

# **EUROTHERM SEMINAR #116**

## **Innovative solutions for thermal energy storage deployment**

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**University of Lleida**  
**Lleida, Spain**



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© Eurotherm Seminar #116 Innovative solutions for thermal energy storage deployment  
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## Preface

It was a pleasure for Prof. Luisa F. Cabeza and the GREiA research group full team at the University of Lleida (Spain) to organize the ***Eurotherm Seminar #116 “Innovative solutions for thermal energy storage deployment”*** from May 24th to 26th, 2023, in Lleida (Spain).

This seminar did bring together researchers and practitioners from academia and industry, who are working in the rapidly expanding field of thermal energy storage (TES).

The most recent trends in such areas as novel storage materials, advanced storage concepts and configurations, TES for renewable energy systems, TES in buildings and industry, use of advanced techniques such as artificial intelligence in TES, and social, environmental, and educational aspects.

Theoretical, numerical, and experimental approaches will be presented for the entire range of applications, from material characterization to complete storage systems.

We want to thank all participants to the conference.





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## Organic salt hydrates as innovative materials for thermochemical energy storage

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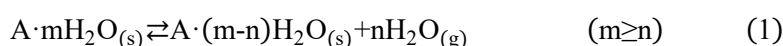
### Abstract

In order to overcome the issues caused by deliquescence in inorganic salt hydrates for thermochemical heat storage applications, it is here proposed and investigated the use of organics salts hydrates, specifically calcium ceftriaxone (CaCf) and calcium lactate (CaL). As main difference among the two salts CaCf presents a bulky organic ligand with different heteroatoms (C<sub>18</sub>H<sub>16</sub>N<sub>8</sub>O<sub>7</sub>S<sub>3</sub><sup>-</sup>) while CaL has a smallest ligand and oxygen as unique heteroatom (C<sub>6</sub>H<sub>10</sub>O<sub>6</sub><sup>-</sup>). Both are characterized by low water solubility, thus more resistance to deliquescence, a tendency to coordinate a high number of water molecules, and stability under operating conditions. The materials' heat storage capacities (595 and 1021 kJ/kg for CaCf and CaL, respectively) are comparable with that of other inorganic salt hydrates, without appreciable efficiency losses in terms of energy as cycles are performed due to unconverted material. These results support the idea of considering hydrated organic salts for effective TCS applications.

**Keywords:** organic salt hydrates, calcium ceftriaxone, calcium lactate, thermochemical heat storage

### 1. Introduction

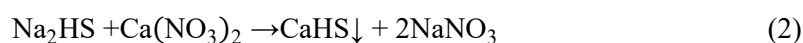
In order to shift towards carbon-free renewable energy sources, which are inherently intermittent, the use of an energy storage technology is essential. In this regard, thermochemical heat storage (TCS) with salt hydrates offers a viable solution for storing heat and re-use it on demand through a reversible reaction [1]:



The solid hydrated salt is converted (endothermic charging step), to the products that consist of a totally or partially dehydrated solid salt and water vapor. The reverse hydration reaction of the salt with water vapor, being exothermic, releases the stored heat when required. These systems, however, suffer of several drawbacks due to their tendency to undergo deliquescence phenomena. Indeed, the hydration reaction often leads to a saturated salt solution rather than a salt hydrate. Hence a deliquescence phenomenon occurs. This can imply chemical instability, mass transfer hindering, and high-pressure drops that would lead eventually to the system failure, but also corrosion issues due to the dripping of the salt solution to other metal components of the systems [2,3]. For moving TCS systems toward a higher technology readiness level, more efforts should be focused on the materials innovation. In this regard, this work aims to explore innovative materials based on highly insoluble organic hydrated salts in order to reduce and/or avoid deliquescence phenomena under operating conditions, able to coordinate a high number of water molecules, and stable under operation conditions [4]. Specifically, calcium ceftriaxone (CaCf) and calcium lactate (CaL) were selected as model compounds for investigation.

