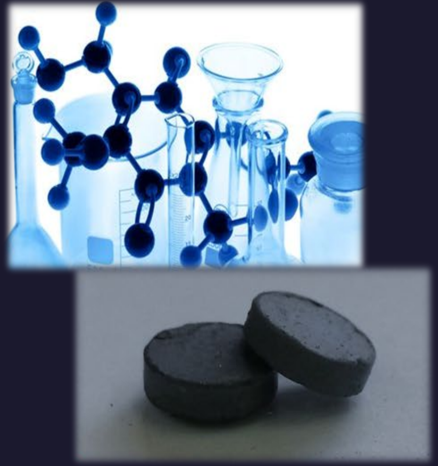
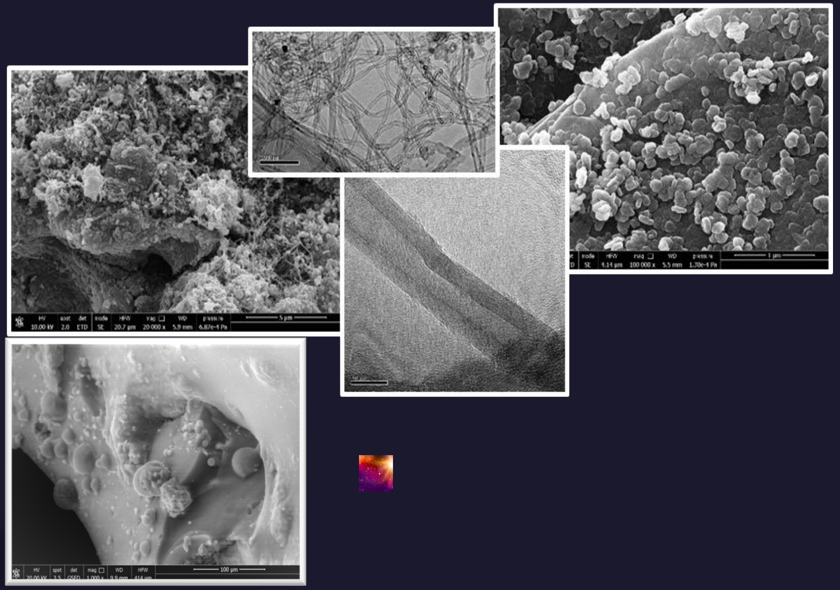
EINDHOVEN UNIVERSITY OF TECHNOLOGY

EIRES SYMPOSIUM
Thermochemical Energy Storage
March 8th 2023, Eindhoven, The Netherland

University of Messina





Synthetic approaches to efficiency enhancement of materials for thermochemical energy storage

Prof. Candida Milone, PhD

Outlines

- **Thermochemical Materials for middle-temperature ranges**
  - $Mg(OH)_2$ /Carbon hybrids
  - Metal doping of $Mg(OH)_2$
- **Thermochemical Materials for low-temperature ranges**
  - Confinement of $LiCl\cdot H_2O$ in a vapor-permeable foam
  - Towards Organic Salt Hydrates with more resistance towards deliquescence

About $Mg(OH)_2$

- $Mg(OH)_2$ is a suitable TCM for storing heat at low-medium temperature (250-400 °C)
- Low cost largely available material
- Non-toxicity of the reactants and products

$$Mg(OH)_{2\ (s)} \leftrightarrow MgO_{\ (s)} + H_2O_{\ (v)}$$

$$Q = \pm\ 1389\ \mathrm{kJ/kg}_{Mg(OH)_2}$$

Drawbacks

Poor heat transfer properties of the reactants ($Mg(OH)_2$ and MgO)

→ Decrease the overall conversion

Cohalescence of the MgO product which leads to grain growth and loss of pore volume

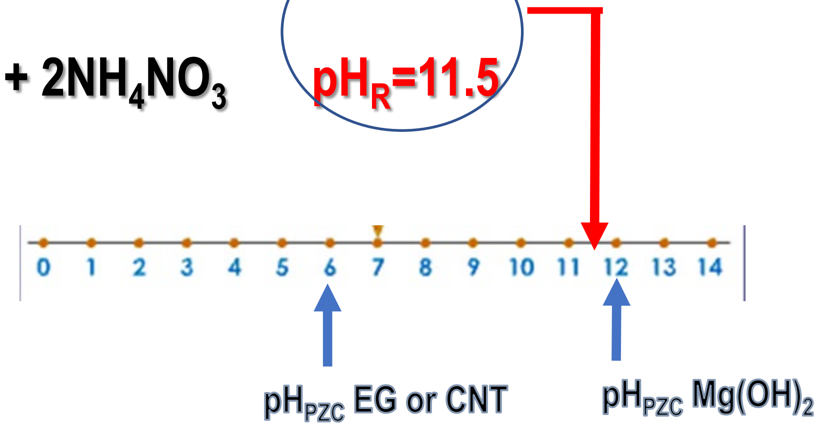
→ Poor durability to the charging/discharging cycles

$Mg(OH)_2$ /Carbon hybrids

Deposition precipitation of **Magnesium Hydroxide over thermal conductive Carbonaceous support**

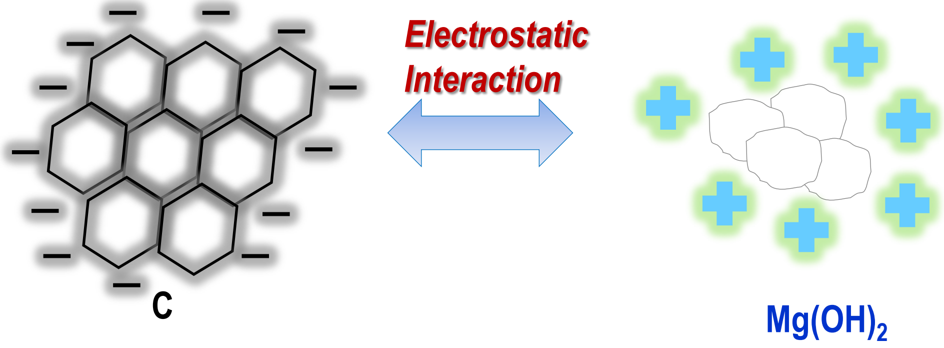
- **Expanded Graphite (EG)**
- **Carbon Nanotubes (CNTs)**

$$Mg(NO_3)_2 + 2NH_4OH \xrightarrow[\text{CNTs}]{\text{EG or}} Mg(OH)_{2\,(s)} + 2NH_4NO_3 \qquad pH_R=11.5$$



•What we expect

- Improvement dispersion of $Mg(OH)_2$ on the carbonaceous support
- Increase of the exposed active phase
- Improvement of the heat transfer properties of the storage medium
- Reduction of the MgO sintering during the dehydration reaction

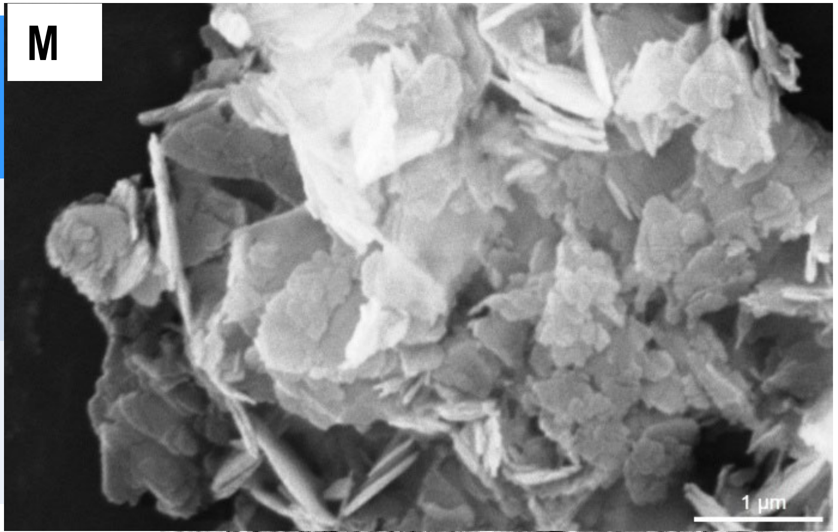


$Mg(OH)_2$ /Carbon hybrids

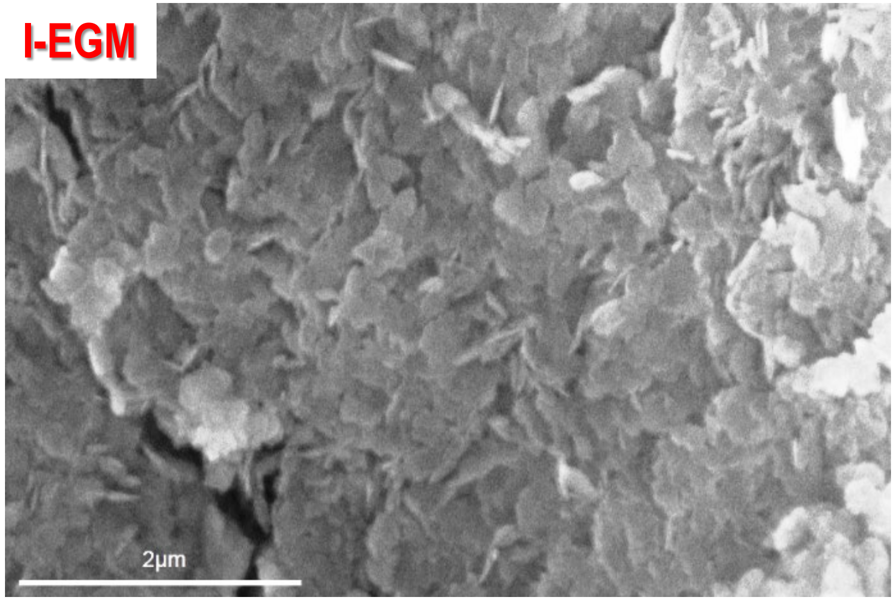
$Mg(OH)_2$ and Expanded Graphite hybrid

Code	***Composition***	***Synthesis method***	***$Mg(OH)_2$ (wt.%)***
M	$Mg(OH)_2$	precipitation	100
I-EGM	$Mg(OH)_2$-EG	impregnation	50
DP-EGM	$Mg(OH)_2$-EG	deposition-precipitation	50

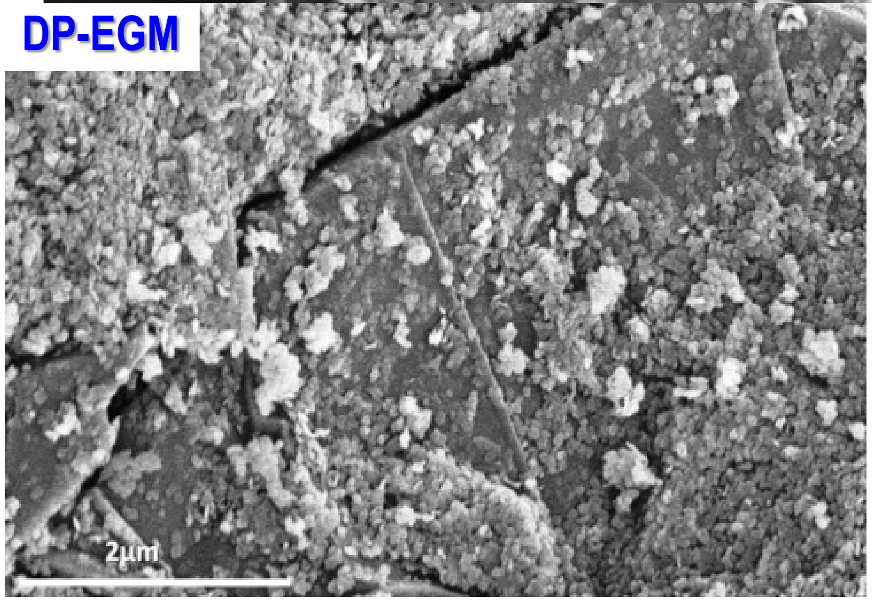
M



I-EGM



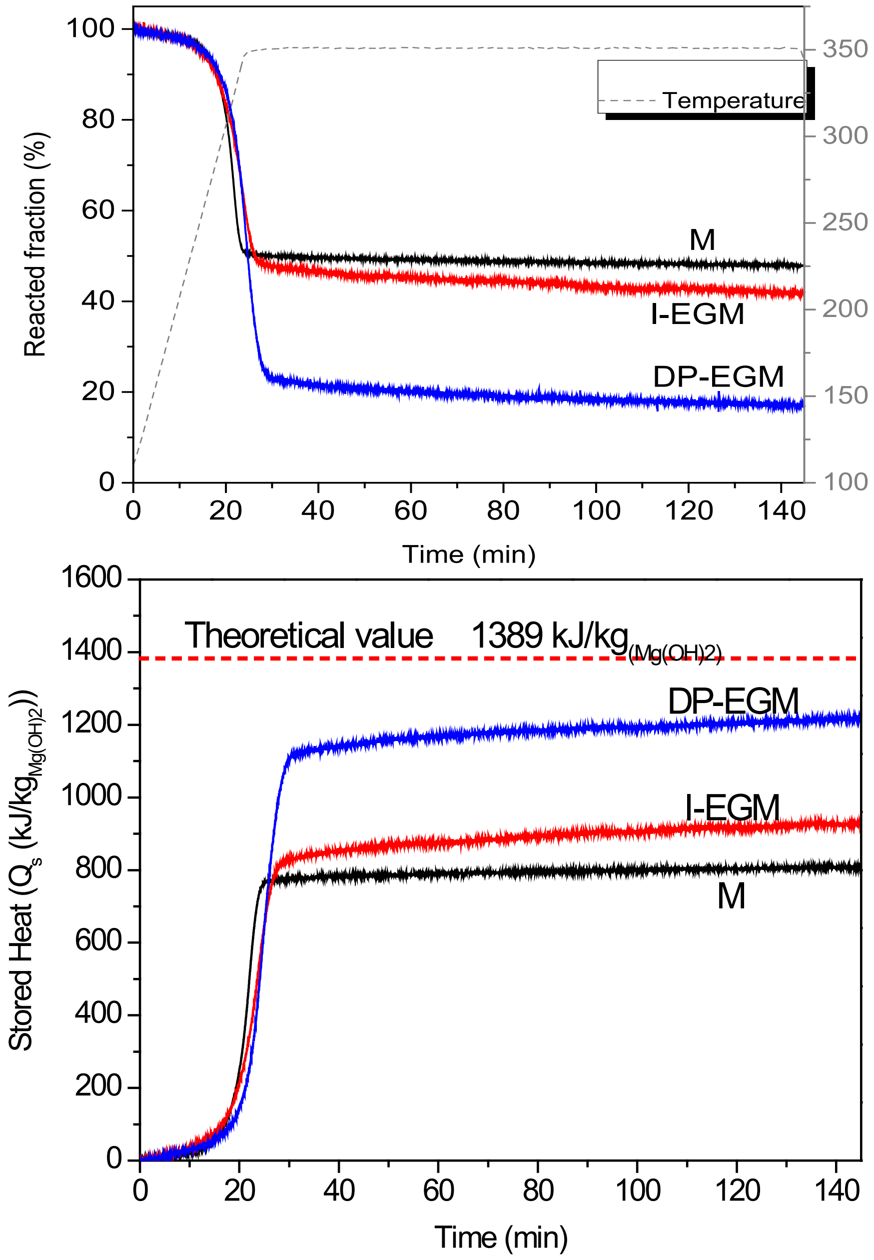
DP-EGM



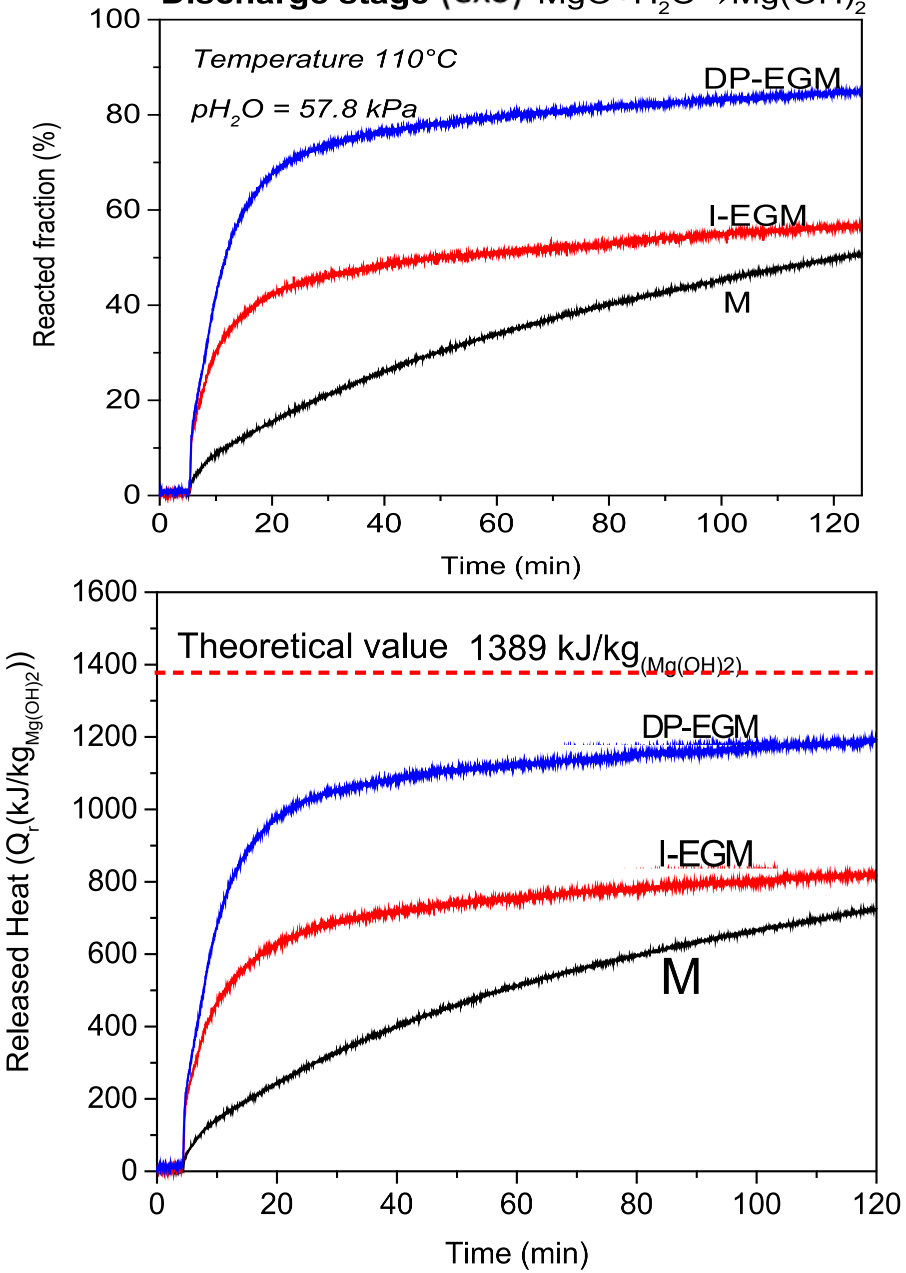
C. Milone et al. Applied Energy 162 (2016) 31–39

