma Aldrich and stored at ambient conditions for this duration) which has significant phase segregation, and the second product was procured from Sigma Aldrich with a purity of 98%. The phase change temperature for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is in the range of $30\text{ }^\circ\text{C}$ [7]. The products were utilized without adding any thickeners.

2.1 Preparation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

The preparation method of the reformed $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is shown in Fig. 1. The stratified sample can be seen with two different phases solid and liquid phase during its crystallization phase. The sample resulted after storing it at ambient conditions for almost 11 years where it experienced temperature above its phase change equilibrium temperature, difference in the atmospheric pressure, and humidity which has probably triggered the phase segregation for this product. The stratified sample of the salt hydrate was placed in an oven with a temperature of $210\text{ }^\circ\text{C}$ for the dehydration process. The complete dehydration of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is done at $200\text{ }^\circ\text{C}$ which is confirmed by Karunadasa et al. [8]. All the water molecules are removed by keeping the sample at $210\text{ }^\circ\text{C}$ for 1 h. This process was followed by mixing mass concentrations of 50.7% dry CaCl_2 and 49.3% distilled water. The solution was mixed for 30 mins, and it was cooled down at room temperature for further characterization. No additional heating was utilized during the mixing process as it has a negative impact on the preparation process [9].

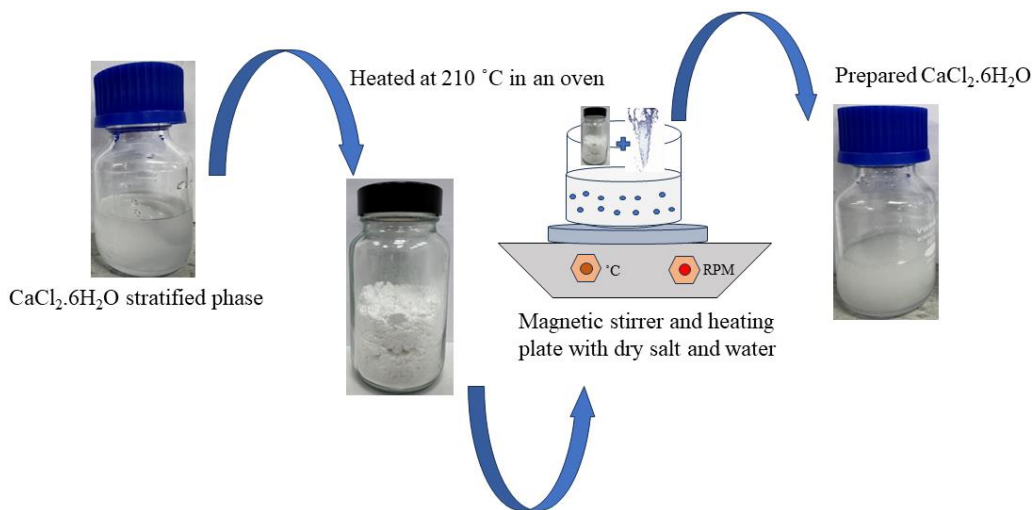


Fig. 1 Preparation methodology for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

2.2 Thermal stress test

The thermal stress test was conducted in a controlled temperature oven (DHG-9032) with an uncertainty of $\pm 0.5\text{ }^\circ\text{C}$. To investigate the effect of the temperature on the PCM stability, a 35 g sample is placed in glass bottles and subjected to temperatures higher than its phase change equilibrium temperature. The oven was adjusted to $50\text{ }^\circ\text{C}$, $20\text{ }^\circ\text{C}$ higher than the phase change equilibrium temperature, and three samples were tested. The trial lasted ninety days, with one different sample removed every thirty days. To determine if the PCM was stable, further

characterization was performed with differential scanning calorimetry (DSC) on the removed sample to investigate its thermal properties.

2.3 Characterization of the PCM

The thermograph obtained by the DSC (MICRO-DSC7-EVO, SETARAM) provides precise information on the thermal characteristics of the PCM. The temperature program ranges from -30 to 50 °C, with a linear ramp of 0.5 °C/min. The DSC analysis was performed for the CaCl₂.6H₂O sample prepared from dry CaCl₂ and commercial products to compare the results. Each sample removed from the thermal stress experiment was analyzed. The DSC sample after the thermal stress experiment was collected from the bottom of the container, once the entire sample was melted, without taking other samples from different levels of the container. The DSC was used for a total of 4 cycles per test. The first thermal cycle in the DSC helped the sample to have good thermal equilibrium with the system. The thermal properties were presented as the average thermal characteristic of the three following thermal cycles with an uncertainty of ±0.2 °C for the phase change temperature and 1.3% for the phase change enthalpy. The uncertainty was estimated by doing a DSC study on distilled water and comparing the standard data available for the sample.