### 2. Materials and methods

CaCf was prepared by precipitation using disodium ceftriaxone hemiheptahydrate as the precursor:



While CaCL was purchased from Sigma Aldrich, (purity >98%,  $[\text{CH}_3\text{CH}(\text{OH})\text{COO}]_2\text{Ca} \cdot 5\text{H}_2\text{O}$ ) in form of fine powder. The initial water content and thermal stability were evaluated by thermogravimetric analysis coupled with a mass spectrometer. The heat storage capacity was also estimated from Differential Scanning Calorimetric (DSC) analysis. A full hydration/dehydration cycle in a controlled (temperature, relative humidity) and measurable (mass change) environment has been performed through a thermogravimetric dynamic vapor sorption system (DVS Vacuum Surface Measurement Systems) to verify the salts dehydration/hydration reversibility. The structural integrity of the molecules was verified by X-ray diffraction and Fourier-Transform Infrared Spectroscopy. Morphological observation of the salts and in their dehydrated and re-hydrated forms was carried out by an environmental scanning electron microscope (ESEM, FEI Quanta 450) operating with an accelerating voltage of 2 kV under low vacuum conditions.

### 3. Results and discussion

As deduced from TG-MS analysis (not reported here from brevity), the initial water content is 7 and 5  $\text{H}_2\text{O}$  molecules for CaCf and CaL, respectively. Both investigated materials begin to release water from 35 °C and are thermally stable up 150 °C, when the dehydration is concluded. Despite the smaller water content, the estimated heat storage capacity for CaL (1021 kJ/kg) is almost double than that of CaCf (595 kJ/kg). The materials undergo a significant structural modification during the dehydration/hydration cycle. The fresh salts, with their initial water content, have a crystalline structure, while after dehydration they became amorphous (Figure 1).

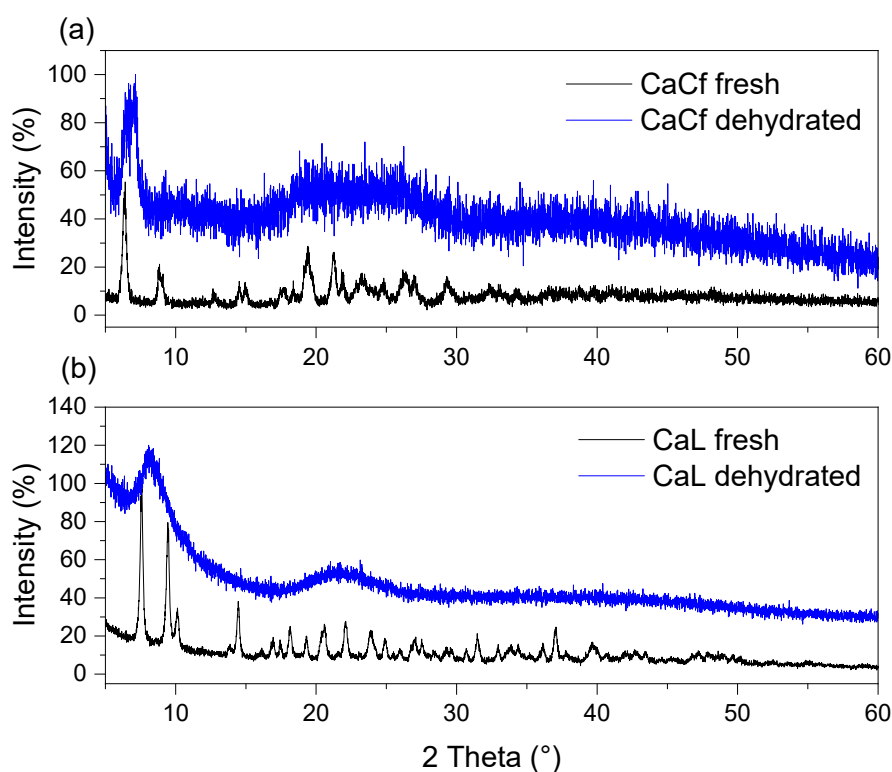


Figure 1. XRD analysis of fresh and dehydrated (a) CaCf and (b) CaL.

