Thermophysical characterization and thermal cycling stability of two TCM: $CaCl_2$ and zeolite

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Abstract

At this moment, the global energy consumption in buildings is around 40% of the total energy consumption in developed countries. Thermal energy storage (TES) is presented as one way to address this energy-related problem proposing an alternative to reduce the gap between energy supply and energy demand. One way to store energy is using thermochemical materials (TCM). These types of materials allow accumulating energy through a chemical process at low temperature, almost without heat losses. In addition, it is a stable way to perform the heat storage and TCM can be implemented for seasonal storage or/and long term storage. This study compares the cyclability, from the thermophysical point of view, $CaCl_2$ which follows a chemical reaction and zeolite which follows a sorption process to be used as TCM for seasonal/long term storage. The main results show that the chemical reaction TCM is more energy-efficient than the sorption TCM. The $CaCl_2$ calculated energy density is 1.47 GJ/m^3, being the best option to be considered to be used as TCM, even though the dehydration process of the zeolite is simpler and it occurs at higher temperatures its calculated energy density is only 0.2 GJ/m^3.

1. Introduction

In the current scenario, the importance of reducing energy consumption in the building sector is a key point as it involves more than 40% of total energy consumption implying up to 22% of CO_2 emissions in Europe [1].

Thermal energy storage (TES) is presented as one way to address this energy problem proposing an alternative to reduce the gap between energy supply and energy demand [2,3]. Thermal energy storage has been investigated since 60's by several researchers: e.g. Gupta and Garg [4] developed a model to predict the thermal performance of domestic solar water heaters; Buchberg [5] stated an annual simulation of system performance including the house, a flat plate solar collector, and a water heat storage unit incorparting storage system. Moreover, Abhat in 1983 [6] wrote the first review on low temperature thermal energy storage materials.

There are three methods to store thermal energy. The first one is using the sensible heat (SH-TES) when one thermal gradient is applied which was the first method to store energy investigated and e.g. Bauer reviewed in 2013 the material aspects of Solar Salt for sensible heat storage [7] and Rezaie at al. [8] performed an energy analysis of systems to store energy with grid configuration concluding that there is no restriction on the TES size for series configurations. The second method to store energy is using latent heat from phase change of several materials (LH-TES). The materials used to store energy using this method are known as phase change materials (PCM) [9] and have been investigated in several applications: solar cooling [10], solar power plants [11], buildings [12], cold storage [13], etc.

Finally, the last and most efficient way to store energy is by using thermochemical materials (TCM). These types of materials allow accumulating energy through a chemical process at low temperature and almost without heat losses being the one with the highest accounted energy density. In addition, it is a stable way to perform the heat storage and TCM can be implemented for seasonal storage or/and long term storage [14].

TES systems containing TCM are being extensively investigated. Recently, Energy research Centre of the Netherlands - ECN [15] has developed a new system applying an open sorption concept where the volume used was a packed bed containing 17 dm^3 of sorption material. The ECN system is able to generate 150 W of thermal power and

the effective energy storage density achieved is approximately 0.5 GJ/m^3. In addition, Deutsches Zentrum fur Luft (DLR) [16] has developed a solar-heated rotary kiln using cobalt oxide as TCM. This system is able to provide high mass flow rates and high amounts of active material where thirty cycles were performed and results showed that this is a proper system for thermochemical storage.

The main used materials to store energy as TCM are salt hydrates and sorption materials like zeolites. In a previous study [17], working principles and operating conditions were successfully tested in our zeolite-based reactor set-up. Muller et al. studied the water adsorption on zeolite NaA [18] and Bruce et al. studied and estimates of the thermochemical properties of zeolitic water at low temperature [19]. Moreover, Wilkins et al. studied the fat to store solar energy through calcium clorhide [20]. However, these kinds of materials have not been compared before in the issues concerning the thermochemical storage. Thermochemical storage was classified by N'tsoukpoe et al. [21] and it was shown that this method to store energy uses a chemical reaction, a sorption process or a combination of both routes, as shown in Figure 1.

Additionally, Yu et al. [22] compare the volume needed to implement a system containing different materials for thermal energy storage using sensible, latent, sorption, and chemical reaction heat. This classification is shown in Figure 2 and it highlights that a thermochemical storage following a chemical reaction will need 10 times less volume to operate as storage system in comparison with a thermochemical storage using a sorption process. Therefore, we turn our attention to reaction storage technology.

