SORPTION FRIENDS III

Mission Innovation Heating and Cooling – Sorption Heat Pump Systems

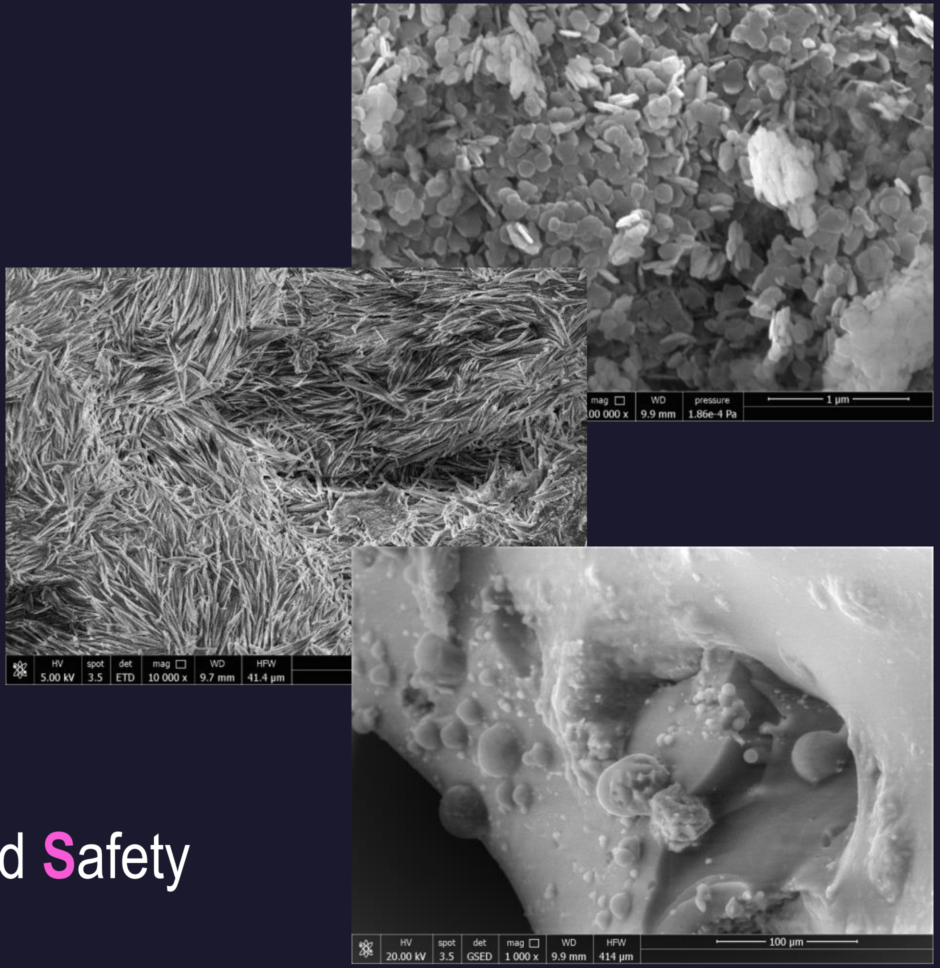
Sorption Friends III

1st to 4th May 2023 Taormina ME, Italy

Università degli Studi di Messina

DIPARTIMENTO DI INGEGNERIA

Main research activities of TREESMAT Group on sorbent materials



University of Messina

Luigi Calabrese

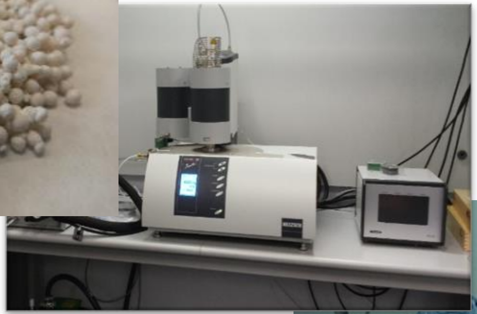
Technology and Research on Energy, Environment and Safety MATerials

TREES-MAT: Labs

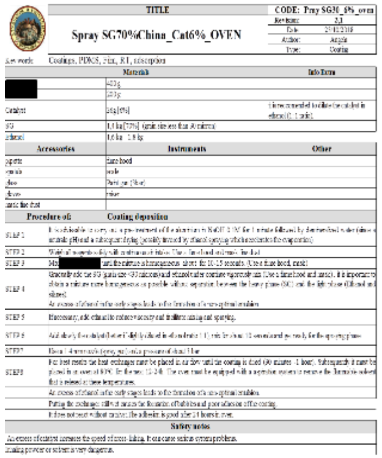
TREES-MAT: Activities

Synthesis

characterization



manufacturing


TITLE

Spray SG70%China_Cat6%_OVEN

Materials | Info Extra

Accessories | Instruments | Other

Procedure of: | Coating deposition

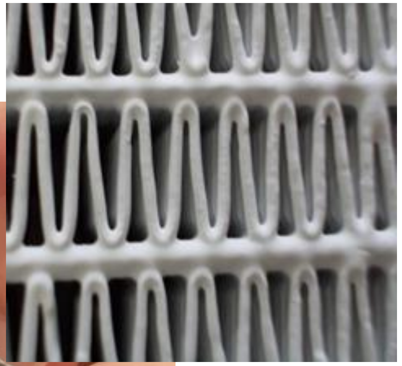
Safety notes

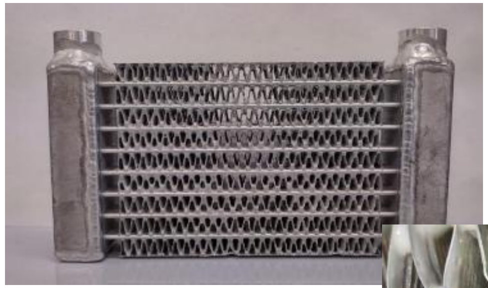
Test Protocols

Testing & Validation	synthesis and characterization of sorbent materials
TCM materials and Coatings	Composite sorbents for AHP

