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Newly designed metal foam-salt hydrate composite for thermochemical heat storage --Manuscript Draft--

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Abstract:	<p>Thermochemical heat storage system based on the sorption mechanism between water vapor and hygroscopic salts is considered to be a promising technology. However, hygroscopic salts have drawbacks such as swelling and agglomeration of the crystalline salt particles during hydration/dehydration cycles, which progressively leads to decreasing specific reaction surface and kinetics of heat and mass transfer, thus resulting in poor cyclic performance and stability.</p> <p>In this paper we propose a composite material, based on open-cell metal foam as host matrix, containing calcium chloride as hygroscopic salt dispersed in the pores. An open-cell metal foam host matrix improves the heat and mass transfer kinetics thanks to the porous structure and the high thermal conductivity, and offers additional advantages related to elevated mechanical strength, which would ensure mechanical resistance of the composite. The composite showed significant improvement in thermochemical performance compared to that of bulk calcium chloride powder in hydration/dehydration cycles. For cyclic stability, composites presented a slight increase and stabilization of thermal energy released upon cycles, while salt showed a substantial and continuous degradation of 78.5% in performance after 12 cycles. For heat released, composites outperformed considerably the bulk calcium chloride in almost all cycles. At the 12th cycle, the heat released of composites improved substantially to 5~6 times that of bulk calcium chloride powder. Observations by in situ environmental scanning electron microscope hydration/dehydration cycles demonstrate that swelling and deliquescence induce moderate redistribution of salt hydrates within the metal foam while preserving the essential open porosity of the matrix. It efficiently prevents extensive salt agglomeration and loss of specific reaction area, which explains the amelioration of the composite's thermochemical properties and cyclic stability. In conclusion, the metal foam-salt hydrate composite developed in our work is suitable and promising for thermochemical energy storage, offering both mechanical and thermochemical advantages.</p>
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Newly designed metal foam-salt hydrate composite for thermochemical heat storage

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Abstract

Thermochemical heat storage system based on the sorption mechanism between water vapor and hygroscopic salts is considered to be a promising technology. However, hygroscopic salts have drawbacks such as swelling and agglomeration of the crystalline salt particles during hydration/dehydration cycles, which progressively leads to decreasing specific reaction surface and kinetics of heat and mass transfer, thus resulting in poor cyclic performance and stability.

In this paper we propose a composite material, based on open-cell metal foam as host matrix, containing calcium chloride as hygroscopic salt dispersed in the pores. An open-cell metal foam host matrix improves the heat and mass transfer kinetics thanks to the porous structure and the high thermal conductivity, and offers additional advantages related to elevated mechanical strength, which would ensure mechanical resistance of the composite. The composite showed significant improvement in thermochemical performance compared to that of bulk calcium chloride powder in hydration/dehydration cycles. For cyclic stability, composites presented a slight increase and stabilization of thermal energy released upon cycles, while salt showed a substantial and continuous degradation of 78.5% in performance after 12 cycles. For heat released, composites outperformed considerably the bulk calcium chloride in almost all cycles. At the 12th cycle, the heat released of composites improved substantially to 5~6 times that of bulk calcium chloride powder. Observations by in situ environmental scanning electron microscope hydration/dehydration cycles demonstrate that swelling and deliquescence induce moderate redistribution of salt hydrates within the metal foam while preserving the essential open porosity of the matrix. It efficiently prevents extensive salt agglomeration and loss of specific reaction area, which explains the amelioration of the composite's thermochemical properties and cyclic stability. In conclusion, the metal foam-salt hydrate composite developed in our work is suitable and promising for thermochemical energy storage, offering both mechanical and thermochemical advantages.

Keywords

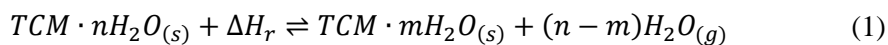
Thermochemical heat storage; Sorption; Selective water sorbent; Metal foam; Calcium chloride

1. Introduction

The global energy crisis has been exacerbated by a combination of factors such as the rapid economic rebound after the Covid-19 pandemic, extreme weather events, disrupted conventional energy supplies and geopolitical reasons, triggering an unprecedented momentum in the development of renewable energy. The soaring prices of conventional fossil energy sources have increased the competitive price benefit of renewable energy while raising awareness of the energy security advantages offered by domestically produced renewable energy worldwide. According to the International Energy Agency 2022 report on renewable energies, driven by existing and new policies introduced in China (the 14th Five-Year Plan), the European Union (the REPowerEU plan), the United States (the US Inflation Reduction Act), renewable energy capacity is expected to grow by 2400 GW, which accounts for more than 90% of global electricity capacity expansion over 2022-2027. It is anticipated that renewable energy overtakes coal as the world's largest source of electricity generation by early 2025 and its share of the electricity mix increases by 10% within five years to reach 38% in 2027 [1, 2].

Among all the renewable energies, the usage of solar energy is a current common trend worldwide for generating electricity via photovoltaics (PV) or by concentrating solar power (CSP) as well as for thermal applications related to space heating in domestic sectors [3, 4]. For both CSP plants and thermal applications such as heating buildings using solar energy, it is essential to be equipped with low-cost and reliable thermal energy storage (TES) system to cope with the mismatch between energy demand and supply, thereby compensating for the intermittent nature of renewable energy and providing energy on-demand [5]. There are mainly three existing TES technologies depending on the relevant physicochemical mechanisms, which are (1) sensible heat storage (SHS) [6, 7], (2) latent heat storage (LHS) [8, 9], and (3) thermochemical heat storage (THS) [10, 11]. SHS and LHS are considered as relatively mature technologies that have been developed and reached commercial implementation. Yet, thanks to their high energy density, small heat losses, flexibility for daily to seasonal heat storage, and significant cost reduction, the THS technology has attracted more attention and experienced prompt development in the past decades [7, 12-14].

Compared to storage mechanisms based on solely chemical reactions, THS systems based on sorption mechanisms have the advantage of low activation energies and are therefore suitable for low-temperature applications, such as domestic heating [3]. The sorption THS system can be applied either in open or closed systems [15]. For an open system, the reactant gas is directly provided from (or released to) the surrounding environment. Water vapor in the ambient air is the most convenient and cost-effective reactant gas. When compared to other open systems, the THS systems based on water vapor sorption/desorption are therefore the most simple, stable and environmentally friendly ones [16]. The open THS systems based on the reversible gas-solid reactions between thermochemical materials (TCM) and water vapor can be described as followed:



The optimal operation of TES depends to a large extent on the selection of a suitable TCM. An appropriate TCM should meet certain requirements, such as high energy storage density, elevated cycling stability, suitable operating temperature, stable mechanical properties, low or

1 non-toxicity and environmental neutrality, economic viability, and appropriate heat and mass
2 transfer properties [3, 7, 17, 18]. As promising TCMs, pure hygroscopic salt hydrates and
3 mixed salt hydrates have been widely studied in recent decades [19-24]. The ability of salt
4 hydrates and water vapor systems to operate at a relatively low temperature suits well for
5 applications such as seasonal and long-term energy storage. However, despite the generally
6 high energy density offered by pure or mixed salt hydrates, problems related to high costs,
7 restrictive operating conditions and the possible toxicity of certain salt prevent their large-
8 scale deployment without special treatments [25-27]. Additionally, hygroscopic salts present
9 non-negligible disadvantages such as excessive swelling and agglomeration during
10 hydration/dehydration cycles, as well as potential deliquescence phenomenon if the relative
11 humidity exceeds the deliquescence relative humidity (DRH), which progressively degrade
12 heat and mass transfer efficiency and lead to poor cyclic stability [28-30].
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16 To alleviate the limitations mentioned above and to make more efficient use of the high
17 energy density of hygroscopic salts, a family of composite sorbents named selective water
18 sorbents (SWS) or composite “salt in porous matrix (CSPM) has been proposed and designed
19 by Aristov et al [31, 32]. The concept is to impregnate hygroscopic salts in a porous host
20 matrix with open pores. This combined structure will limit excessive volume changes due to
21 swelling and agglomeration by confining the salt crystals to the open pores, hence preventing
22 loss of the reaction specific surface. In addition, the presence of pores also provides more
23 efficient pathways for mass and heat transfer, which would both promote the kinetics of
24 hydration/dehydration reaction [33]. The most commonly investigated composites concerned
25 CaCl₂, LiCl, MgSO₄, MgCl₂, SrBr₂ salts, and host matrices with a pore size smaller than 50
26 nm, such as zeolites, silica gels, carbon-based materials, alumina, vermiculites and metal-
27 organic frameworks (MOF) [34-43]. Despite the promising possibilities offered by these
28 different composite systems to be applied to different applications under various operation
29 conditions, these works still haven’t been considered for commercial deployment because of
30 problems related to inappropriate charging temperature, low thermal conductivity and
31 possible leakage of the salt solution after deliquescence [28, 44, 45].
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38 This paper presents an original CSPM type of SWS, specifically designed for thermochemical
39 energy storage. The composite consists of open-cell metal foam with a pore size of about 350
40 μm as host matrix and calcium chloride as hygroscopic salt dispersed in the pores. Calcium
41 chloride has been proposed as a promising TCM for decades, both as pure salt hydrate and as
42 impregnated salt in composite form. It is an affordable industrial by-product offering many
43 advantages such as high energy storage density, low cost, non-toxicity, and suitability for
44 low-temperature operation conditions [46-51]. Open-cell metal foams are composed of
45 interconnected pores that form a network in the structure [52]. A metal foam host matrix
46 improves the heat and mass transfer kinetics thanks to the porous structure and the high
47 thermal conductivity, and offers additional advantages related to elevated mechanical strength,
48 which would ensure the mechanical resistance of the composite. What’s more, the mechanical
49 strength and relatively low density of metal foam serving as host matrix ensure the possibility
50 of manufacturing lightweight and durable components, adapted to handling, stacking and
51 mounting operations, which are necessary for adequate dimensioning and fabrication of
52 flexible and polyvalent thermochemical reactors for future industrial and commercial TCM
53 applications. Besides, the reticulation of large open porosity, with several hundred-
54 micrometer pore sizes, provides large open volumes allowing for swelling of salt hydrates
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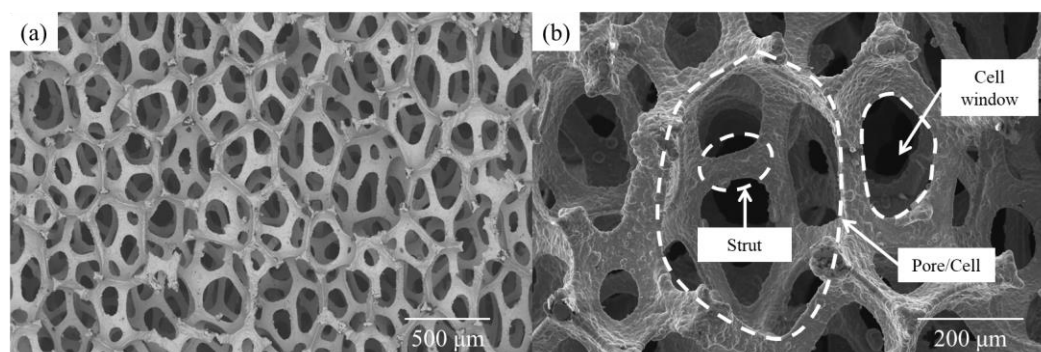
1 without occluding pore spaces, and hence preserving the mass transfer kinetics. Therefore,
2 metal foam–salt hydrate composites meet all requirements for the heat and mass transfer
3 process which are essential for the good performances of thermochemical composites [53].
4 Additionally, metal foams can be produced using recycled metal materials, which offers
5 additional environmental advantages [54].
6

