Toward new low-temperature thermochemical heat storage materials: Investigation of hydration/dehydration behaviors of MgSO4/Hydroxyapatite composite
Minh Hoang Nguyen, Mohamed Zbair, Patrick Dutournié, Antonella Gervasini, Cyril Vaulot, Simona Bennici

To cite this version:

HAL Id: hal-03856103
https://hal.science/hal-03856103
Submitted on 16 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
Toward New Low-Temperature Thermochemical Heat Storage Materials: Investigation of Hydration/Dehydration Behaviors of MgSO₄/Hydroxyapatite Composite

Minh Hoang Nguyen ¹,², Mohamed Zbair ¹,², Patrick Dutournié ¹,², Antonella Gervasini ³, Cyril Vaulot ¹,², and Simona Bennici ¹,²,*

¹ Université de Haute-alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France; minh-hoang.nguyen@uha.fr; mohamed.zbair@uha.fr; patrick.dutournie@uha.fr; cyril.vaulot@uha.fr; simona.bennici@uha.fr
² Université de Strasbourg, France
³ Dipartimento di Chimica, Università degli Studi di Milano, via Camillo Golgi, 19, 20133 Milano, Italy, antonella.gervasini@unimi.it

*Corresponding author: simona.bennici@uha.fr; Tel.: +33 (0)3 89336729

Highlights

- MgSO₄-hydroxyapatite composite materials were synthesised using impregnation method.
- Physical characteristics of different composite materials were characterized.
- Hydration kinetic and water uptake of different samples were investigated.
- Composite salt of 20 wt% has a good stability over 20 hydration/dehydration cycles.

Abstract:

A new two-component (composite) water sorbent MgSO₄/Hydroxyapatite has been developed for sorption-based solar heat storage. The matrix of the composite is a hydroxyapatite (HAP) material with ordered structure, high surface area of 111.3 m²/g and mesopore dimensions centered at 45 nm. The composites, prepared by wet-impregnation of HAP with MgSO₄, have lower specific surface area and similar mesopore dimensions as the matrix. The maximum water sorption capacity of HAP is 0.039 g/g, while the composite (20-MgSO₄/HAP) possesses 3.7 times higher maximum
water sorption capacity due to the presence of the salt in the matrix. The HAP composite containing 20% MgSO₄ achieved the highest heat of hydration 464 J/g. A long-term cycling (dehydration at 150 and hydration at 30 °C at a relative humidity of 60%) confirms a comparatively good stability of the composite.

**Keywords:** Thermochemical storage of solar heat; magnesium sulfate; hydroxyapatite; water sorption; adsorption kinetics.

1. Introduction

Solar energy is considered a viable alternative to conventional energy sources, and its potential applications in residential and industrial surroundings have been extensively studied [1,2]. Though, the imbalance between energy supply and demand makes it difficult to put into practice. Thermal energy storage (TES) is an evolving technology and an effective way to achieve long-term solar energy use [3,4]. Latent heat storage, sensible heat storage, and thermochemical heat storage (TCHS) are three types of system using TES technologies. While latent and sensible heat storage have been extensively studied in recent decades [5,6], there have been few studies on TCHS, which is highly competitive and have been attracting growing interests due to higher energy storage density and negligible heat loss over long storage periods [7,8]. Based on the reversible sorption reaction, heat is stored following the endothermic reaction (charging) and this energy can be retrieved later on from the exothermic reaction (discharging) for many practical applications in particular in the building sector. In these application the most common configuration is based on the sorption phenomena of a sorbate (often water) on a sorbent (generally a solid material).

The solid thermochemical storage material has to be chosen carefully to ensure a good working system. Basically, it must possess certain properties such as high energy density, high affinity for the sorbate (water in most cases), a high mass and heat transfer with a charging temperature as low as possible to fit in residential applications.
In addition, the material needs to be eco-friendly, non-toxic and inexpensive. With these criteria, salt hydrates appear to be a promising storage materials. SrBr₂, MgCl₂, and MgSO₄ hydrates are among the best potential salt hydrates, with MgSO₄ hydrate having the highest theoretical heat storage density of 2.8 GJ/m³ and a low charging temperature (<150 °C), which is suitable for building applications with solar collectors, being the most cost-effective, and, most importantly, having a dehydration temperature that matches well with the thermal solar collectors. Furthermore, to broaden the applications panel, the salt’s relative humidity of deliquescence (RHD) is a crucial metric to consider. The RHD is the relative humidity limit at which the salt will dissolve in the adsorbed water in proportion to temperature, resulting in absorption into the material. Excessive water absorption permits more water to be absorbed, increasing the amount of heat generated by the process. The production of saline solution, on the other hand, might produce corrosion issues. The deliquescence process of MgSO₄, nH₂O, for example, will not occur below 80% relative humidity (RH) at temperatures ranging from 10 to 80 °C since it is thermodynamically stable at this temperature and humidity range. The major drawbacks of this system are the overhydration, the formation of aggregates occurring during rehydration, the kinetic hindrance limiting the mass and heat transfer, and the poor cyclability. Consequently, the system’s full potential could not be reached and, as a result of these constraints, the energy storage capacity was low. One way to take advantage of the MgSO₄'s great potential is to make composites by dispersing the salt in a porous matrix to avoid swelling and aggregates formation, which represent one of the main materials' drawbacks. To overcome these issues, efforts have been focused on the development of high-performance composite materials using porous matrix and salt hydrates.

