Study of the solidification behaviour of calcium chloride hexahydrate by in-situ X-ray computed tomography

Jorge Martinez-Garcia¹, Damian Gwerder¹, Dario Guarda¹,², Benjamin Fenk¹, Anastasia Stamatiou¹, Jörg Wortlicheck¹ and Philipp Schuetz¹

1 Lucerne University of applied sciences and arts, Competence centre for thermal energy storage, Horw, Switzerland, jorge.martinezgarcia@hslu.ch
2 Department of Management and Engineering, University of Padova, Italy

Abstract

Calcium chloride hexahydrate (CaCl₂.6H₂O) is a stablished inorganic salt hydrate-based phase change material (PCM) with interesting properties for low temperature latent heat thermal energy storage (LHTES) applications. However, its phase transition during melting and solidification exhibits a complex behaviour with supercooling and phase segregation effects, which critically limit their practical applications. Experimental approaches enabling tracking of the solidification process in this PCM are thus crucial for a deeper understanding of these adverse effects and to design efficient LHTES. In this study, a novel method based on dynamic X-ray computed tomography (XCT) is used to monitor the solidification process in CaCl₂.6H₂O through sequences of XCT images. The method was tested with a sample of 60g of CaCl₂.6H₂O with density of 1.71 g/cm³ and purity higher than 98%. The results reveal that solidification of CaCl₂.6H₂O occurs through the fusion of crystalline structures initially appearing at the side and the bottom surfaces of the sample which grow over time. In the experiment performed, the solidification process is found to be incomplete, which is frustrated after 385 min of starting the solidification. This frustration was preceded by a change in the total solidification rate which is here estimated from the transient liquid volume fraction curve computed via image processing analysis. Quantitative estimation for the crystals size is also reported.

KEYWORDS: Phase change materials; Calcium chloride hexahydrate; Solidification; X-ray computed tomography (XCT); Image processing analysis.

1. Introduction

Salt hydrates are considered a very promising class of inorganic phase change materials (PCMs) for latent heat thermal energy storage applications. Owing to its high volumetric phase change enthalpy, low toxicities, good thermal conductivity, and low cost, they are particularly suitable for low temperature heat storage applications, such as heat pump systems. However, despite the plethora of advantages, undesired problems such as, phase...
separation, volume change, supercooling, corrosion and leakage occurring during thermal cycling, impose restrictions on their practical applications. A particularly interesting class of materials are salt hydrates which excel in volumetric storage density and comparably low prices compared to organic storage materials [1]. Among the potential salt hydrate PCM candidates, calcium chloride hexahydrate (CaCl\textsubscript{2}.6H\textsubscript{2}O), has attracted much attention in the past and still has multiple open issues for additional investigation and improvement. It has many advantages, such as a suitable phase transition temperature at around 29 °C, a considerable large heat enthalpy (170-190) kJ/kg and solid and liquid density of 1710 kg/m\textsuperscript{3} and 1560 kg/m\textsuperscript{3}, respectively. It also has good thermal conductivity of about 0.58 W/mK and 1.08 W/mK for liquid and solid phase and a working temperature range in the human comfort, making it an ideal PCM candidate for building applications (e.g., for space heating) [2]. Despite this, CaCl\textsubscript{2}.6H\textsubscript{2}O faces a major challenge, in that supercooling and semi-congruent melting lead to undesirable phase separation, which cause variation of their thermochemical properties and thus decrease its performance with increasing the number of heating/cooling cycles [3]. Understanding solidification and melting processes of CaCl\textsubscript{2}.6H\textsubscript{2}O is therefore of utmost importance for its research and technological development [4].

X-ray computed tomography (XCT) is a powerful and no destructive technique which allows the inspection of the entire three-dimensional (3D) volume of a material at different length scales. Recent advances in conventional laboratory XCT equipment have enabled short acquisition times (~10-20s), which allow to perform in-situ XCT imaging of dynamic processes [5]. These improvements have opened new opportunities for monitoring melting and crystallization processes in PCMs from time-lapse (4D) volumetric XCT image measurements. Kholer et. al. applied for the first time dynamic XCT to study phase formation on the magnesium chloride hexahydrate PCM [6]. Martinez-Garcia et al. and Guarda et al. studied the solidification of ice PCM and validated a developed enthalpy-porosity model from time-lapse XCT measurements [7,8]. A methodology to quantify relevant PCM parameters (e.g., liquid volume fraction and volume changes) during the solid-liquid phase change from volumetric XCT image sequences has been recently proposed and used to track the solidification front of calcium chloride hexahydrate and eicosane PCMs [9,10]. This contribution demonstrates XCT as a suitable non-destructive method to track the liquid-solid phase change in PCMs. Here, results recently reported by Martinez-Garcia et al. [9] are used and extended to study the solidification behaviour of CaCl\textsubscript{2}.6H\textsubscript{2}O. It is shown how the crystal growth process in CaCl\textsubscript{2}.6H\textsubscript{2}O during solidification occurs. Quantitative estimation for the crystal size growth and the total crystallisation rates are also provided and discussed.