$Mg(OH)_2$ /Carbon hybrids

Charge stage (endo): $Mg(OH)_2 \rightarrow MgO + H_2O$



Discharge stage (exo) $MgO + H_2O \rightarrow Mg(OH)_2$



$Mg(OH)_2$ /Carbon hybrids

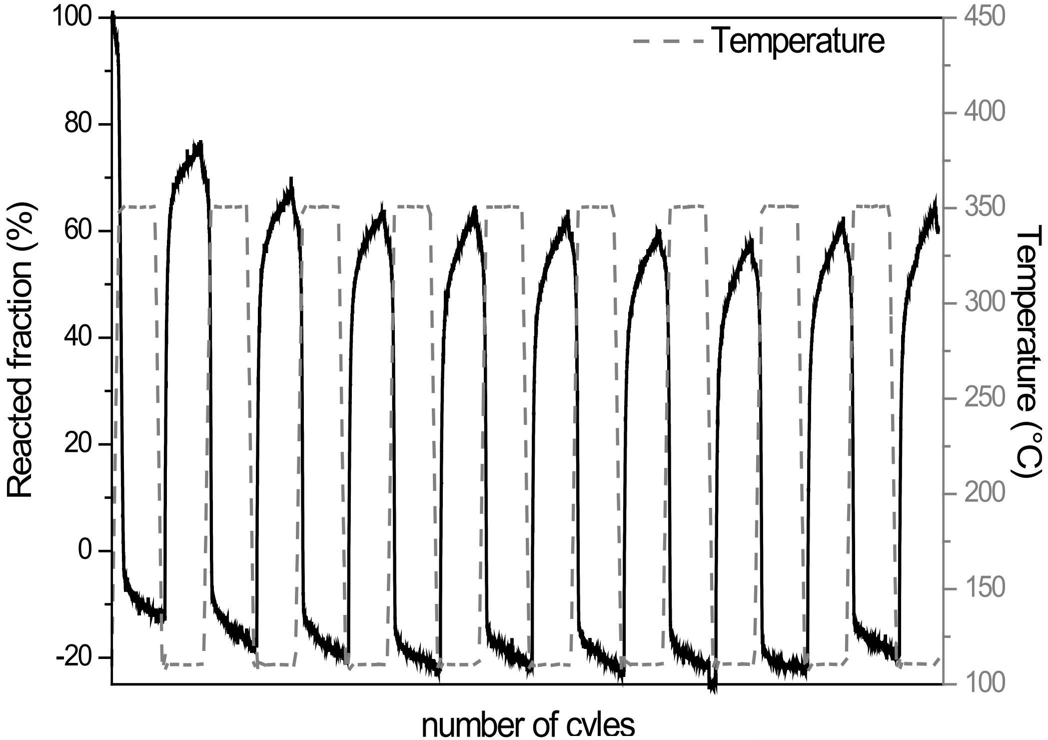
The best performance of DP-EGM with respect to I-GM samples can be ascribed to :

a) the smaller $Mg(OH)_2$ particle size which in turn increases the exposed active phase then the conversion;

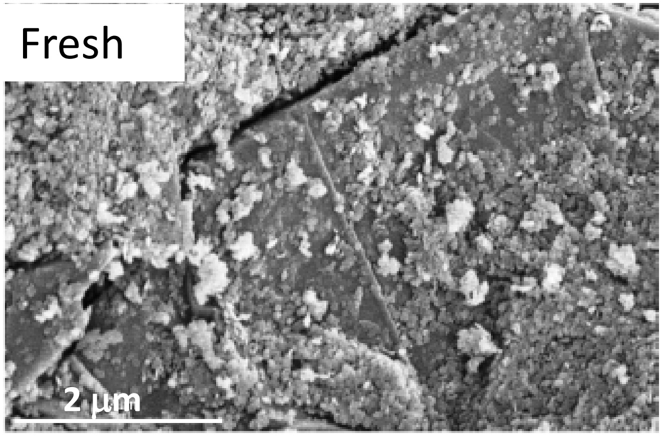
b) the loosely packed layer of $Mg(OH)_2$ over EG surface which favors the H_2O diffusion

Mg(OH)$_2$ /Carbon hybrids

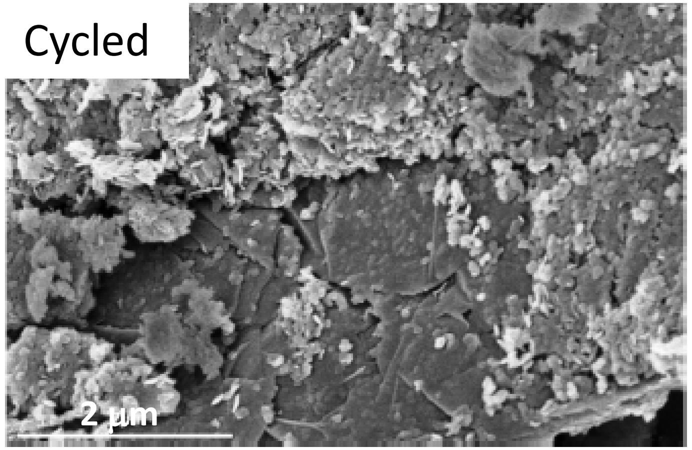
DP-EGM Cyclability



Fresh



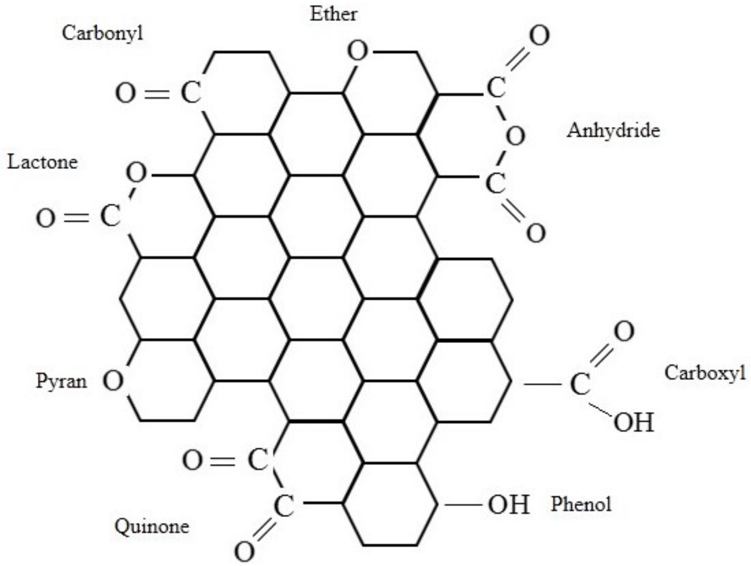
Cycled

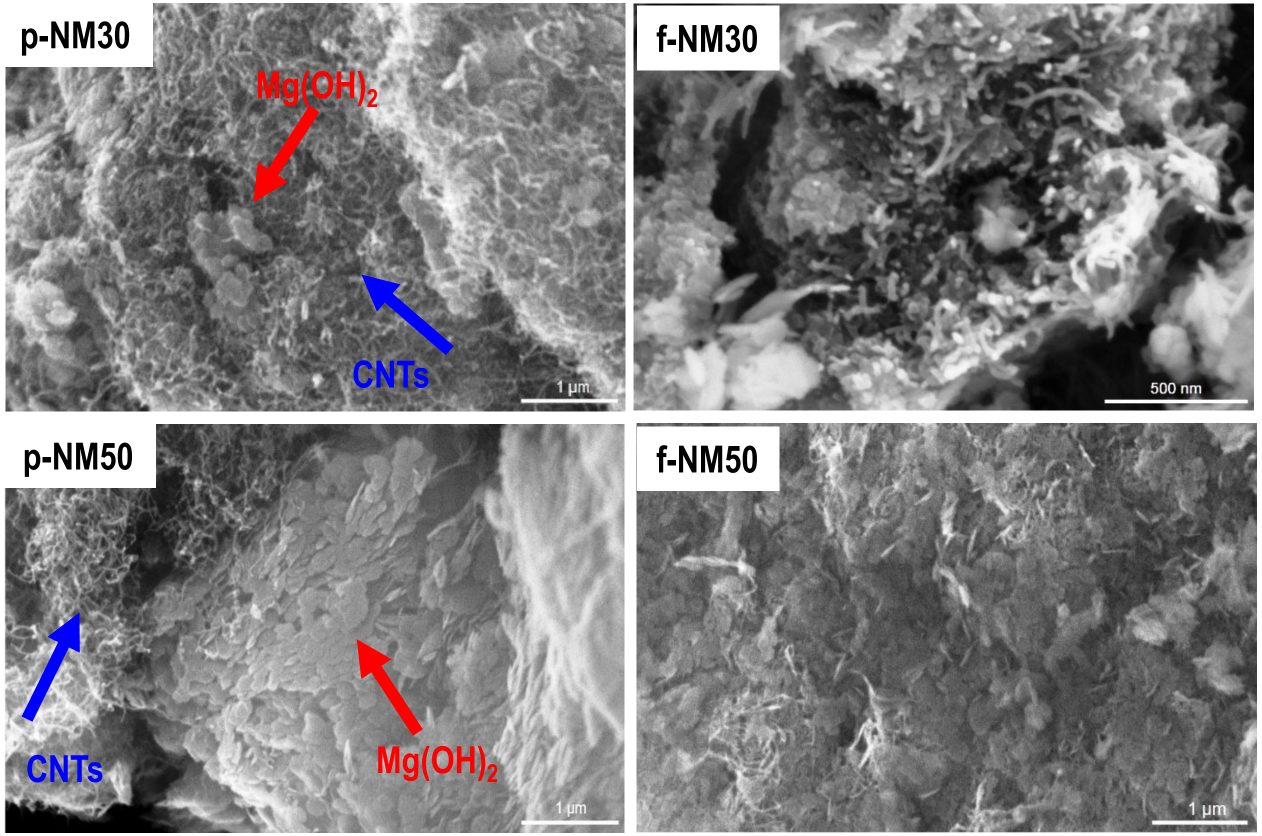


$Mg(OH)_2$ /Carbon hybrids

$Mg(OH)_2$-Carbon nanotubes CNTs hybrids prepared by DP

Code	*CNTs type*	*$Mg(OH)_2$ (wt.%)*
M	-	100
p-NM50	pristine	52.0
f-NM50	functionalized	50.5
p-NM30	pristine	35.5
f-NM30	functionalized	32.4





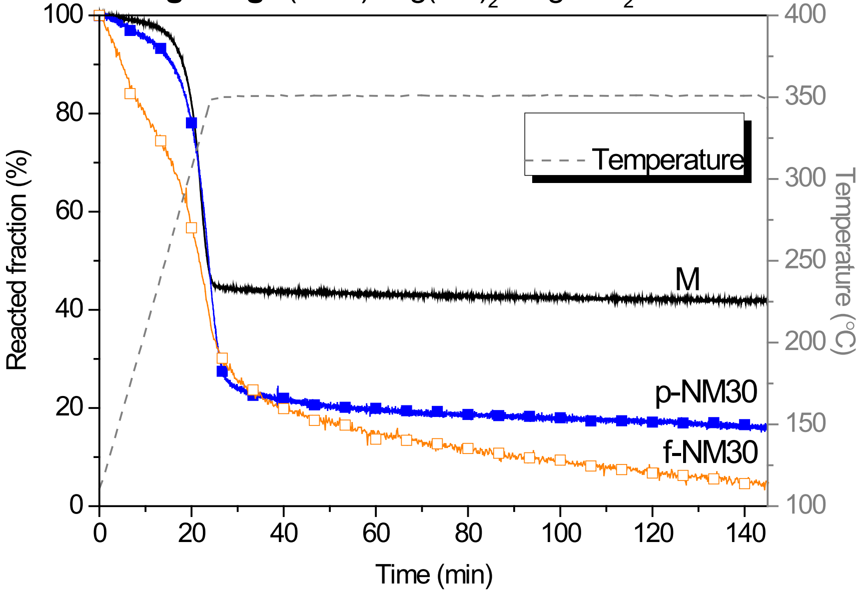
C. Milone et al. / Applied Energy 181 (2016) 232–243

$Mg(OH)_2$ /Carbon hybrids

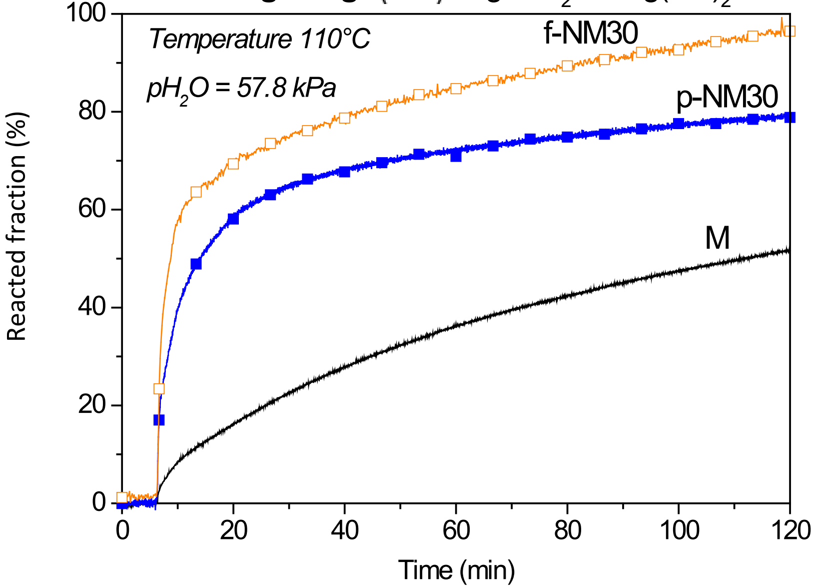
Thermochemical performance

Samples Code	$Mg(OH)_2$ (wt.%)	Dehydration conversion (%)	Hydration conversion (%)
M	100	51.9	49.9
p-NM50	52.0	76.2	71.0
f-NM50	50.5	85.9	81.4
p-NM30	35.5	83.5	79.9
f-NM30	32.4	95.2	96.5

Charge stage (endo): $Mg(OH)_2 \rightarrow MgO+H_2O$

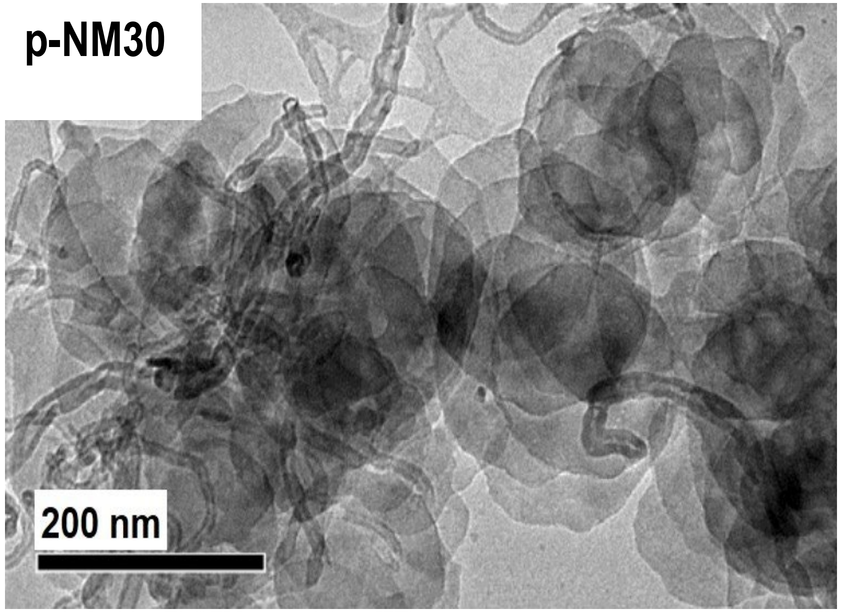


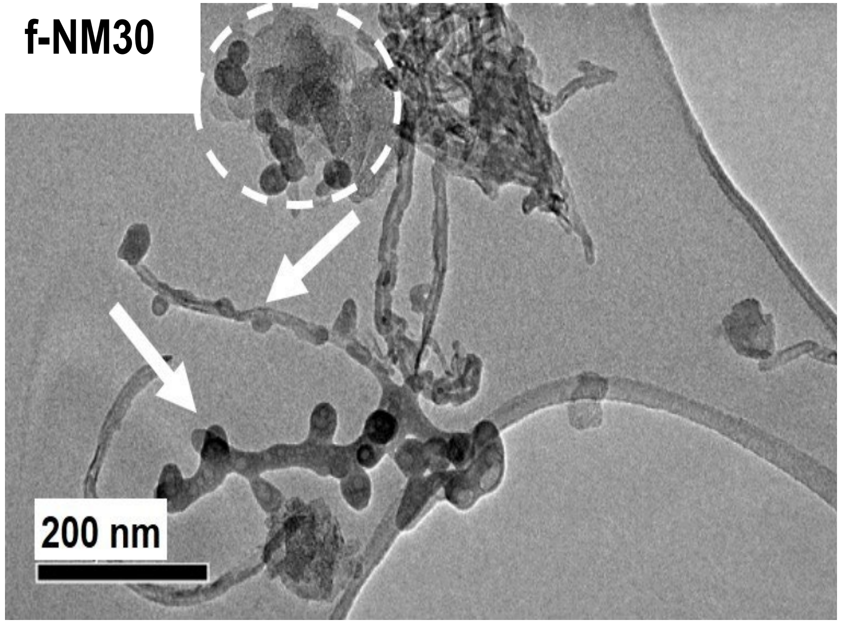
Discharge stage (exo): $MgO+H_2O \rightarrow Mg(OH)_2$