The composite sorbents are also known as "composite salt in porous matrix" (CSPM), a term used by Yuri Aristov et al. However, if composite sorbents are subjected to a wet environment for an extended period of time and the collected water is
insufficient to be held inside the pores, they are at risk of solution leakage. As a result, developing a porous matrix with an ultrahigh pore volume to load a high content of salts and store a big amount of collected water is extremely important in order to avoid the risk of liquid leakage.

For that reason, several sorbent materials as a matrix for hydrated salts, such as silica gel [19,20], activated alumina [21], zeolite [22,23], MOFs [24], vermiculite [25], and expanded graphite [26,27], has received considerable attention. However, in order to be an appropriate material for TES applications, the matrix must fulfill a number of criteria, including cheap cost, a low regeneration temperature, a high storage density, and good mass and heat transfers that enable long-term storage with high efficiency and an easier recovery of the heat by different means (air vector, solid/liquid, solid/air heat exchangers).

Despite the fact that a variety of innovative composite sorbents for heat storage have been developed [24,28–32], there is still a significant gap between the materials and their practical applications. As supporting matrices, for example, different zeolites, which are aluminosilicate minerals having microporous structures for moisture adsorption, are commonly used. Wang et al. [22] performed the solution impregnation approach to create the MgSO₄@zeolite-13x composite thermochemical sorbent. They indicated that the sorbent contained 8% by weight MgSO₄ performed better at a high RH of 80%, with no salt crystals visible on the surface. However, the low ESD of about 600 J/g and cyclability need to be further improved. MgSO₄@zeolite has been proven to be financially viable for home interseasonal energy storage, however it may not entirely fulfill a household's heating requirement [30]. The adsorption capacity of MgSO₄@zeolite sorbent, on the other hand, would considerably decrease if the hydration temperature is above 50 °C [4], implying that the maximum discharge temperature in the application would not exceed 50 °C. Zhang et al. [33] produced a range of form-stable cylindrical structures using zeolite-13X as a matrix. The sample with the optimal mass ratio (zeolite-13X: CaCl₂: MgSO₄ = 10: 54: 36) exhibited a
gravimetric-ESD of 1410 J/g at a dehydration temperature of 250 °C, and the value reduced by 20% after 20 dehydration-hydration cycles. Although zeolites are common and inexpensive matrices, inherent defects such as a high charging temperature (>200 °C) and a low thermal conductivity.

Aristov et al. [18] studied different composites by embedding hygroscopic salts (e.g., CaCl₂ and LiBr) in mesoporous and microporous silica gels. The salts were distributed rather than bulk, which helps to reduce swelling and agglomeration and to speed up mass and heat transmission. The pore structure and chemical content of the host matrix materials have a significant impact on the heat storage capacity of salt/porous matrix composites [34], therefore choosing the right host porous material is crucial. By impregnating CaCl₂ into SBA-15 pores, Ponomarenko et al. [35] produced a composite material that could adsorb 0.47 g/g. Courbon et al. [36] presented an improved synthesis process for silica gel and CaCl₂ composites. The energy storage density was 300 Wh/kg, and the cycle loading uptake was 0.4 g/g. Whiting et al. [37] investigated the use of zeolite as a porous matrix to increase MgSO₄ heat storage. When impregnated with MgSO₄, the zeolite Na–Y with the largest surface area (780 m²g⁻¹) and total pore volume (0.32 cm³g⁻¹) produced the highest heat of hydration (1090 J/g).

The water sorption process on expanded vermiculite/CaCl₂ composites was researched by Aristov and coworkers [38], who claimed that impregnation of CaCl₂ into expanded vermiculite can increase the water sorption capacity even at low water vapor pressure. However, expanded vermiculite’s surface area is low (9 m²g⁻¹), making it unsuitable for salt loading and mass transfer. Although these porous materials can increase the heat storage capacity of organic salts, they have low pore size and it is hard to modulate their structures and properties.

Shi et al. [24] made-up CaCl₂-based metal-organic frameworks (MOFs) composites with a high storage energy of 1274 J/g with moderate stability via 17 continuous adsorption/desorption cycles. Palomba and coworkers encapsulate LiCl into silica gel to improve the dynamic behavior of a long-term adsorption heat storage with a maximum useful heat of 450 J/g [39]. Calabrese [40] designed a silicone foam/MgSO₄...
composite and shown that this material improved mechanical stability and cycle performance considerably.

It is obvious from the above literature study that there are still improvements to be made in TES materials for heat storage. Certainly, the studies on composites appear to be too diverse. However, various flaws, such as vermiculite's low heat conductivity, zeolite's high desorption temperature, and MOFs' poorer thermo-mechanical characteristics, must be addressed.

The type of porosity (micro/meso) is a significant element in composite design, according to these studies. The salt may plug the pores if they are too tiny, preventing water molecules from diffusing and lowering energy storage capacity. Other materials, such as mesoporous activated carbon or silica-gels, have also been shown to be excellent supports. Salt may be incorporated through their large pores, increasing their energy storage capacity while preventing pore obstruction [41,42]. Aside from the high surface area and the existence of mesoporosity, strong thermal conductivity is a significant consideration in selecting the best support. This parameter is critical for the heat transport phenomena to be optimized.

A porous host matrix with a large pore size structure (mesoporous) is needed to improve the composite material's water uptake. In this study, in addition to the commonly used porous materials (zeolites, silica gel, and so on), a new host matrix is used: hydroxyapatite (HAP), a calcium phosphate apatite with a developed mesoporous structure [43].