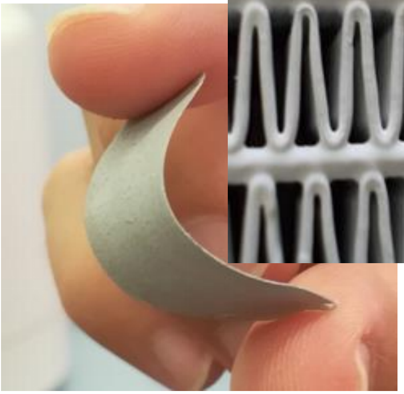
Sorbent Materials

Zeolite sorbent coatings





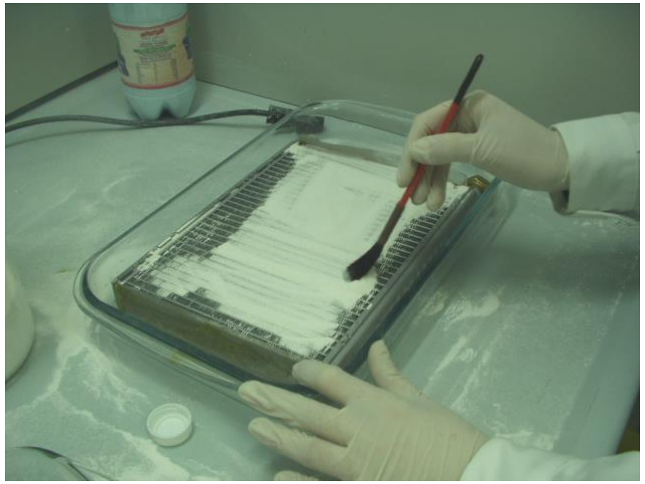
TCM coatings



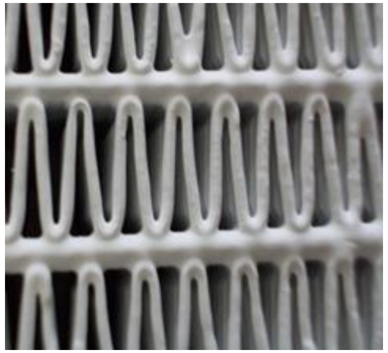
Flexible coatings

Composite sorbent coatings for AHP

- The coating process enhances the heat transfer rate and power density compared to granular adsorber
- Mechanical and adsorption stability of the coated adsorbers
- possibility of easily coat complex heat exchanger geometries



Coating Adsorber

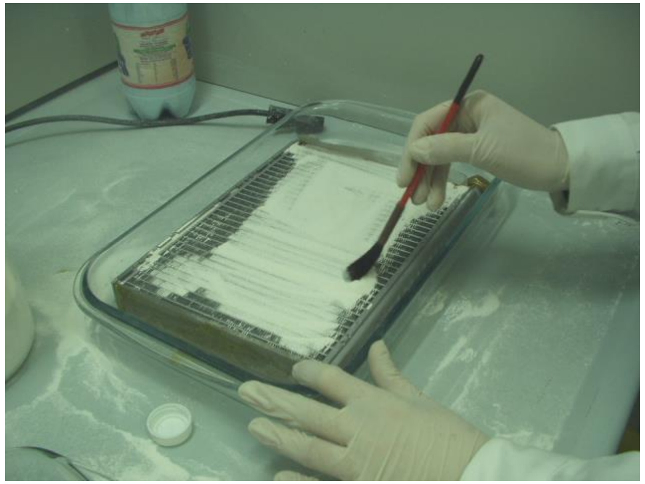


Silane-Zeolite composite coatings

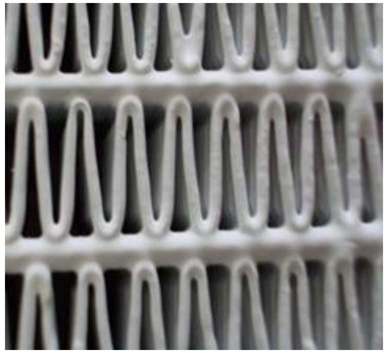
About Porous Sorbent coatings

Drawbacks

- low zeolite amount in the adsorber, due to the limited coating thickness
- Brittle behaviour of zeolite coating
- Durabiity issues