Mg(OH)$_2$ /Carbon hybrids

TEM analysis

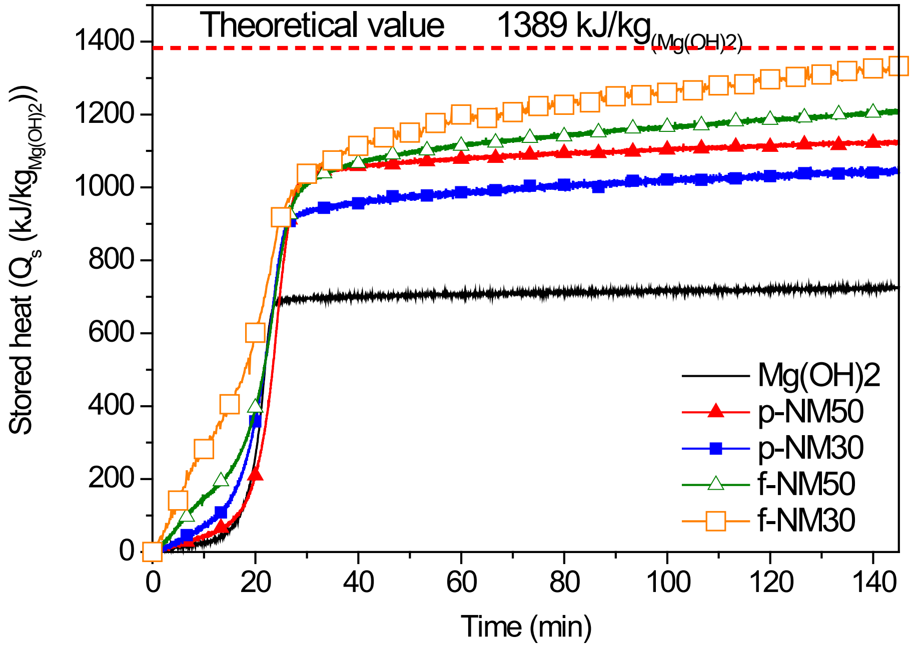


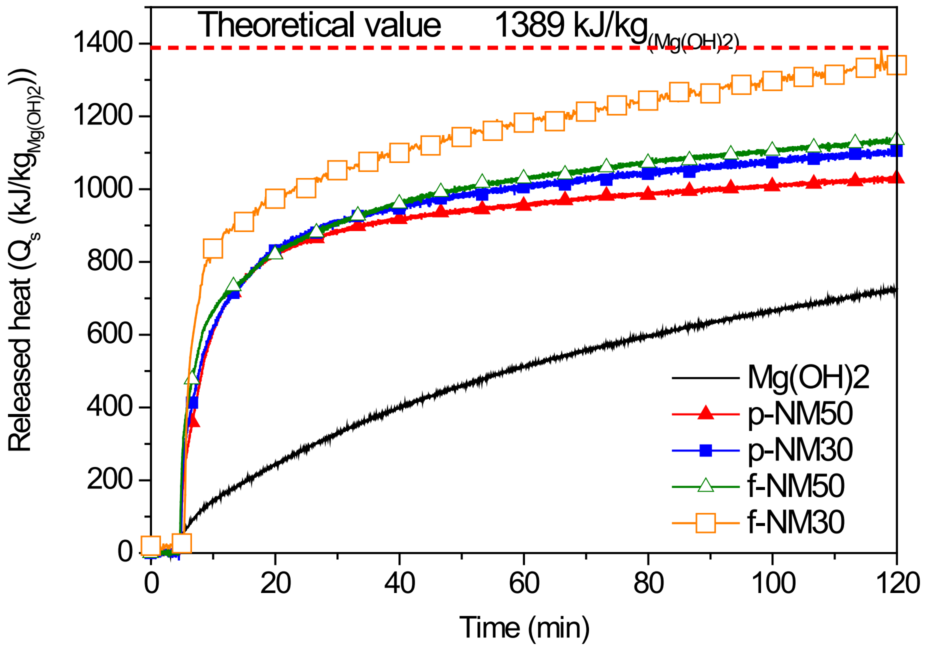


- ✓ In case of p-NM30 sample Mg(OH)$_2$ particles precipitate as self-standing roundish platelet with irregular contour.
- ✓ In f-NM30, Mg(OH)$_2$ deposits on f-CNTs and grows on forming a coral-like morphology (white arrow); it is also evident the presence of some Mg(OH)$_2$ agglomerates (white circle).
- ✓ It also should be noted that as an effect of functionalization a significant lowering of Mg(OH)$_2$ particle size occurs

$Mg(OH)_2$ /Carbon hybrids

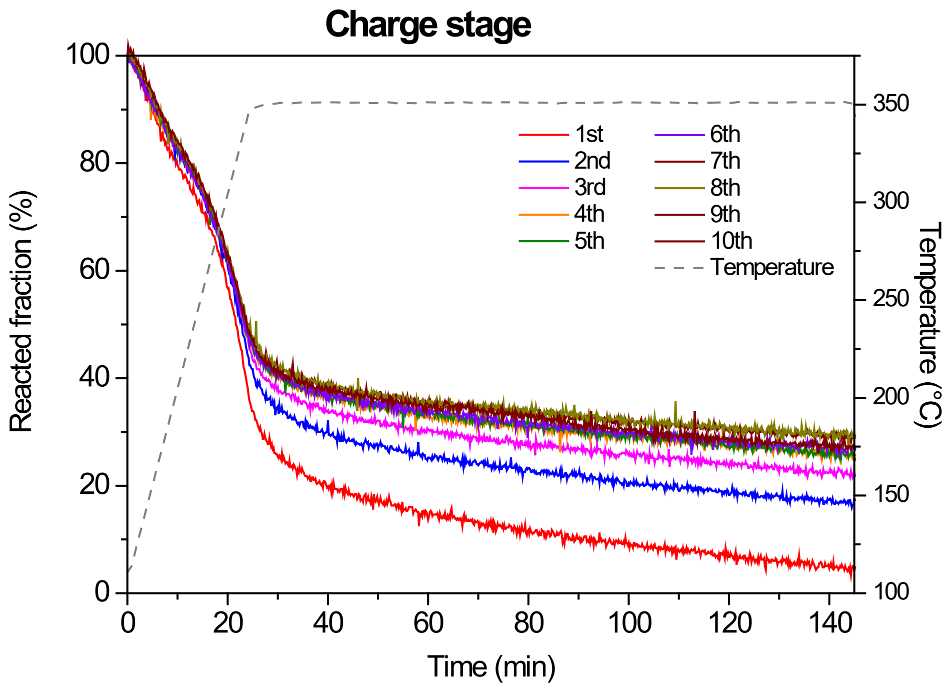
Heat storage/output capacities

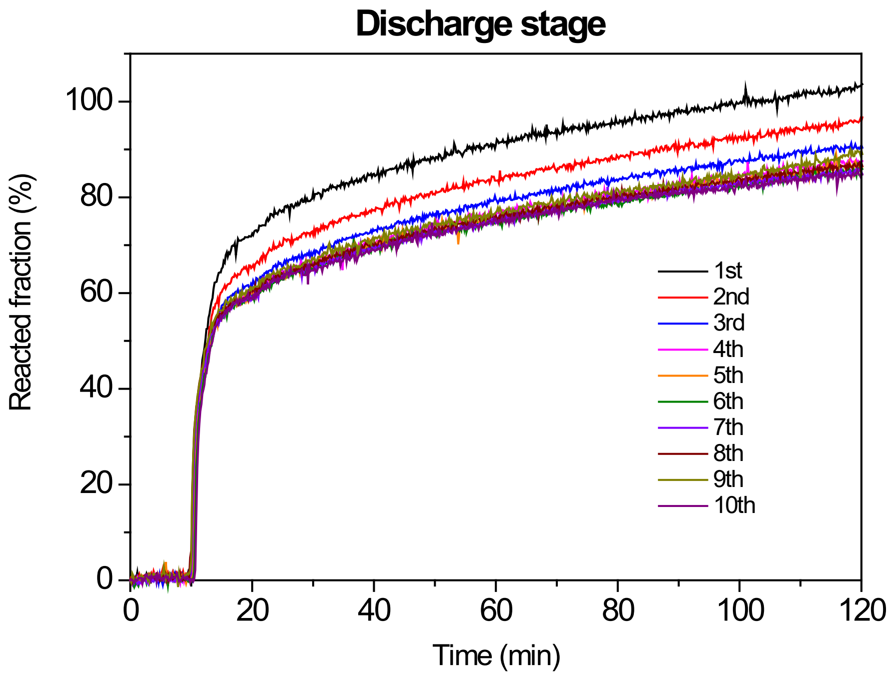


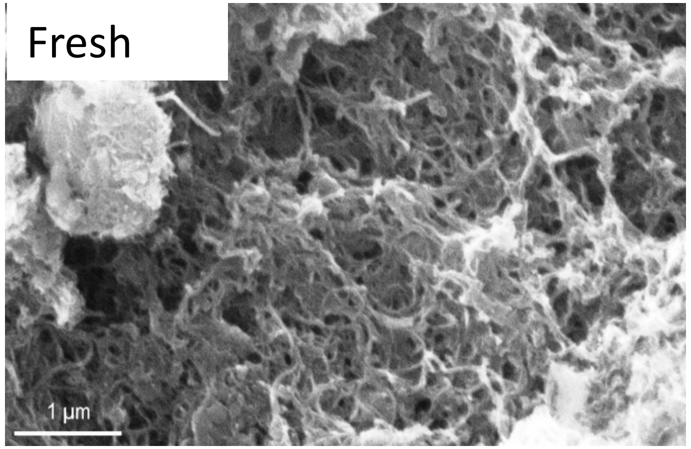


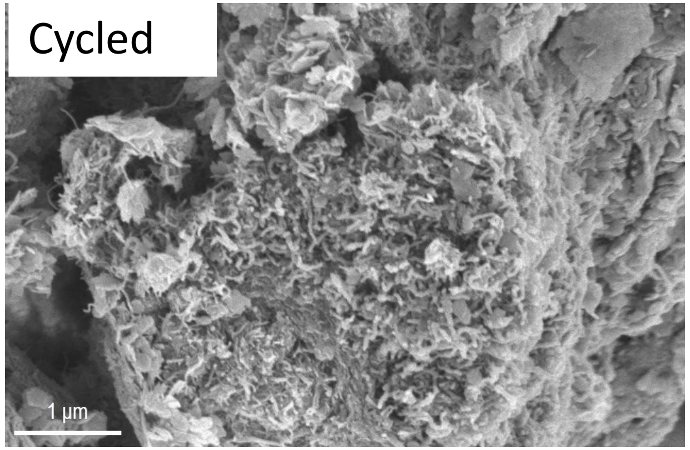
$Mg(OH)_2$ /Carbon hybrids

f-NM30 Cyclability


Charge stage


Discharge stage





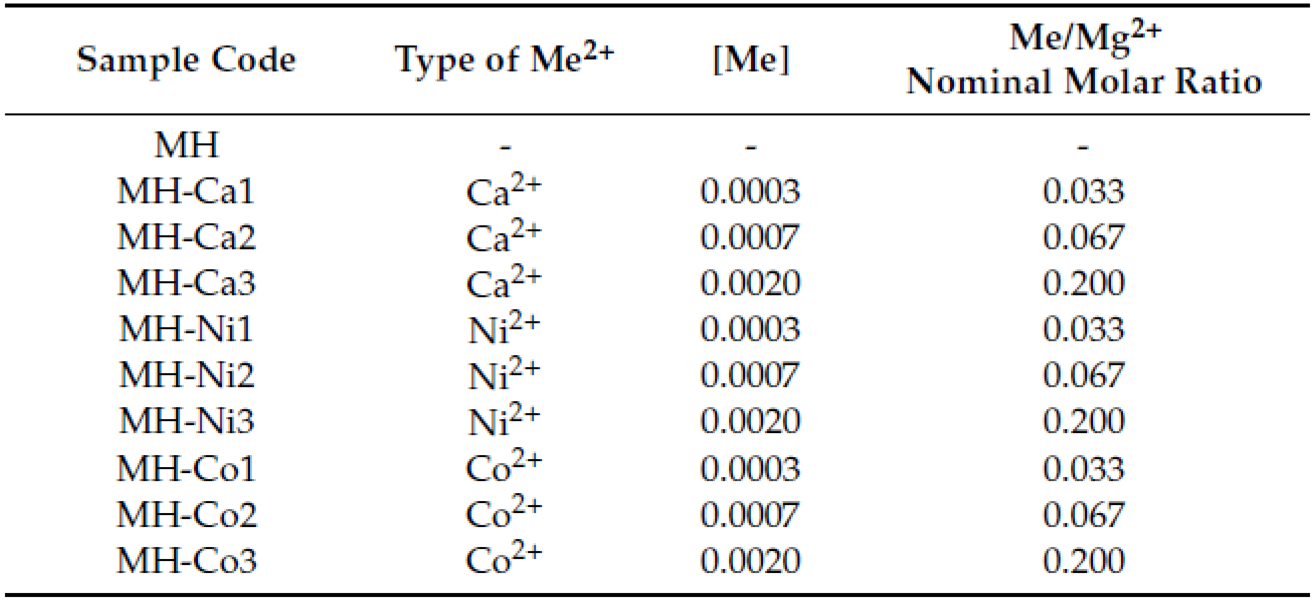
Metal doping of $Mg(OH)_2$

The purpose of this work is to investigate the influence of metal (**Ca^{2+}, Co^{2+} and Ni^{2+}**) doping in $Mg(OH)_2$ synthesis on its structural and morphological properties and consequently on its thermochemical behavior.

Me^{2+}	Ionic radius (pm)
Ca^{2+}	100
Mg^{2+}	72
Ni^{2+}	69
Co^{2+}	65

Materials preparation : Precipitation

$$Mg(NO_3)_2 + 2NH_4OH \xrightarrow{Me^{2+}} Mg(OH)_{2\,(s)} + 2NH_4NO_3 \qquad pH_R=11.5$$



Sample Code	Type of Me^{2+}	[Me]	Me/Mg^{2+} Nominal Molar Ratio
MH	-	-	-
MH-Ca1	Ca^{2+}	0.0003	0.033
MH-Ca2	Ca^{2+}	0.0007	0.067
MH-Ca3	Ca^{2+}	0.0020	0.200
MH-Ni1	Ni^{2+}	0.0003	0.033
MH-Ni2	Ni^{2+}	0.0007	0.067
MH-Ni3	Ni^{2+}	0.0020	0.200
MH-Co1	Co^{2+}	0.0003	0.033
MH-Co2	Co^{2+}	0.0007	0.067
MH-Co3	Co^{2+}	0.0020	0.200

E. Mastronardo et al./ Nanomaterials **2018**, 8, 573;

Metal doping $Mg(OH)_2$

Under preparation condition nor Ca^{2+} neither Co^{2+} and Ni^{2+} hydroxides form because

- in case of Ca^{2+} supersaturation conditions, necessary to have the $Ca(OH)_2$ formation are not reached;
- in case of Ni^{2+} and Co^{2+} complexes formation with amino ligands avoid precipitation

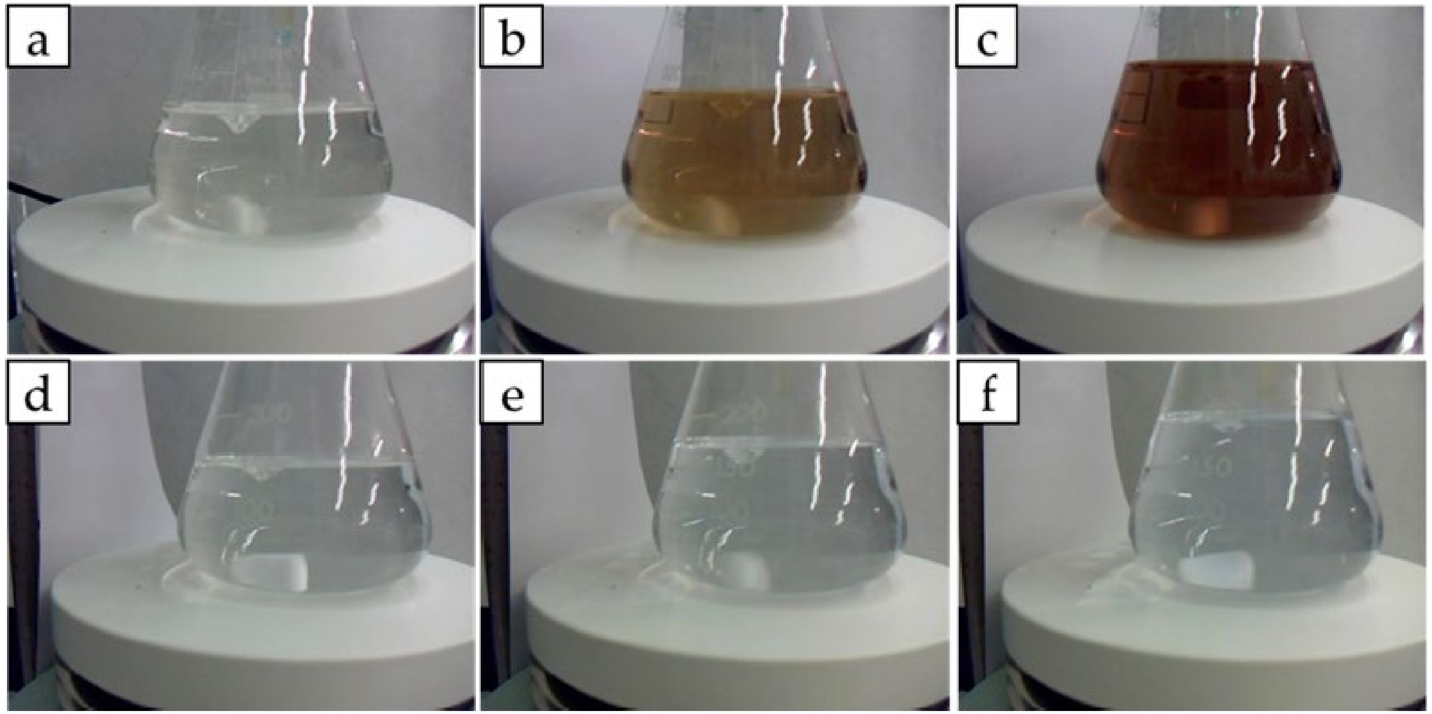


Figure 1. Formation of cobalt and nickel hexamine complexes. Starting aqueous Co^{2+} solution 0.002 M (**a**); Upon addition of $NH_4(OH)$ (**b**) and after mixing for 24 h (**c**). Starting aqueous Ni^{2+} solution 0.002 M (**d**); Upon addition of $NH_4(OH)$ (**e**) and after mixing for 24 h (**f**).