HAP - Ca_{10}(PO_4)_6(OH)_2, is a well-known biomaterial of the calcium phosphate family with high biocompatibility. Recently, Hu et al. [44] discovered that a HAP nanowire membrane could be used as a separator, especially for high-temperature Li-ion battery applications. Because of its low cost, superior compatibility with surrounding materials, and higher adsorption ability, nanoscale HAP is regarded as one of the most significant biomaterial adsorbents. HAP can be used also as an adsorbent to absorb heavy metal ions like Pb^{2+}, Cu^{2+}, and Cd^{2+}, which are attributed to the ion Ca^{2+} in
solution through metal cations [45]. HAP is also regarded as one of the most promising adsorption materials for absorbing different organic and inorganic pollutants [46]. Amedlous et al. [47] have been used natural mesoporous hydroxyapatite as support for copper loading as eco-friendly Fenton-like catalyst to effectively remove organic dyes. Furthermore, Wang et al. [48] determined that HAP has a thermal conductivity of 0.15 to 0.20 W/m K, indicating that it has a high heat transfer capacity. As a consequence, employing HAP as a porous matrix for hygroscopic salts is valuable, as it will allow to better understand water sorption and heat transport in composite materials.

For all the above-mentioned reasons and to the best of our knowledge, this is the first work which reports the use of HAP as adsorbent in TCHS application. Incorporation of MgSO₄ in HAP matrix may increase the total charge storage capacity and potentially overcome its limitations. In addition, the HAP shows a low density and mesoporous structure, which is very conducive to its application in TCHS system [49]. The OH-group in HAP can form hydrogen bonds with water which inhibits the leakage of the salt [48]. In this study, composites designed by impregnation of MgSO₄ on a HAP support were prepared, characterized, and their performance assessed. In addition to the heat of hydration released, the experimental kinetic data were examined. The goal was to produce composite materials with high energy density storage with a fast reaction kinetics.

2. Materials and Methods

2.1. Composite materials preparation

2.1.1 Hydroxyapatite (HAP) preparation

Hydroxyapatite synthesis was carried by using pure reagent-grade salt precursors, namely, calcium nitrate tetra hydrate, Ca(NO₃)₂·4H₂O (>99.0% from Merck ACS); and ammonium dihydrogen phosphate, (NH₄)H₂PO₄ (>98.0% from Sigma-Aldrich).
Stoichiometric hydroxyapatite was synthesized by the conventional co-precipitation method by fixing the Ca/P molar ratio of the reagents in solution at 1.67, operating by the procedure reported in Campisi work [50]. For the preparation of ca. 4 g of stoichiometric hydroxyapatite, 250 mL of an aqueous solution containing 0.167 mol of Ca(NO₃)₂·4H₂O was added to 250 mL of a 0.1 mol of (NH₄)H₂PO₄ solution placed in a 4-neck round flask and maintained under stirring at 80°C. During the synthesis, the pH value was maintained at value of 10 by an appropriate addition of a 28-30% NH₄OH solution (from Sigma-Aldrich). The formed precipitate was slowly filtered, washed with hot water, and dried first at 50 °C under vacuum and then at 120 °C for 8 h. The grain size of HAP obtained is in the range of 0.5-1 mm with a density of 3.16 g/cm³.

2.1.2 Composite materials (MgSO₄/HAP) preparation

Incipient Wetness Impregnation (IWI) method [51] was used for embedding MgSO₄ (MgSO₄·7H₂O 99.9 % from Sigma-Aldrich) inside HAP adsorbent. This traditional method consists of only filling the pores of the HAP with an aqueous solution of MgSO₄. To do this, the HAP support was firstly oven-dried at 150 °C to remove any trace of water from the pores. An aqueous solution of MgSO₄ was then applied on the dried support (room temperature and pressure) until it starts to get wet. The impregnated materials were then dried at 150 °C for 12 h. Accordingly, two composites were prepared by IWI and then labelled as x-MgSO₄/HAP (1st column in Table 1) with x is the theoretical content of MgSO₄ in the composites. The first composite contains 5 wt% of MgSO₄ and the second one contain 20 wt% of MgSO₄ which is the maximum amount that can be integrated inside HAP. The experimental salt content was determined by means of X-Ray Fluorescence. The density of HAP is 3.16 g/cm³ and the density of anhydrous MgSO₄ is 2.66 g/cm³. With the law of mixture, the density of the composites would be 3.07 g/cm³ for the 20-MgSO₄/HAP and 3.14 g/cm³ for the 5-MgSO₄/HAP.
2.2. Physicochemical characterizations methods

X-Ray Diffraction (XRD) analyses were performed on the compacted powder of the samples on a diffractometer PANalytical MPD X’Pert Pro, equipped with a Pixcel real-time multiple strip detector, operating with an angular aperture of 3.347° 2θ in 3° to 80° 2θ range, and using CuKα radiation with 0.15418 nm wavelength. Diffractograms were recorded at 22 °C with a step size of 0.013° 2θ and a scan time of 220 s per step.

A wavelength dispersion X-Ray Fluorescence (WDXRF) spectrometer (from PANalytical, Zetium) was used to perform the XRF measurements on pellets made of 0.2 g of the sample.