7 This paper focuses first on the synthesis of appropriate metal foam-salt hydrate composite.
8 Secondly, we evaluate their thermochemical properties during hydration/dehydration cycles
9 and compare them with that of bulk salt hydrate powders. At last, the evolution of the
10 thermochemical properties of composites is addressed based on their thermomechanical
11 characteristics and in particular their microstructural/morphological evolution. For that
12 purpose, we performed experimental measurements by differential scanning calorimetry
13 (DSC) and in situ environmental scanning electron microscope (ESEM) observations.
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17 2. Experimental methodology

18 2.1. Starting materials

19 Commercial nickel foam (Recemat BV) and aluminum foam (American Elements) with an
20 average pore size of 350 μm were used as the host matrices of the composites (see Fig. 1).
21 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (VWR Chemicals, AnalaR NORMAPUR® Reag. Ph. Eur.) was used as the
22 thermochemical active phase of the composite.
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40 Fig. 1. (a) Backscattered Electron (BSE) image (x40 magnification) and (b) SEM image (x127 magnification) of
41 commercial nickel foam used in this study for synthesizing the composite, with essential elements (pore/cell,
42 and cell window) of open-cell metal foam marked in dashed lines.
43

44 2.2. Synthesis of composite

45 The deposition of CaCl_2 particles into the metal foam matrix was realized by the deposition-
46 precipitation process. The metal foams were cut into pieces in the form of panels, measured,
47 and weighed before depositing CaCl_2 . They were then immersed in an oversaturated solution
48 of calcium chloride at room temperature. Dispersion of salt particles was achieved by stirring
49 continuously and intensively the metal foam in the CaCl_2 solution for approximately 5 min.
50 Then the composites were subjected to moderately flushed by compressed air to remove the
51 excess salt dispersion from the pores and to avoid complete saturation of the porosity. The
52 final step consisted of placing the composites in an oven for more than 48 h at 90 °C.
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57 2.3. DSC: thermal properties analysis

58 The thermal properties analysis of the composite was realized by performing thermal cycling
59 tests on a DSC device (Micro-DSC VII, SETARAM). The DSC device was equipped with a
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1 double chamber that serves as the calorimetric block. It contained one vessel for the sample
2 and a second one for reference. Both vessels consisted of an 850 μl cylindrical crucible made
3 of Hastelloy®. They were sealed with elastomer seals retained by anti-extrusion rings. The
4 heat flow measurement sensor consisted of a high-sensitivity planar flow meter, which
5 surrounded the two experimenting vessels and kept a tight thermal connection to the
6 calorimetric block, ensuring identical temperature between the experimenting vessels and the
7 calorimetric block. The temperature sensor was composed of Peltier elements with Joule
8 effect calibration and provided measurement accuracy of a level up to ± 0.07 °C for the
9 temperature range between -45 °C and 120 °C.
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11
12 We performed cyclic thermal experiments on a nickel foam- CaCl_2 composite sample under
13 vacuum conditions. The sample was heated up to 115 °C and cooled down to -40 °C at the
14 heating/cooling rate of 0.5 °C/min for 4 cycles. The temperature range was chosen to cover
15 the temperature range of possible working conditions for the composite serving as
16 thermochemical material for thermal energy storage. To reduce the errors related to the
17 thermal lag between the sample and the sensor, a relatively low heating and cooling rate of
18 0.5 °C/min was chosen [55]. The thermal properties of the composite were then analyzed
19 based on the DSC curve recorded during the crystallization and melting process of the salt.
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22 **2.4. Calorimeter: thermal analysis during hydration/dehydration cycles**

23 **2.4.1. Experimental setup**

24
25 Heat flow measurements during hydration and dehydration cycles were carried out on a
26 Calvet-type calorimeter (C80, SETARAM). The sample and reference vessels of 12.5 ml
27 were connected to a gas circulation tubing circuit. They were surrounded by 3D Calvet
28 sensors based on thermocouples with Joule effect calibration which provided a temperature
29 measurement accuracy of ± 0.1 °C and precision of ± 0.15 °C. The operating temperature
30 range was between the ambient temperature and 300 °C.
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34 The metal foam-salt composite samples were kept dry in the oven at 90 °C and re-weighed
35 before use. Samples were then placed directly into the sample vessel of the calorimeter and
36 sealed to prevent the hydration of the sample due to ambient air humidity. Every two samples
37 of metal foam-salt composite panels were stacked in the sample vessel to simulate their
38 practical industrial application conditions. For our experiment, we chose to perform the
39 hydration/dehydration cycles at an isothermal condition at 23 °C. A bottle of dry nitrogen gas
40 ($\text{N}_2 \geq 99.999\%$, ALPHAGAZ™ 1 Nitrogen, Air Liquide) was connected to two gas circuits
41 controlled by a valve. During the dehydration process, the dry nitrogen gas served as the
42 purge gas. For the hydration process, the dry nitrogen gas passed through a gas bubbler filled
43 with a saturated solution of magnesium nitrate kept at a constant temperature of 23 °C by
44 water bath, which allowed the nitrogen gas to be humidified to a constant relative humidity of
45 54% [56]. The nitrogen gas then passed a flowmeter (R-2-15-AA, Sho-Rate™ 1355,
46 BROOKS) connected to the gas inlet tube of the sample vessel for measuring the gas flow
47 rate. It can be controlled by adjusting the switch knob of the gas circulation tube attached to
48 the sample vessel. For both the cyclic hydration and dehydration processes, the gas flow rate
49 was controlled at 128 ml min^{-1} . Note that the inlet pipe connecting to the entrance of the
50 sample vessel was heated by a water bath glass tube and was heat-insulated to ensure that the
51 humidified gas could still enter the reaction chamber at the temperature of 23 °C so that the
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fluctuations of heat flow in the reaction chamber due to temperature differences could be avoided. The gas outlet tube of the sample vessel was then linked to a vacuum pump to realize the gas circulation throughout the experimental setup. At the beginning and the end of each hydration/dehydration process, we waited for at least 15 min for the signal to stabilize. The schematic of the experimental setup is shown in Fig. 2.

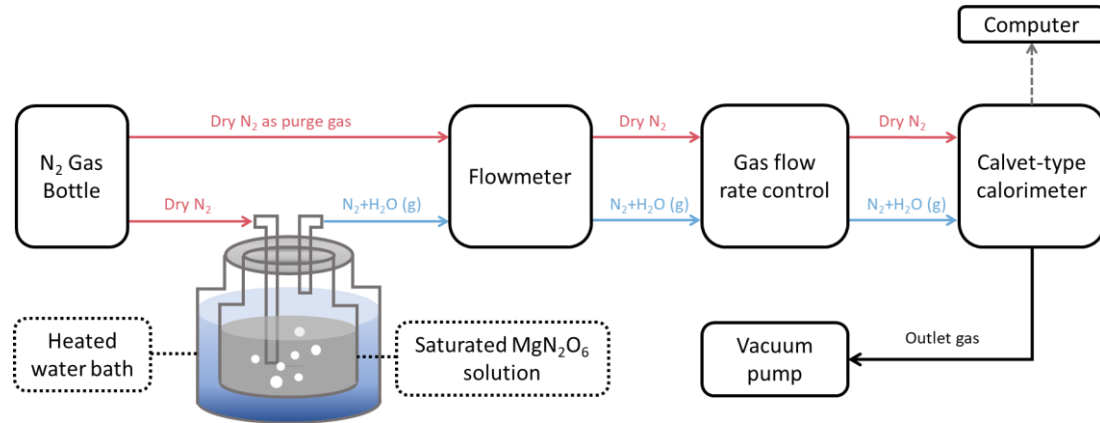


Fig. 2. Schematic diagram of the experimental setup.

2.4.2. Experimental procedures

For analyzing the thermal cycling performance of the composite and compare its performance with that of bulk CaCl_2 salt during hydration and dehydration cycles, we performed experiments on three kinds of samples, which were nickel foam- CaCl_2 composite (48.5 wt% CaCl_2), aluminum foam- CaCl_2 composite (21.0 wt% CaCl_2) and bulk CaCl_2 salt powder. We designed two kinds of experimental procedures described as follows.

1) Long hydration/dehydration cycles

To avoid the possibly irreversible structural damage of the composite related to leakage of CaCl_2 due to possible deliquescence during complete hydration, each composite sample was partially hydrated by the circulation of hydrated nitrogen gas with a constant relative humidity at 54% for different hydration duration Δt_{hydr} under isothermal conditions for 12 cycles (see Table 1). After every hydration, the samples were completely dehydrated by the circulation of dry nitrogen. The time necessary to completely dehydrate the sample depended on the hydration duration, the type of sample, and the mass content of salt in the composite. The same experimental procedure was applied to bulk salt powder for comparison.

Cycle number	Hydration duration Δt_{hydr} (min)
1	360
2	180
3	180
4	180
5	90
6	90
7	90
8	90
9	45
10	45
11	45
12	360

Table 1. Long hydration/dehydration cycles experimental procedure.

2) Short hydration/dehydration cycles

1 In this procedure, each sample was hydrated by the circulation of hydrated nitrogen gas with a
2 constant relative humidity at 54% for 45 min under isothermal conditions and was completely
3 dehydrated by the circulation of dry nitrogen after every hydration process. Six cycles of this
4 experiment were performed for each kind of sample, and two repetition tests were conducted.