This structural modification in case of CaL is also accompanied by a substantial morphological modification, as inferred by SEM micrographs. From the DVS dehydration/hydration cycle (Figure 2) is evident that for both salts the re-hydration reaction is fully reversible, despite a broad hysteresis between dehydration and hydration phases thus indicating a kinetic barrier. Indeed, generally, the presence of hysteresis between the sorption and desorption isotherms indicates that the water diffusion through the material structure is slower when the lattice re-arranges upon hydration [5].

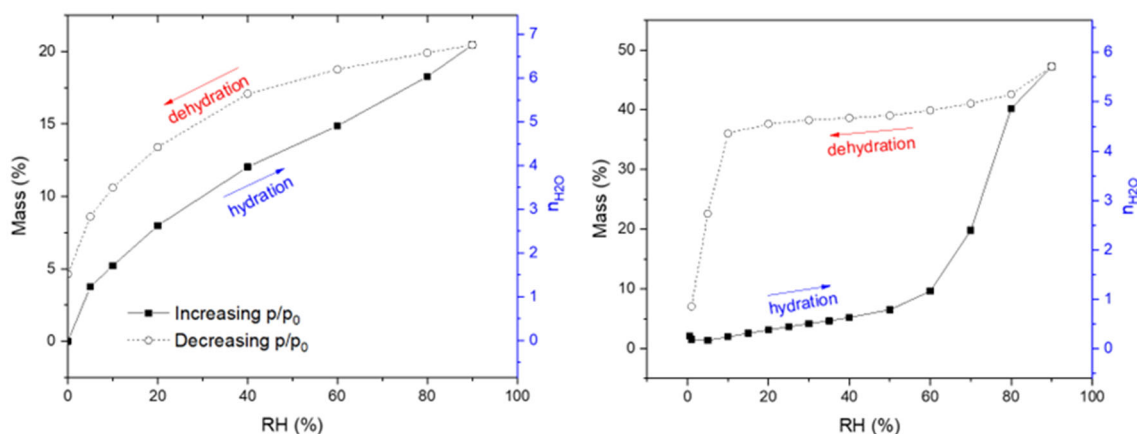


Figure 2. DVS analysis of (a) CaCf and (b) CaL.

This is applicable to both CaCf and CaL, which, as already observed, transform from a completely amorphous structure to a more ordered one when they convert from the dehydrated to the hydrated form. Due to this hysteresis, it can be deduced that at equal temperatures, the difference in the relative humidity conditions under which the heat storage occurs and those at which the release phase takes place is extreme, thus avoiding the dispersion of the accumulated heat in the case of required intermediate operating conditions.

What is more, both investigated salts do not exhibit deliquescence even at 90% of relative humidity (RH) and 30 °C. FT-IR analyses carried out on the fresh salts as well as on their dehydrated and rehydrated forms do not show any decomposition.

#### 4. Conclusions

The investigated organic salts hydrate, CaCf and CaL, in contrast to their inorganic counterparts, are stable upon exposure at an RH of 90% at 30 °C, assuring no drawbacks related to deliquescence and, at the same time, fully rehydrating at low temperature. No decomposition is observable under the operating conditions. The materials' heat storage capacities are comparable with that of other inorganic salt hydrates, without appreciable efficiency losses in terms of energy as cycles are performed due to unconverted material. Such encouraging results support the idea of considering hydrated organic salts for effective TCS applications, breaking new ground for this field of research. Further studies are ongoing for a better understanding of the materials' kinetic behavior and their stability upon several hydration/dehydration cycles.

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