Coating Adsorber

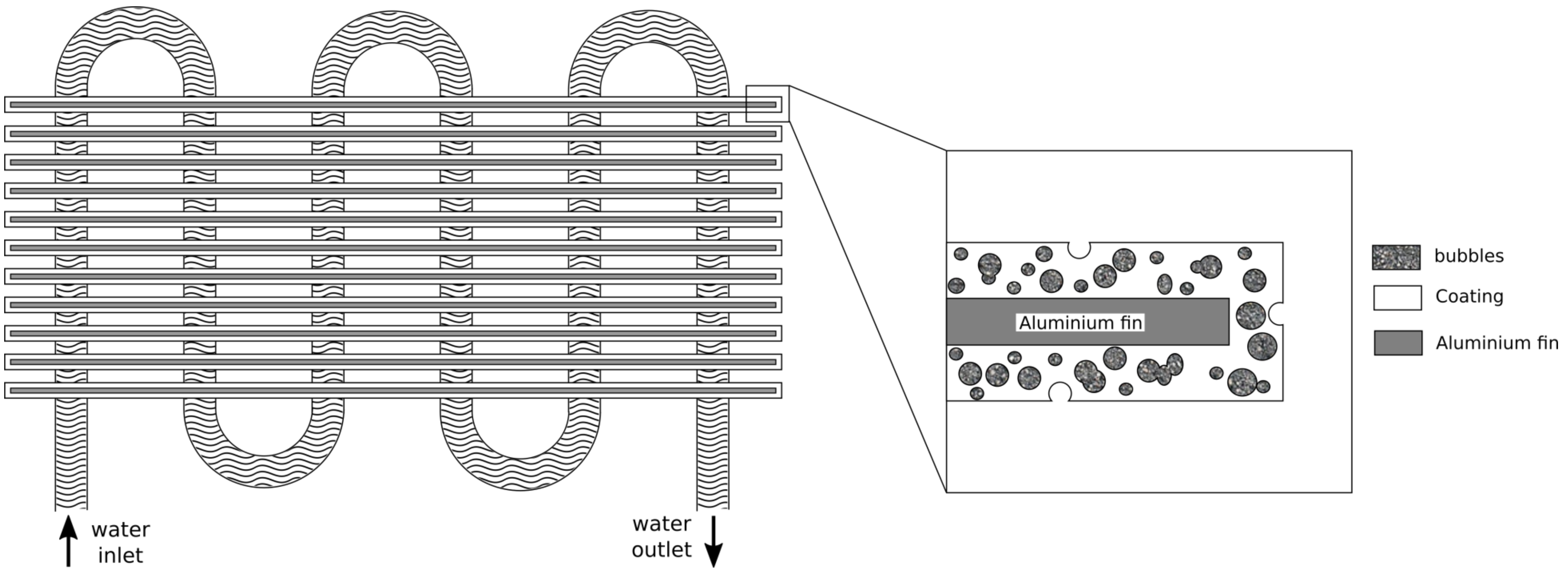


Strategies

to design porous sorbent coatings with high stability and durability for coated HEX without reducing mass flow rate.

Proof of Concepts (1)

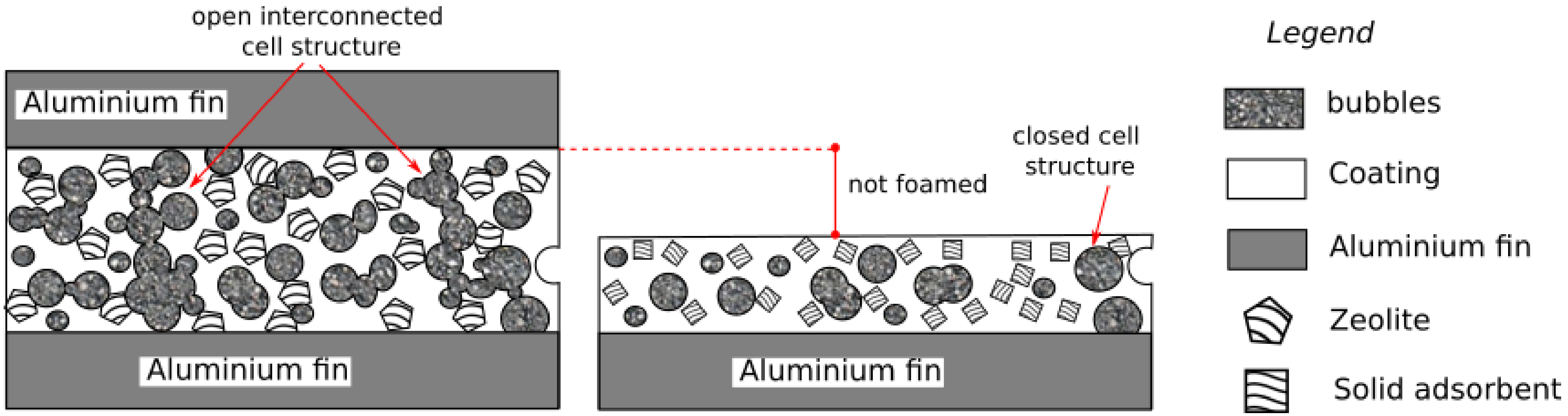
To tailor a new sorbent flexible composite coating with a macro-porous morphology with suitable film ability and good heat and mass transfer capacity.



