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Thermophysical characterization of sorption TCM

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Abstract

Thermochemical materials (TCM) are proposed for thermal energy storage as one of the future options to achieve lower energy consumption in buildings and other industrial applications, as well as to store energy from solar energy. In this study, the thermophysical properties of two TCM, CaCl₂ and zeolite, are determined with TGA and DSC and samples are cycled 4 times with TGA. Results show that the material with the highest energy density is the salt, CaCl₂. Moreover, both materials under study present noble cyclability.

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1. Introduction

Nowadays, the total energy consumption of the world is up to 40% in buildings sector, being responsible of 22% CO₂ emissions, according to the International Energy Agency (IEA) [1].

Thermal energy storage is proposed as one of the alternatives to address this energetic problem by reducing the gap between energy supply and energy demand [2].

Thermochemical materials (TCM) are materials which can store energy by a reversible endothermic/exothermic process, and products are easily separated [3,4]. As a reversible reaction, when products are placed in contact again and under the suitable reaction conditions, the stored energy is then released. In addition, the storage is performed at ambient temperature and, therefore, no thermal insulation is required.

The most common materials used as TCM are salt hydrates with high theoretical energy density but also significant corrosion problems when they are brought in contact to metals [3]. On the other hand, zeolites have been

widely studied as sorption/desorption materials to be used as TCM [5,6]. The thermophysical characterization using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) of CaCl_2 and zeolite are presented in this study.

The main objective of this study is to compare the thermophysical properties of both TCM (zeolite and CaCl_2) and to determine the material that is able to store higher energy amounts, taking into account the temperature process and calculating the theoretical energy density.

2. Materials and methodology

The first material analyzed is one of the most studied TCM: CaCl_2 . The most stable structures of this material have 2, 4 or 6 coordination water molecules (showing orthorhombic, monoclinic or trigonal structure, respectively). CaCl_2 density is $1830 \text{ kg}\cdot\text{m}^{-3}$ and the melting temperature of the tetrahydrate is $45.3 \text{ }^\circ\text{C}$ [7].

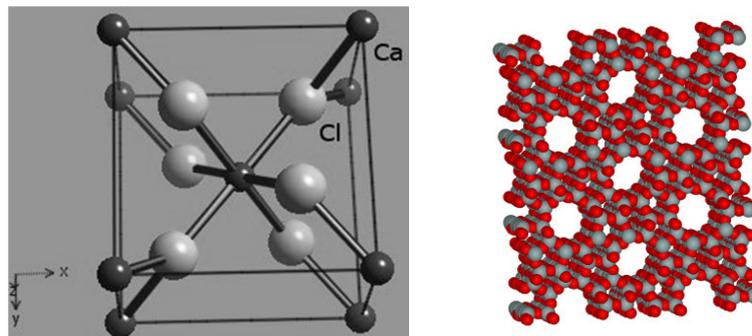


Figure 1. CaCl_2 anhydride (left) and zeolite anhydride (right) crystalline structure

The other material analyzed was zeolite 5A (Sigma Aldrich) which is a sorption material used as TCM. This material does not show corrosion problems when it is put in contact with metals due to its chemical nature and inertness, and its sorption/desorption process is described as reliable [8]. The zeolite density is $900 \text{ kg}\cdot\text{m}^{-3}$.

3. Methodology

Thermophysical characterization was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

TGA is a calorimetric technique widely used to evaluate the degradation of materials and processes involving mass changes on the samples when the materials are exposed to increasing temperatures. TGA was performed using a TGA/SDTA 851e device from Mettler Toledo under $20 \text{ ml}\cdot\text{min}^{-1}$ N_2 atmosphere. The used crucible was a $100 \text{ }\mu\text{L}$ aluminum crucible and the material fills the crucible volume completely.

TCM were cycled 4 times with TGA and the open crucibles containing the samples were left on the TGA tray during 3 days between measurements in order to guarantee the sample rehydration, the mass stabilization, and the experiment reproducibility. A dynamic mode was applied by using a $10 \text{ K}\cdot\text{min}^{-1}$ heating rate between $40 \text{ }^\circ\text{C}$ and $240 \text{ }^\circ\text{C}$ for CaCl_2 and between $50 \text{ }^\circ\text{C}$ and $400 \text{ }^\circ\text{C}$ for zeolite because this material needs this temperature range to finish its desorption thermal process. Furthermore, analyses were performed in triplicate in order to confirm the reproducibility.