Metal doping $Mg(OH)_2$

Assuming a $Mg(OH)_2$ growth based on the model of **anion** coordination polyhedron (a) , the presence of doping **cation** through electrostatic interaction could cause structure distorsion

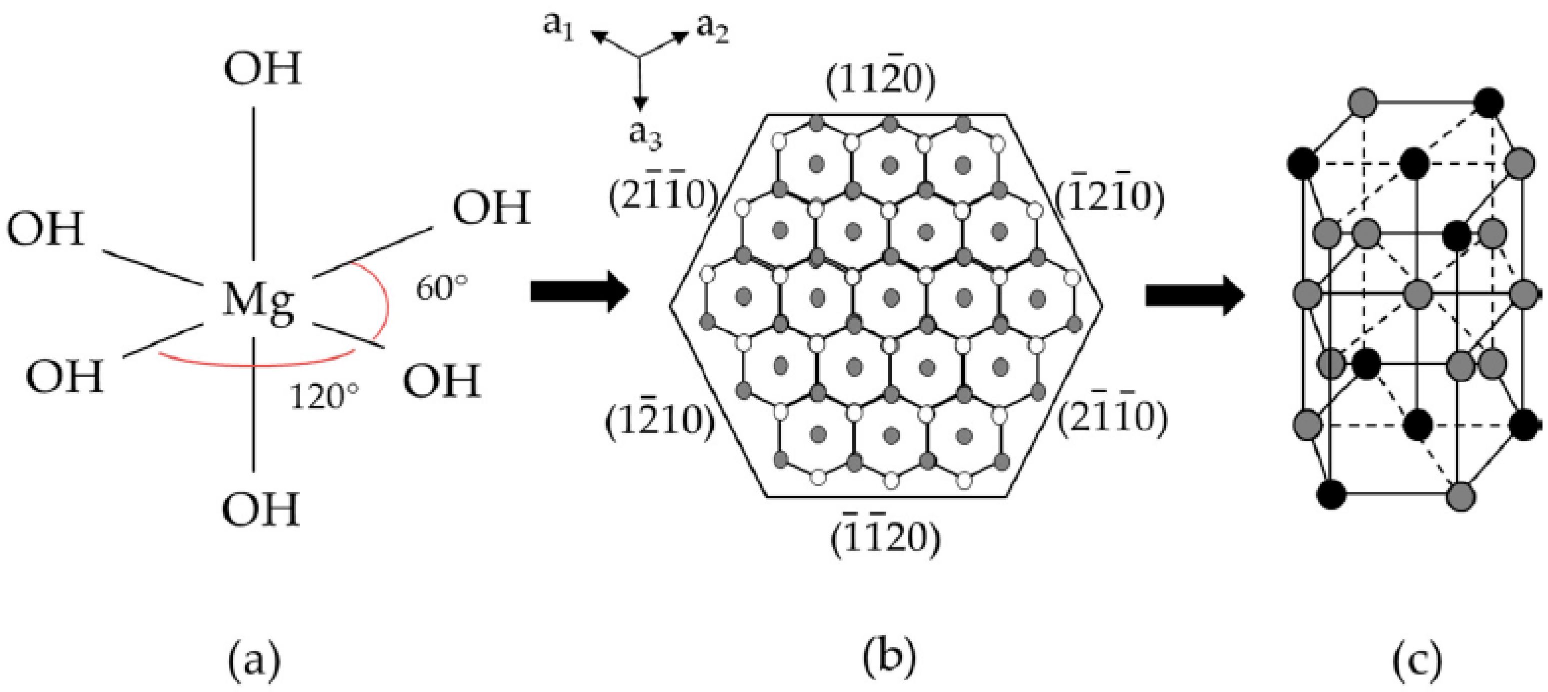
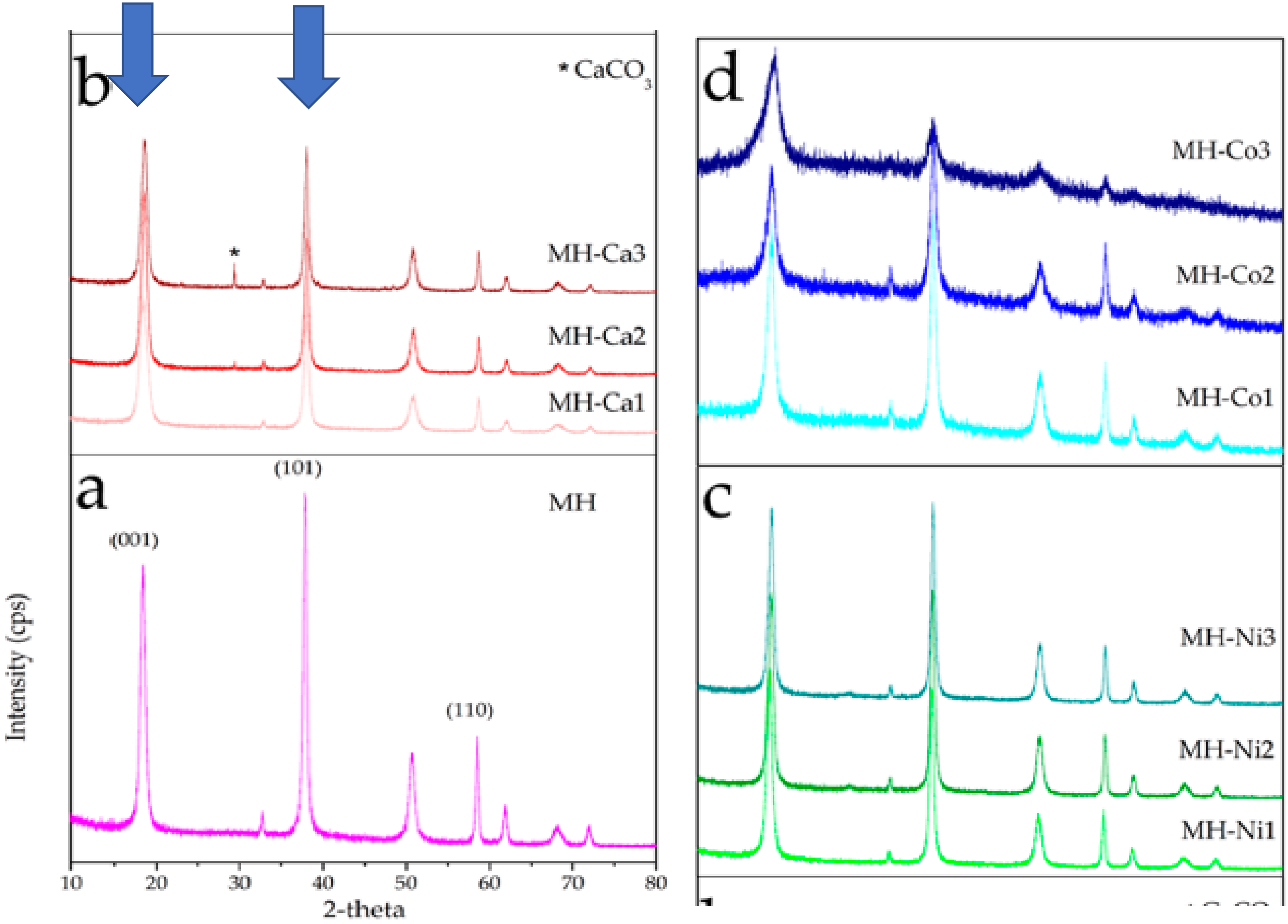


Figure 5. $Mg(OH)_2$ growth, based on the model of anion coordination polyhedron (ACP). Growth unit (**a**); Large dimension growth units in the same face (**b**); Hexagonal structure (**c**).

Metal doping $Mg(OH)_2$



Signals of hexagonal brucite are present.

Intensity ratio I_{001}/I_{101} increase.

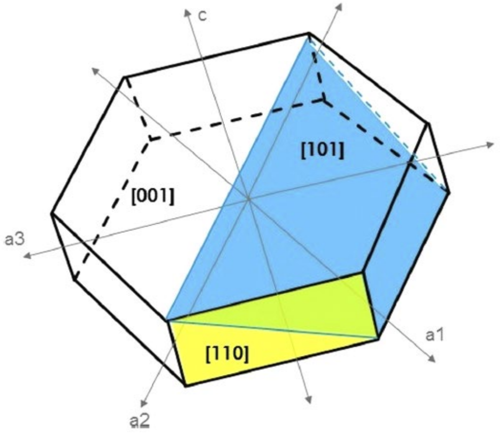
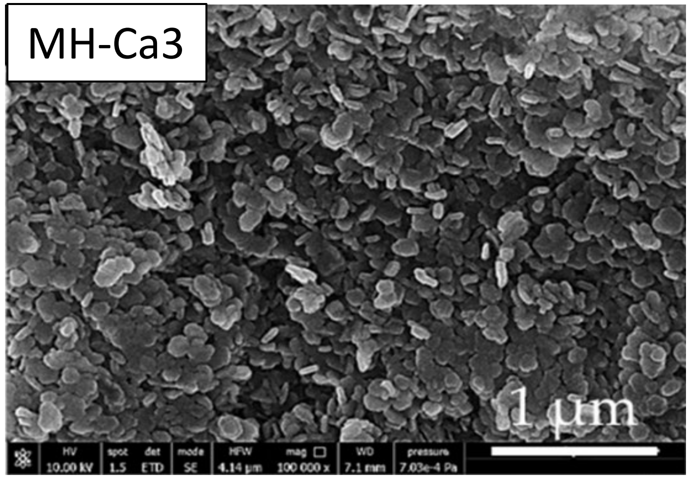


Fig. A.1. $Mg(OH)_2$ crystal model.

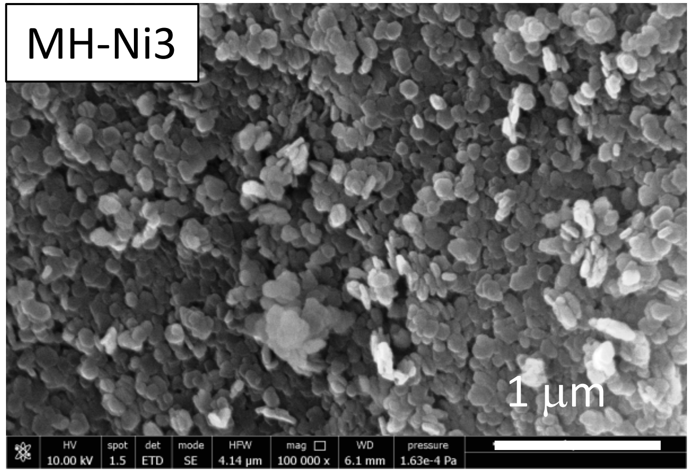
Co induced brucite amorphization

Metal doping $Mg(OH)_2$

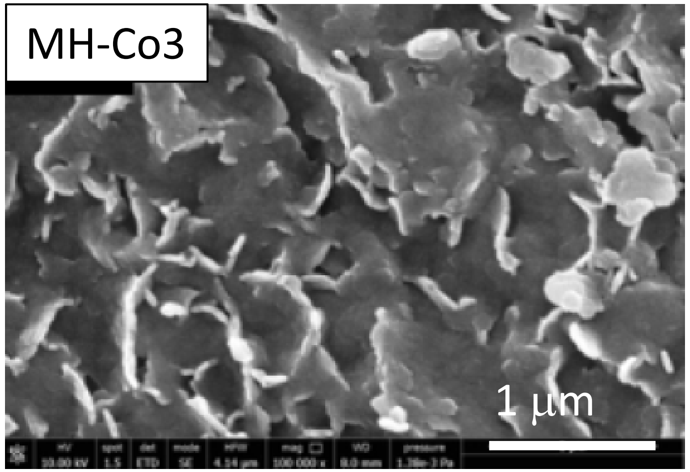
MH-Ca3



MH-Ni3

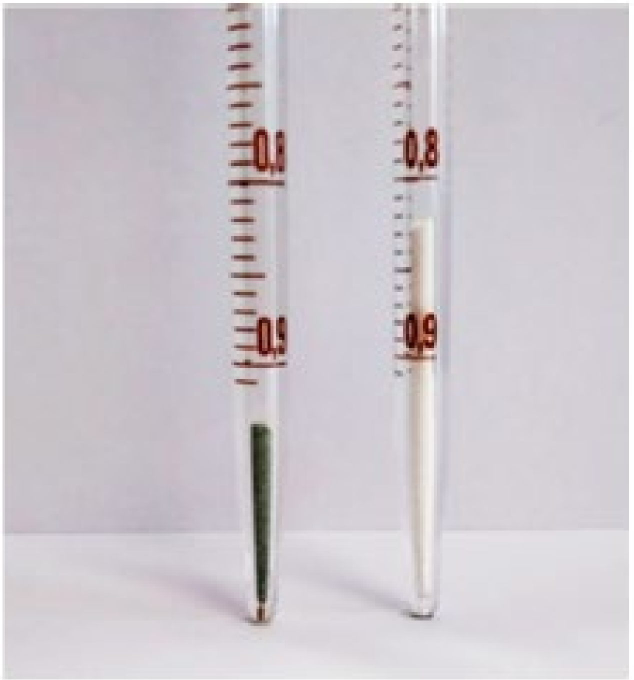


MH-Co3



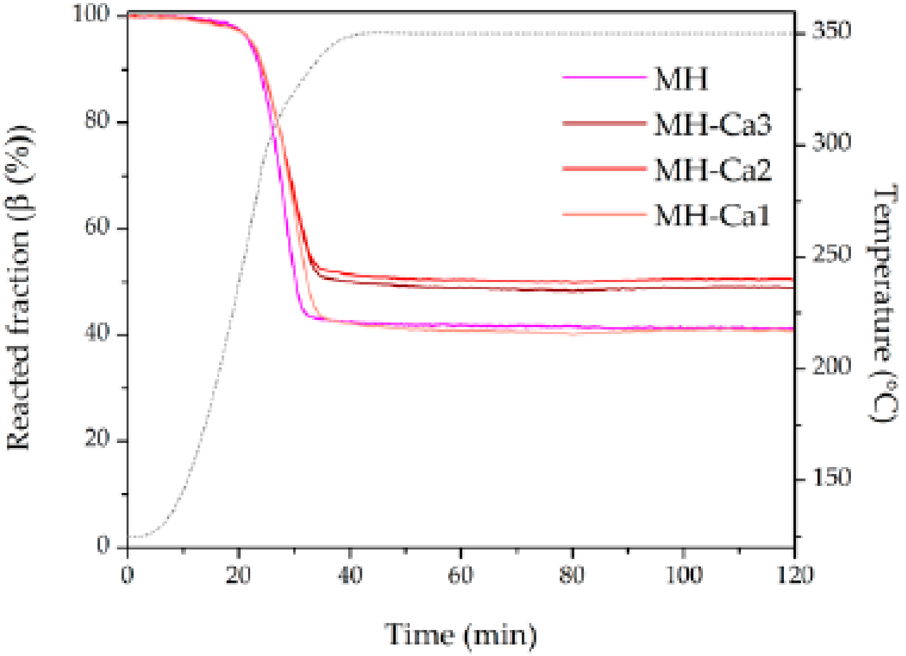
SEM analysis is in agreement with the XRD results that evidence the amorphization of MH-Co.

Metal doping $Mg(OH)_2$

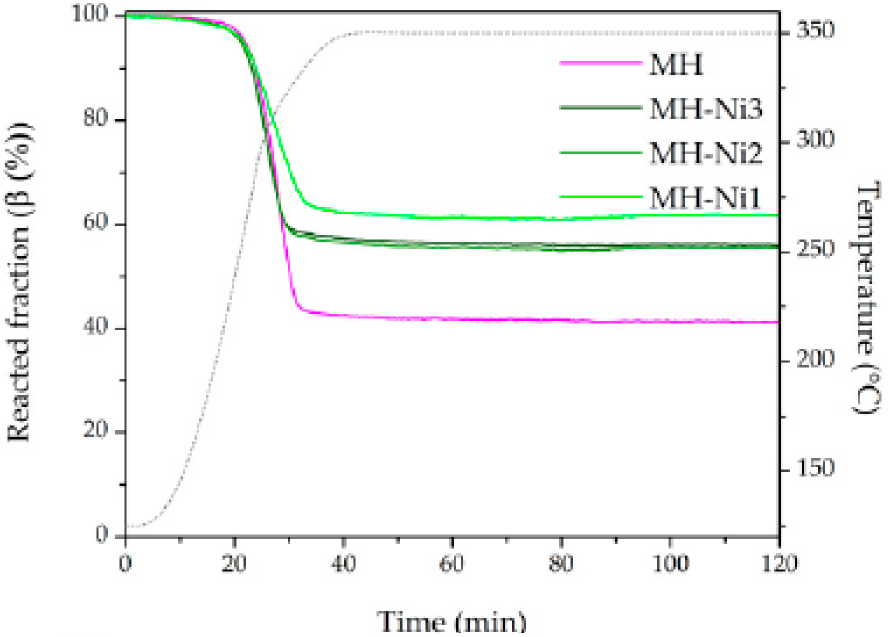


Volume occupied by ~69 mg of MH-Co3 (on the left) and MH (on the right) samples.