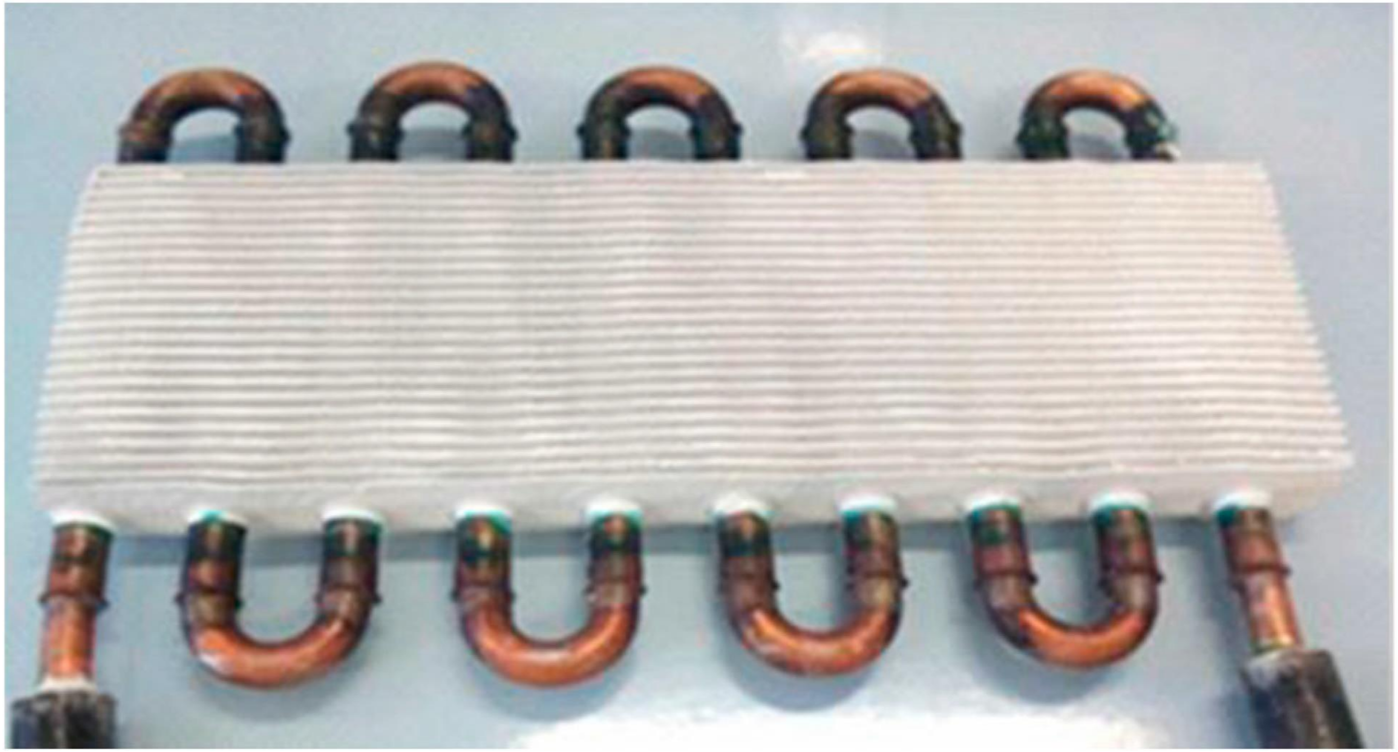
Sorption Technologies

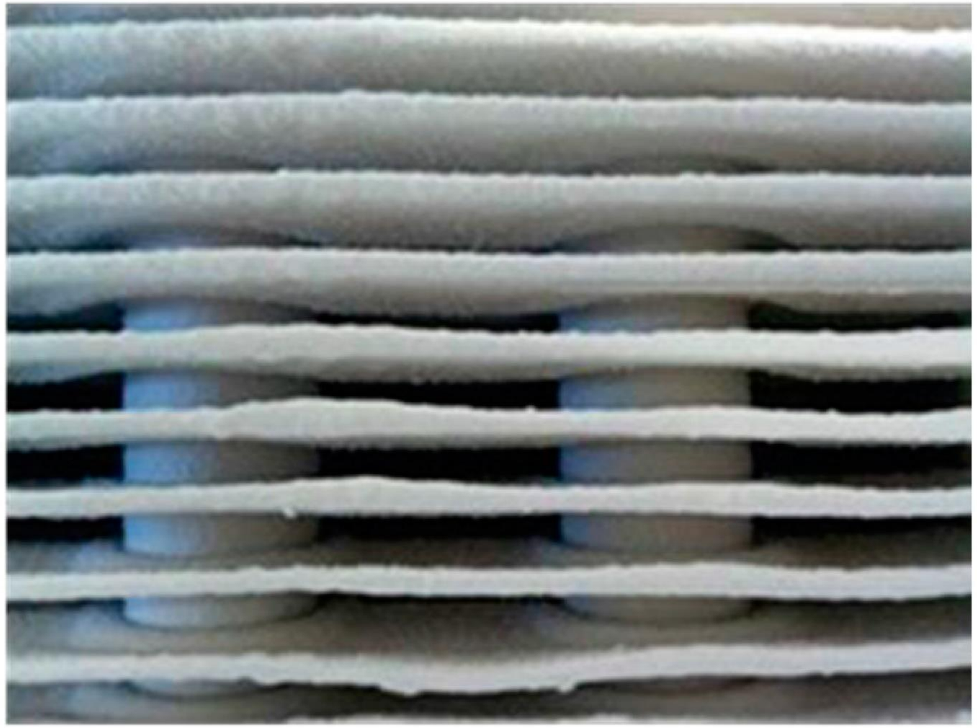
Proof of Concepts (1)

To tailor a new sorbent flexible composite coating with a macro-porous morphology with suitable film ability and good heat and mass transfer capacity.