On the other hand, DSC analysis was performed in order to elucidate the exact temperature from the processes that are taking place (phase change, recrystallizations, reactions, etc.) and the energy involved in such processes. Furthermore, it can easily discern whether a process is endothermic or exothermic. DSC measurements were performed using a Mettler DSC 822e device under $20 \text{ ml}\cdot\text{min}^{-1}$ N_2 atmosphere. The applied heating rate for TCM characterization was $10 \text{ K}\cdot\text{min}^{-1}$ between $40\text{-}240 \text{ }^\circ\text{C}$ for CaCl_2 and between $50\text{-}400 \text{ }^\circ\text{C}$ for zeolite.

In addition, the theoretical energy density was calculated following the equation 1, where ρ_{en} is the theoretical energy density, ρ is the density of each TCM [4] and ΔH is the energy involved in the chemical energy release process (chemical reaction or sorption process).

$$\rho_{en} = \rho \cdot \Delta H \quad (1)$$

4. Results and discussion

Figure 2 shows the TGA profile (percentage of mass loss vs. - Temperature/time) obtained for CaCl_2 hydrated when it is applied $10 \text{ K}\cdot\text{min}^{-1}$ heating rate. It is shown that at the beginning it is not registered the first part of the water released but at the end, the three samples achieved the same mass loss. Moreover, TGA curves of CaCl_2 show two processes: the first dehydration is achieved around $100 \text{ }^\circ\text{C}$ and the second process takes place around $150 \text{ }^\circ\text{C}$. Full hydration has occurred around $240 \text{ }^\circ\text{C}$.

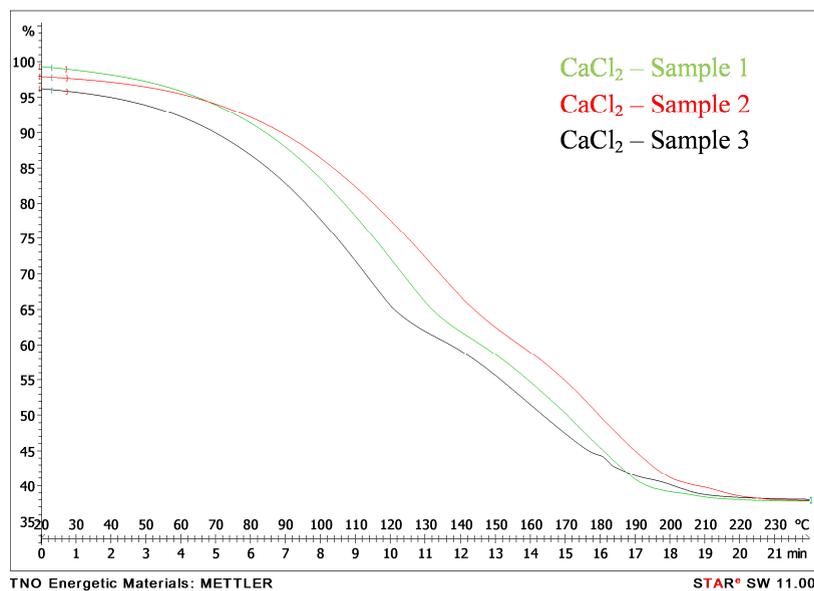


Figure 2. TGA curves of three CaCl_2 samples cycled once with TGA

Table 1 summarizes these TGA results. Mass loss (%) standard deviation is lower than 0.6% indicating the experimental analyses achieved the reproducibility between experiments. Furthermore, the moles of water lost were calculated taking into account the mass loss and the molecular weight of the TCM.

In addition, Figure 3 shows the TGA profile (percentage of mass loss vs. Temperature/time) obtained for zeolite spheres when the same heating rate is applied. It is shown that the three samples in this figure have the same profile. Note that this process is finished around $400 \text{ }^\circ\text{C}$ while CaCl_2 process is finished at $240 \text{ }^\circ\text{C}$.

Table 1. Results obtained with TGA measurements: mass loss and moles of water lost of TCM under study