5
6 Heat flows during these cycles were recorded and the quantity of thermal energy released
7 during each hydration/dehydration cycle was obtained by integrating the heat flow signal over
8 the time duration of each experiment. Experimental errors were estimated according to the
9 data acquired through repetition tests as well as resolution limitations of the instrument given
10 by manufacturers.

11 **2.5. SEM: in situ hydration/dehydration cycling test**

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13 In situ hydration/dehydration cycling tests of the metal foam-salt composites were performed
14 using a scanning electron microscope (FEI QUANTA 650 FEG-ESEM) to investigate their
15 microstructural evolution. The observation and the image recording in real-time during the
16 process were done under controlled relative humidity (RH), which was made possible with
17 the environmental scanning electron microscope (ESEM) mode and using a gaseous
18 secondary electron detector (GSED) [57, 58]. In addition to RH control, the ESEM mode also
19 allowed for avoiding coating the poorly conductive salt particles with conductive metal foam,
20 hence preserving their original characteristics.

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22 The nickel foam-CaCl₂ composite sample (7 mm × 7 mm × 1.4 mm) fresh out of the oven was
23 mounted on a cooling stage using the Peltier effect with a thermocouple in contact with the
24 sample's upper surface to monitor the actual temperature of the sample. For reproducing the
25 experimental conditions of thermochemical tests mentioned in section 2.4, the sample was
26 controlled at a constant temperature of 23 °C by adjusting the temperature of the Peltier stage.
27 During the hydration process, the humidity around the sample was gradually increased from 0
28 to about 54% RH. This was achieved and controlled by increasing the vapor pressure in the
29 scanning electron microscope (SEM) chamber. Likewise, for the dehydration process, the
30 humidity was decreased to 0 by reducing the vapor pressure in the chamber. Highly resolved
31 images (3072 × 2207 pixels per image with a pixel size of 0.08 μm) were taken for the region
32 of interest (ROI) at the initial and final states for both hydration and dehydration cycles.
33 Lower resolution images (1536 × 1113 pixels per image with a pixel size of 0.77 μm) were
34 also recorded automatically every 5 seconds during the hydration/dehydration cycles.

35 **3. Results and discussion**

36 **3.1. Thermal properties analysis of the composite**

37
38 Thermal properties and thermal cyclic reliability of metal foam-salt composite were analyzed
39 by DSC. Fig. 3 presents the DSC curves of nickel foam-CaCl₂ composite during 4 cycles of
40 heating and cooling in the temperature range of -40 °C and 115 °C at a constant rate of 0.5
41 °C/min. The onset temperature, offset temperature, and peak maximum temperature of
42 melting and crystallization, as well as their average value for 4 heating/cooling cycles, are
43 listed in Table 2. Fig. 3 shows that one exothermic peak with an onset temperature of 18.2 ±
44 0.8 °C during the cooling process and one endothermic peak with an onset temperature of 44.3
45 ± 0.2 °C during the heating process were detected, which corresponded to the crystallization
46 and the melting of salt embedded in the metal foam, respectively. The onset crystallization
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temperature and onset melting temperature detected is compatible with the values for calcium chloride tetrahydrate reported in the literature [59, 60]. The difference between onset crystallization temperature and onset melting temperature is defined as the supercooling degree ΔT_s of a phase change material and can be expressed by a hysteresis equation [61] :

$$\Delta T_s = T_M - T_C \quad (2)$$

where T_M and T_C are the melting and crystallization temperatures, respectively. As shown in Table 2, $\Delta T_s \approx 26$ °C was detected for the composite during the heating and cooling process. It is also notable that the supercooling degree of the first cycle (~ 27.5 °C) was nearly 2 °C higher than that of the following cycles (~ 25.5 °C). It is possible that during the first melting process, the salt particles were redistributed in the host matrix in a way favoring nucleation during the following cycles, for instance by revealing more open pores as well as metal foam struts, thus resulting in a lower supercooling degree [62, 63].

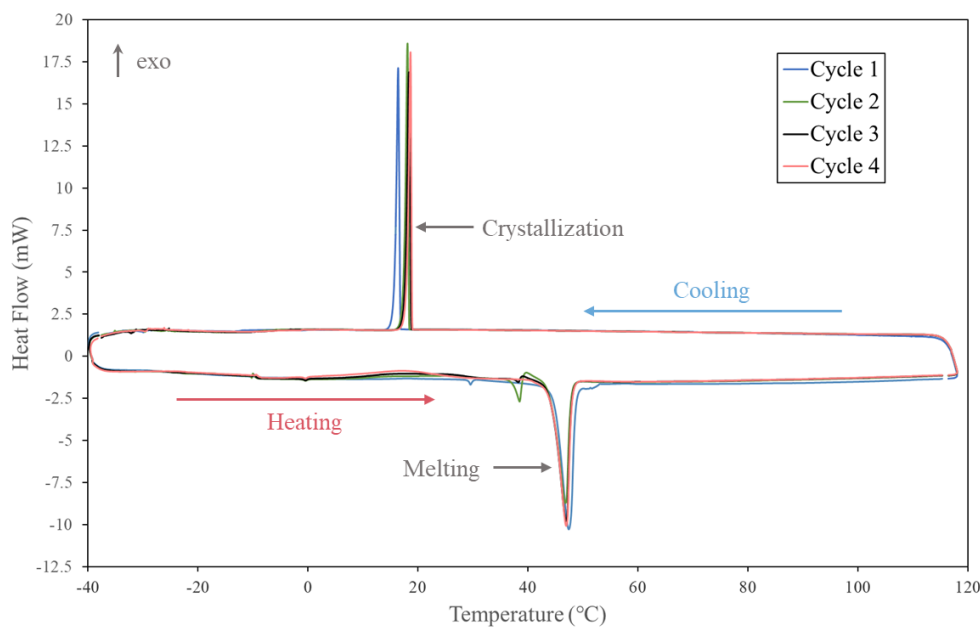


Fig. 3. DSC curves of nickel foam-salt composite during 4 cycles of heating and cooling.

It can be clearly seen in Fig. 3 that except for the first cycle, the DSC curves for the following 3 cycles are closely coincident with each other, indicating that the enthalpy of fusion and crystallization almost remained unchanged during heating and cooling cycles. In addition, the phase change temperatures were rather steady (see Table 2). These results demonstrate that the composite has sufficiently good cycling thermal reliability over a large temperature range of -40 °C and 120 °C.

Cycle No.	Heating			Cooling		
	Onset T_M (°C)	T_{Peak} (°C)	Offset T_M (°C)	Onset T_C (°C)	T_{Peak} (°C)	Offset T_C (°C)
1	44.5	47.6	48.6	16.8	16.4	15.7
2	44.1	47.0	47.8	18.4	18.1	17.4
3	44.2	47.1	47.9	18.8	18.4	17.7
4	44.2	47.1	47.9	18.9	18.7	17.9
Average	44.3 ± 0.2	47.2 ± 0.2	48.1 ± 0.3	18.2 ± 0.8	17.9 ± 0.9	17.2 ± 0.9

* T_M = melting temperature, T_C = crystallization temperature, T_{Peak} = peak maximum temperature

Table 2. Thermal properties of composite by DSC cyclic tests.

3.2. Thermochemical performance during hydration/dehydration cycles

3.2.1. Analysis of long hydration/dehydration cycles

We present in Fig. 4 the typical curves of heat flow over time during the hydration/dehydration process of both composite and bulk salt powder. The curves obtained for the nickel foam-CaCl₂ composite and the aluminum foam- CaCl₂ composite had identical forms, so here we present the curves of the nickel foam-CaCl₂ composite as an example. In fact, it can be seen in Fig. 4 that the curves obtained for bulk salt powder and composites also have similar forms. For curves obtained during the hydration process (see Fig. 4a and c), the signal of heat flow stabilized during the first 15 min which provided us with a steady state baseline value of the heat flow ϕ_{bl} for evaluating the integration of heat flow over time. Then the humidified nitrogen entered the reaction vessel at t_i and a rapidly increasing heat flow signal was detected. The heat flow reached a maximum peak value of ϕ_p in 5-7 min and then decreased slowly over time. The circulation of humidified nitrogen was stopped at t_f when the humidification process time reached the target duration set by our experimental plan (Table 1). Then the heat flow signal dropped immediately and rapidly. It gradually stabilized near the baseline in 30 min. For the following dehydration process (see Fig. 4b and d), the dry nitrogen gas entered the reaction vessel after the signal stabilized. The circulation of dry nitrogen continued until the signal of heat flow gradually returned to the baseline. During the whole process, the temperature of the sample was controlled at 22.76 °C.

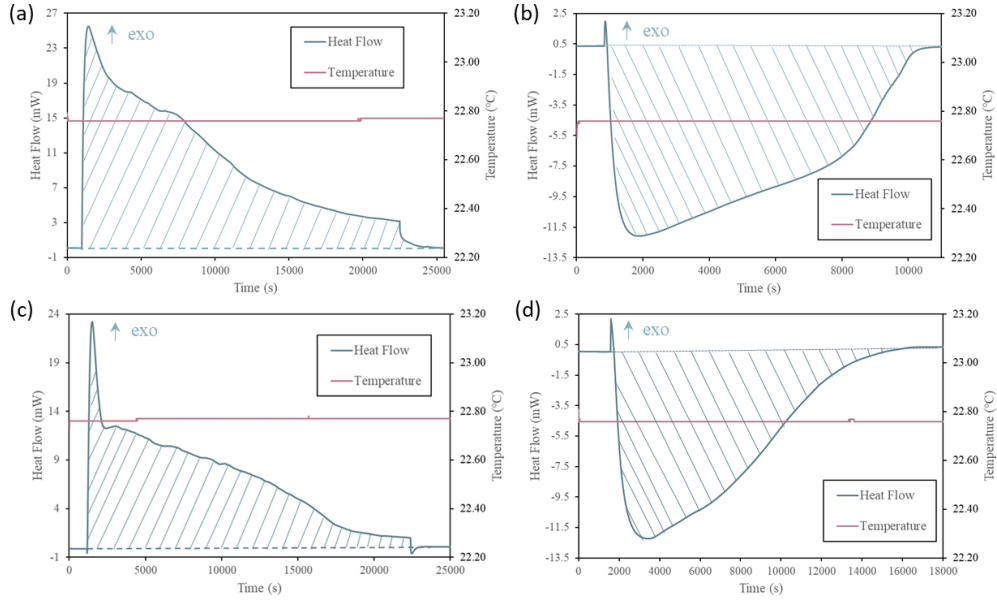


Fig. 4. Typical curves of heat flow over time during (a) hydration and (b) dehydration process of bulk calcium chloride powder and during (c) hydration and (d) dehydration process of composite (here we present the curves of nickel foam-CaCl₂ composite for example).

