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Characterization of hydration levels of salt hydrate using X-ray computed tomography

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Characterization of hydration levels of salt hydrate using X-ray computed tomography

Benjamin Fenk[1], Anastasia Stamatiou[1], Dario Guarda[2], Jorge Martinez-Garcia[1], Philipp Schütz[1], Damian Gwerder[1], Poppy O'Neill[1], Rebecca Ravotti[1], Simone Mancin[2], Ludger Fischer[1] and Jörg Worlitschek[1]

[1] Competence Centre for Thermal Energy Storage, Lucerne University of Applied Sciences and Arts, Technikumstrasse 21, Horw, 6048, Switzerland
[2] Department of Management and Engineering, University of Padova, Str.lla S.Nicola 3, Vicenza, 36100, Italy

benjamin.fenk@hslu.ch

Abstract. Salt hydrates are promising phase change materials (PCMs) for energy storage due to their high enthalpy of fusion and cost-effectiveness. However, they face challenges like segregation. X-ray computed tomography (XCT) is suggested for non-destructive analysis to assess the formation of segregation. But first, the feasibility of using XCT to distinguish between different hydration levels of salt hydrates needs to be investigated. This study compares XCT gray values of anhydrous and salt hydrate samples, particularly sodium acetate (SA) hydrates, to understand the influence of hydration level on XCT images, aiming to assess XCT's suitability for salt hydrate investigation.

1. Introduction

Energy storage is a critical component in the pursuit of sustainable and efficient energy solutions, and the utilization of phase change materials (PCMs) has emerged as a promising avenue for addressing this need [1-3]. Among the various PCM candidates, salt hydrates have garnered increasing attention due to their remarkable enthalpy of fusion and cost-effectiveness. Despite their potential, salt hydrates present challenges, particularly segregation, which is the formation and separation of different hydration levels within the base material. The occurrence of segregation during thermal cycling of the salt hydrate results in altered local properties of the PCM, such as melting point and density [4,5]. The main concern is the change of the melting point, which results in a decreased energy storage capacity of a system at a given temperature.

So far, there are limitations for tracing this phenomenon due to the opaque appearance of the salt hydrate in its solid phase. However, it is possible to observe the segregation in a non-destructive and dynamic manner by using X-ray computed tomography (XCT) [6]. XCT systems allow the investigation of internal structures of an object by visualizing its local densities. Since the density of the salt hydrate changes for different hydration levels, it is possible to identify PCM segregation.
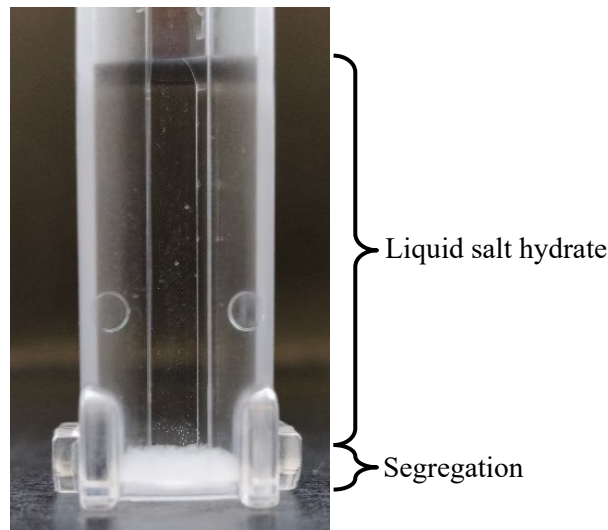
Figure 1. Segregation of salt hydrates.

2. Objectives

The central objective of this work is to employ XCT for developing characterization methods, specifically comparing gray values in XCT measurements between pure reference samples and other salt hydrate samples. Through this comparative analysis, the study seeks to explain how variations in gray values correspond to changes in hydration levels. By delving into these relationships, the suitability of XCT for characterizing salt hydrates for PCM applications can be assessed.

The chosen model system for this investigation is sodium acetate (SA) hydrates. The insights gained from this model system are expected to contribute to the broader understanding of salt hydrate characteristics.

3. Materials and Methods

3.1. Sample materials

Materials with a similar density will be represented with a very similar gray value in the data from the XCT measurements. This means that a salt hydrate with a relatively large density difference between its hydration levels must be chosen. The materials utilized in this study include sodium acetate trihydrate (SAT) and anhydrous sodium acetate (SA). SAT has been studied as a PCM by many researchers and has, in its solid state, a density difference of over 5% to solid SA [7-9]. All the materials were bought from Sigma-Aldrich with a purity ≥99.0%. Due to high porosity of the SA particles obtained from Sigma-Aldrich, a second SA sample was created by placing a small portion of SA in an aluminum oxide crucible, melting it at 310 °C and letting it solidify again. This resulted in larger flakes of anhydrous sodium acetate without any trapped air.