High-resolution micrographics were acquired by a Scanning Electron Microscope (SEM) from JEOL, JSM-7900F model. The semi-quantitative chemical analysis and atomic composition mapping of the sample was performed by means of Energy Dispersive X-ray (EDX).

\[
\text{N}_2 \text{ adsorption/desorption isotherms of support and composites at } -196 \, ^\circ\text{C were acquired in a ASAP 2420 device from Micrometrics (Micromeritics, Norcross, GA, USA). The samples were previously degassed at 150 } ^\circ\text{C for 12 h and then, again at 150 } ^\circ\text{C for 2 h directly in the calorimetric cell before analysis. The specific surface area was calculated applying the Brunauer, Emmett and Teller (BET) equation } (S_{\text{BET}}) (0.01<p/p^o<0.40). \text{ The mesoporous volumes } (V_m), \text{ external surface (ext) and microporous surface } (S_m) \text{ were determined by applying the t-plot method (thickness range: 0.35-0.50). Finally, the pore size distribution (PSD) was determined using Barrett, Joyner and Halenda (BJH) method applied on the desorption branch of the isotherms.}
\]

2.3. Hydration/dehydration experiments
A Sensys TG-DSC (Thermogravimetry coupled to differential scanning calorimetry) apparatus, equipped with a Wetsys flow humidity generator both from Setaram (Figure 1) were used to measure the heat released and the water adsorption amounts (measured by the microbalance) of the HAP and its composites. Prior to the hydration process, the samples (~10 mg) were dehydrated at 150 °C by increasing the temperature from 30 to 150 °C at 5 °C/min under a flow of dry air (30 mL/min) with a subsequent isotherm of 3 h at 150 °C to ensure a complete dehydration. Then, each sample was cooled down to 30 °C and, once having attained a stable thermal (DSC signal) baseline, the relative humidity (RH) of the air flow was increased to 60 % (equivalent to a water vapor partial pressure of 2.55 kPa). The hydration process was set for 8 hours in order to completely rehydrate the material – the complete rehydration was reached when the DSC signal returned to the baseline. Figure 2a depicts the temperature profile used for all the calorimetric experiments. These conditions were selected to be as close to a real-life residential application as possible: 150 °C is the average working temperature that can be reached using a flat-plate solar heat collectors [37,52] and 30 °C is close to the indoor air temperature during the discharging phase [53]. To accurately calculate the dehydration/hydration heat, the dehydration/hydration process for each sample was performed after stabilizing the DSC and TGA signals. Blank experiments with empty crucibles in the same conditions were also performed. The signals (DSC and TGA) of the blank experiment were then subtracted from the sample experiment. The dehydration/hydration heat (J/g_{sample}) were finally obtained by integrating the surface of the subtracted curves (see Figure 2b as an example).
**Figure 1.** A Sensys TG-DSC apparatus equipped with a microbalance and connected to a humidity regulator Wetsys by a thermal transfer line (from Setaram).

**Figure 2a.** Thermal cycle used for the TG-DSC/WETSYS analyses.
Figure 2b. Example of DSC peaks for hydration and dehydration (after subtraction of the
blank analysis performed in the same conditions) for the 20-MgSO₄/HAP sample. The
(yellow area) represents the heat.

3. Results and discussion

3.1. Structural properties of the composite materials

Table 1 summarizes the chemical composition obtained using the WDXRF method as
well as the textural parameters ($S_{\text{BET}}$, $S_{\text{ext}}$, $S_{\text{ms}}$, $V_p$, and $V_{\text{meso}}$, where $S_{\text{ext}}$ is the external
surface and $V_{\text{meso}}$ is the mesoporous volume). With increasing MgSO₄ loading, the $S_{\text{BET}}$
and $V_p$ (total pore volume) values of the HAP and related composites show a
significant decrease. This might be explained by the pore blocking by MgSO₄ and then
a decrease in the pore accessibility by the N₂ molecules. Actually, the initial $V_p$ (0.664
cm³/g) diminished by 25% (0.499 cm³/g) after the impregnation of 4.11% MgSO₄ and it
shrank to only 0.358 cm³/g after HAP was incorporated by 17.27% MgSO₄. HAP
support and prepared composites display type IV isotherm according to Ref. [54]. We
can observe that the deposition of MgSO₄ do not impact the isotherm shape even if by
increasing the quantity of impregnated salt, the adsorbed volumes decrease. (Figure
3a). The adsorption curves appear slightly convex at a very low p/p° (insert in Figure
3a), representing a minor part of microporosity in the different materials (Type I
isotherm). A type IV isotherm is particularly identified by capillary
condensation/evaporation at high relative pressures (from 0.8 – 1.0 p/p°) interpreted
by a hysteresis loop. In the present cases, the adsorption and desorption branches
appear relatively parallel, and the phenomena seems to finish at about p/p° = 0.8. This
behavior is relatively typical of type H1 hysteresis [55]. The type IV isotherm with a
type H1 hysteresis and the p/p° range of the hysteresis highlight the presence of
mesopores (eventually macropores) with a large distribution in the porous structure
of the composite. The pore size distribution (PSD) of the composites and pure HAP
shown in Figure 3b has been obtained by applying the BJH method to the desorption
branches of N₂ adsorption/desorption isotherms [56]. The composites maintain the
same unimodal, but large (between 10 and 200 nm), distribution as the HAP (only the pore volume is diminished) with peaks centered at around 45 nm. This distribution confirms the predominance of the large mesopores and macropores in the composites porous structures. Since the PSD of the composites is maintained, the size of the pore entrance is not affected. This result suggests the filling and complete blocking of several pores by aggregates of salt particles; no narrowing of the pores due to the deposition of salt can be deduced.