3. Results and discussion

DSC characterization of the PCM

The phase change process for solidification and melting of CaCl₂.6H₂O prepared from dry CaCl₂ is shown in Fig. 2. The onset phase change equilibrium temperature (solid to liquid) $T_{\text{onset,m}}$ was 30.6±0.2 °C whereas the phase change equilibrium enthalpy $\Delta_{\text{fus}}H$ was 177±2 J/g. For the liquid-to solid phase change (solidification curve), two peaks are present. The onset crystallisation temperature of the first one is $T_{\text{onset,s}} = -17.0\pm 0.2$ °C and for the second one $T_{\text{onset,s}} = -22.0\pm 0.2$ °C. The total phase change enthalpy is $\Delta_{\text{sol}}H = 146\pm 2$ J/g. The two peaks in the crystallization process can be due to fact that the initial composition of the sample prepared from dry CaCl₂ could be slightly different from the ratio of one CaCl₂ molecule to six molecules of water. It also can be due to the supercooling which can trigger crystallization of one part of the salt water mixture and the whole crystallization process is completed with the second peak. The difference in the phase change temperature values between melting and crystallization is due to the degree of supercooling which is quite large for the small volume of PCM (approximately 10 µl) in the cell of the DSC. Due to the erratic behavior of the degree of supercooling and the fact that the temperature of crystallization is linked to the volume, the crystallization process is not considered in this work and the results presented were deduced by analyzing the phase change process during melting. The thermal properties reported in this work have the same tendency as reported by other research groups [7,10]. As already mentioned, the first thermal cycle was performed to have a good thermal equilibrium between the sample and the system. Then the average values over the next cycles of the thermal properties are presented.

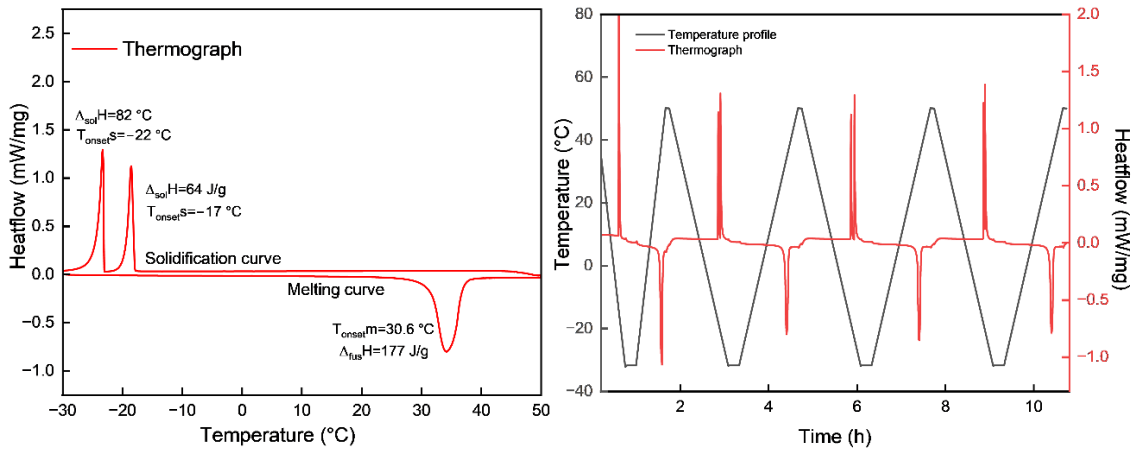


Fig. 2 DSC thermograph of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (prepared in lab)

In Fig. 3 the endothermic and exothermic thermographs for the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ commercial product are shown. The results show similar values to the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sample prepared in the laboratory. The onset phase change equilibrium temperature (solid to liquid) $T_{\text{onset},m}$ was 30.4 ± 0.2 °C whereas the phase change equilibrium enthalpy $\Delta_{\text{fus}}H$ was 184 ± 2 J/g. The onset crystallization temperature (liquid to solid) $T_{\text{onset},s}$ was -20.7 ± 0.2 °C, and its phase change enthalpy $\Delta_{\text{sol}}H = 156 \pm 2$ J/g. The same phenomenon explained in the previous section is repeated in the third thermal cycle of the DSC where two peaks in the crystallization process are evidenced. The results show the thermal properties of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ prepared from dry CaCl_2 are in an acceptable range compared to the commercial product.