2. Material and Methods

2.1 Sample material

To generate the calcium chloride hexahydrate sample used in this study, commercial available calcium chloride hexahydrate with a purity greater than 98% was purchased from Sigma Aldrich. To create the sample, 60 g of CaCl\textsubscript{2}.6H\textsubscript{2}O with a density of 1.71 g/cm\textsuperscript{3} was filled into a glass vial, which was closed with an airtight screw on cap. A water bath at 50 °C was used to fully melt the sample before placing it in the XCT device.
2.2 XCT measurements and image processing

The entire liquid-solid phase transition during the crystallisation of the CaCl$_2$.6H$_2$O sample was monitored through sequences of XCT measurements performed on an industrial XCT device, Diondo D2, Hattingen, Germany (see Figure 1a-b). The experiment was performed with the source (XWT-225 TCHE+) in high power mode with an acceleration voltage of 160 kV and a filament current of 188 µA. The sample (cf. Fig. 1c) was placed on the rotatory stage of the XCT device where it solidified at a temperature of around 29 °C, meanwhile sequences of XCT measurements were performed at time intervals of 7.5 min. A total of 8 frames were averaged at each rotation point of the sample with a total integration time of 80 ms. The source-detector and source-object distance were set to 447 mm and 154 mm, respectively, giving an isotropic voxel size of 103 µm. For each time step, the resulting projections were converted into a 3D image stack with cross-sections of 352×352×1268 voxels using the CERA (Siemens Healthineers, Erlangen, Germany) reconstruction software with a beam hardening correction setting of 4. The chosen voxel size value was selected to clearly discern the features of interest in this study (i.e., liquid and solid PCM phases), while keeping a reasonable measurement speed and preventing artefacts. The data analysis was carried out in GeoDict®2022 and ImageJ-2.0 softwares. All algorithms used in this contribution were implemented in Python 3.7, supported by the tools provided by the image processing libraries, scikit-image and OpenCV and the GeoDict®2022 software.

3. Results and discussion

Exemplary cross-sections obtained from the dynamic XCT experiment are shown in Figure 2(a). As it can be seen from the Figure, the density difference between solid and liquid PCM phases was sufficient to clearly differentiate both phases. Solid and liquid PCM phases were quantified by applying the Otsu’s thresholding algorithm to the XCT image stacks [9]. As it can be seen from Figure 2(b), the quality of the segmented data is very good, capturing fine details, as for example, small solid PCM crystals apparently suspended in the liquid PCM phase. These features can be better visualized in Figure 3a where semi-transparent 3D rendering of the XCT imaging data allows to see internals snapshots of the crystallisation process.
As it can be seen from Figure 3a, the crystallization of \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) occurs through the fusion of crystalline structures initially appearing at the lateral surface and at the bottom of the sample and then growing over time. Noteworthily, the crystal cluster formed at the center of the bottom surface whose sizes increase remarkably over time until a merge with the solid surrounding takes place forming a solid homogenous structure. To have a quantitative measure of the crystal growth process, the size of the biggest crystal in the cluster was monitored in time. A quantitative measure of its size was estimated as the Euclidean distance between the extreme points of the crystal, which was computed from the image data collected during the dynamic XCT experiment. As it can be seen from Figure 3b, the growth process for this crystal occurs in three different stages. In the initial stage, a sudden occurrence of the crystal cluster take place during the first 34 min where the biggest crystal reaches the size of roughly 2.25 cm. Afterward, the crystal growing speed decreases and the growth process runs roughly linear in the \((y, z)\) plane during the next 247 min, until it reaches a saturation stage where the crystal reaches a maximum size of 4.48 cm.

It should be also noted from Figures 2a and 3b that the solidification of the examined \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) sample is accompanied by a notable volume shrinkage and moreover, is incomplete. This incompleteness is evidenced by the presence of a small amount of liquid \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) that remains until the end of the experiment. Computation of the transient liquid volume fraction curve reveals that the PCM liquid fraction decreases linearly until a constant liquid frication value of 0.022 (See Figure 4a). From the curve it is deduced that the solidification starts at \( t = 26 \) min with an average crystallization rate of \( R_1 = -0.025 \) (%vol/min) which is increased to \( R_2 = -0.008 \) (%vol/min) during the period from 340 min to 382 min (see Figure 4b).

3. Conclusions

The present work confirms that quantitative study of the solidification behaviour of PCMs
is possible using \textit{in-situ}, time-lapse XCT. The capabilities of XCT for such a study was here demonstrated for a sample of the commercial CaCl$_2$.6H$_2$O PCM. It was shown that liquid and solid phases can clearly be separated, and that the evolution of the crystal growth process can be tracked in time.

![Figure 3](image)

**Figure 3.** (a) Semi-transparent 3D rendering of the crystal formation (grey regions) in CaCl$_2$.6H$_2$O at different times. (b) Size of the biggest crystal localised at the bottom surface of the sample (see dotted arrows in Figure 3a) as function of time.

![Figure 4](image)

**Figure 4.** (a) Transient liquid volume fraction curve computed from the XCT imaging data shown in Figure 2b. R1 and R2 denotes the regimens where different crystallisation rates were found. (b) Total crystallisation rate computed as the average of the local slopes (i.e., time derivatives) of the liquid volume fraction.

Quantitative estimate for the crystals size and the total crystallization rate were also computed from the collected 4D XCT imaging data. The presented non-destructive XCT
method is thus proposed as a novel tool for the analysis of PCMs and their integration in LHTES.

**Acknowledgements**

The authors would like to thank the Swiss National Science Foundation for the support of the acquisition of the LuCi instrument (Grant 206021-189608) and the support of the research projects Cutaway (Grant 200021E-183684) and Investigation of Salt Hydrates Segregation with XCT (Grant 200021-201088).

**References**