![Graph](image)

**Figure 3.** (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of HAP and its composites with MgSO₄.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgSO₄ content (wt%)</th>
<th>(S_{BET}) (m².g⁻¹) (^a)</th>
<th>(S_{ext}) (m².g⁻¹) (^b)</th>
<th>(S_{m}) (m².g⁻¹) (^b)</th>
<th>(V_p) (cm³.g⁻¹) (^c)</th>
<th>(V_{meso}) (cm³.g⁻¹) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAP</td>
<td>-</td>
<td>111.3</td>
<td>99.6</td>
<td>11.7</td>
<td>0.664</td>
<td>0.659</td>
</tr>
<tr>
<td>5-MgSO₄/HAP</td>
<td>4.11</td>
<td>93.9</td>
<td>83.3</td>
<td>10.6</td>
<td>0.499</td>
<td>0.494</td>
</tr>
<tr>
<td>20-MgSO₄/HAP</td>
<td>17.27</td>
<td>63.1</td>
<td>63.1</td>
<td>0</td>
<td>0.358</td>
<td>0.358</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated using the BET equation at \(p/p^0\) between 0.01 and 0.40.

\(^{b}\) Determined using the \(t\)-plot method with thickness range 3.5-5 Å.

\(^{c}\) Determined from the amount of N₂ adsorbed at \(p/p^0=0.99\).
The crystallinity and phase identification of the prepared samples were determined using XRD. The XRD patterns of all samples (Figure 4a) revealed a pure HAP phase (Ca_{10}(PO_4)_6(OH)_2), with all reflections identical to the reference database (ICDD 00-064-0738). Nonetheless, an unidentified peak at around 20° 2θ was observed on the XRD pattern of 20-MgSO_4/HAP (Figure 4a). To verify the source of such peak, the sample was exposed to ambient air for 30 hours. Further hydration occurred, and then the intensity of this peak increased alongside the appearance of additional peaks between 17-20° 2θ (Figure 4b). These peaks have been identified using database of X’Pert HighScore Plus software and they were assigned to MgSO_4.6H_2O (ICDD 00-024-0719) (Figure 4b). On the other hand, no additional MgSO_4 reflections were observed in the XRD patterns, suggesting that an amorphous MgSO_4.yH_2O phase (y < 6) could be present in the sample [57]. In fact, the amorphicity of the MgSO_4.yH_2O phase was confirmed after analyzing the diffractograms of MgSO_4 during the dehydration process up to 150 °C (Figure 4c). At first, at 25 °C the sample showed high crystallinity. Then the degree of crystallinity gradually decreased increasing the temperature at 44 °C and 55 °C. Finally, the diffractogram shows no crystallinity between 80 and 150 °C. Furthermore, the dehydration was incomplete at this point, leading to the fact that there are amorphous hydrated phases present. This could be related to the blocking of the pores which hinders the initial dehydration (after impregnation) of the hydrated salt confined in the porous structure [37]. Another suggestion is that the MgSO_4 crystallites could be smaller than the detection limit of the XRD spectrometer and so, no well-defined peaks are observed on the XRD patterns.
Figure 4. a) XRD patterns of HAP and its composites, b) Identification of MgSO$_4$.6H$_2$O formation after 30h at ambient air exposition, c) In-situ XRD patterns of MgSO$_4$.7H$_2$O during its dehydration from 25 to 150 °C.
In order to investigate the morphology and the salt deposition homogeneity, SEM analyses were performed. Based on Figure 5 (a and b), different particle sizes with different morphologies have been observed for the both HAP composites. For more insight, the EDX mapping (Figure 6) have been performed in order to have an idea about the possible distribution of the salt on the HAP surface. As seen in Figure 6, the elements Mg and S were homogeneously distributed on the surface of the 5-MgSO$_4$/HAP. However, for the 20-MgSO$_4$/HAP sample (Figure 7), if the distribution of Mg and S elements on the surface was still homogenous on most of the HAP grains, some particles (highlighted by yellow dotted circles) presented a higher concentration of Mg and S, which relates to higher loading of MgSO$_4$, indicating the formation of salt aggregates on the surface of HAP. The presence of aggregates could potentially block the pore network, thus reducing the reaction surface between water vapor and salt.

Figure 5. SEM images of a) 5-MgSO$_4$/HAP and b) 20-MgSO$_4$/HAP.
3.2. TG-DSC analysis for hydration behaviors

The hydration heat released and water sorption capacities of the HAP support and its composites were measured respectively by TG-DSC under controlled RH, regulated by a Wetsys apparatus. From the variation of the heat flow and the mass of the sample as a function of time, the heat released upon hydration (Figure 8a) and the water adsorption capacity (defined as “w.,” in Equation (1)) (Figure 8b) were deduced. The amount of heat produced and water uptake in both prepared composites increased as the salt concentration in the composites increased. This is probably due to the fact that,
the more salt was dispersed onto the porous structure, the more active sites were generated for the exothermic reaction between salt particles and water vapor. The hydration behavior of MgSO$_4$ was also experimented with the same temperature profile.

$$w_e = \frac{m_h - m_d}{m_d}$$  (1)

where $w_e$ is the water adsorption capacity ($g_{H_2O}/g_{sample}$ or g/g in short), $m_h$ (g) and $m_d$ (g) correspond respectively to the final mass of the hydrated sample and the dehydrated sample. For MgSO$_4$, the water uptake is expressed as $g_{H_2O}/g$ of dehydrated salt and for the composite is expressed as $g_{H_2O}/g$ of dehydrated composite.