The quantity of thermal energy Q released/restored during the hydration/dehydration process is estimated as follows:

$$Q(t) = \int_{t_i}^{t_f} [\phi(t) - \phi_{bl}] dt \quad (3)$$

The normalized quantity of thermal energy Q_N released/restored during each cycle is defined as follows:

$$Q_N = \frac{Q}{m_{CaCl_2}} \quad (4)$$

where m_{CaCl_2} is the mass of $CaCl_2$ contained in each sample.

The normalized thermal energy Q_N released during 12 cyclic hydration processes (see Table 1) for bulk $CaCl_2$ salt powder, nickel foam- $CaCl_2$ composite, and aluminum foam- $CaCl_2$ composite are presented in Fig. 5. For the first cycle of 360 min hydration, the bulk $CaCl_2$ powder outperformed the other two composite significantly by reaching 1074.3 kJ/kg^{salt} in terms of thermal energy released during this time range, while for nickel foam- $CaCl_2$ composite, the value was 730.8 kJ/kg^{salt} and 811.0 kJ/kg^{salt} for aluminum foam- $CaCl_2$ composite. Yet, in the following cycles, especially from the 5th cycle, the performance of bulk $CaCl_2$ powder exhibited a clear disadvantage compared to the other two composites. For a hydration time range of 90 min (cycle N°5, 6, 7 and 8), the average Q_N released by nickel foam- $CaCl_2$ composite and by aluminum foam- $CaCl_2$ composite was 705.3 kJ/kg^{salt} and 525.7 kJ/kg^{salt}, which improved 146.1% and 83.5% respectively compared to that of bulk $CaCl_2$ powder (286.5 kJ/kg^{salt}). In the following cycles, for hydration time range of 45 min (cycle N°9, 10, 11), the advantage of composites' performances became increasingly apparent. In particular, the composite with aluminum foam as the matrix released up to 351.2 kJ/kg^{salt} for the average Q_N of these 3 cycles, which was 4.9 times more than the amount released by bulk $CaCl_2$ powder (72.0 kJ/kg^{salt}), while the nickel foam- $CaCl_2$ also released up to 4.0 times more thermal energy than the bulk salt powder, which was 288.3 kJ/kg^{salt}. Then, in the last cycle, we reproduced exactly the same experimental conditions of the first cycle, which means the samples were re-humidified for 360 min as in the first cycle, to investigate how the samples performed after 11 hydration/dehydration cycles. Results showed that nickel foam- $CaCl_2$ composite provided a Q_N of 903.9 kJ/kg^{salt}, which improved 23.7% compared to that of the first cycle, while aluminum foam- $CaCl_2$ composite provided a Q_N of 834.1 kJ/kg^{salt} in the 12th cycle, which slightly increased by 2.8% compared to the first cycle. In contrast, Q_N of bulk $CaCl_2$ powder decayed by 63.2% after 11 cycles, by providing a Q_N of only 395.8 kJ/kg^{salt} in the 12th cycle.

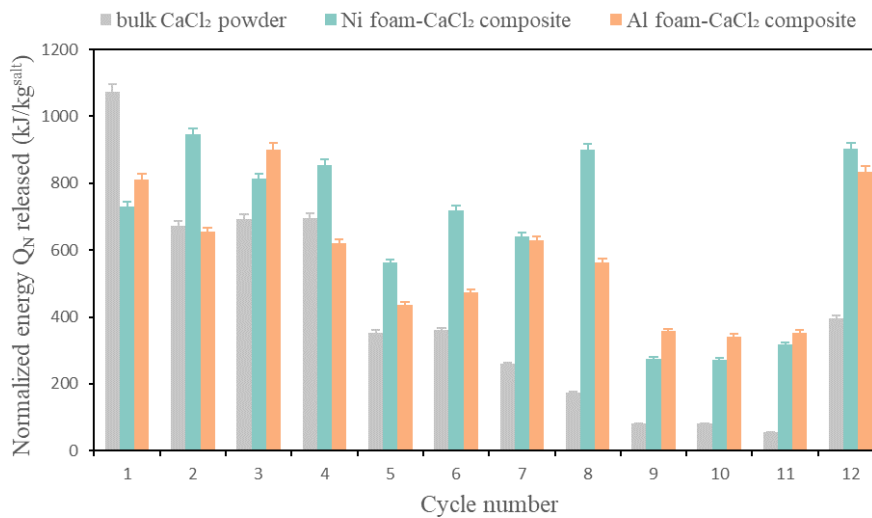


Fig. 5. Normalized thermal energy released during 12 cyclic hydration/dehydration processes of nickel foam- $CaCl_2$ composite, aluminum foam- $CaCl_2$ composite, and bulk $CaCl_2$ powder.

In order to better compare the trends in performance of these 3 kinds of samples during the 12 hydration/dehydration cycles by eliminating the influence on Q_N due to the difference in hydration time during different cycles, the values of normalized thermal energy Q_N released for each kind of sample were calculated and compared for the first 45 minutes of each humidification as presented in Fig. 6. Although bulk CaCl_2 powder provided the highest Q_N in the first cycle, it is clearly seen that the performance of bulk CaCl_2 powder decreased from the 2nd cycle and continued to decline sharply after 6 cycles, resulting in a performance degradation of 78.5% at the 12th cycle compared to the 1st cycle (from 265.6 to 57.2 kJ/kg^{salt}). While the performance of both composites was found to be much more stable. Both composites provided a lower Q_N compared to the bulk CaCl_2 powder in the first cycle, however, in the following cycles, the composites showed superior performance and enhanced cycling stability. After 12 cycles, Q_N improved from 179.3 to 299.6 kJ/kg^{salt} for nickel foam- CaCl_2 composite and from 225.6 to 346.5 kJ/kg^{salt} for aluminum foam- CaCl_2 composite, which indicates a 67.1% and a 53.6% increase in Q_N , respectively. Moreover, there wasn't any tendency for Q_N to degrade for both composites after these 12 cycles. The results also demonstrate that for the first 45 min of the 12th cycle, Q_N of nickel foam- CaCl_2 composite and of aluminum foam- CaCl_2 composite improved substantially to 5.2 and 6.1 times that of bulk CaCl_2 powder.

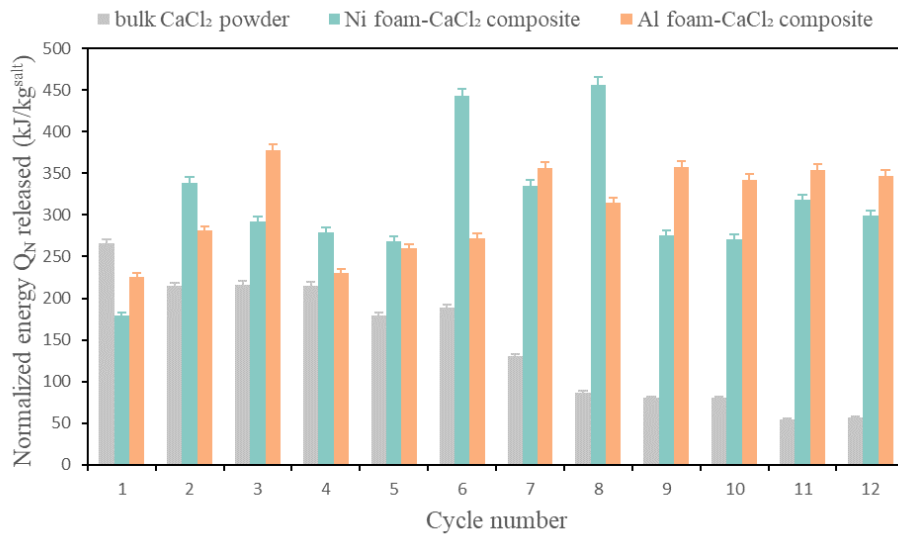


Fig. 6. Normalized thermal energy released during the first 45 min of each humidification process for 12 hydration/dehydration cycles of nickel foam- CaCl_2 composite, aluminum foam- CaCl_2 composite, and bulk CaCl_2 powder.

The results obtained from the long hydration/dehydration cycles provided us with fundamental data allowing for comparison of the cyclic thermal properties for bulk CaCl_2 powder, nickel foam- CaCl_2 composite, and aluminum foam- CaCl_2 composite.

For bulk CaCl_2 powder, though it provided relatively high thermal energy in the first hydration process, Q_N dropped substantially and continuously during the following humidification cycles due to deliquescence and agglomeration, inducing specific surface loss, which yielded poor cyclic stability [46, 64].

Conversely, on the one hand, for nickel foam- CaCl_2 composite and aluminum foam- CaCl_2 composite, there was no degradation in terms of Q_N after 12 cycles of hydration/dehydration.

On the other hand, surprisingly, both of them showed a significant increase in Q_N in the last and longest cycle of hydration (N°12) compared to the first longest cycle (N°1). In general, except for the first cycle, the thermal energy released by the composites compared to that by the bulk salt was substantially improved in all the rest of the cycles, and this advantage tended to increase with the number of cycles. This clearly demonstrate that the composites combining a hygroscopic salt (such as calcium chloride) dispersed in metal foam as a host matrix exhibited excellent cyclic stability and superior thermal energy storage capability compared to bulk CaCl_2 powder. This improvement is undoubtedly attributable to the use of the metal foam as a porous matrix, which might have preserved the salt particles from agglomeration and compaction effects related to deliquescence and swelling during hydration cycles. As a result, the metal foam matrix might have preserved the specific reaction surface and provided more efficient pathways for mass and heat transfer.