The study presented in this paper, one substance that undergoes a chemical reaction with water and one substance that uses a chemisorption process with water are compared. Thereby, the main objective of this study is to compare and discern the most appropriate material to be used as TCM under the defined analysis conditions, taking into account its cyclability. Thermophysical properties were analysed using thermogravimetrical analysis (TGA) and differential scanning calorimetry (DSC).

2. Materials and Methodology

2.1. Materials

In this study, two of the most studied TCM are compared. The first material analyzed is $CaCl_2$. It is a salt hydrate and the most stable crystalline structures of this substance have 2, 4 or 6 coordination water molecules (showing orthorhombic – $T_m=176°C$, monoclinic – $T_m=43.5 °C$ or trigonal structure – $T_m=29.9 °C$, respectively) [23]. Furthermore, $CaCl_2$ used in this study has 1830 kg·m^{-3} [24]. $CaCl_2$ follows a chemical reaction during its hydration/dehydration process.

On the other hand, zeolites are ceramic sorption materials that do not present corrosion problems when are put in contact with metals and its sorption process is extremely stable. The zeolite used in this study is zeolite 5A commercialized by Sigma Aldrich. Moreover, zeolite follows a sorption/desorption process to hold/release water molecules [25].

During the charge process (which is the process studied in this paper), the hydrated TCM is heated up and the energy stored is absorbed by the TCM being an endothermic reaction/process. Figure 3 presents a schematic description of the basic mechanism that TCM under study follows, being a chemical reaction in the case of $CaCl_2$ and a sorption process for zeolite.

2.2. Methodology

Several researchers have been studied and characterized the substances here selected to be used as TCM which are under study [24,25].

Thermogravimetrical analysis – TGA

TGA is a widely used technique to characterize thermally TCM as it provides information on whether a material is stable or it decomposes when it is cycled, how the reaction products are charged and discharged, if the reaction is completely reversible, if the material has the same number of water moles before each cycle, etc.

The analyses for the thermogravimetrical material characterization were performed using a TGA/SDTA 851e device from Mettler Toledo under 20 ml·min^{-1} N_2 flow. The crucibles used to contain the samples were 100 μl aluminium crucibles. In addition, the

TCM samples fully filled the crucible volume. A dynamic mode was applied by using a 10 K·min⁻¹ heating rate between 40 ºC and 240 ºC for $CaCl_2$ and from 50 ºC to 400 ºC for zeolite, because in a preliminary test, it was observed that the zeolite did not finish the dehydration process under the described conditions. The accuracy of TGA equipment is ± 0.02 mg.

Furthermore, both TCM under study were cycled 4 times each and sample preparation was required before reaching the thermophysical characterization in order to guarantee the TCM rehydration achieving a stable/constant composition, because their sample mass is strongly dependent on ambient humidity. For that reason, the samples were prepared and left for at least three days in experiments tray before being analyzed. Moreover, analyses were performed in triplicate in order to confirm the reproducibility.

On the other hand, the moles of water lost per mole of dried TCM were calculated taking into account the Eq. (1) where n_w is the moles of water lost, m_w is the mass of water lost, $M_{TCM,dry}$ is the molecular weight (zeolite: 398 g·mol⁻¹; $CaCl_2$: 110 g·mol⁻¹), $m_{TCM,dry}$ is the mass of the dried salt and M_w is the molecular weight of water (18 g·mol⁻¹).

$$n_w = \frac{m_w \cdot M_{TCM,dry}}{m_{TCM,dry} \cdot M_w} \qquad \textbf{(1)}$$

Differential Scanning Calorimetry - DSC

Differential Scanning Calorimetry - DSC is one of the most powerful techniques to characterize thermally substances in order to obtain their melting point, melting enthalpy as well as the specific heat capacity. DSC has been widely used to characterize TES materials as e.g. in the study performed by Günter et al. [26] and Barreneche et al. [27].