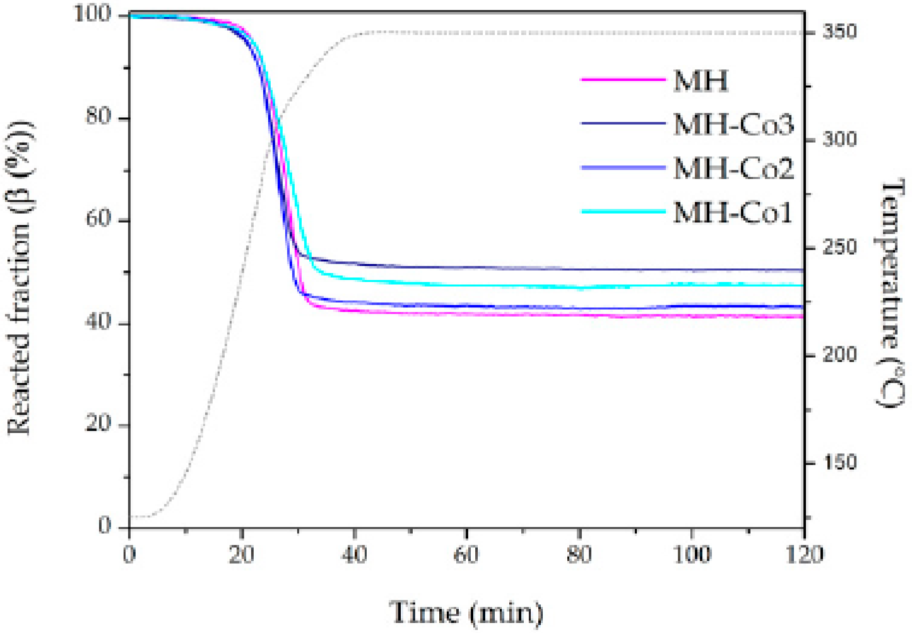
Metal doping $Mg(OH)_2$



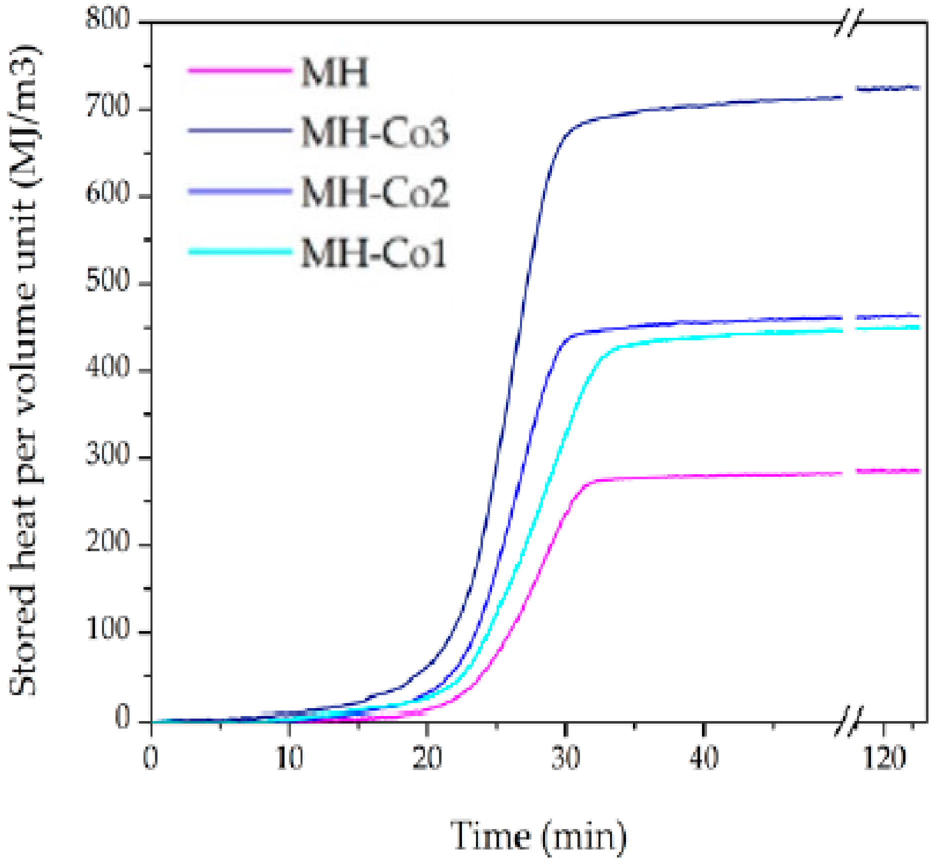
Dehydration reaction (endo): $Mg(OH)_2 \rightarrow MgO + H_2O$

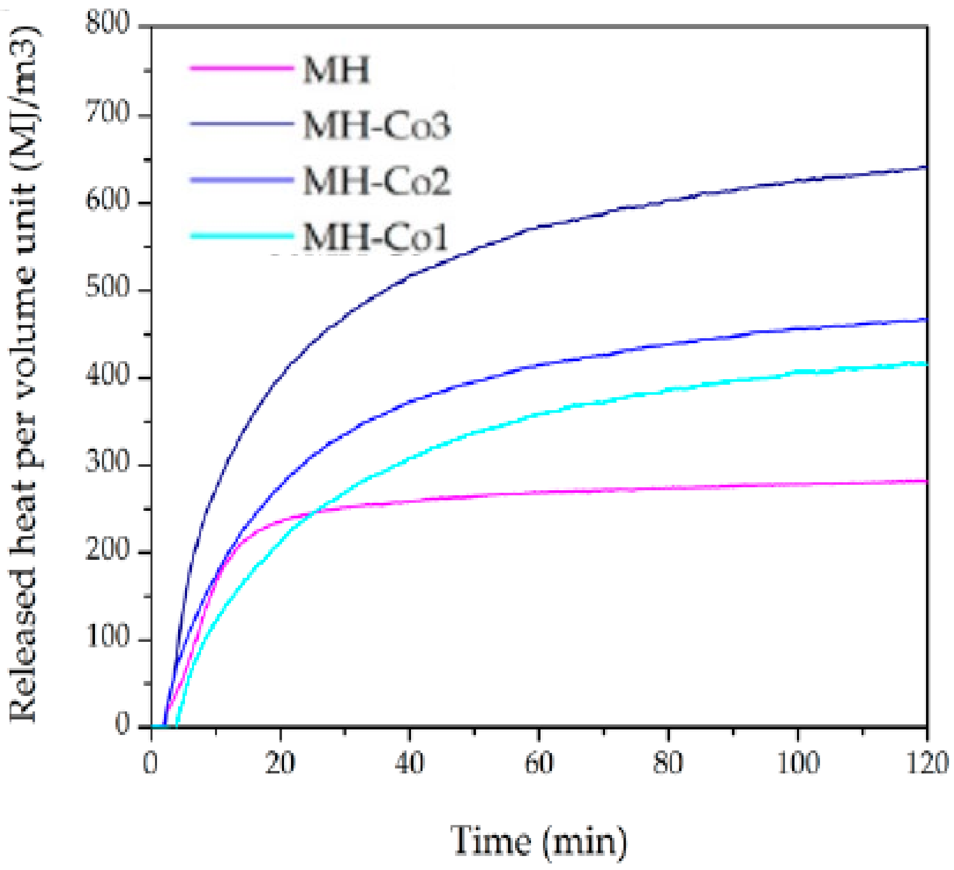


Dehydration reaction (endo): $Mg(OH)_2 \rightarrow MgO + H_2O$



Metal doping $Mg(OH)_2$





Thermochemical Materials for low-temperature ranges

$$Salt \cdot mH_2O_{(s)} + nH_2O_{(g)} \underset{\text{Charging}}{\overset{\text{Discharching}}{\leftrightarrow}} Salt \cdot (m+n)H_2O_{(s)}$$

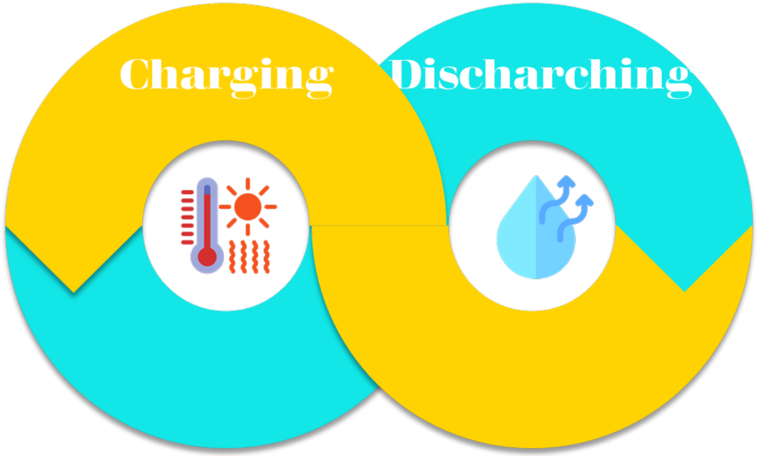
Drawbacks of Inorganic Salt Hydrates (ISH)

Deliquescence

→ Chemical instability, Corrosion issues, Limits the operating range

Agglomeration and swelling

→ Poor durability to the charging/discharging cycles



Strategies

1) Confinement of the inorganic salt hydrate in a vapor-permeable foam
2) Finding suitable candidates among organic salt hydrates with more resistance towards deliquescence

Silicone vapor-permeable foam

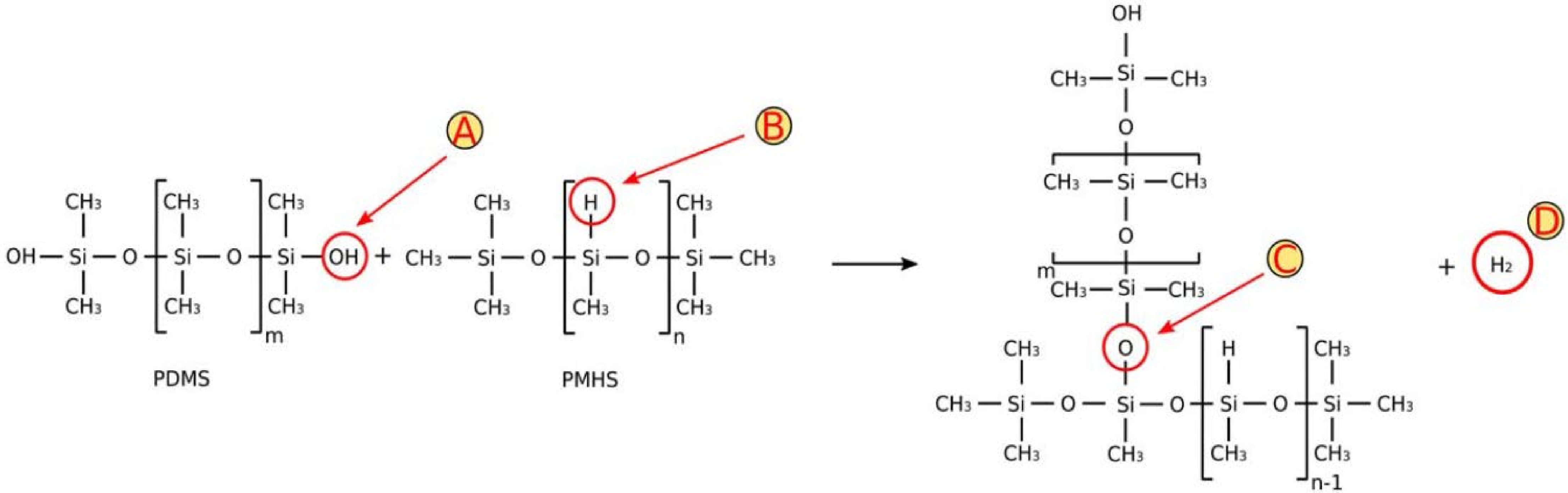
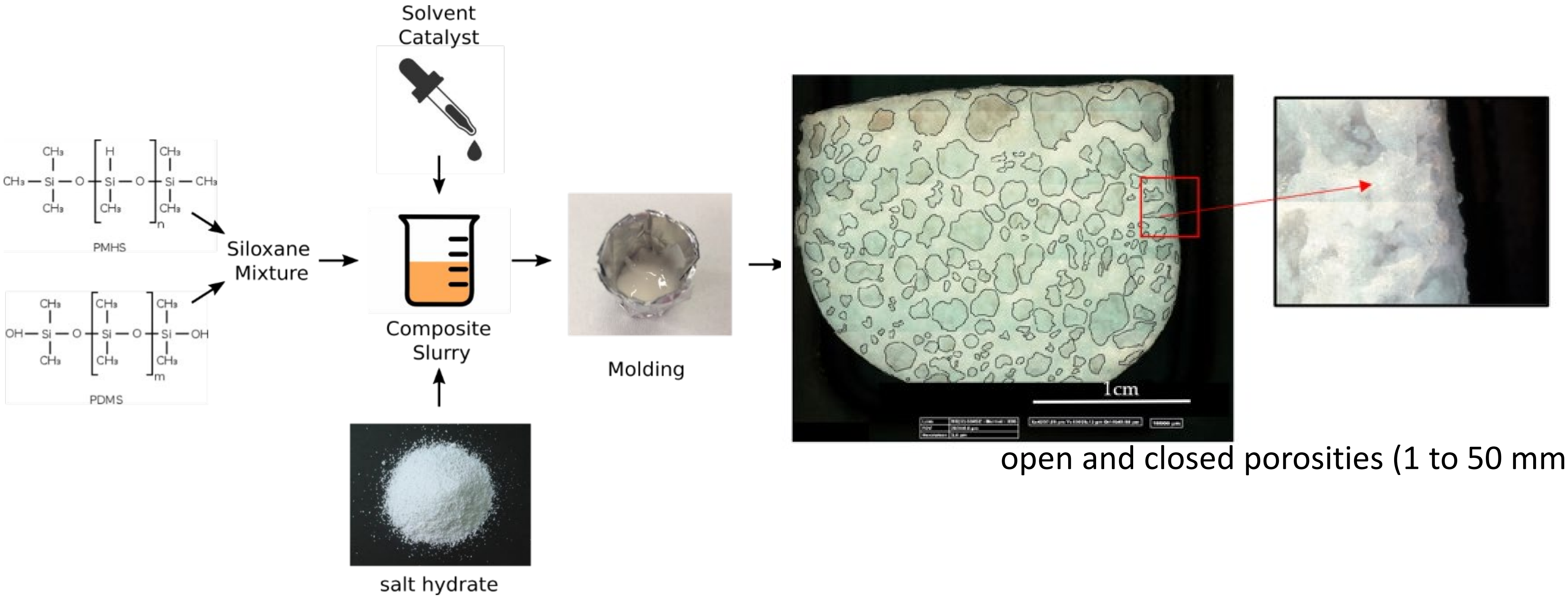


Figure 2. Scheme of dehydrogenative coupling reaction of PDMS and PMHS. [Color figure can be viewed at wileyonlinelibrary.com]