We define $\phi_{p,N}$ the normalized peak maximum heat flow during the hydration process as follows:

$$\phi_{p,N} = \frac{\text{Max}[\phi(t)]}{m_{\text{CaCl}_2}} \quad (5)$$

In the case of composites, the value of $\phi_{p,N}$ is considered to be strongly influenced by the spatial distribution, size, and morphology of salt crystals deposited in the composite. As for bulk salt, it is also considered to be influenced by the degree of dispersion and agglomeration of the salt crystals. In both cases, the value of $\phi_{p,N}$ can be seen as an implicit indicator of the heat and mass transfer efficiency of each sample. Fig. 7 illustrates the $\phi_{p,N}$ of hydration process for these three kinds of samples during 12 hydration/dehydration cycles. For all samples, the trends of $\phi_{p,N}$ were almost the same as these of the respective Q_N during hydration over 12 cycles. For the bulk salt, the average of $\phi_{p,N}$ was $64.4 \text{ W/kg}^{\text{salt}}$ and the maximum $\phi_{p,N}$ for the 12 cycles appeared during the first hydration process. $\phi_{p,N}$ continued to decrease in the following cycles and reached by the last cycle a degradation of 73.5%, as compared to its maximum value obtained at the first cycle. This indicates that during the initial phase of the experiment, the bulk salt particles were more uniformly dispersed in the sample vessel, providing a larger specific surface area for hydration. As the cycles progressed, the bulk salt underwent deliquescence and agglomeration, resulting in a decreasing surface area and thus reducing its cycling stability in terms of Q_N , as shown in Fig. 6 and in terms of $\phi_{p,N}$, as shown in Fig. 7. For nickel foam- CaCl_2 composite and aluminum foam- CaCl_2 composite, the average of $\phi_{p,N}$ over 12 cycles were $140.2 \text{ W/kg}^{\text{salt}}$ and $139.9 \text{ W/kg}^{\text{salt}}$ respectively, which was about 2.2 times higher than that for the bulk salt. In addition, no evidence of $\phi_{p,N}$ degradation was detected in either composite throughout the 12 cycles and the minimum $\phi_{p,N}$ was that of the first hydration for both composites, resulting in an increase of 27.5% and 51.9% in terms of $\phi_{p,N}$ in the last cycle for nickel foam- CaCl_2 composite and aluminum foam- CaCl_2 composite, respectively.

The conclusions drawn from Fig. 7 regarding $\phi_{p,N}$ correspond well to the previous conclusions regarding Q_N , which illustrate the influence of the distribution and deposition morphology of the salt particles on the cyclic stability and energy storage properties, validating the superiority offered by open-cell metal foams as a host matrix for the composites.

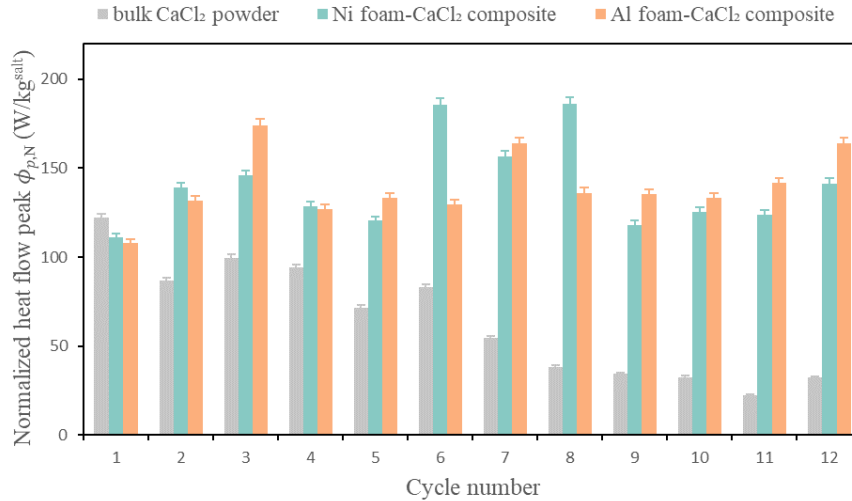


Fig. 7 Normalized peak maximum heat flow of hydration process during 12 hydration/dehydration cycles of nickel foam-CaCl₂ composite, aluminum foam-CaCl₂ composite, and bulk CaCl₂ powder.

These results also suggest that during the first hydration cycle, the topological parameters (spatial distribution and morphology) of the salt particles deposited in the composites have evolved in a way improving the thermochemical performances. We can also infer that if the topological evolutions continued in the following cycles, it did not affect the performances of the composites in thermochemical terms (Q_N) related to the specific reaction area, nor in kinetic terms ($\phi_{p,N}$) related to mass transfer capability, which means the portion of accessible open pores in the metal foam did not decrease during the cycles, thus leading to a better performance in terms of cyclic stability and quantity of thermal energy released.

3.2.2. Analysis of short hydration/dehydration cycles

In order to better verify the superior performance of the metal foam-CaCl₂ composites compared to that of bulk CaCl₂ salts, 2 repetition experiments were performed for each kind of sample. The experiment consisted of 6 cycles, as described in section 2.4.2, where the samples were humidified for 45 minutes per cycle with other experimental conditions remaining unchanged, and the normalized thermal energy Q_N released during the process was then calculated and analyzed. Experimental errors were analyzed according to the data acquired through repetition tests.

Fig. 8 illustrates that from the 2nd cycle onwards for both composites Q_N was significantly higher than that of bulk CaCl₂ powder. For cycle N^o2 to N^o6, the improvement of normalized thermal energy Q_N released by aluminum foam-CaCl₂ composite to bulk CaCl₂ powder was between 77.9% to 129.6%, while for nickel foam-CaCl₂ composite, the improvement was between 54.5% to 85.9% (see Fig. 9). For nickel foam-CaCl₂ composite, Q_N varied from 256.7 kJ/kg^{salt} (N^o1) to 314.3 kJ/kg^{salt} (N^o6), which increased by 22.4%, with the highest Q_N appeared in the 4th cycle (323.2 kJ/kg^{salt}). As for aluminum foam-CaCl₂ composite, Q_N increased from 299.3 kJ/kg^{salt} (N^o1) to the highest of 389.5 kJ/kg^{salt} (N^o6), achieving an improvement of 30.1%. In general, the results confirm an improved cyclic stability of the composites in comparison with bulk CaCl₂ powder. After the first hydration, it can be seen that for both composites Q_N stabilized or slightly increased, while it decreased for bulk CaCl₂ powder. These opposite evolutions relate to microstructural changes of the reactive material

which we will further discuss in section 3.3.

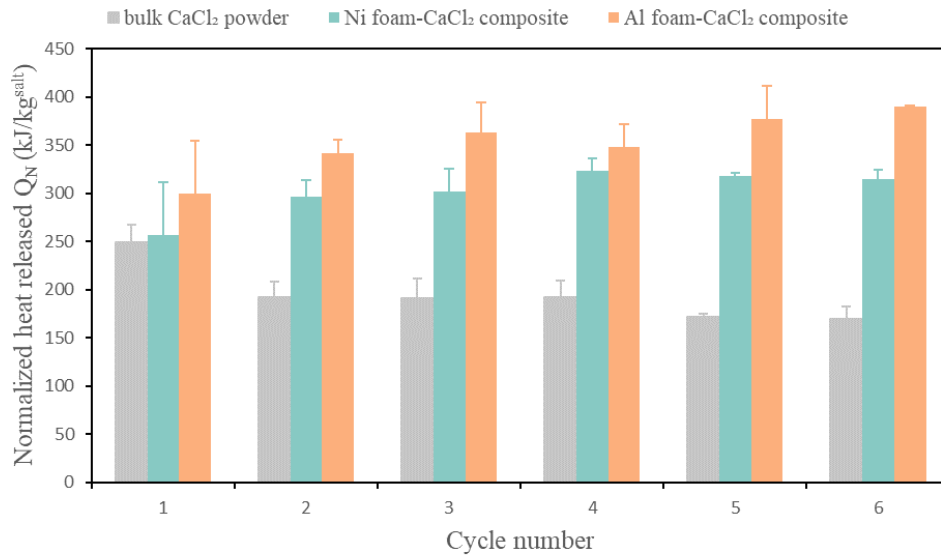


Fig. 8. Normalized thermal energy released during 6 short hydration/dehydration cycles (45 min hydration) of nickel foam-CaCl₂ composite, aluminum foam-CaCl₂ composite, and bulk CaCl₂ powder.

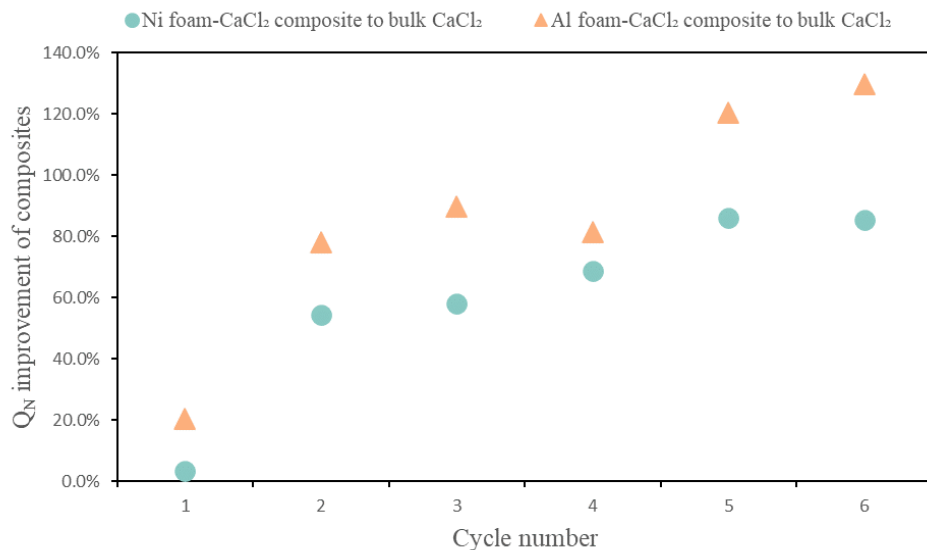


Fig. 9. Q_N improvement of composites compared to bulk CaCl₂ powder during 6 short hydration/dehydration cycles.

The results of the short hydration/dehydration cycle experiments once again verified the superior quantity of thermal energy stored/released and enhanced cycling stability of composites compared to bulk salt powder under the same experimental conditions. Compared to the previous experimental results concerned with long cycles, we found that after the first cycle of hydration, the bulk salt did not show strong degradation of performances during the short hydration/dehydration cycles. This observation is consistent with time-dependent microstructural evolution, related to the swelling of hydrated salt crystallites and corresponding agglomeration/compaction, which naturally depends on the number and duration of cycles.