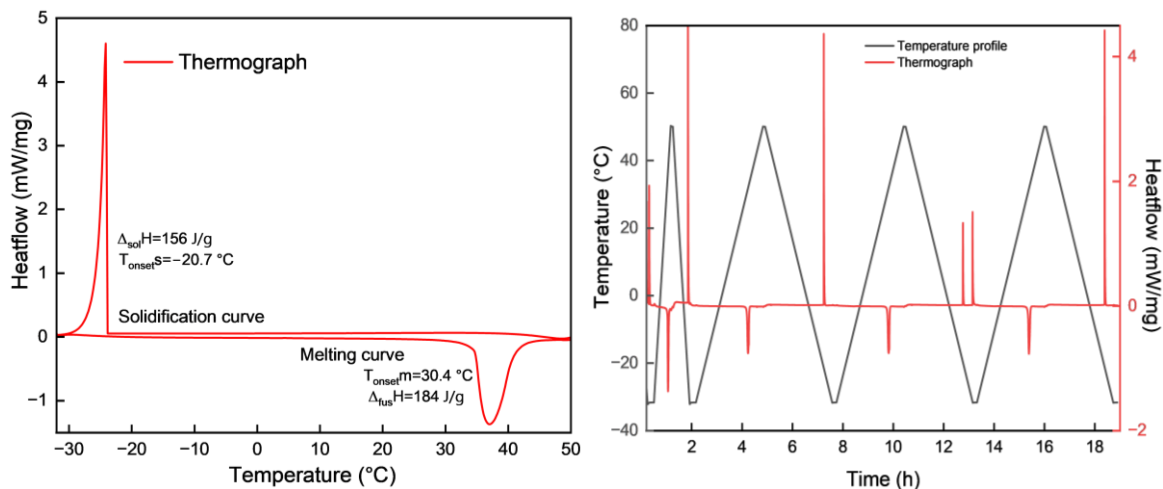


Fig. 3 DSC thermograph of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich product)

Thermal stress analysis of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

The thermal stress test results are shown in Fig. 4 and Fig. 5. Due to the erratic behavior of the degree of supercooling only the melting process is presented. Fig.4 depicts the result for the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sample which was prepared from dry CaCl_2 . The DSC thermograph for the three samples that were analyzed after 30, 60, and 90 days did not show much variation in the thermal properties of the sample. The result indicates that the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sample that was prepared in the laboratory did not show much variation in the thermal properties. A small bump was evidenced in the thermograph which represents the 30 days thermal stress experiment. The small bump could indicate the starting of a phase segregation. Therefore, it was concluded that

if the temperature of the latent heat thermal energy storage system increases to 50 °C due to thermal fluctuation the thermal properties will not vary much but it can be responsible for starting a phase separation which can be increased further. In addition, the small bump in the thermograph after 30 days has less impact on the thermal properties. The maximum variation in the thermal properties evidenced was 1.63% for the phase change temperature and 4.5% for the phase change enthalpy.