The DSC characterization of TCM under study was performed applying a 10 K·min⁻¹ dynamic heating rate between 40 ºC and 240 ºC for $CaCl_2$ and between 50 ºC and 400 ºC for zeolite. The study was performed by using 40 μl aluminium crucibles containing 10 mg $CaCl_2$ ·4H₂O mass. The crucibles were pierced by using a robot at the same moment that the experiment started. The experiments were carried out under 20 ml·min⁻¹ N₂ flow by using a DS 822e device from Mettler Toledo. In addition, the

heating rate used was switch to 2 K/min and 5 K/min in order to measure the thermal behaviour changes when the final application uses a different heating/cooling rate.

The measurements were performed under controlled room conditions: 21 ºC and 34% humidity). The accuracy of this equipment is ± 0.5 ºC and ± 3 J·g⁻¹.

3. Results

TGA results of one sample cycled 4 times are shown in Figure 4, where normalized mass loss (%) vs. temperature is presented. The four cycles follow similar profile and the final result is the same: around 38% of anhydrous $CaCl_2$ remains inside the crucible. Therefore, thermal measurements of the $CaCl_2$ are repeatable as the reported results show (see Figure 4, Figure 5, and Table 1), presenting equal mass loss (%).

In addition the same thermal dehydration behaviour was followed by zeolite: all samples followed exactly the same profile and the final result was identical: 87.7% wt zeolite mass remained in the crucible at the end of the fourth experiment.

On the other hand, triplicate analyses were performed in order to assure the reproducibility of the TGA results. In this case, Figure 5 shows the zeolite thermal performance for three different samples during the first cycle. Results obtained for 3 different samples of $CaCl_2$ followed the same TGA curve.

The obtained mass loss results for $CaCl_2$ and zeolite are summarized in Table 1. Note that the standard deviation is lower than 2% showing that $CaCl_2$ is cyclable under the studied conditions (T = 21 ºC, 34% humidity).

DSC results are shown in Figure 6 for both TCM under study. The difference between TCM is important because DSC curves of zeolite are quite flat but an energy-related process is taking place.

However, $CaCl_2$ results show that there are two different peaks which correspond to two energy-related processes. The peak integration corresponds to energy involved in those processes. The first peak is related to the solid-liquid phase change from $CaCl_2·6H_2O$, TGA curves (see Figure 4) show that there is not mass loss at 50 ºC. The expected phase change temperature is 45.3 ºC, however, the obtained one is higher, around 50 ºC. This result is due to the experimental conditions used: the heating rate is not slow enough to achieve the thermal equilibrium in the sample. Moreover, the

second peak regards to dehydration water loss which takes place applying heat to $CaCl_2$.

On the other hand, zeolite has only one peak which corresponds to the zeolite dehydration; besides this process shows a broad peak. Note that this energy-related process is almost finished at 400 ºC.

The energy involved in these processes was calculated following Eq. 2, where ρ_{en} ($GJ \cdot m^{-3}$) is the energy density, ρ is the material density ($kg \cdot m^{-3}$) and ΔH is the energy involved in the process ($kJ \cdot kg^{-1}$):

$$\rho_{en} = \rho \cdot \Delta H \qquad \qquad \textbf{(2)}$$

For both materials, the temperature and the theoretical energy density are listed in Table 2 yielding both endothermic processes (chemical reaction and sorption process). In addition, the main results showed that the investigated salt hydrate has a much higher energy density than the investigated sorption material.

The effect of the heating rate was evaluated performing DSC analyses using three different heating rates (2 $K \cdot min^{-1}$, 5 $K \cdot min^{-1}$ and 10 $K \cdot min^{-1}$) between 40 ºC and 240 ºC for $CaCl_2$ and between 50 to 400 ºC for zeolite. Resultant DSC curves (Cp vs. temperature) are shown in Figure 7 and Figure 8, respectively.

As it is observed for the $CaCl_2$, the peak reaction temperature applying 10 $K \cdot min^{-1}$ heating rate is 186 ºC. However, this reaction temperature for analyses performed using slower heating rate is 165 ºC. Thus, the measured temperature of reaction depends on the heating/cooling rate applied and this fact has to be taken into account during the design step. In addition, the energy density (calculated following Eq. 1) is varied depending on the heating rate used. The calculated energy density is 1.47 $GJ \cdot m^{-3}$ applying 10 $K \cdot min^{-1}$, 1.50 $GJ \cdot m^{-3}$ applying 5 $K \cdot min^{-1}$ and 1.31 $GJ \cdot m^{-3}$ applying 2 $K \cdot min^{-1}$. Thereby, the energy density also decreases when the heating rate is slower.