	Mass loss (%)	Moles of water lost (moles)		Mass loss (%)	Moles of water lost (moles)
CaCl ₂ (1 st cycle) (1)	61.98	10.05	Zeolite spheres (1 st cycle) (1)	13.40	3.43
CaCl ₂ (1 st cycle) (2)	61.34	9.78	Zeolite spheres (1 st cycle) (2)	13.40	3.41
CaCl ₂ (1 st cycle) (3)	60.51	9.45	Zeolite spheres (1 st cycle) (3)	13.40	3.43
CaCl ₂ (2 nd cycle) (1)	60.99	9.64	Zeolite spheres (2 nd cycle) (1)	13.00	3.43
CaCl ₂ (2 nd cycle) (2)	60.76	9.55	Zeolite spheres (2 nd cycle) (2)	13.00	3.43
CaCl ₂ (2 nd cycle) (3)	59.87	9.20	Zeolite spheres (2 nd cycle) (3)	13.00	3.43
CaCl ₂ (3 rd cycle) (1)	60.94	9.62	Zeolite spheres (3 rd cycle) (1)	13.00	3.36
CaCl ₂ (3 rd cycle) (2)	61.23	9.74	Zeolite spheres (3 rd cycle) (2)	13.00	3.36
CaCl ₂ (3 rd cycle) (3)	60.53	9.46	Zeolite spheres (3 rd cycle) (3)	13.00	3.31
CaCl ₂ (4 th cycle) (1)	61.56	9.88	Zeolite spheres (4 th cycle) (1)	13.00	3.30
CaCl ₂ (4 th cycle) (2)	61.15	9.71	Zeolite spheres (4 th cycle) (2)	13.00	3.28
CaCl ₂ (4 th cycle) (3)	61.88	10.01	Zeolite spheres (4 th cycle) (3)	12.00	3.23
Average	61.06	9.67	Average	13.02	3.37
St. Deviation	0.60	0.24	St. Deviation	0.37	0.07

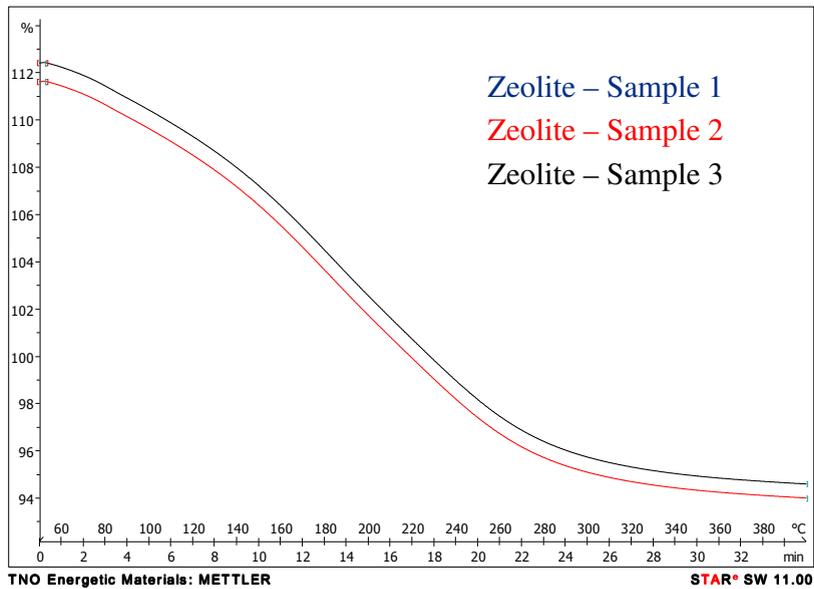


Figure 3. TGA curves of three zeolite spheres samples cycled once with TGA

On the other hand, DSC results are shown in Figure 4 for CaCl_2 . In this figure one can see that CaCl_2 shows two energetic processes: the first one is related to the phase change of CaCl_2 tetrahydrate which has a melting point around 50 °C because there are no mass changes related with an energetic process. The second one is due to the moles of crystallization water loss during the sorption process.