3.2. Sample container

A custom container for the salt hydrates was designed and fabricated in this work. Its most important function is to seal the salt hydrate from its environment and prevent any moisture exchange between the two, otherwise, the desired hydration level cannot be assured. The container is a three-piece design. In the center, there is a round plate with several holes in a circular pattern. A disc with markings on it is attached to the center piece with adhesive and each hole in the center piece is filled with PCM. To seal the container, another disc is glued on top of the stack. PMMA was chosen as the container material due to the density difference to the PCM and its ability to be laser-cut.
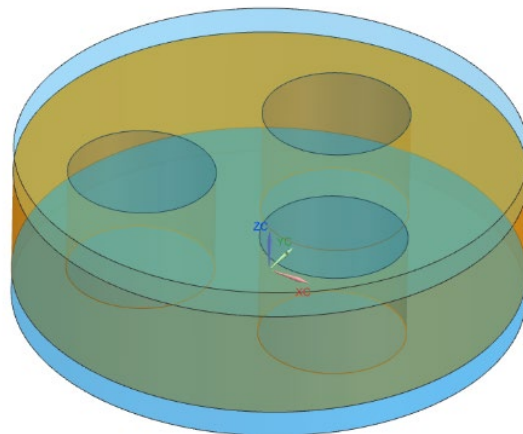
Figure 2. Sample holder with three sample positions.
Lids in blue, center piece in orange.

3.3. X-ray computed tomography (XCT)

XCT was employed for characterizing different hydrate levels of the PCM. Specifically, the commercial micro XCT system d2 from Diondo was utilized. The samples were mounted on an 360° rotation stage. For the reconstruction, software from Diondo, based on Siemens CERA, was used. During the reconstruction, the radiographies are converted into an image stack with inverted pixel intensities, meaning that high-density regions will be represented as lighter pixels and low-density regions as darker pixels [10].
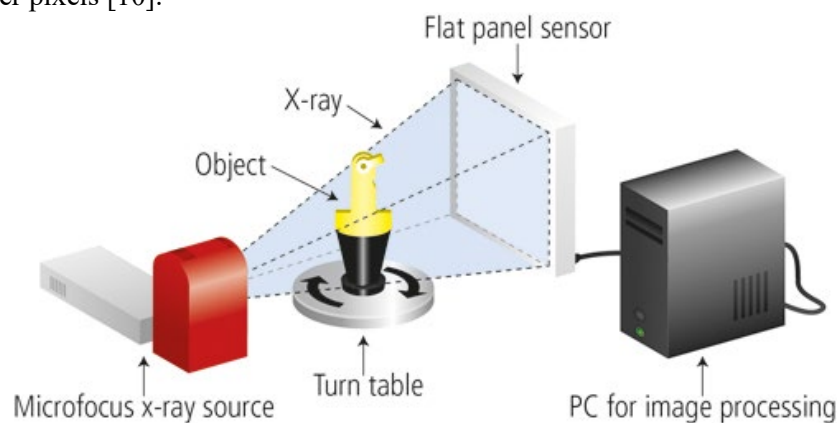
Figure 3. Components of a XCT system [11]

3.4. Data analysis

The reconstructed images were further processed in Fiji (Fiji Is Just ImageJ) by importing individual slices of the sample and analyzing the gray value of each PCM. For this, the sections containing PCM were extracted and a segmentation between the PCM and the surrounding air was performed using Otsu's algorithm [12]. Then, the mean gray value of each PCM was exported and compared to one another.

4. Results

The results from the analysis are shown in Table 1. Even tough SA has a higher density as SAT, the mean gray value of SA grains is lower than the one of SAT. Also, the relatively high standard deviation of the SA grain's mean gray value stands out. Comparing the gray value of SA flakes to SAT shows another result. Both mean gray values and standard deviations are almost equal.

**Table 1.** Densities and gray values of SA and SA.

Salt hydrate	Density [g/cm^3]	Mean gray value [-]	Standard deviation [-]
Anhydrous sodium acetate (grains)	1.53	28826	1333
Anhydrous sodium acetate (flakes)	1.53	31166	767
Sodium acetate trihydrate	1.45	31159	572