For the composites, we found performance trends similar to those shown during the long

1 cyclic process (Fig. 6). In both cyclic processes, the Q_N was minimum for the first cycle, then
2 increased for the following. It is therefore presumed that the metal foam-salt composites need
3 a certain duration of time to optimize their thermochemical properties. This time-lapse
4 represents a maturation period, during which the microstructure evolves owing to topological
5 changes concerning salt hydrate deliquescence, swelling, agglomeration, and local
6 redistribution within the metallic foam.
7

8 This interpretation is strengthened by the fact that the thermal energy released during the first
9 hydration of the composites varied relatively widely for different samples under the same
10 experimental conditions. For example, the error in Q_N of the first hydration was 21.5% for the
11 nickel foam-CaCl₂ composite and 18.4% for the aluminum foam-CaCl₂ composite.
12 Conversely, during the subsequent cycles, the error for different samples decreased
13 considerably and the thermochemical properties became relatively stable. The larger
14 differences in thermochemical performances during the initial hydration might be due to
15 differences in the initial distribution of salt crystallites in the metal foam, resulting from the
16 preparation process. Such differences are expected to vanish after the maturation period of the
17 first hydration, owing to salt hydrate deliquescence redistribution within the metallic foam
18 network.
19

20 In section 3.3, we will specifically address the possible reasons and explanations for the
21 superior performance and the enhanced cyclic stability of the designed composites by
22 characterization based on in situ ESEM hydration/dehydration cycling test.
23

24 **3.2.3. Apparent energy density of Ni/Al foam-CaCl₂ composite**

25 In this part, the apparent energy density of two kinds of metal foam-CaCl₂ composites using
26 nickel foam and aluminum foam are compared. We define the apparent energy density E_d as
27 follows:
28

$$29 E_d = \frac{Q}{V_{sample}} \quad (6)$$

30 where Q is the quantity of thermal energy released/restored during the hydration/dehydration
31 process as defined in equation (3) and V_{sample} is the total volume of the composite sample.
32

33 Fig. 10 presents the energy density of both composites in hydration/dehydration cycles. It is
34 clear that the E_d of nickel foam-CaCl₂ (48.5 wt%) composite exceeded that of aluminum
35 foam-CaCl₂ (21.0 wt%) composite in both long and short hydration/dehydration cycles
36 (experimental procedure described in section 2.4.2). In long hydration/dehydration cycles (as
37 shown in Fig. 10a), as hydration duration Δt_{hydr} differed from 45 min to 360 min for
38 different cycles, the E_d of Ni foam-CaCl₂ composite was between 82.3 MJ/m³ (N°10 - Δt_{hydr}
39 of 45 min) and 286.9 MJ/m³ (N°2 - Δt_{hydr} of 180 min), while the E_d of Al foam-CaCl₂
40 composite was between 78.5 MJ/m³ (N°10 - Δt_{hydr} of 45 min) and 206.8 MJ/m³ (N°3 -
41 Δt_{hydr} of 180 min). During the 12th cycle (Δt_{hydr} of 360 min), Ni foam-CaCl₂ composite
42 provided a E_d of 274.2 MJ/m³, improved by 43% compared to that of Al foam-CaCl₂
43 composite, which provided a E_d of 191.5 MJ/m³. The results of short cycles (Δt_{hydr} of 45
44 min) shown in Fig. 10b once again confirmed the superiority of Ni foam-CaCl₂ composite
45 over Al foam-CaCl₂ composite in terms of energy density. E_d provided by Ni foam-CaCl₂
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composite was between 76.6 MJ/m³ (N°1) and 96.4 MJ/m³ (N°4), with an average E_d of 90.0 MJ/m³ for 6 cycles. While E_d provided by Al foam-CaCl₂ composite was between 65.8 MJ/m³ (N°1) and 84.6 MJ/m³ (N°6), with an average E_d of 76.8 MJ/m³ for 6 cycles. An improved E_d of 17% was obtained for Ni foam-CaCl₂ composite compared to Al foam-CaCl₂ composite for 6 cycles of hydration/dehydration process with Δt_{hydr} of 45 min for each cycle. The summary of E_d of both composites for all cycles are shown in Table 3.

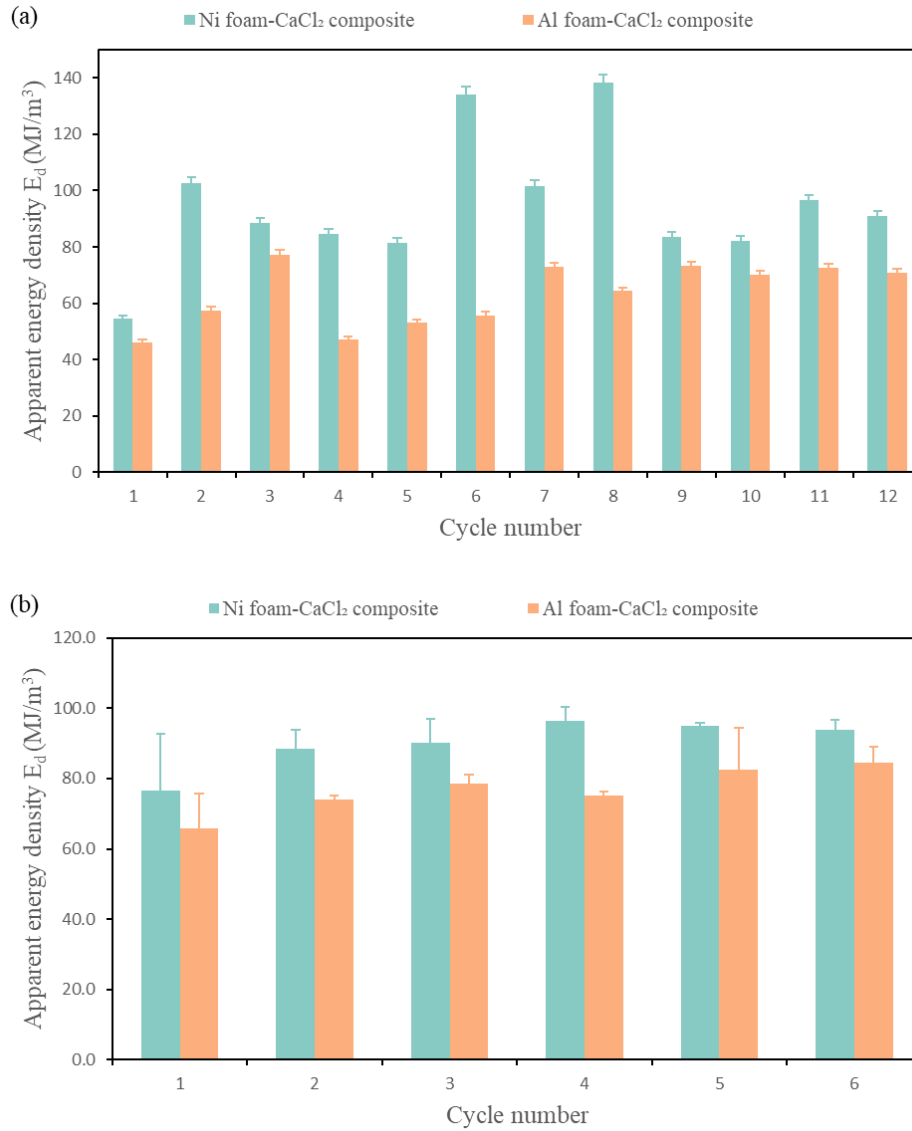


Fig. 10. Energy density of nickel foam-CaCl₂ composite and aluminum foam-CaCl₂ composite in (a) 12 hydration/dehydration cycles of different hydration duration and (b) 6 hydration/dehydration cycles of 45 min hydration duration.

Obviously, the difference in apparent energy density of these two composites mainly derives from the different morphology and microstructure of the host matrix (metal foam), especially the porosity. The porosity of nickel foam used is about 96%, while the porosity is about 40% for aluminum foam. The difference in porosity greatly affected the content of salt deposited in the metal foam, thus affecting the apparent energy density.

From the perspective of cyclic stability and thermochemical energy density, the most effective thermochemical composite is the nickel foam-CaCl₂. Such composite, based on

nickel foam as host matrix offers the highest porosity proportion as well as appropriate pore size and would be a promising choice for thermochemical heat storage systems. However, the source, cost, and mechanical properties should also be taken into account. Not to mention the corrosion problem of metal [65-67]. These aspects still need further exploration.

Cycle No.	Apparent energy density E_d (MJ/m ³)			
	Ni foam-CaCl ₂ composite		Al foam-CaCl ₂ composite	
	Long cycle	Short cycle*	Long cycle	Short cycle*
1	221.7	76.6	186.2	65.8
2	286.9	88.4	150.4	74.0
3	246.8	90.1	206.8	78.5
4	259.0	96.4	142.3	75.3
5	170.4	94.9	100.1	82.4
6	218.4	93.7	108.8	84.6
7	194.1	-	144.3	-
8	272.8	-	129.5	-
9	83.6	-	82.1	-
10	82.3	-	78.5	-
11	96.5	-	81.3	-
12	274.2	-	191.5	-

*Average value calculated from repetition tests.

Table 3 Apparent energy density results of both composites for all cycles.

3.3. Performance improvement mechanism of composites

In this section, we present results obtained during hydration/dehydration cycling tests, performed with in situ ESEM, in order to investigate the topological behavior of salt hydrates in the composite. The aim is to observe possible redistribution of salt during hydration processes and to provide explanations for the performance improvement in terms of cyclic stability and quantity of thermal energy released during hydration of metal foam-salt composites compared to bulk salt powder.

As introduced in section 2.5, the experimental conditions of cyclic hydration/dehydration tests performed in the differential scanning calorimeter were reproduced during in situ ESEM observation with images recorded every 5 seconds. Fig. 11 illustrates the continuous evolution of the sample surface as the relative humidity increased from 0 to approximately 54% under an isothermal condition for the nickel foam-CaCl₂ composite. In the region of interest (ROI) presented in Fig. 11, it is clearly seen that not all the open pore spaces of the metal foam matrix were filled with salt at the initial state, which ensured that the water vapor could pass smoothly through the metal foam and thus come into contact with the salt crystallites distributed within the metal foam, thereby promoting the hydration process and releasing the thermal energy. Besides the open pores of the metal foam, we observed the entrapped salt particles at the initial state with 0.4% RH, where the cross-sections of the metal foam struts protruding from the salt layer were also clearly visible, as shown in Fig. 11a. By adjusting the chamber pressure, we control the relative humidity for the hydration and dehydration process. As the hydration process began, the salt on the surface of the sample gradually absorbed water with increasing humidity. When the RH reached about 45%, we observed the part of the salt layer denoted by the dashed line shrieked and formed a hole (see Fig. 11b). This hole formed on the surface salt layer continued to expand as the RH increased to 51.4% (see the part circled by the dashed line in Fig. 11c). When the relative humidity reached 54.7%, which was approximately the same condition as in the cyclic hydration/dehydration tests for thermal

analysis (54% RH), we stopped raising the vapor pressure in the SEM chamber. The sample was kept under this condition for about 30 minutes, during which no further changes in the ROI were detected. Fig. 11d showed that compared to lower RH conditions, the hole in the salt layer continued expanding before the RH reached 54.7%, which is also indicated by the higher proportion of metal foam struts that can be observed under the surface salt layer compared to the former states. As no further changes in the ROI were detected under this condition for 30 min, it may be considered that the hydration reaction was completed and the subsequent redistribution of salt hydrates within the metallic foam network has been achieved. This suggests that once a certain hydration degree is reached, the redistribution and relocation process of the surface salt layer stops. This in turn means that hydration kinetics are very fast and may be achieved within a few minutes.