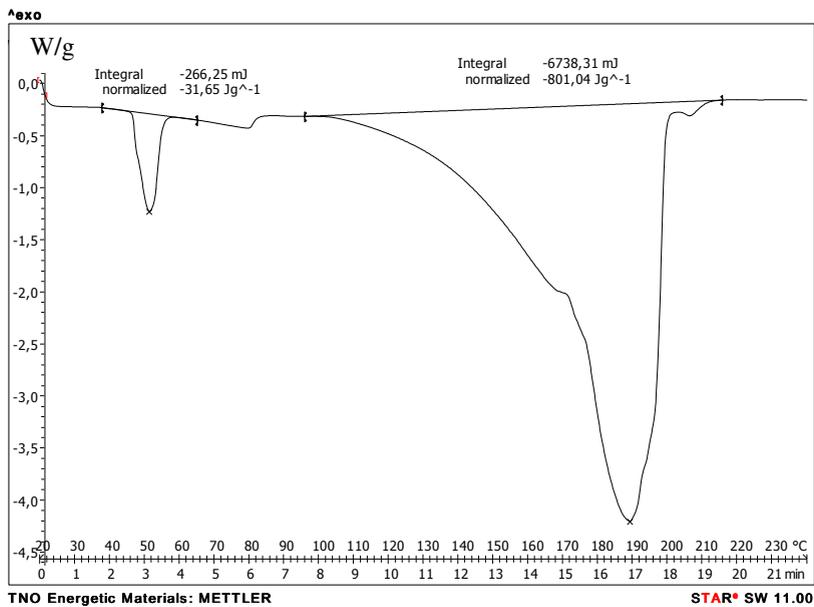


Figure 4. DSC curve for CaCl_2 : heat flow vs. Temperature/time

Moreover, the DSC profile for zeolite spheres is given in Figure 5 and the zeolite spheres DSC results show only one energetic step which concerns the desorption process. It clearly shows a much slower process that is not even finished at 400 °C (heat flow is not stable).

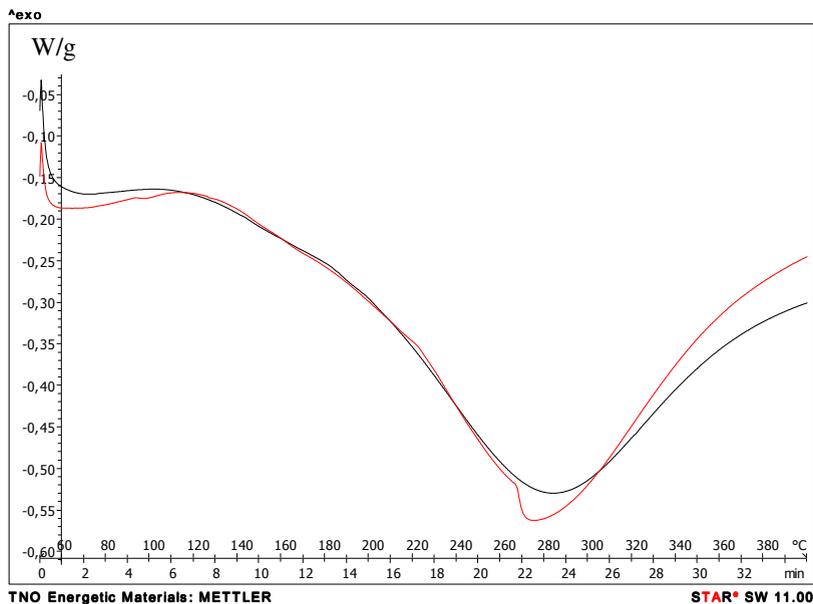


Figure 5. DSC curve for zeolite spheres: heat flow vs. Temperature/time

Finally, DSC results are summarized in Table 2 where the integration of each peak, the energy involved in each process, is listed as well as the theoretical energy density calculated following Eq. 1. DSC results show that the TCM with the highest energy density is the salt in comparison to the zeolite spheres.

Table 2. DSC results and calculated energy density of TCM under study

Material	Peak 1		Peak 2		Energy density (GJ/m ³)
	Energy (J/g)	Temperature (°C)	Energy (J/g)	Temperature (°C)	
CaCl ₂	32	50.1	801	190.0	1.47
Zeolite	No peak	No peak	141	274.0	0.18

The hydrated CaCl₂ stable structure allows 6 water molecules in the crystal lattice, but the melting point shown by DSC results is around 50 °C which is closer to the CaCl₂·4H₂O melting point. Taking into consideration the TGA results it is observed that the first mass loss step is due to the combined evaporation of loose and crystal water molecules (6 moles) and the second step is due to the dehydration reaction (4 moles). In zeolite, this distinction cannot be made as it is a more continuous process.

5. Conclusions

CaCl₂ loses more water during the dehydration process (chemical reaction) than zeolite (desorption) because CaCl₂ has deliquescent behaviour and it is able to adsorb much more H₂O per unit mass. The reproducibility of charging/discharging processes is achieved because the sample cyclability of both materials is completed (standard deviation of mass loss (%) between sample analyses is lower than 0.6% for CaCl₂ being the highest one).

The temperatures at the end of desorption processes are quite different (DSC peaks were found at 190 °C for CaCl₂ and 274 °C for zeolite) and this is a key point to take under consideration during TCM selection, because the final temperature of dehydration governs total energy density when the respective materials are used; a lower dehydration temperature means that a greater part of the available energy of the material is used at a certain collector temperature. Moreover, CaCl₂ theoretical energy density is considerably higher than zeolite: 1.47 GJ/m³ and 0.18 GJ/m³, respectively.

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