However, these values are lower than their respective calculated ones which are shown in Table 2. The calculated values are performed by simple addition of the contribution of the MgSO$_4$ salt and of the HAP support based on their respective content in the composites. This can be explained with the presence of the partially amorphous hydrated phases of MgSO$_4$.yH$_2$O (absence of crystalline phase in the XRD patterns) [57,58]. The storage density of these partially hydrated are lower compared to the anhydrous MgSO$_4$, therefore the heat released of the composite is less significant. Moreover, the bare HAP presents a very low hydration heat that did not contribute greatly to the enhancement of heat storage density. Besides that, because of the pore blocking, there could be a certain amount of salt that cannot be reached by the water vapor (Figure 8c). Thus, the hydration energy released as well as the water uptake did not meet expectations. The performance of 20-MgSO$_4$/HAP was also compared with other sulfate-support composites previously reported in literatures. Table 3 shows that the 20-MgSO$_4$/HAP has good energy storage density and has a potential to be a candidate for medium and low temperature applications.
Figure 8. a) Hydration behavior of MgSO₄ and HAP composites at 30 °C and 60 %RH b) Water uptake curves of HAP support and composites (T_{discharge} = 30 °C; RH = 60 %; 24 h of hydration) c) Water adsorption mechanism on the storage material and d) Dehydration behaviour of MgSO₄ and HAP composites from 30 to 150 °C under dried air.
Figure 8d shows the dehydration behavior of MgSO₄ and HAP composites. The MgSO₄·7H₂O decomposed at around 61 °C and produced an unstable phase that eventually decomposed to form MgSO₄·H₂O with a mass loss of 46% and a dehydration enthalpy of 2.75 kJ/g_dried salt. The difference in the behavior of the composites can be explained by the good dispersion of the salt into the HAP pore structure. The decrease in dehydration temperature can also be due to the change in their crystallinity after impregnation into the HAP support [59]. This result confirmed that the use of HAP can be beneficial for certain applications.

Table 2. Experimental results and calculated values of MgSO₄, HAP and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat released (J/g_sample)</th>
<th>Heat released calculated (J/g_sample)b</th>
<th>Water adsorption (g/g)</th>
<th>Water adsorption calculated (g/g)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄ a</td>
<td>2588</td>
<td>-</td>
<td>0.809</td>
<td>-</td>
</tr>
<tr>
<td>HAP</td>
<td>114</td>
<td>-</td>
<td>0.039</td>
<td>-</td>
</tr>
<tr>
<td>5-MgSO₄/HAP</td>
<td>166</td>
<td>216</td>
<td>0.049</td>
<td>0.071</td>
</tr>
<tr>
<td>20-MgSO₄/HAP</td>
<td>464</td>
<td>541</td>
<td>0.155</td>
<td>0.172</td>
</tr>
</tbody>
</table>

a Determined experimentally by TG-DSC/Wetsys.
b Calculated by addition of the heat contribution of MgSO₄ salt and HAP support in each sample.

Table 3. Performance comparison of 20-MgSO₄/HAP and other sulfate-supported composites.

<table>
<thead>
<tr>
<th>Material components</th>
<th>Operating conditions</th>
<th>Energy storage density (J/g)</th>
<th>Reference</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-MgSO₄/HAP</td>
<td>T_{hyd} = 30 °C; RH = 60 %</td>
<td>464</td>
<td>This paper</td>
<td>2021</td>
</tr>
<tr>
<td>30-MgSO₄/Diatomite (D30)</td>
<td>T_{hyd} = 25 °C; RH = 80 %</td>
<td>460</td>
<td>[60]</td>
<td>2021</td>
</tr>
<tr>
<td>60-MgSO₄/Diatomite (D60)</td>
<td>T_{hyd} = 25 °C; RH = 85 %</td>
<td>773</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50-MgSO₄/Expanded graphite (EG50)</td>
<td>T_{hyd} = 25 °C; RH = 85 %</td>
<td>496.4</td>
<td>[61]</td>
<td>2021</td>
</tr>
<tr>
<td>MgSO₄/13x with %MgSO₄ up to 20%</td>
<td>T_{hyd} = 25 °C; RH = 60 %</td>
<td>510-575</td>
<td>[22]</td>
<td>2019</td>
</tr>
<tr>
<td>MgSO₄/zeolite (laboratory pilot)</td>
<td>T_{hyd} = 25 °C; RH = 85 %</td>
<td>401</td>
<td>[4]</td>
<td>2018</td>
</tr>
<tr>
<td>MgSO₄/zeolite Modernite</td>
<td>T_{hyd} = 22 °C; RH = 50 %</td>
<td>507</td>
<td>[62]</td>
<td>2013</td>
</tr>
</tbody>
</table>
3.3. Hydration kinetic modeling

Figure 9 shows the water uptake curves for the HAP support and two prepared composites. Similarly, they all display an initial short and fast water sorption rate during the first 30 minutes of hydration. However, after the initial fast adsorption, the kinetic curve of the 5-MgSO₄/HAP composite is similar to the curve of the support HAP which quickly reached the water sorption equilibrium only after 2 h of hydration. While for the 20-MgSO₄/HAP composite, after the initial fast adsorption, the kinetic curve slowed down significantly and then barely reached the equilibrium after over 7 h of hydration. This behavior is shown to be strongly impacted by the amount of salt deposited. When more salt was deposited, water vapor diffusion could become problematic as it takes more time for water vapor to reach entirely salt particles.