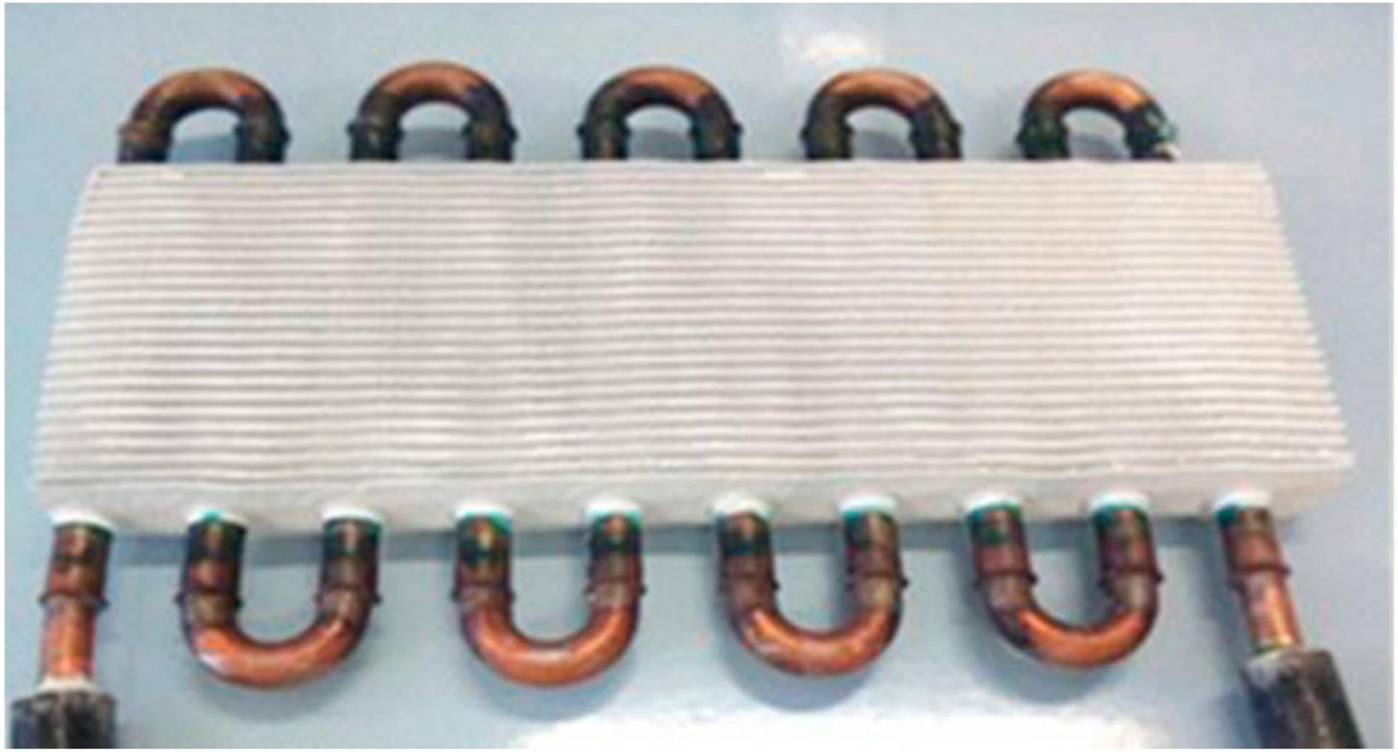


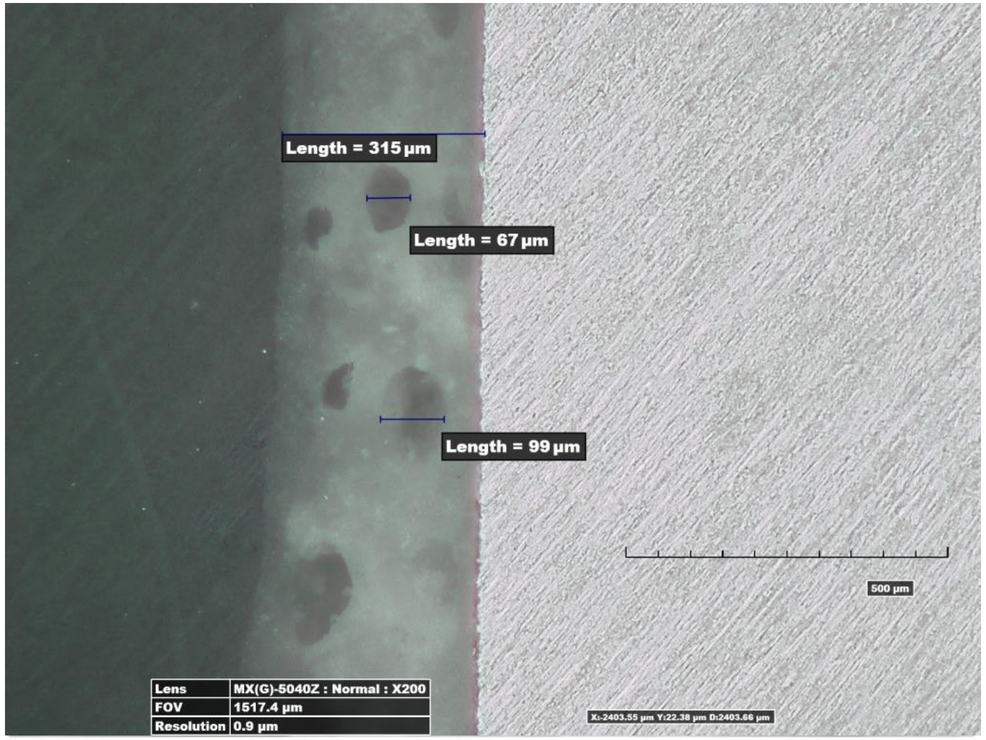
Results & Discussion





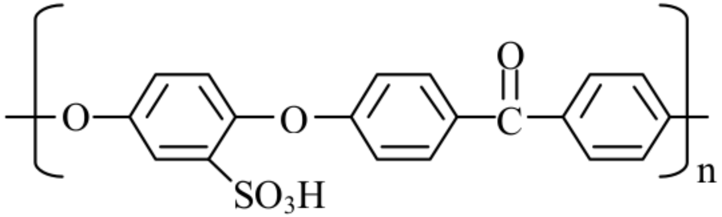
Results & Discussion



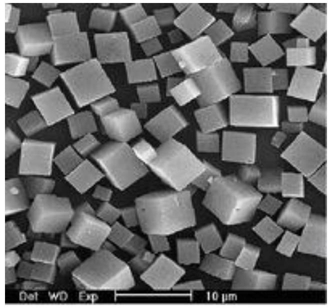


Proof of Concepts (II)

To tailor a new sorbent flexible composite coating with a micro-porous morphology with suitable film ability and good heat and mass transfer capacity.