Silicone vapor-permeable foam filled with LiCl



Solvent
Catalyst

Siloxane
Mixture

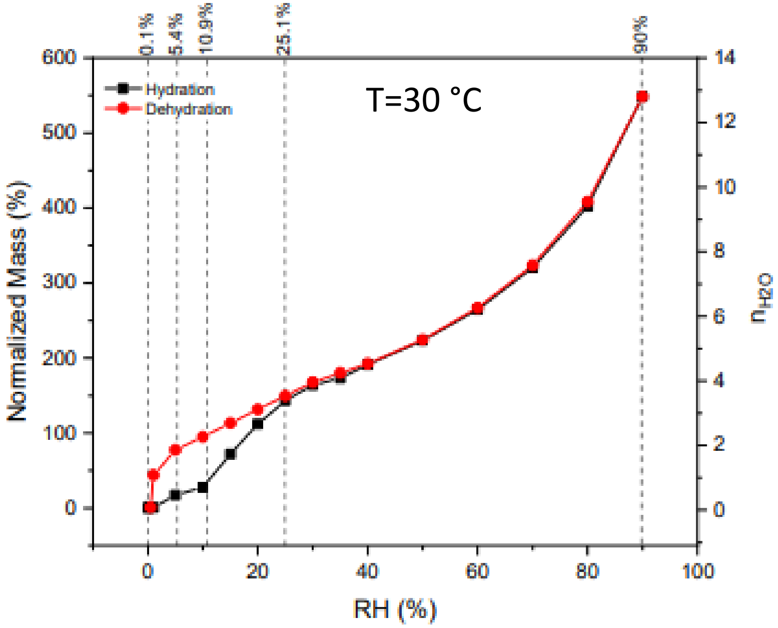
Composite
Slurry

Molding

salt hydrate

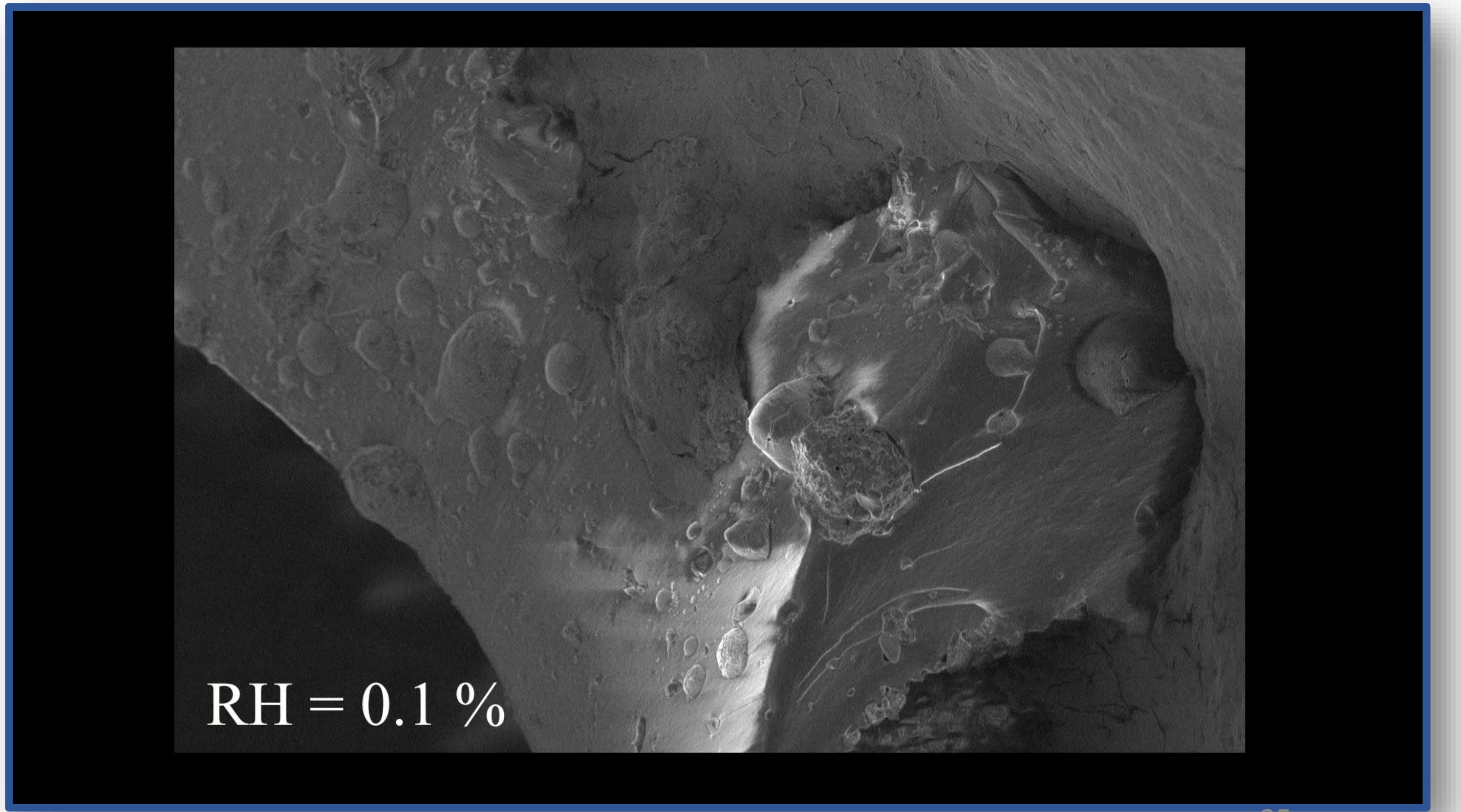
open and closed porosities (1 to 50 mm)

$LiCl\cdot H_2O(s) \rightleftarrows LiCl(s) + H_2O$



Hysteresis occurs in the RH range of 0–25%
above this RH value, the hydration and dehydration profiles overlap.

Sample	L-100	L-60
Salt content [wt.%]	100	60
Sorption enthalpy [J/g]	4500	3150
Foam Density [kg/m^3]	-	657
Volumetric energy density [GJ/m^3]	2.7	2.1



C Milone et al. Appl. Sci. 2022, 12 (3), 1510

Organic salt hydrates as a paradigm for novel TCS materials that matches:

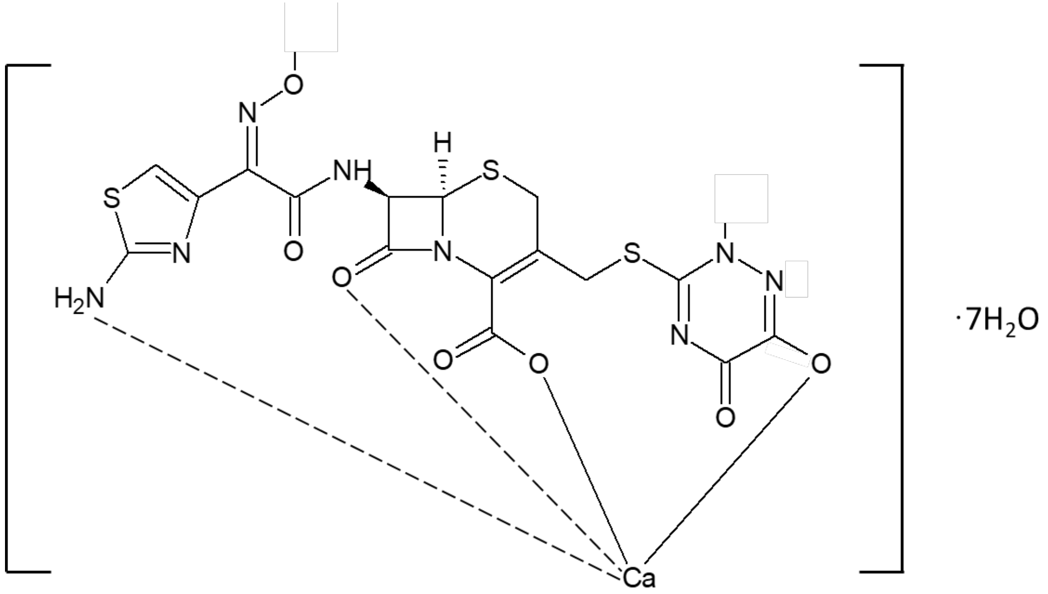
- **low water solubility**,
- **tendency to coordinate a high number of water molecules**
- **stability under operating conditions**.

What we expect:

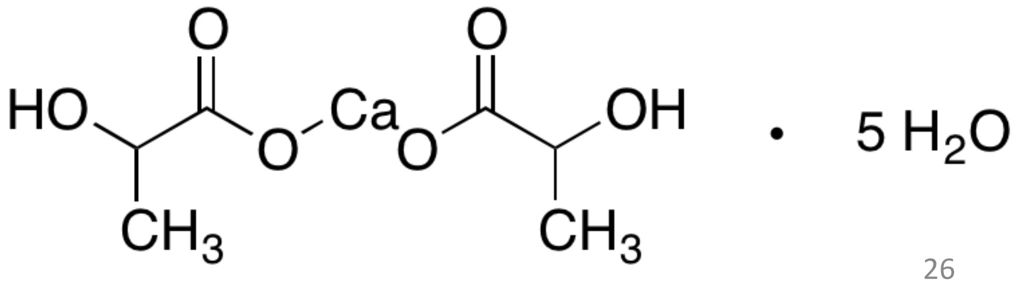
Higher resistance towards deliquescence
Less agglomeration
Higher cyclability

Model compounds investigated:

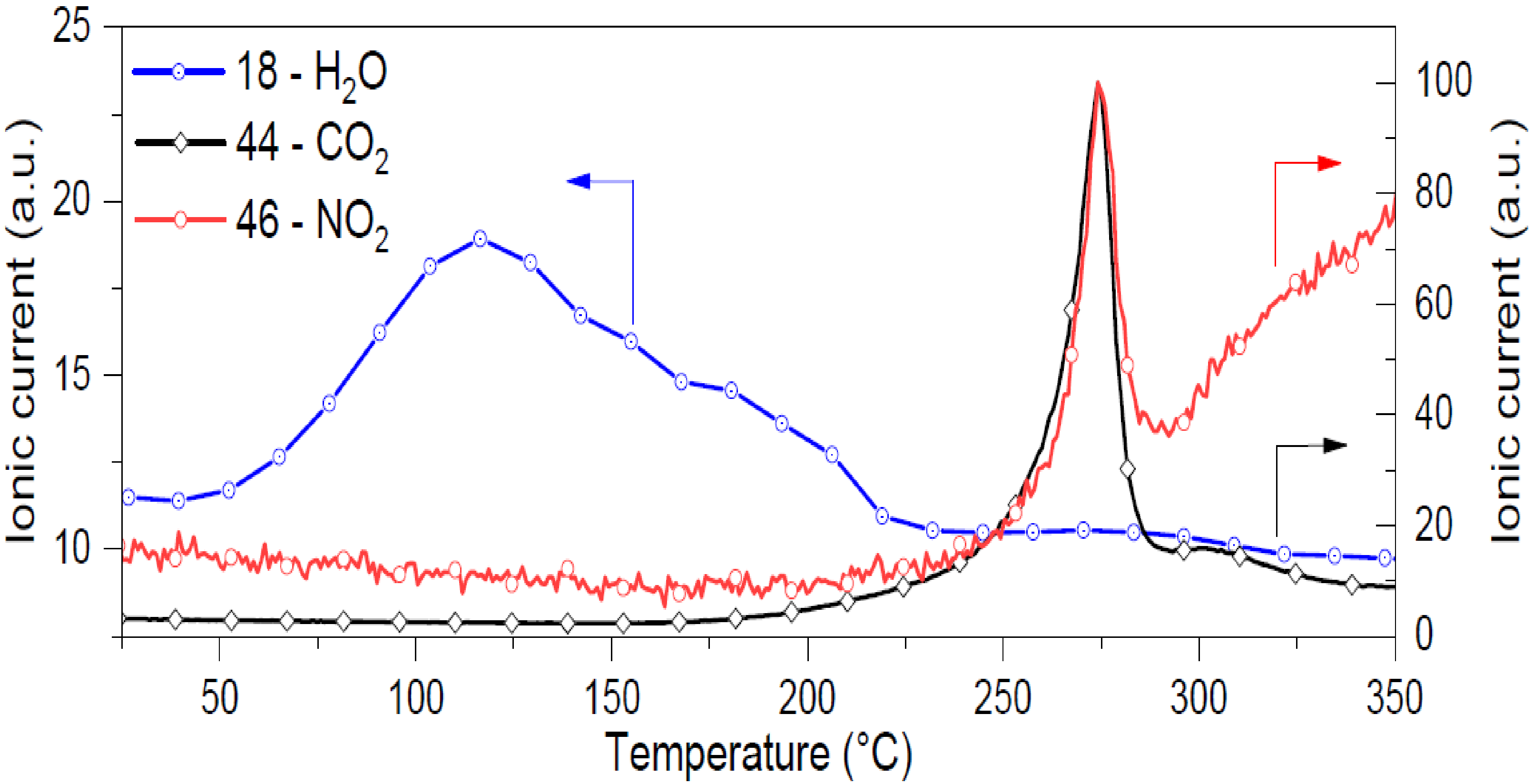
1) Calcium ceftriaxone heptahydrate (CaCf)



2) Calcium Lactate Pentahydrate (CaLP)