To investigate the kinetics of water uptake, several kinetic models were tested (Table 4). Among all of these kinetic equation models, six kinetic models showed a poor fitting based on on the correlation coefficient R²: Elovich model (0.70-0.94), Vermeulen model (0.95-0.97) and Unipore model (0.17-0.78). With the exception of the pseudo-first order (PFO) and pseudo-second order (PSO), which are two well-known kinetic models [63–65]. The fitting results are reported in Figure 9 and the obtained kinetic parameters are listed in Table 5.

### Table 4: Non-linear kinetic adsorption models.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Equation</th>
<th>Description of parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo First Order (PFO)</td>
<td>( w_t = w_e[1 - \exp(-K_1 t)] )</td>
<td>( w_t ) is the water uptake at time ( t ) (g/g), ( w_e ) is the water uptake at equilibrium (g/g), ( t ) is the hydration time (h), ( K_1 ) and ( K_2 ) are respectively the rate constant of the PFO and PSO models (s⁻¹).</td>
<td>[63–65]</td>
</tr>
<tr>
<td>Pseudo Second Order (PSO)</td>
<td>( w_t = \frac{w_e^2 K_2 t}{1 + w_e K_2 t} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elovich</td>
<td>( w_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) )</td>
<td>( \alpha ) is the initial adsorption rate (mg/g min), and ( \beta ) is the extent of the surface coverage and activation energy of the process</td>
<td>[65,66]</td>
</tr>
<tr>
<td>Vermeulen</td>
<td>( w_t = w_e \sqrt{1 - \exp\left(-\frac{4\pi^2 D_v t}{d_p^2}\right)} ) ( D_v ) is the diffusion coefficient; ( d_p ) is the particle radius</td>
<td>[67,68]</td>
<td></td>
</tr>
<tr>
<td>Unipore</td>
<td>( w_t = w_e \times 6 \left(\frac{D_e \times \pi}{\pi}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ight)^{0.5} ) | ( D_e ) is the the diffusion coefficient | [69] |</p>
Figure 9. Adsorption kinetics fitting results of MgSO₄, HAP support and two composites with 5% and 20% salt content. (Hydration temperature: 30°C; RH: 60%; sample mass: ~10 mg; MgSO₄ density: 2.66 g/cm³; HAP density: 3.16 g/cm³; 20-MgSO₄/HAP density: 3.07 g/cm³; 5-MgSO₄/HAP density: 3.14 g/cm³).

Table 5. The kinetic parameters obtained by different adsorption kinetic models.

<table>
<thead>
<tr>
<th></th>
<th>MgSO₄</th>
<th>HAP</th>
<th>5-MgSO₄/HAP</th>
<th>20-MgSO₄/HAP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-First-Order (PFO)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>We (g/g)</td>
<td>0.815</td>
<td>0.038</td>
<td>0.048</td>
<td>0.146</td>
</tr>
<tr>
<td>K₁ (10⁴ s⁻¹)</td>
<td>1.133</td>
<td>10.24</td>
<td>8.347</td>
<td>2.069</td>
</tr>
<tr>
<td>R²</td>
<td>0.996</td>
<td>0.988</td>
<td>0.993</td>
<td>0.997</td>
</tr>
<tr>
<td><strong>Pseudo-Second-Order (PSO)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>We (g/g)</td>
<td>0.909</td>
<td>0.040</td>
<td>0.051</td>
<td>0.176</td>
</tr>
<tr>
<td>K₂ (10⁴ s⁻¹)</td>
<td>1.794</td>
<td>462.5</td>
<td>288.1</td>
<td>13.16</td>
</tr>
<tr>
<td>R²</td>
<td>0.957</td>
<td>0.953</td>
<td>0.962</td>
<td>0.977</td>
</tr>
</tbody>
</table>
It can be seen from Figure 9 that the PFO model described better the adsorption processes of all samples than the PSO model (with $R^2$ coefficients of around 0.99). From the kinetic rate constant $K_1$ obtained from the PFO model, the hydration kinetics can be classified as following order (from fastest to slowest): HAP $>$ 5-MgSO$_4$/HAP $>$ 20-MgSO$_4$/HAP $>$ MgSO$_4$. The MgSO$_4$ presents a slow kinetic compared to others materials (Figure 9). The salt required 15 hours to attain a stable hydration state, which is twice the rate of the 20-MgSO$_4$/HAP composite. This well-known slow hydration kinetic of the MgSO$_4$ was already investigated. According to Linnow et al. [15], when exposed to humid air, a thin layer of hydrated salt forms quickly on the support surface, restricting water vapor diffusion and thereby slowing the reaction rate. The HAP support presents a fastest kinetic which is probably due to the fast physical adsorption process during hydration. The impregnation of MgSO$_4$ has then a significant impact on this speed. In the case of the 5-MgSO$_4$/HAP composite, the kinetic was slightly impacted when the salt was integrated in the HAP porous structure. However, when the surface coverage of the salt was extended, as in the case of the 20-MgSO$_4$/HAP composite, the hydration kinetic significantly slows down (rate constant $K_1$ 4 times lower) (Figure 10). As aforementioned, these behaviors are related to the difficulty of water vapor to diffuse inside the material pore network, in particular composites with higher salt content. Another result is that the slow kinetic of MgSO$_4$ was greatly improved as it was dispersed in the porous matrix HAP (the kinetic rate constant of the composites are higher than MgSO$_4$). This latter could have a remarkable value in residential applications, because it will reduce considerably the hydration time and thus improve the operating flexibility of the overall storage system.
Figure 10. Influence of the salt content on the kinetic rate constants.