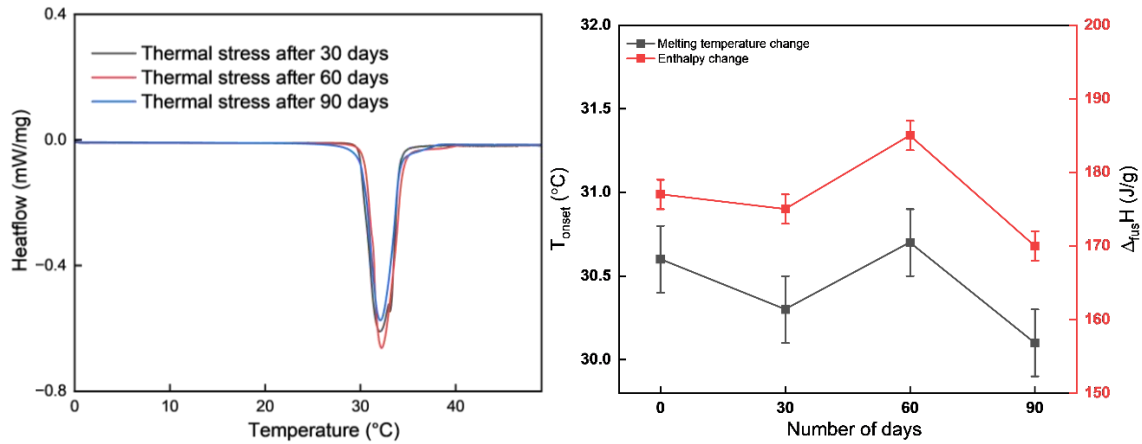


Fig. 4 Thermograph of the melting peaks of CaCl₂.6H₂O (prepared in the lab)

Fig. 5 shows the thermal stress results for the commercial product utilized in this study. The same protocol was followed for this test as described earlier. The result did not show any considerable variation in the thermal properties due to the influence of the temperature. In the melting process, there is a small bump which indicates perhaps the starting of a phase segregation. This possible start of a phase segregation was detected but the thermal properties of the PCM were not altered significantly. Afterwards, when the samples are visually inspected two phases can be observed, which strengthens the hypotheses of phase segregation. However, there is no significant change in the thermal properties of the sample. This could be due to the fact that the samples were first melted and a small portion of the sample which was taken from the bottom of the container was investigated. The maximum variation in thermal properties for the commercial product was 0.32% for phase change temperature and 2.7% for the phase change enthalpy. In this study, the sample that is reformed was from a product that was procured 11 years ago whereas the commercial product was newly purchased. The partial results show the calcium chloride hexahydrate reformed from dry CaCl₂ shows good repeatability of thermal properties, but further tests will be performed in future work to investigate the phase segregation by taking the DSC samples from different levels of the container. If the phase segregation existed in the sample the density of the sample at different levels in the container would not be the same. Therefore, the DSC sample should be taken from different levels of the container to better investigate the influence of the phase segregation.

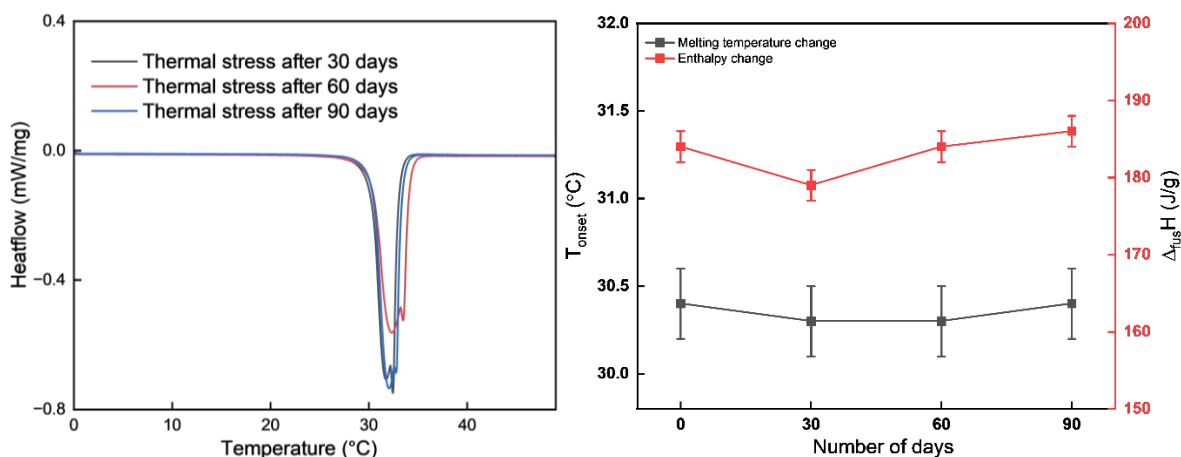


Fig. 5 Thermogram of the melting peaks of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich product)