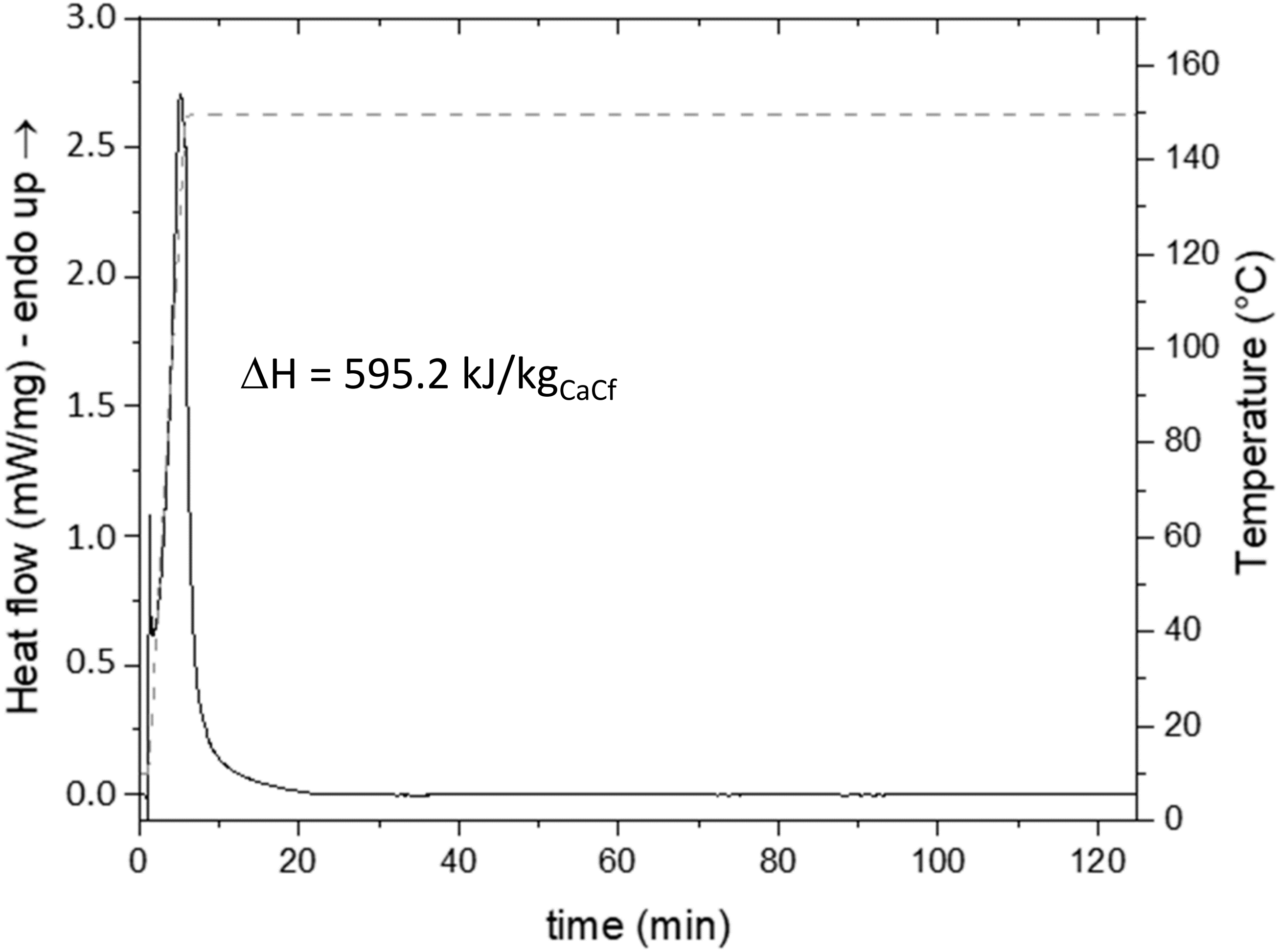
About CaCf



E. Mastronardo,…, C. Milone, Energies ***2022****, 15(12), 4339*

About CaCf

Heat Storage Capacity



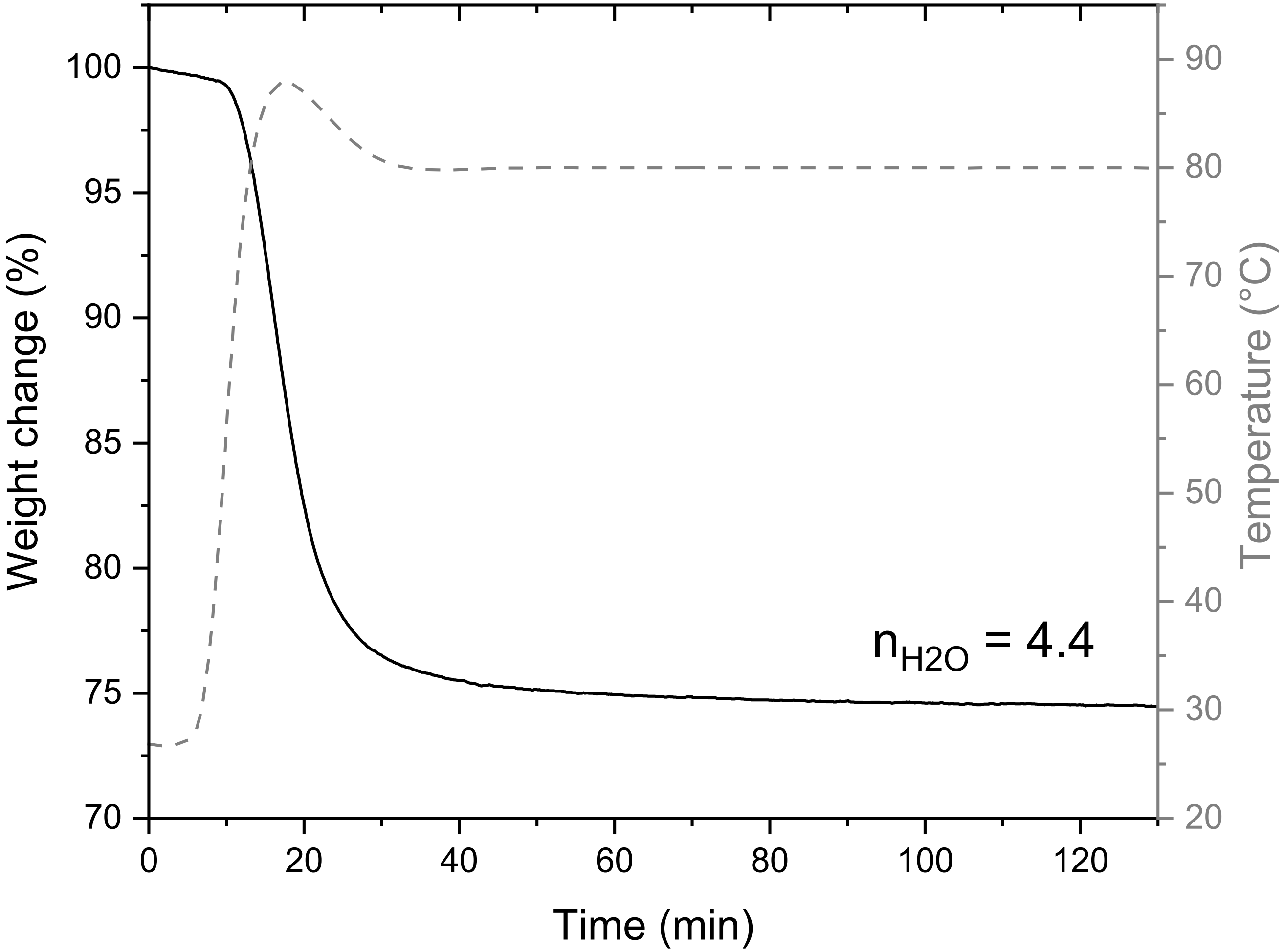
$\Delta H = 595.2\ kJ/kg_{CaCf}$

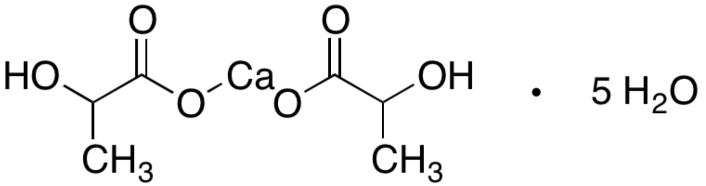
Energy density = 278 kWh/m^3

Operating Temperature range: 20-150°C

*E. Mastronardo,…, C. Milone, Energies **2022**, 15(12), 4339*

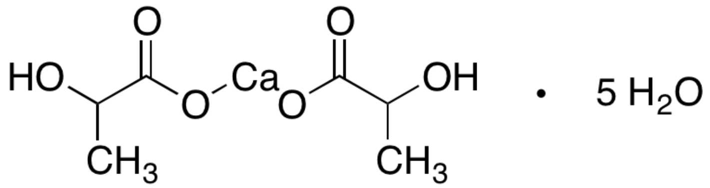
About CaLP

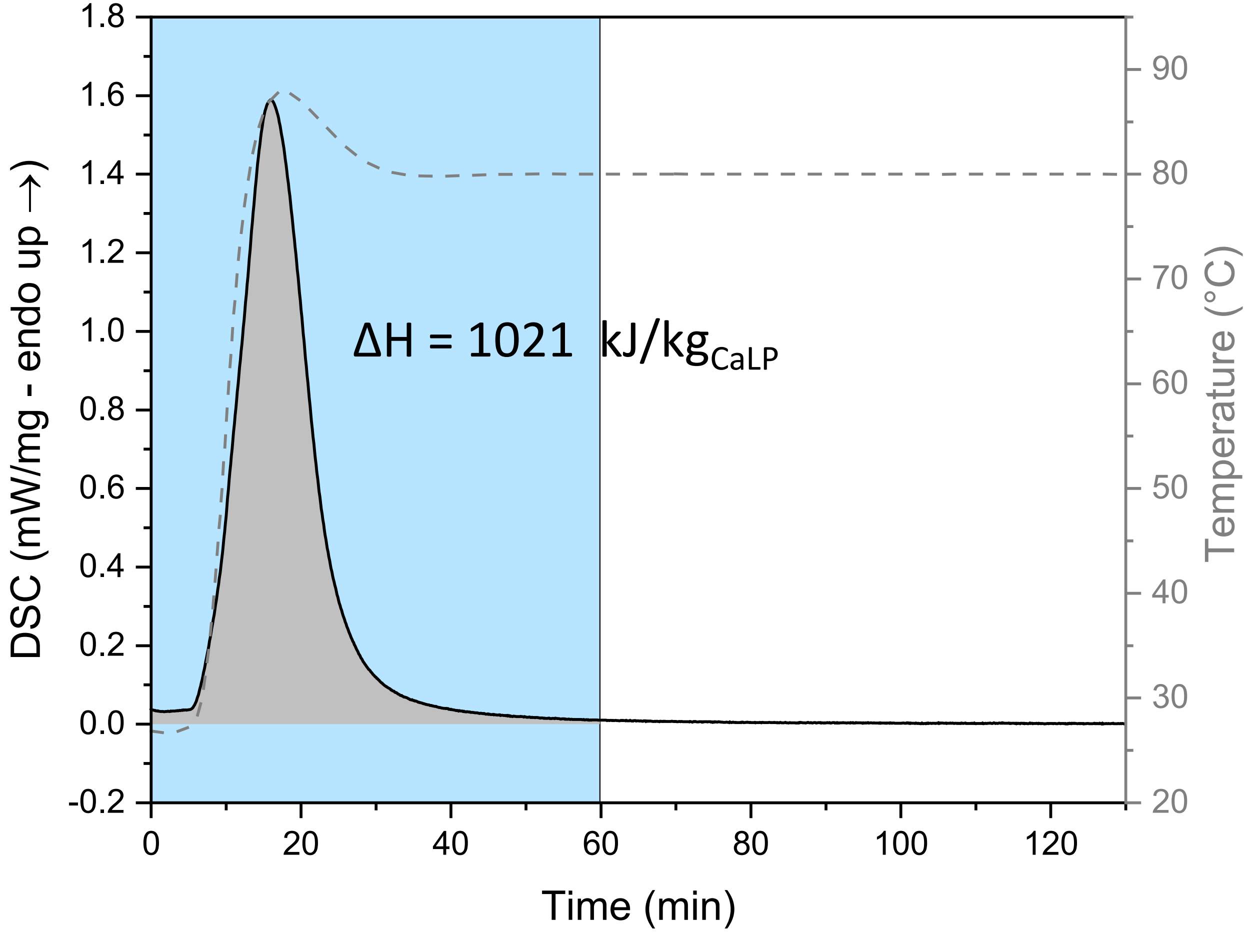

Weight change (%)
100
95
90
85
80
75
70
Temperature (°C)
90
80
70
60
50
40
30
20
0
20
40
60
80
100
120
Time (min)
n_{H2O} = 4.4


HO
O
O
Ca
O
O
OH
CH_3
CH_3
• 5 H_2O

About CaLP

Heat Storage Capacity





Energy density = 425 kWh/m^3

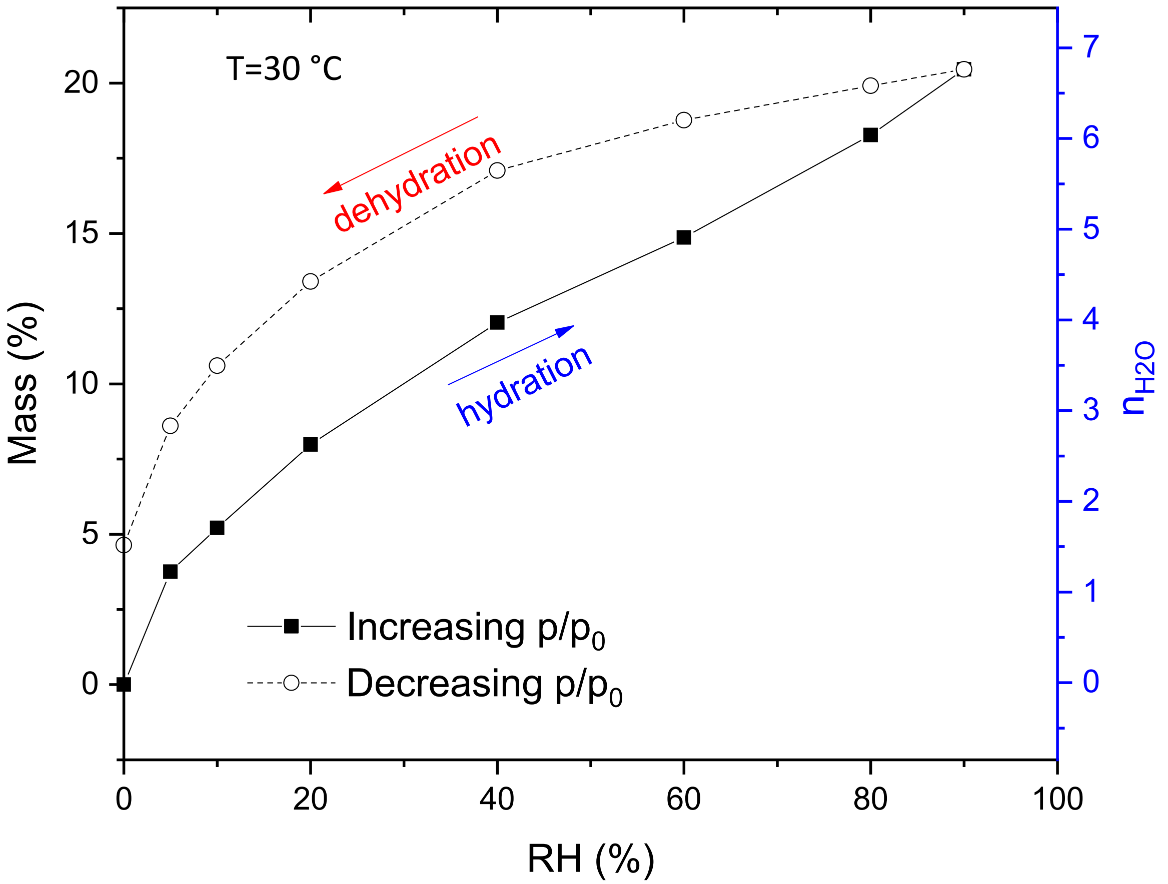
Operating Temperature range: 20-80°C

Advantages:

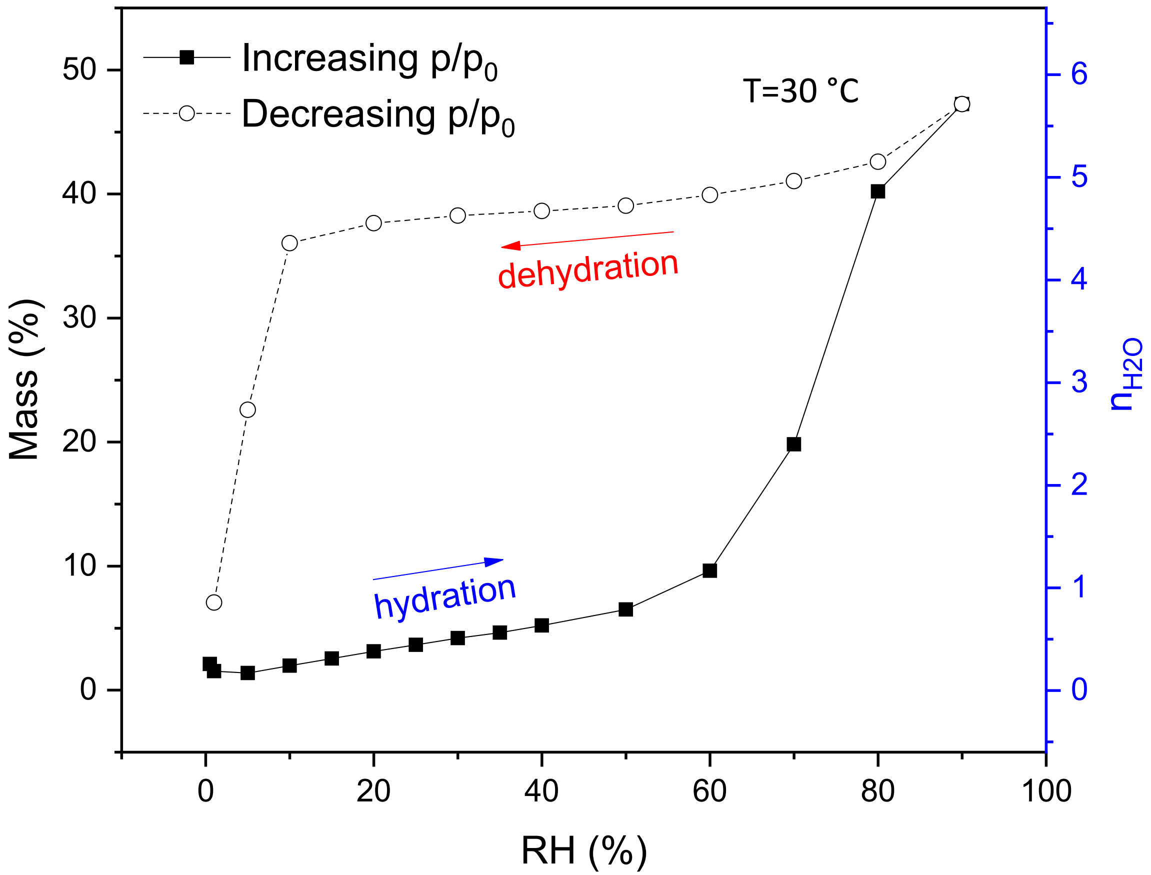
- Inexpensive
- Environmentally safe
- Non-corrosive
- Large availability

Comparison of Ca-based Organic Salt Hydrate

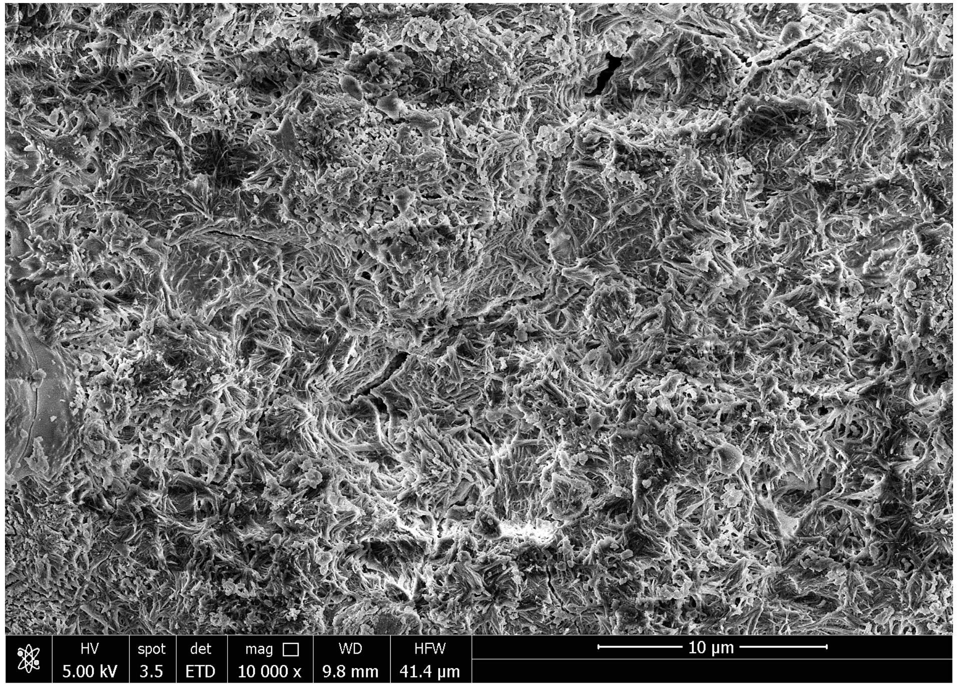
CaCf



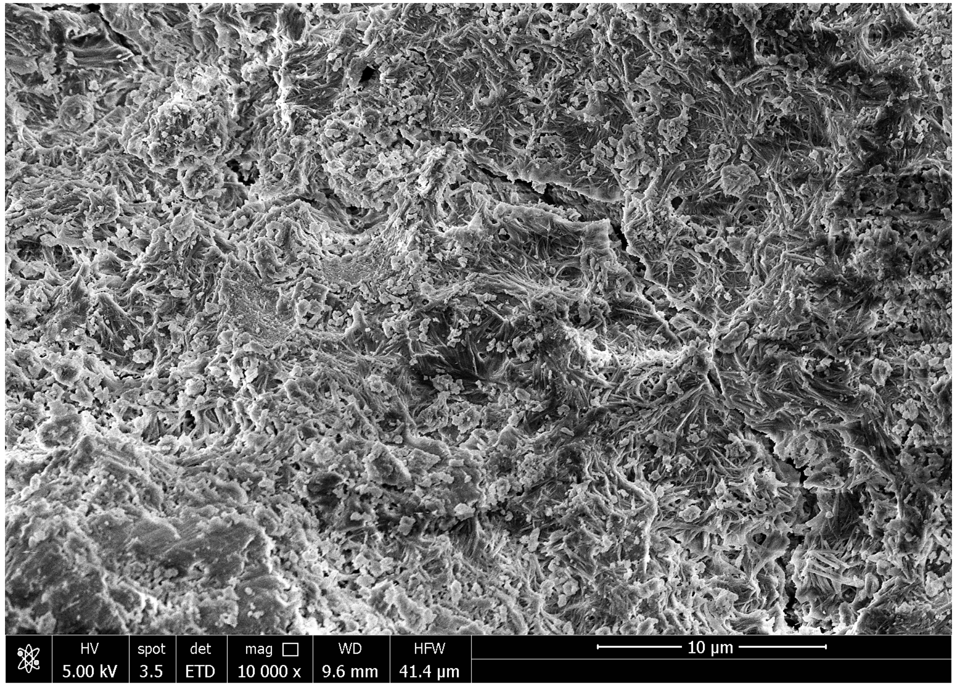
CaLP



CaLP

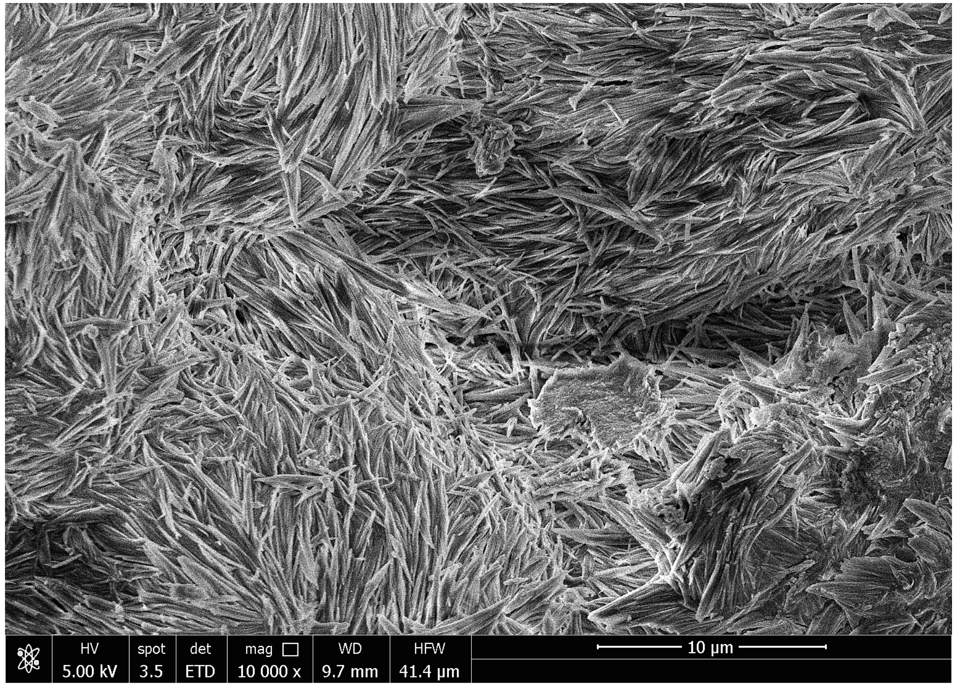


Fresh



Dehydrated

Rehydrated



Comparison of Ca-based Organic Salt Hydrates with ISH

Compound	n	Q^M (kJ/kg)	Q^V (kWh/m³)	T_{deh} (°C)	T_{hyd} (°C)	Ref.
$CaCf \cdot 7H_2O$	4.3	595	279	150	30	this study
$CaLP \cdot 5H_2O$	4.4	1021	425	60-80	30	this study
$SrBr_2 \cdot 6H_2O$	5	948	434	52	45	[3–5]
$SrCl_2 \cdot 2H_2O$	1	302	164	52	46	[3–5]
$MgSO_4 \cdot 6H_2O$	4	986	558	91-123	10	[3–5]
$MgCl_2 \cdot 6H_2O$	1.3	352	153	104	61	[4,6]
$CaCl_2 \cdot 2H_2O$	2	837	542	111	63	[4,6]
$LiCl \cdot H_2O$	1	1041	486	80	73	[4]
$K_2CO_3 \cdot 1.5H_2O$	1.5	580	355	65	59	[4]
$Na_2S \cdot 5H_2O$	3	1120	781	73	66	[3,4]

Conclusions

- Strategies for enhancement of thermochemical performance of already studied thermochemical materials have been shown.