S-PEEK



SAPO 34

graphite

Permeable thermoplastic Matrix

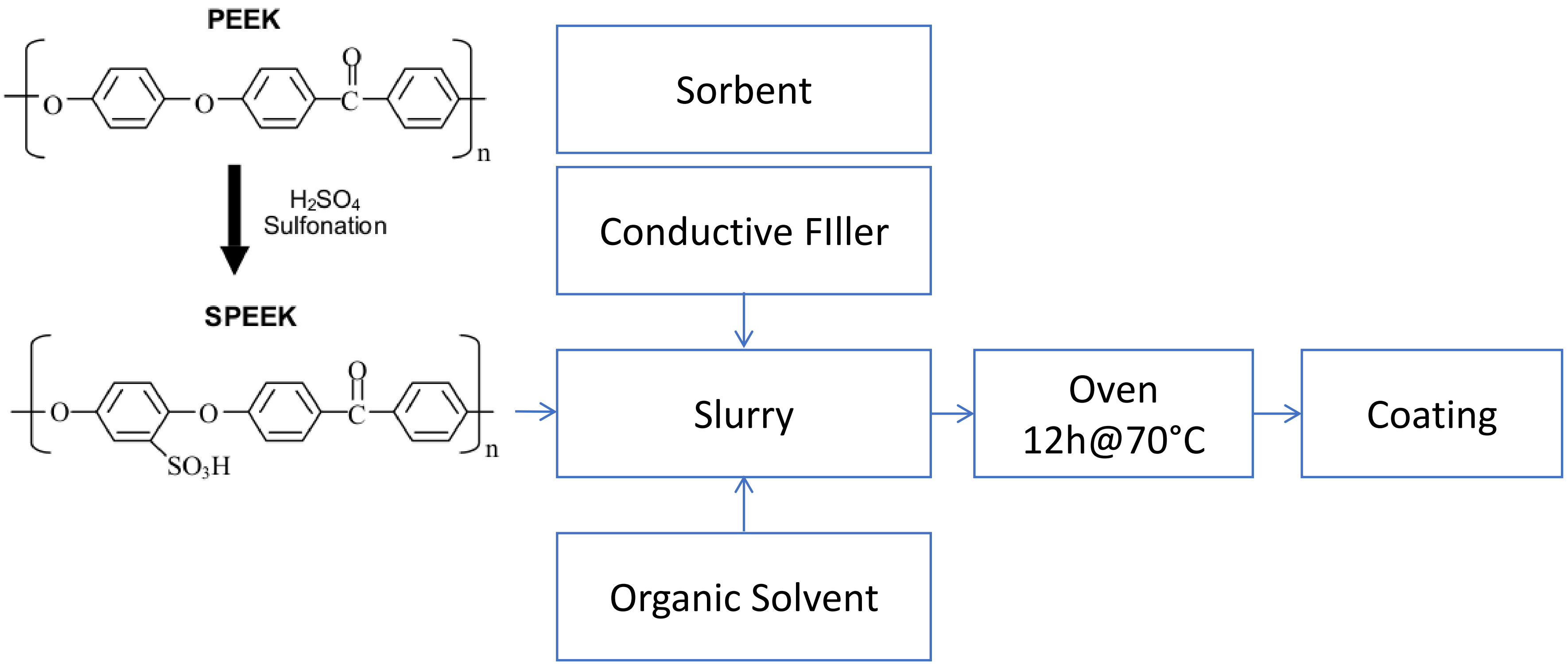
Adsorbent material

Thermal conductive filler

Patent n° 102015000044739

Proof of Concepts (I)

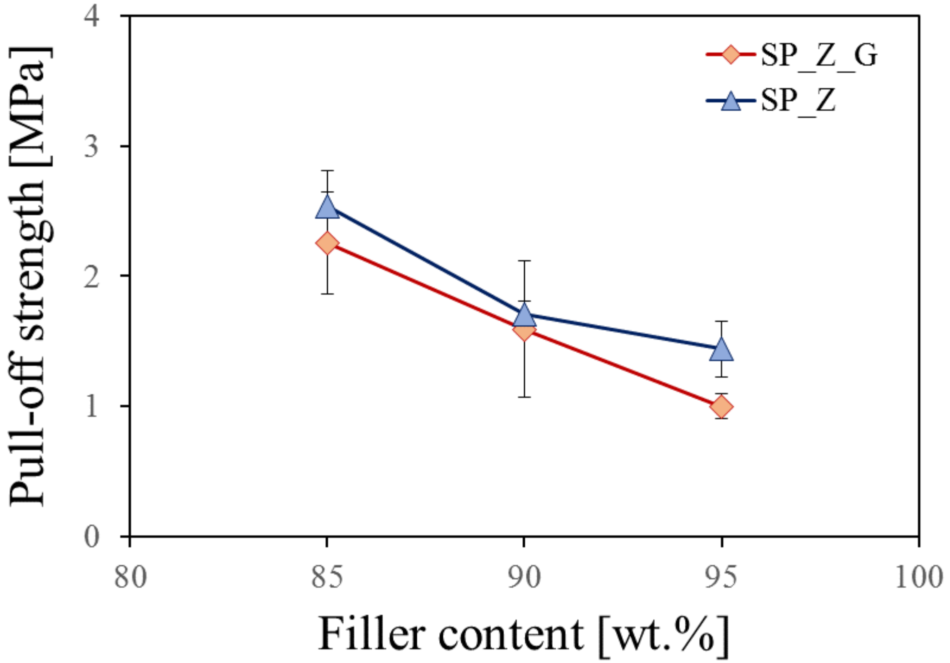
to design a sorbent coating with a microstructural porous morphology