On the other hand, results obtained for zeolite showed that the highest heating rate the lowest process temperature: 279.3 ºC (10 $K \cdot min^{-1}$), 251.2 ºC (5 $K \cdot min^{-1}$), and 225.6 ºC (2 $K \cdot min^{-1}$). The process of release and uptake of water is a key point during the selection of TCM because final dehydration temperature will determine the total energy

stored by a certain application, then, this fact is a key point to take into consideration during the TCM selection step.

Finally, the peak is sharper when the slower heating rate is used and the calculated energy density decrease when the heating rate is slower (0.18 $GJ \cdot m^{-3}$ when 10 $K \cdot min^{-1}$ is applied, 0.17 $GJ \cdot m^{-3}$ working with 5 $K \cdot min^{-1}$, and 0.15 $GJ \cdot m^{-3}$ when 2 $K \cdot min^{-1}$ heating rate is applied.

In summary, from the thermophysical point of view the chemical reaction TCM is more energy efficient than the sorption TCM as shown by the much higher calculated energy density as was state by N'tsoukpoe et al [21] (see Figure 9). Moreover, the heating rate used will change the thermal performance of the material. Therefore, the realest heating rate must be used to characterize thermally the materials. The closer to real condition, the better characterization.

Thereby, the salt hydrate is the best substance to be considered to be used as TCM (see right upper corner of Figure 9), even though the dehydration process of the zeolite is simpler but it will be completed at higher temperatures.

4. Conclusions

Based on the results presented in the previous section it can be concluded that both materials tested had no change after being performed four thermal cycles.

In addition, three repetitions were carried out of each sample and the results showed that the reproducibility of the charging/discharging process is assured under analysis conditions obtaining a standard deviation of mass loss lower than 0.6%.

On the other hand, the energy involved in the $CaCl_2$ dehydration process is almost 10 times higher than the energy obtained for zeolite being 1.47 $GJ \cdot m^{-3}$ and 0.18 $GJ \cdot m^{-3}$ (one order of magnitude higher), respectively. Thereby, salt hydrates lose more water moles during chemical reaction than sorption materials. Final process temperatures for all these materials are different and it is a key point to take into account for the selection of the energy storage material for a given application.

Moreover, applying different heating rates to perform the DSC analyses, it was observed that the peak reaction temperature for $CaCl_2$ applying 10 $K \cdot min^{-1}$ heating rate is 186 °C. However, the lower the heating rate applied the lower the peak reaction

temperature. Thus, the measured temperature of reaction depends on the heating/cooling rate applied and this fact has to be taken into account during the design step of the storage system. The same trend was obtained for zeolite.

Finally, considering the materials under study, CaCl2 is the best candidate because present better thermophysical properties (ρ_{en}).. However, other parameters as the corrosion behaviour as well as de degradation process must be studied for this substances in order to discern which is the best candidate to be implemented in a storage system.

Acknowledgments

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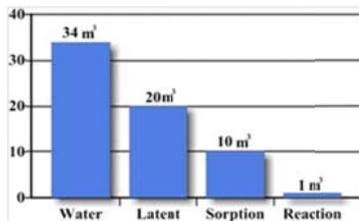Figure 1. Thermochemical storage classification [21]

Figure 2. Volume required for thermal storage of 1850 kWh using different materials for TES [22]
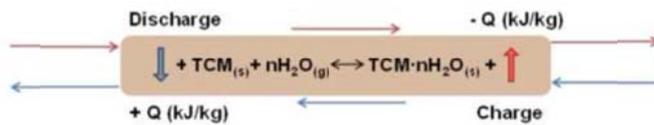