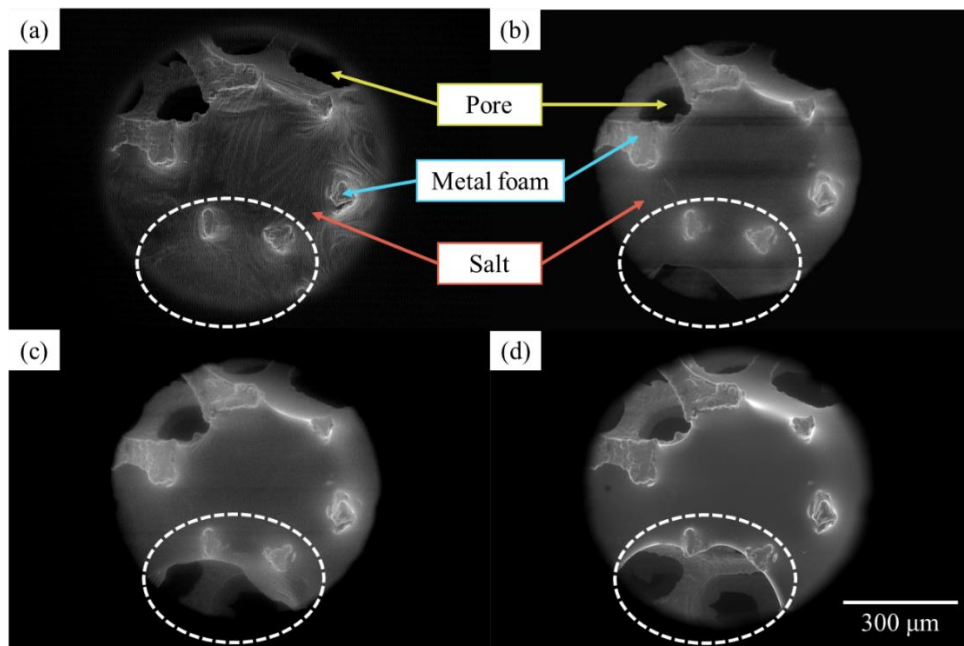


Fig. 11. GSED images (x107 magnification) of the nickel foam- CaCl_2 composite sample surface with the relative humidity increasing from (a) 0.4%, (b) 45.3%, (c) 51.4%, to (d) 54.7% under isothermal condition. The redistribution of salt during the variation of humidity is circled in a dashed line.

A different nickel-based composite was observed at higher magnification, with a smaller horizontal field width (HFW) of 250 μm chosen as the region of interest (ROI), in order to focus on the evolution of the interfaces between the metal foam and the salt layer during hydration/dehydration cycles (Fig. 12). At the initial state with a relative humidity of 0.4%, as shown in Fig. 12a, a layer of dry salt crystals could be observed tightly surrounding the strut of the metal foam. The fine fissures formed during sample preparation and drying for preservation were visible on the surface of the salt layer. At this point, there were no observable open pores of the metal foam in the ROI. Then the vapor pressure was raised in the SEM chamber for the relative humidity to increase. During the increase of relative humidity, the deliquescence of the salt was observed at approximately 30% RH, which is in accordance with the deliquescence relative humidity (DRH) of hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) at about 23 $^\circ\text{C}$ [68-70]. Fig. 12b illustrates the ROI after 30 min's stabilization when RH reached 54.7%. In this figure, the deliquescence of the salt layer after the first hydration process can be clearly seen. It is also worth noting in Fig. 12b that the salt which was originally located in the left area of the ROI, surrounding the strut of metal foam, separated from it along the struts

and redistributed in the host matrix, thus forming a hole in the salt layer revealing the original pores and struts of metal foam (see the part marked in circle). In the next step, the relative humidity was reduced to 0.4% then remained at this RH for 30 min to dry the samples. As shown in Fig. 12c, the salt layer that still surrounded the struts of the metal foam after the first hydration process dehydrated and formed a salt layer with a thickness gradient. Compared to Fig. 12b, the hole formed during the first hydration process remained unchanged (the part marked in circle) and no additional holes in the salt layer were formed in the ROI during this process. The second hydration cycle was then carried out and the ROI after the second hydration process is presented in Fig. 12d. It can be clearly seen that the salt layer was again deliquescent, allowing the salt to flow in the metal foam either along the struts or through the pores. The change in the thickness of the salt layer in the ROI allowed us to see the shape of the metal foam strut (see the mark in blue dashed lines in Fig. 12d). Most notably, another hole was formed in the salt layer in the upper part of the ROI (marked in circles in Fig. 12d), indicating that the salt layer continued to relocate in the metal foam matrix during this second hydration process, as was observed during the first hydration process (shown in Fig. 12b).

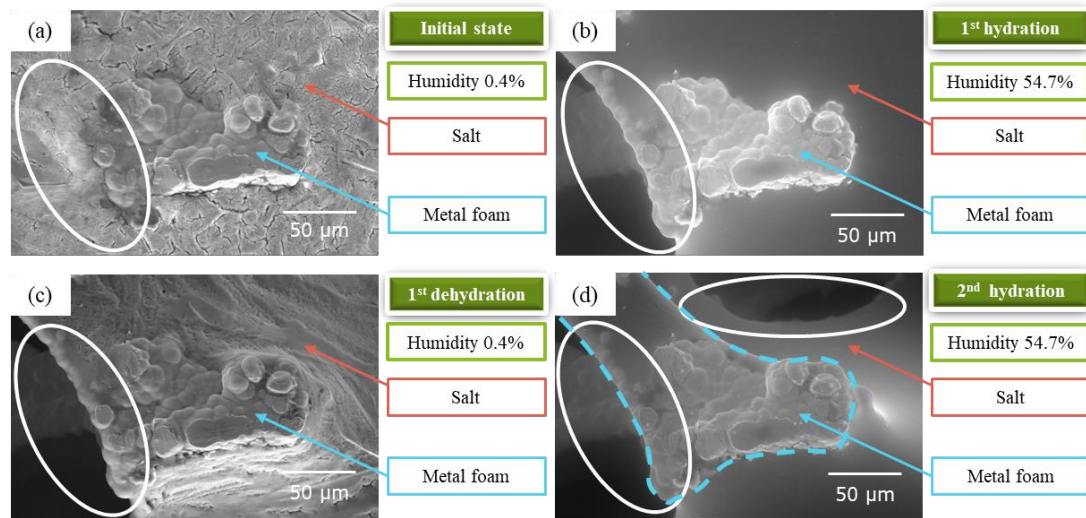


Fig. 12. GSED images (x508 magnification) of the nickel foam-CaCl₂ composite sample surface during 2 hydration/dehydration cycles with (a) the initial state (0.4% RH), (b) after first hydration (54.7% RH), (c) after first dehydration (0.4% RH) and (d) after second hydration (54.7% RH) under isothermal condition. The redistribution of salt during the hydration/dehydration cycles is marked in circle.

Observations from in situ hydration/dehydration cycle tests on nickel foam-CaCl₂ composites show that after sample preparation and drying process, the salt tended to be deposited surrounding the struts of the metal foam pores or in the metal foam cells. The distribution of salt crystallites was irregular, some of the pores of the metal foam were filled, while others remained open. During the hydration process at a constant temperature (approximately 23°C), CaCl₂ became deliquescent when the relative humidity reached about 30%. The resulting gel-like salt flowed along the struts driven by surface tension forces and hence redistributed homogeneously in the metal foam. Most importantly, the redistribution favored restoring the open porosity. According to observation, this reorganization mechanism of the salt may be activated during each hydration process. It can also be inferred that as the number of hydration/dehydration cycles increases, the distribution of salt in the metal foam matrix tends to homogenize the salt dispersion along the metal foam struts, hence reaching a stable topology, with an optimum surface to volume ratio and preserving the interconnections of the

foam porosity.

By observing at different scales, it is noted that not all the deliquescent salt necessarily redistributes during the first hydration process, as shown in Fig. 13. By comparing the initial state (Fig. 13a) and the state after the first hydration process (Fig. 13b), it is clearly observed that the salt completely embedded in a small cell ($< 200 \mu\text{m}$) remained trapped even after hydration and deliquescence. This local behavior is contrasting with observations shown in Fig. 11, where the deliquescent salt massively migrated from a larger cell ($> 300 \mu\text{m}$). However, the smaller cell in Fig. 13 was nearly complete and offered only a cell window to the observation surface, while the large pore shown in Fig. 11 was incomplete and largely opened to the observation surface. These observations indicate the strong role of capillary effects and suggest that the local structure of the foam will control the actual salt redistribution. This aspect highlights the microstructural importance of the metal foam, for instance, the size and the size distribution of the metal foam cells, or the size of the struts and cell windows.

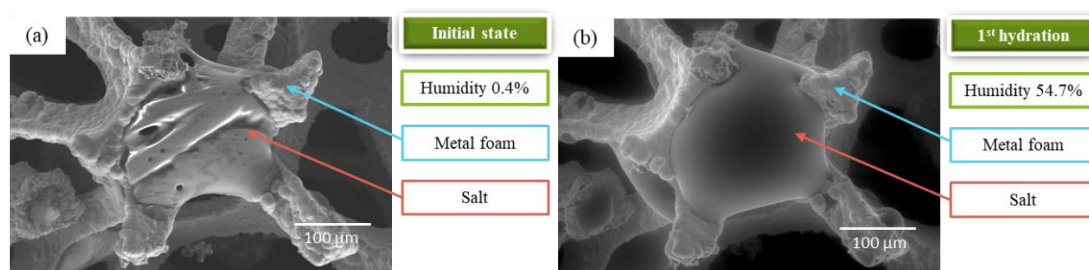


Fig. 13. GSED images (x254 magnification) of the nickel foam- CaCl_2 composite sample surface focused on the interface of salt and metal foam with (a) the initial state (0.4% RH) and (b) after first hydration (54.7% RH).