Synthesis

Patent n° 102015000044739

Results & Discussion

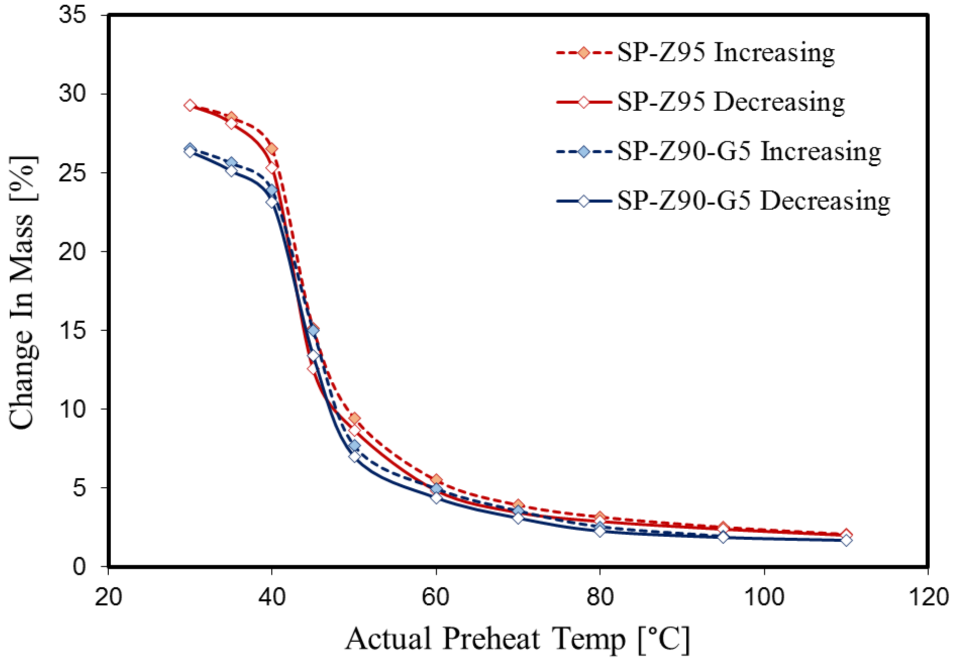


Adhesive fracture

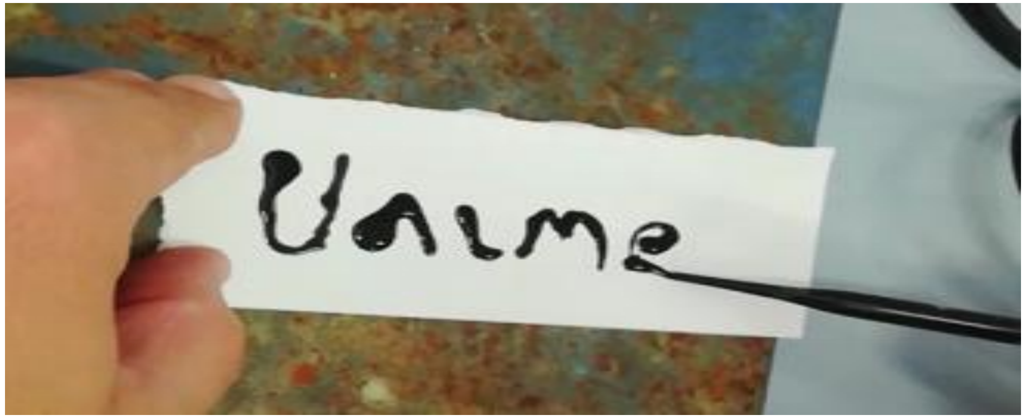
The water uptake curve is characterised by the typical S-shape adsorption trend.

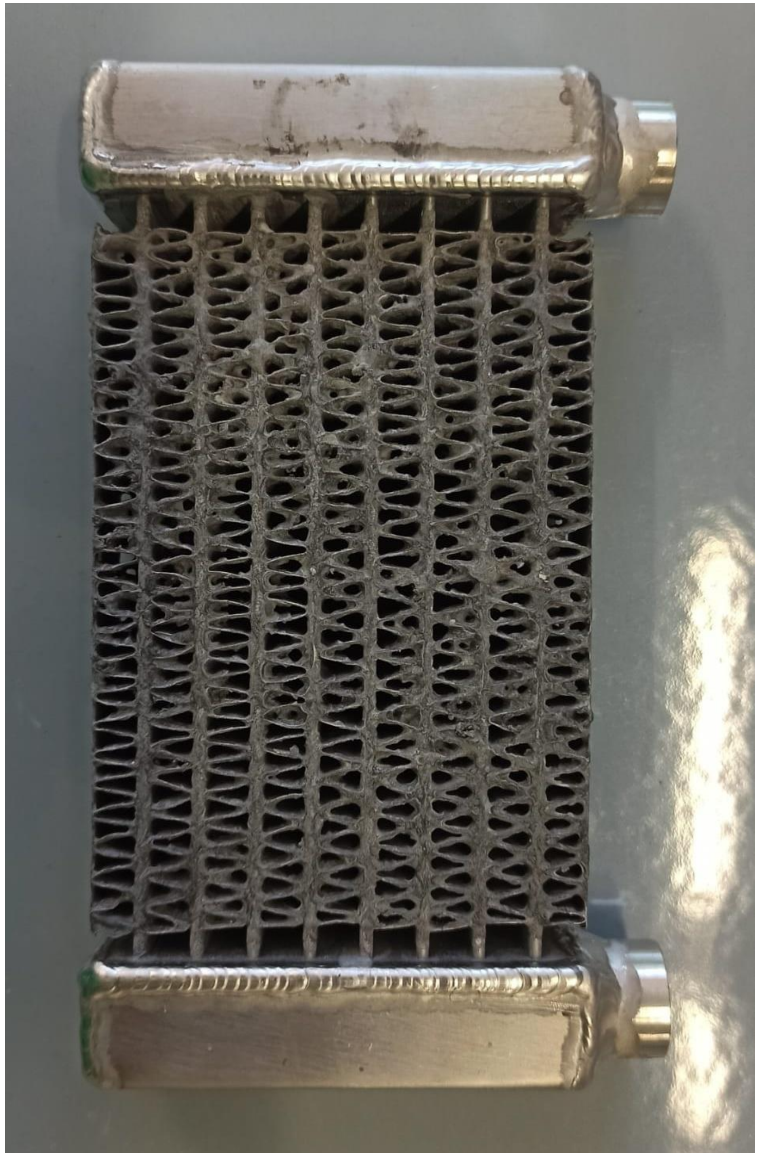
An increase of water uptake can be observed, according with SAPO-34, at about 45°C.