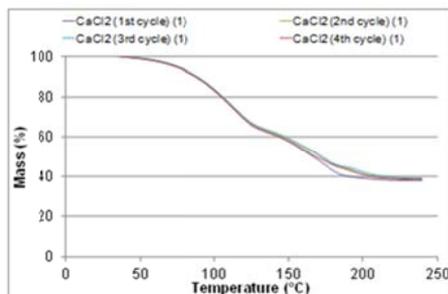Figure 3. Scheme of TCM hydration/dehydration process
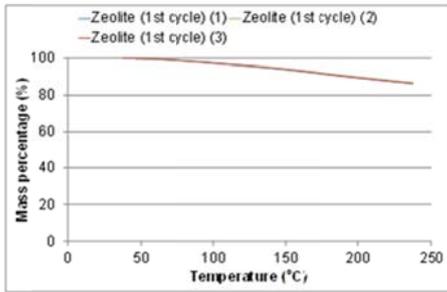

Figure 4. CaCl$_2$ cycled 4 times in TGA device

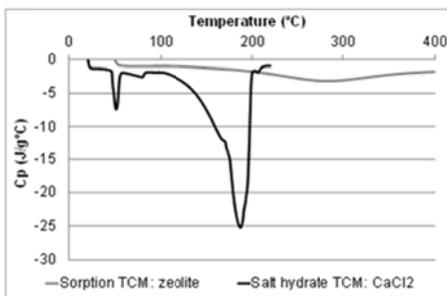Figure 5. TGA curves of three zeolite spheres sample cycled once with TGA

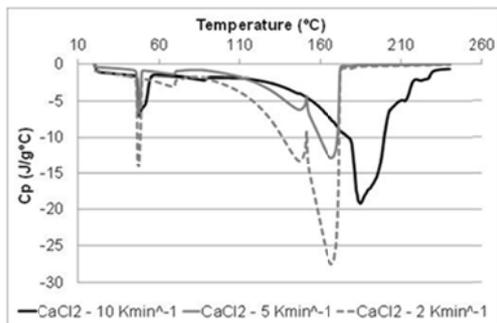Figure 6. DSC curve for $CaCl_2$: Cp vs. time applying 10 K·min^{-1}

Figure 7. $CaCl_2$ DSC curves performed applying three different heating rate (10 K·min^{-1}, 5 K·min^{-1} and 2 K·min^{-1})
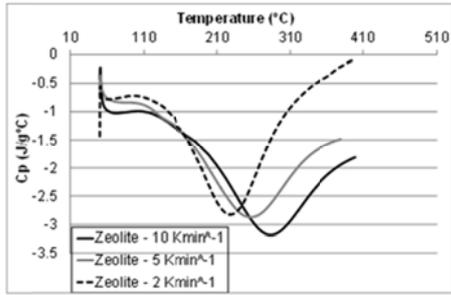
Figure 8. Zeolite DSC curves performed applying three different heating rate (10 K·min^{-1}, 5 K·min^{-1} and 2 K·min^{-1})
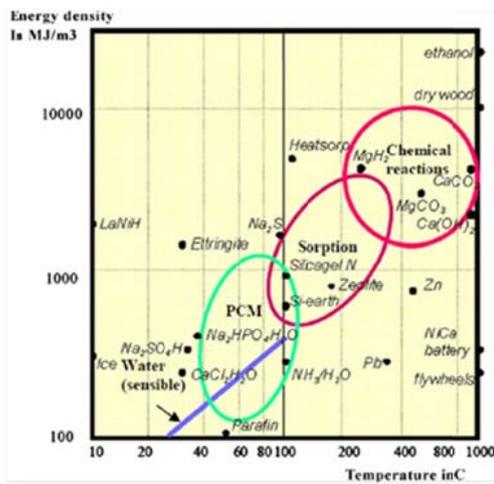

Figure 9. Energy density (MJ·m^{-3}) from several materials used as thermal energy storage. Highligted: Phase change materials (PCM), sorption TCM, and chemical reaction TCM [21]

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

	Mass loss (%)	Moles of water lost (moles)	Final process temperature (ºC)
CaCl2	61.1 ± 0.6	9.7 ± 0.2	200
Zeolite	13.1 ± 0.2	3.4 ± 0.1	400

Table 2. DSC results and calculated energy density obtained for $CaCl_2$ and zeolite

Material	Energy (J·g^{-1})	T (°C)	Energy (J·g^{-1})	T_{peak} (°C)	Energy density (GJ·m^{-3})
$CaCl_2$	- 32	50.1	801	190.0	1.47
Zeolite	---	---	141	274.0	0.18