The conclusions obtained from observations during the in situ hydration/dehydration cycling test give a reasonable explanation and a possible mechanism for the improvements of the composites compared to bulk salt in terms of thermochemical performance. The enhanced performance of the metal foam-salt composite can be partially attributed to the porous structure of the metal foam. On the one hand, the porous matrix serves for salt deposition. On the other hand, the open pores increase the specific reaction area, which facilitates mass and heat transfer while effectively avoiding the degradation of performance due to salt swelling and agglomeration. What's more, thanks to the pore size of the selected metal foam and the proportion of free pores after each cycle, the host matrix ensures that the salt can be relocated and reorganized in the composite even if agglomeration or even deliquescence occurs, which greatly enhances its cyclic stability as well as the mass and heat transfer efficiency. The composite offers a dynamic microstructure, with local topological evolutions during hydration cycles, while allowing the maintenance of statistically stable proportions of interconnected open pores and specific reaction areas. In this case, the global thermochemical performances might remain stable over time. Without the metal foam serving as host matrix, the cyclically swelling salt crystallites would undoubtedly lead to progressive compaction, with loss of open porosity and specific reaction area, which would lead to progressively decreasing thermochemical performances. Actually, these contrasting scenarios for composites and bulk salt powder are wholly supported by our thermochemical measurements (section 3.2).

The observations from the in situ experiments can also explain some of the conclusions drawn from the thermal analysis experiments related to composite performance. In section 3.2, results suggested that for both composites the minimum value of the normalized thermal

1 energy released Q_N during cycles usually occurred at the first hydration process and tended to
2 increase and stabilize in the subsequent cycles. Meanwhile, the experimental data presented in
3 section 3.2.2 showed relatively large errors in Q_N of the first hydration process for both
4 composites during repetition tests on different samples. Based on the in situ ESEM
5 observations, this is possibly due to the differences in the position of salt deposited on the
6 surface of the sample during the preparation and drying process, as well as the percentage of
7 free open pores remaining in the composite after salt deposition. All these factors resulted in a
8 greater variation in performance exhibited by the initial hydration process for different
9 samples. However, as seen in the in situ hydration/dehydration experiment, salts without
10 sufficient structural support provided by the initial deposition location are more likely to
11 relocate after the first cycle of hydration. It can be presumed that as the hydration/dehydration
12 cycle continues, salts continue to relocate and reorganize, thus resulting in a more dispersed
13 and rational deposition in the composite, which increases the specific surface area while
14 leaving more pathways for heat and mass transfer, thus improving and gradually stabilizing
15 the performance of the composites after the first hydration. This mechanism well explained
16 the experimental results mentioned in 3.2, where Q_N was usually at a minimum during the
17 first hydration cycle, and the reduction of the experimental error in the different samples to a
18 reasonable range after a few cycles. This also confirms our conjecture based on the results of
19 the thermal experiments, that the first cycle can be considered as an activation (or maturation)
20 cycle, allowing for an optimum salt redistribution, hence ensuring the most effective salt
21 topology in terms of the specific reaction area, which in turn ensures the stability of the
22 thermochemical heat capacity during further cycling.
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30 In addition, the metallic framework of the metal foam provides improved thermal
31 conductivity and mechanical strength to the overall system. All of the above results indicate
32 that the metal foam-salt hydrate composite introduced in this paper is a suitable and
33 promising thermochemical material.
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37 4. Conclusion

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39 To overcome the drawbacks of pure calcium chloride as thermochemical material, this study
40 presented a newly designed metal foam-salt hydrate composite consisting of open-cell metal
41 foam with a pore size of 350 μm as host matrix and calcium chloride as hygroscopic salt
42 dispersed in the pores for thermochemical heat storage. The aim was to investigate the
43 feasibility of the newly designed composite as a TCM and to compare its performance with
44 that of pure calcium chloride. The main results are shown as follows:
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46

47 (1) A method for dispersion of salt in open-cell metal foam was developed using an
48 oversaturated salt solution and by immersing the metal foam sample in. Intensive and
49 continuous stirring was required to achieve an even distribution of salt. The composite sample
50 should be kept in the oven for more than 48 h at 90 °C before experiments.
51
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53 (2) Metal foam-salt composites showed significant improvement in terms of cyclic stability
54 and quantity of thermal energy released/stored compared to bulk calcium chloride in both
55 long and short hydration/dehydration cycles. For cyclic stability, composites presented a
56 slight increase and stabilization of thermal energy released upon cycles, while salt showed
57 substantial and continuous degradation in performance. For heat released during hydration,
58 composites outperformed considerably the bulk calcium chloride in all cycles, except for the
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1 first cycle, which may be considered as an activation cycle allowing to reach the optimum
2 composite microstructure. The result also indicated that for discharging/charging the same
3 amount of thermal energy, metal foam-salt composites were more efficient than bulk calcium
4 chloride.

5
6 (3) Nickel foam-CaCl₂ composite provided better performance in terms of apparent energy
7 density as compared to aluminum foam-CaCl₂ composite. The difference in energy density of
8 these two composites mainly derives from the different porosity of the host matrix (96% for
9 nickel foam, 40% for aluminum foam). The difference in porosity greatly affects the salt
10 content deposited in the metal foam, thus affecting the energy density.

11
12 (4) After confirming the feasibility of the designed metal foam-salt composite as TCM and its
13 improvement in thermochemical performance compared to that of bulk salt powder, the
14 performance enhancement mechanism of the composite was investigated by in situ ESEM
15 hydration/dehydration cycling test. The observation indicated that the open-cell metal foam
16 with a pore size of 350 μm provided sufficient salt deposition sites, allowing the salt to be
17 relocated and reorganized in the metal foam cells even after deliquescence during the
18 hydration process while preventing the swelling and agglomeration of salt, which effectively
19 increased the cyclic stability of the composite. In addition, large open volumes and multiple
20 flow paths provided by the metal foam increased the specific reaction surface, favored heat
21 and mass transfer, and ensured no volume change even if swelling and agglomeration of salt
22 occurred. Moreover, metal foam provided high thermal conductivity. All of the above-
23 mentioned advantages led to a significant improvement in the thermochemical performance of
24 the composite compared to that of bulk salt powder.

25
26 In conclusion, the metal foam-salt hydrate composite developed in our work is suitable and
27 promising for thermochemical energy storage, offering both mechanical and thermochemical
28 advantages. On the one hand, the metallic foam ensures structural integrity allowing for
29 flexible industrial handling of thermochemical storage units. On the other hand, the metal
30 foam guarantees the microstructural stability of the reactive material, hence preserving an
31 economically durable life span of the composite. At last, the thermochemical composites
32 presented in this work have a low environmental footprint. The reactive salt hydrates are
33 environmentally friendly and allow for total recycling along with the metal foam. Moreover,
34 this work helps to open up innovative possibilities for research in sorption thermal energy
35 storage systems and also helps to understand the thermochemical performance improvement
36 mechanism of the composite thermochemical material.

37 38 39 40 41 42 43 44 45 46 47 **Acknowledgments**

48
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54 55 56 57 58 59 **References**

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Highlights

- Composite material based on metal foam and CaCl_2 for thermochemical heat storage is developed.
- Cyclic stability and heat released during hydration are significantly enhanced.
- Evolution of thermochemical performance and improvement mechanism are revealed.
- Offering both mechanical and thermochemical benefits for thermal energy storage.

Cover letter

Dear Editorial Board,

We wish to submit the enclosed manuscript entitled “Newly designed metal foam-salt hydrate composite for thermochemical energy storage” for consideration by *Applied Energy*. We confirm that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere, in whole or in part. We wish to publish this manuscript for the following reasons:

Thermochemical heat storage systems based on the sorption mechanism between water vapor and hygroscopic salts are considered to be a promising technology. However, hygroscopic salts have drawbacks such as swelling and agglomeration of the crystalline salt particles during hydration/dehydration cycles, which progressively leads to decreasing specific reaction surface and kinetics of heat and mass transfer, thus resulting in poor cyclic performance and stability. A family of composite sorbents named Selective Water Sorbents (SWS) have been studied to alleviate the limitations mentioned above, with hygroscopic salts and host matrices with nanoscale pore size (< 50 nm). Despite the high energy density, problems related to inappropriate charging temperature, low thermal conductivity and possible leakage of the salt solution after deliquescence have impeded its large-scale applications.

The novelty of our work is the development of an original SWS composite, based on open-cell metal foam with pore size of 350 μm as host matrix, containing calcium chloride as hygroscopic salt dispersed in the pores. An open-cell metal foam host matrix improves the heat and mass transfer kinetics thanks to the porous structure and the high thermal conductivity, and offers additional advantages related to elevated mechanical strength, which would ensure mechanical resistance of the composite.

The experimental results showed that the composite presented significant improvement in thermochemical performance compared to that of bulk calcium chloride powder in hydration/dehydration cycles. For cyclic stability, composites presented a slight increase and stabilization of thermal energy released upon cycles, while salt showed a substantial and continuous degradation of 78.5% in performance after 12 cycles. For heat released, composites outperformed considerably the bulk calcium chloride in almost all cycles. At the 12th cycle, the heat released of composites improved substantially to 5~6 times that of bulk calcium chloride powder. Observations by in situ environmental scanning electron microscope (ESEM) hydration/dehydration cycles demonstrated that swelling and deliquescence induce moderate redistribution of salt hydrates within the metal foam while preserving the essential open porosity of the matrix. It efficiently prevents extensive salt agglomeration and loss of specific reaction area, which explains the amelioration of the composite’s thermochemical properties and their cyclic stability.

In conclusion, the metal foam-salt hydrate composite developed in our work is suitable and promising for thermochemical energy storage, offering both mechanical and thermochemical advantages.

This work opens up innovative possibilities for research in sorption thermochemical energy storage systems. That’s way we believe that this manuscript fits the aims and scope of *Applied Energy*. Therefore, if we could have the honor of publishing this work in *Applied Energy*, we would greatly appreciate the opportunity to share and discuss this research with all other readers of this journal.

To answer other questions indicated in the Guide for authors, 1) the paper is more appealing to a scientific audience. 2) I’m available as a reviewer for at least three other articles for *Applied Energy* during the current year.

If you require any additional information regarding our manuscript, please do not hesitate to contact me via the resources below. We greatly appreciate your time and consideration.

Sincerely,

Yutong Liu

Ecole Polytechnique

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