In Figure 4, a single reconstructed slice of the whole sample container is shown. For better visibility of the gray value differences, the contrast has been increased in the right image. The gray value variations within the SA grains (1) are clearly visible while the other two samples have a more homogenous appearance.
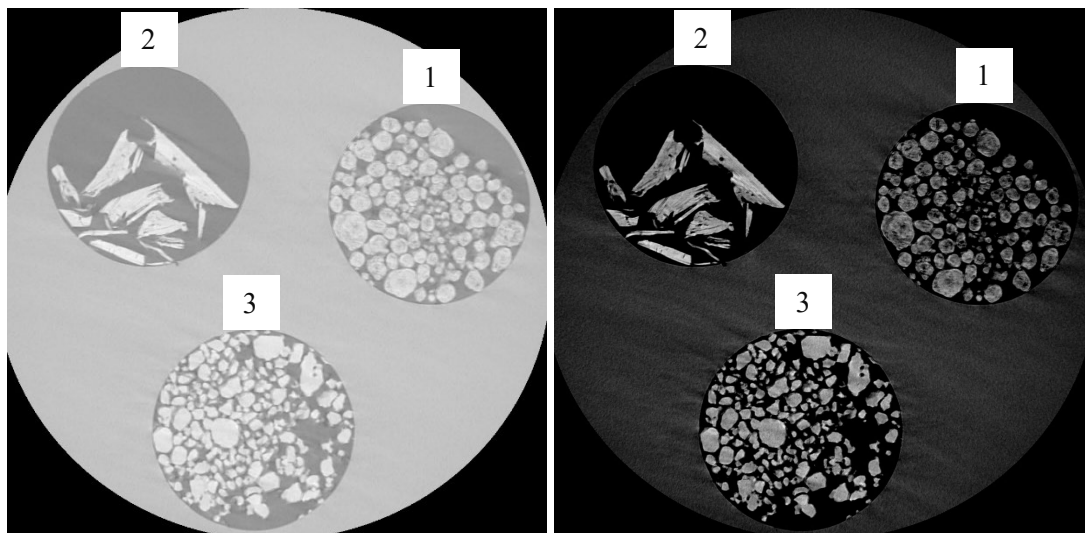
Figure 4. Slice of the XCT measurement. Increased contrast settings on the right. 1: Anhydrous sodium acetate (grains), 2: Anhydrous sodium acetate (flakes), 3: Sodium acetate trihydrate.

Additionally, to the XCT-images, images of the raw materials were taken with a microscope (Figure 5). While the SA grains on the left appear opaque and consist of tiny SA-crystals, similar to a snowball, the SAT on the right is clear and consists of larger homogenous grains.
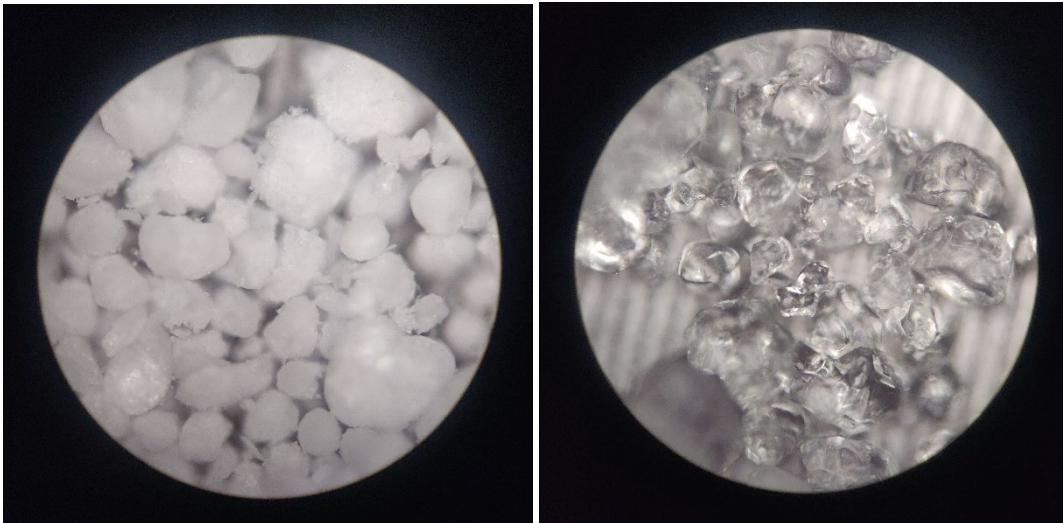
Figure 5. Microscope images of the raw materials from Sigma-Aldrich.
SA grains on the left, SAT on the right.

5. Discussion

The observed differences in mean gray values between SA-grains and SAT, despite the former having a higher density, indicate that the structure of the observed grains plays a crucial role. In the case of the SA-grains, air included in the grains influences the gray value significantly. This is further shown in the standard deviation of the SA-grains and confirmed by inspecting them under an optical microscope.

While melting these grains into larger flakes had a positive effect on the standard deviation, it was still not possible to clearly differentiate the SA and SAT using XCT. A possible reason for this is the used method for determining the gray value. Calculating the mean gray value of every pixel representing the salt hydrate, instead of only a 2D-slice, could lead to better results.

Furthermore, the parameters of the XCT-measurement should be optimized. This might give better contrast and a larger separation between the hydration levels.

6. Conclusion

Even though the results of this work are not as promising as hoped, they are a valuable starting point for characterizing hydration levels of salt hydrates and segregation of those. With improved measurement parameters and post-processing techniques, this approach could help the development of stable, cost-effective and energy dense PCMs.

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