- New idea have been proposed on the use of hydrated organic salts for effective TCS applications, breaking new ground for this field of research.

Acknowledgments

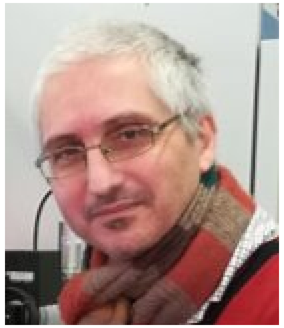
Technology and
Research on
Energy,
Environment and
Safety
MATerials

TREES-MAT

Team

Edoardo Proverbio
Full Professor

Elpida Piperopoulos
Associate Professor



Luigi Calabrese
Associate Professor

Emanuela Mastronardo
Senior Researcher

UNIONE EUROPEA
Fondo Sociale Europeo
Fondo Europeo di Sviluppo Regionale

Ministero dell'Istruzione, dell'Università e della Ricerca

PON
RICERCA E INNOVAZIONE
2014 - 2020

Università degli Studi di Messina

This project has partly funded by

European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

National Project PON 2014-2020 "NAUSICA – Efficient ship through the use of innovative and low carbon technological solutions"

Acknowledgments

Università degli Studi di Messina

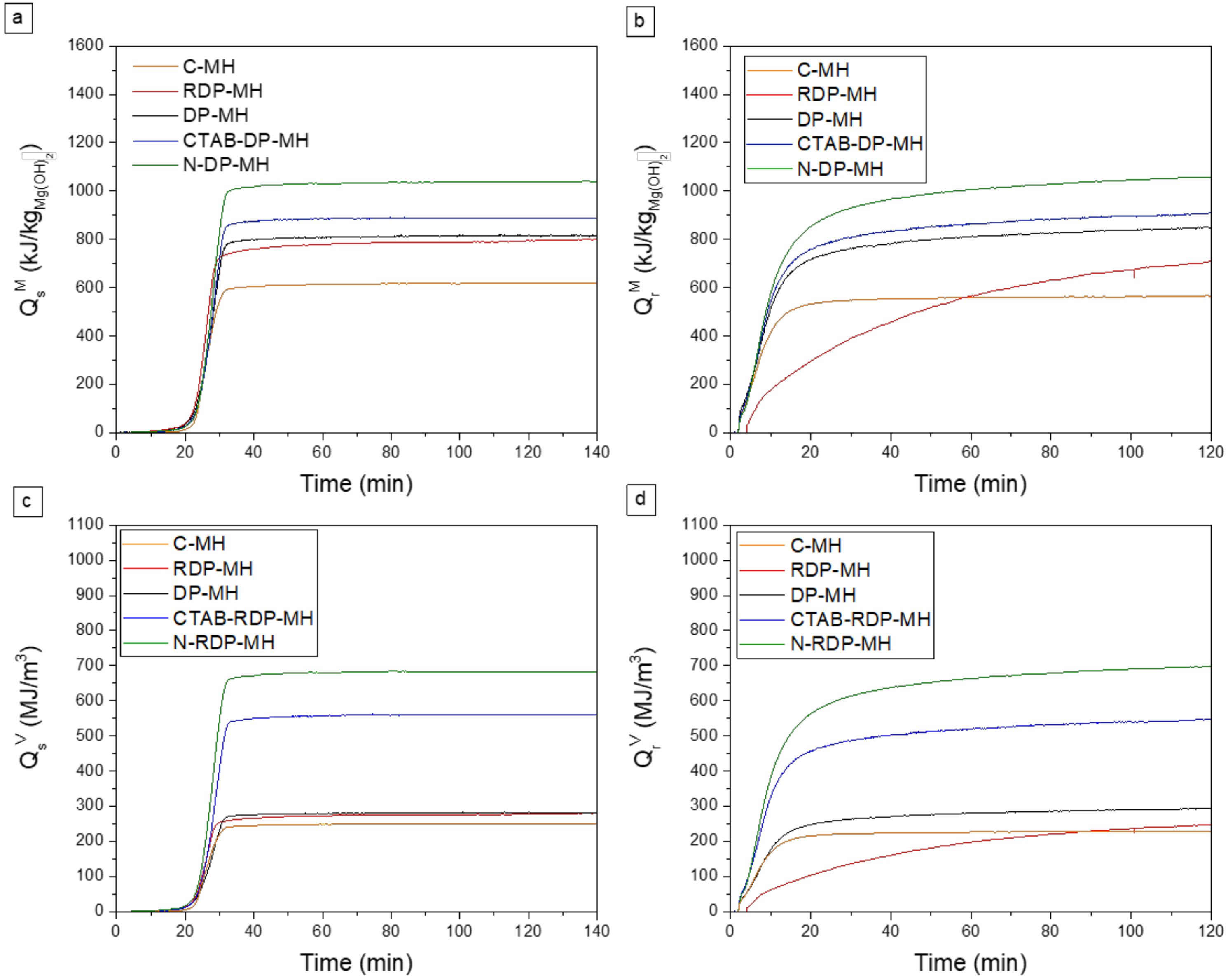
DIPARTIMENTO DI INGEGNERIA

Thank you!

Contact: cmilone@unime.it

EXTRA SLIDES

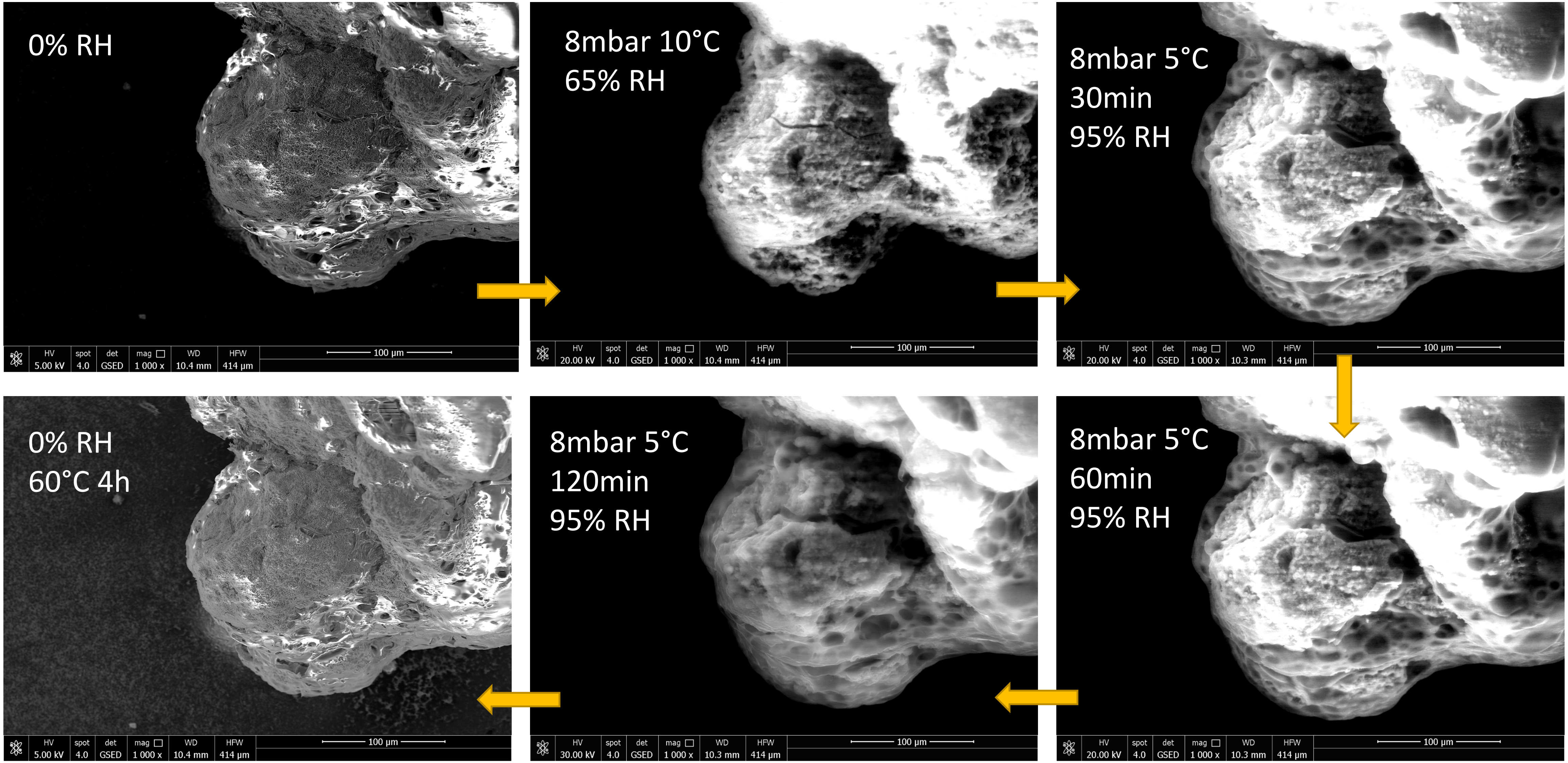
Results & Discussion



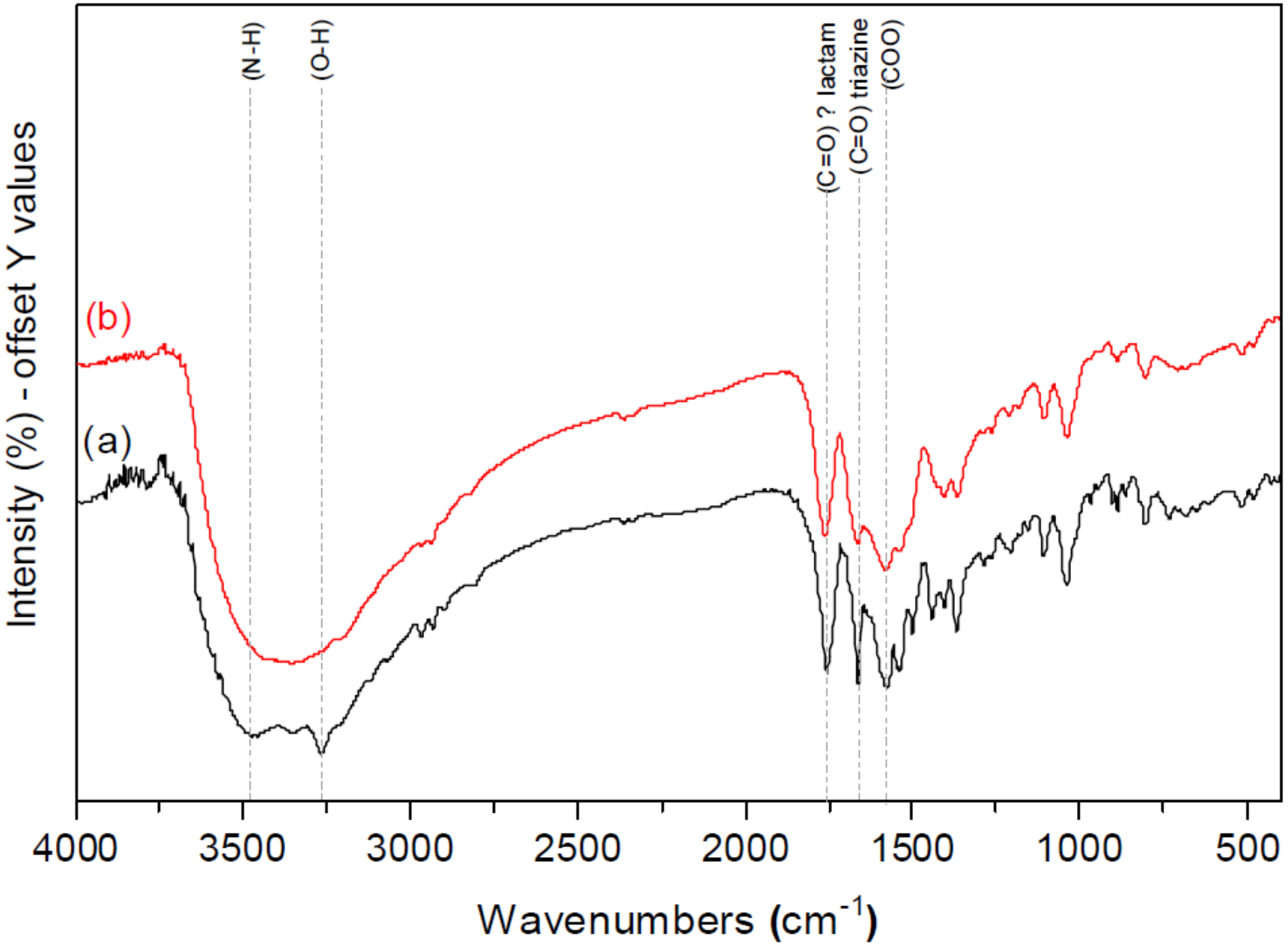
(**a,c**) Stored and (**b,d**) released heat per mass unit and volume unit.

E. Piperopoulos,…, C. Milone, Materials, 2021, 14(5), pp. 1–19, 1091

Environmental ESEM CaLP



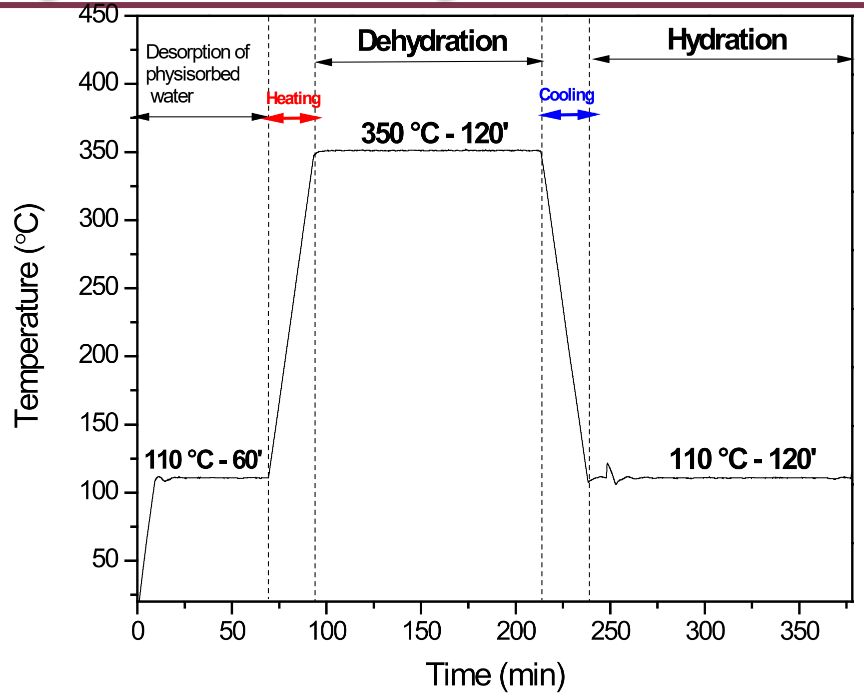
About CaCf



FTIR spectra fresh CaCf (black) and after after thermal treatment at 150 °C for 2 hrs (red)

E. Mastronardo,…, C. Milone, Energies ***2022****, 15(12), 4339*

De/Hydration cycle



Reacted fraction

$$\beta[\%] = \left(1 - \frac{\Delta m_{real}}{\Delta m_{th}}\right) \cdot 100$$

$$\Delta m_{th}[\%] = \frac{M_{Mg(OH)2} - M_{MgO}}{M_{Mg(OH)2}} \cdot 100$$

⟶ theoretical mass change due to the dehydration/hydration of $Mg(OH)_2/MgO$ normalized to the total amount present in the sample

$$\Delta m_{real}[\%] = \frac{m_i - m_{ist}}{m_i} \cdot 100$$

⟶ instantaneous real mass change

$$Q_{s/r}[kJ/kg_{Mg(OH)_2}] = \pm Q \cdot \frac{\Delta\beta_{d/h}}{100}$$

per initial mass unit of $Mg(OH)_2$

- Q [kJ/kg $Mg(OH)_2$] – theoretical heat of dehydration/hydration
- $\Delta\beta_{d/h}$ [%] – dehydration/hydration conversion