4. Conclusion

This study aims to perform stability investigation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, which is often used in building thermal energy storage applications. Two different samples of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ were utilized. The thermal characteristics of the sample prepared from dry CaCl_2 were compared to a new commercial product available from Sigma Aldrich. The results showed the thermal properties of the sample prepared in the laboratory are in the acceptable range. In addition, the impact of temperature was investigated during thermal stress experiment. The thermal stress results indicated that a small bump was obvious in the melting process of all Sigma Aldrich product samples, including the 30 days sample made from dry CaCl_2 , which could suggest the start of phase segregation. The phase segregation in both samples seems very small and did not change the thermal properties considerably. Further characterization techniques (XRD X-ray diffraction) will be followed to look indepth for the phase segregation in these samples. In addition, the sample for DSC analysis will be taken from different levels of the container to better investigate the potential phase segregation of the sample. The findings will be useful for researchers who wish to reform an old $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sample and use it to design a latent heat thermal energy storage system.

References

- [1] M.F. Junaid, Z. ur Rehman, M. Čekon, J. Čurpek, R. Farooq, H. Cui, I. Khan, Inorganic phase change materials in thermal energy storage: A review on perspectives and technological advances in building applications, *Energy Build* 252 (2021) 111443. <https://doi.org/10.1016/J.ENBUILD.2021.111443>.
- [2] S. Marks, An investigation of the thermal energy storage capacity of Glauber's salt with respect to thermal cycling, *Solar Energy* 25 (1980) 255–258. [https://doi.org/10.1016/0038-092X\(80\)90332-1](https://doi.org/10.1016/0038-092X(80)90332-1).
- [3] A.A. El-Sebaili, S. Al-Amir, F.M. Al-Marzouki, A.S. Faidah, A.A. Al-Ghamdi, S. Al-Heniti, Fast thermal cycling of acetanilide and magnesium chloride hexahydrate for indoor solar cooking, *Energy Convers Manag* 50 (2009) 3104–3111. <https://doi.org/10.1016/J.ENCONMAN.2009.08.020>.

- [4] V. V. Tyagi, D. Buddhi, Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage, *Solar Energy Materials and Solar Cells* 92 (2008) 891–899. <https://doi.org/10.1016/J.SOLMAT.2008.02.021>.
- [5] Y. Guo, D. Gao, X. Yu, C. Ma, S. Chen, T. Deng, Thermal energy storage using calcium chloride hexahydrate, *Thermal Science* 22 (2018) 3035–3041. <https://doi.org/10.2298/TSCI170119135G>.
- [6] J. Thakkar, N. Bowen, A.C. Chang, P. Horwath, M.J. Sobkowicz, J. Kośny, Optimization of Preparation Method, Nucleating Agent, and Stabilizers for Synthesizing Calcium Chloride Hexahydrate (CaCl₂·6H₂O) Phase Change Material, *Buildings* 12 (2022). <https://doi.org/10.3390/buildings12101762>.
- [7] Sigma Aldrich, Calcium chloride hexahydrate, (n.d.). <https://www.sigmaaldrich.com/FR/fr/product/aldrich/442909> (accessed February 1, 2024).
- [8] K.S.P. Karunadasa, C.H. Manoratne, H.M.T.G.A. Pitawala, R.M.G. Rajapakse, Relative stability of hydrated/anhydrous products of calcium chloride during complete dehydration as examined by high-temperature X-ray powder diffraction, *Journal of Physics and Chemistry of Solids* 120 (2018) 167–172. <https://doi.org/10.1016/j.jpcs.2018.04.034>.
- [9] J. Thakkar, N. Bowen, A.C. Chang, P. Horwath, M.J. Sobkowicz, J. Kośny, Optimization of Preparation Method, Nucleating Agent, and Stabilizers for Synthesizing Calcium Chloride Hexahydrate (CaCl₂·6H₂O) Phase Change Material, *Buildings* 12 (2022). <https://doi.org/10.3390/buildings12101762>.
- [10] J. Charles, Performance and Stability of CaCl₂·6H₂O-Based Phase Change Materials Heat-Pipe PCM Based Cool Storage for ACC Systems View project, (2018). <https://doi.org/10.13140/RG.2.2.26572.87685>.

Acknowledgment

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska Curie Actions, Grant Agreement No. 945416 and was carried out through the research project KSP PCM-STORE (308847) supported by the Research Council of Norway and industry partners. PCM-STORE aims at building knowledge of novel PCM technologies for thermal energy storage systems.