3.3. Cyclability and stability

To evaluate the cyclability and stability of the 20-MgSO$_4$/HAP composite, the sample has been exposed to a short-cycle hydration/dehydration treatment consisting of 20 cycles between temperatures of 150 °C (Dehydration) and 30 °C (Hydration, at a relative humidity of 60%). In the following step, the heat released for each cycle has been determined as a first benchmark. As it can be seen in Figure 11, there is only a small fluctuations of heat released between each cycle, which confirms the good stability with an average ESD of 472 J/g.
Figure 11. Evaluation of 20-MgSO$_4$/HAP composite stability for 20 cycles of hydration/dehydration.

Figure 12 shows the TGA signals during hydration and dehydration of 5 different cycles in the cyclability test (1$^{st}$, 5$^{th}$, 10$^{th}$, 17$^{th}$, 20$^{th}$). During the hydration reactions, a degradation in water uptake during the first 10 cycles is noted, from 0.188 g/g in the first hydration but down to 0.157 g/g after the 10$^{th}$ hydration. From this point onwards, the water adsorption capacity is stabilized at 0.157 g/g (83.5% compared to 0.188 g/g) until the 20$^{th}$ hydration. The hydration kinetic rate is also reported to be stable at around 1.2.10$^{-4}$ s$^{-1}$ during the cycling experiment.

In terms of dehydration reactions, a loss of 13.26% in mass is recorded in the first dehydration. Over cycling, the dehydration becomes less and less effective, but not significantly since during the last dehydration, a loss of 11.55% (about 87.1% compared to 13.26%) in mass is reported.
Figure 12. TGA curves of 5 different cycles during the cyclability experiment (1st, 5th, 10th, 17th, 20th).

The SEM and EDX mapping (Figure 13) of sample after 20 cycles have been done to verify if there are any changes in term of salts distribution, agglomeration and so on. The results showed that there is no significance difference before and after cycling experiment, which confirm also the morphological stability of the composites. Consequently, these composites can be a base for the development of potential material for TCHS application based on HAP. A research regarding the development of new composites on other HAP types with the objective to enhance the water uptake and increase the amount of deposited salt in order to improve the thermal storage capacity is ongoing.

Figure 13. EDX mapping for 20-MgSO₄/HAP after 20 cycles.
4. Conclusions

Wide pore hydroxyapatite composite materials impregnated with different amounts of MgSO$_4$, as prospective thermochemical seasonal heat storage materials, have been studied using the TG-DSC apparatus. Despite the fact that magnesium sulfate was unable to fully exploit its sorption capacities, a composite containing 20% MgSO$_4$ produced the maximum heat (464 J/g) as compared to HAP impregnated with 5% MgSO$_4$ (166 J/g). The excellent dispersion of MgSO$_4$ increases the storing capability of composite materials. High heat and water storage capabilities are not the only factors to consider when selecting a storage material in thermochemical heat storage systems. A rapid water sorption kinetics is also necessary for the system's usability. Good fitting of the kinetic experimental data with the model equation has been successfully performed, allowing us to determine the rate controlling adsorption mechanism, which is an important factor in thermochemical heat storage system design. The repeated stability of MgSO$_4$-HAP is evaluated, revealing that this two-component sorbent is relatively well constant after 20 dehydration/hydration cycles. In perspective, these promising results open the way to the optimization of a new thermochemical heat storage composite materials’ family based on HAP. New HAP compositions and morphology can be then studied in order to improve the salt dispersion and the water mass transfer.

Author Contributions: Conceptualization and Writing—Original Draft Preparation M. H. N, S.B.; Methodology and Writing—Original Draft Preparation M.Z; Review & Editing—Supervision, S. B., P. D; Preparation of hydroxyapatite material, A. G; Nitrogen physisorption analyses, M.H.N, C. V; Writing—Review & Editing, Supervision, and Project Administration S. B. All authors have read and agreed to the published version of the manuscript.
Funding: - Region Grand Est for providing funding for the acquisition of the TG-DSC equipment within the “STOCKFATAL” project and for the contribution to Mr. Minh Hoang Nguyen’s thesis grant.

- Carnot MICA for funding part of this study in the frame of the STOCKENER project.

- IS2M for the postdoctoral grant of M. Zbair in the frame of the “Projets Structurants” call.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the Carnot Institutes MICA(France) for supporting a part of this study within the STOCKENER; Region Grand Est (France) for providing funding for the acquisition of the TG-DSC equipment, in the frame of STOCKFATAL project, and financing a part of the PhD-grant of Mr. Minh Hoang Nguyen.

All physicochemical characterizations were performed on the IS2M technical platforms. The authors are very grateful to L. Michelin (XRF) and L. Josien (SEM+EDX) for their contribution.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

TES, thermal energy system;

TCHS, thermochemical heat storage;

HAP, hydroxyapatite;

IWI, Incipient Wetness Impregnation;

XRD, X-ray Diffraction;

WDXRF, wavelength-dispersive X-Ray Fluorescence;

SEM, Scanning Electron Microscope;

EDX, Energy Dispersive X-ray;

BET, Brunauer, Emmett and Teller;
PSD, pore size distribution;

BJH, Barrett, Joyner and Halenda;

TG, thermogravimetry;

DSC, Differential Scanning Calorimetry;

RH, relative humidity;

PFO, pseudo-first order;

PSO, pseudo-second order.

References