The adsoprtion performance of zeolite foamed coating is lower than SAPO 34 powder.



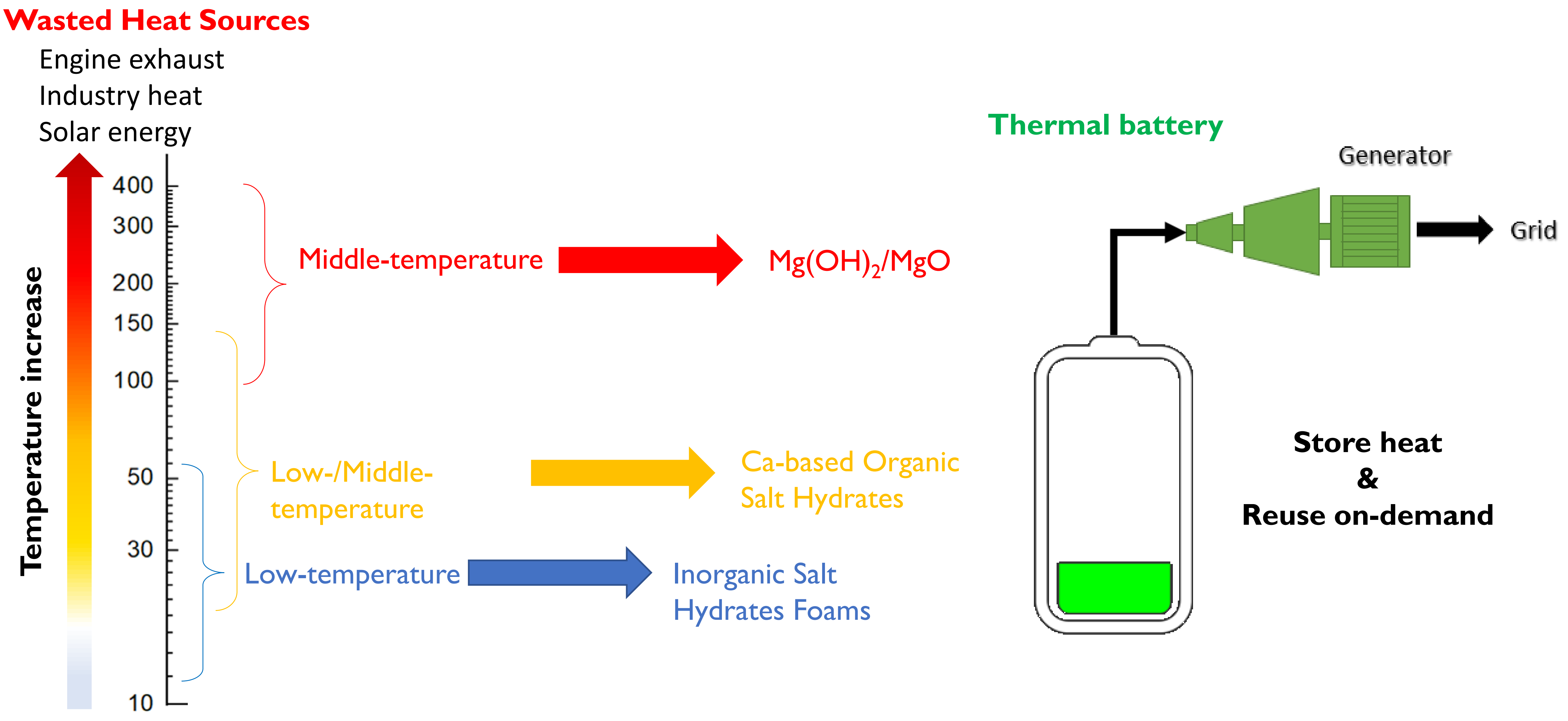
Results & Discussion





Thermochemical heat storage

low- and middle-temperature ranges



About $Mg(OH)_2$

Drawbacks

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

→ Decrease the overall conversion of the system

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

→ Poor durability to the charging/discharging cycles

Strategies

Tuning $Mg(OH)_2$ Structural, Physical, and Morphological Characteristics for Its Optimal Behaviour in a Thermochemical Heat-Storage Application

Proof of Concepts

Tailoring the morphology (primary particle size, surface area, etc.) of $Mg(OH)_2$ through the synthesis routes:

$$Mg(NO_3)_2 + 2NH_4OH \rightarrow Mg(OH)_2 + 2NH_4NO_3$$

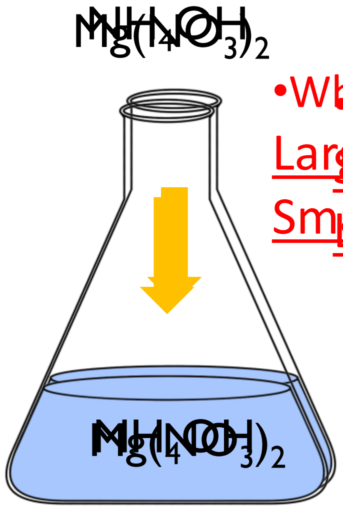
Reverse Deposition-Precipitation (RDP): gradual addition of the magnesium salt solution to the precipitating agent (pH ~11.5), under magnetic stirring

Deposition-Precipitation (DP): gradual addition of the NH_4OH solution to the magnesium salt solution under magnetic stirring

$$Mg(NO_3)_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaNO_3$$

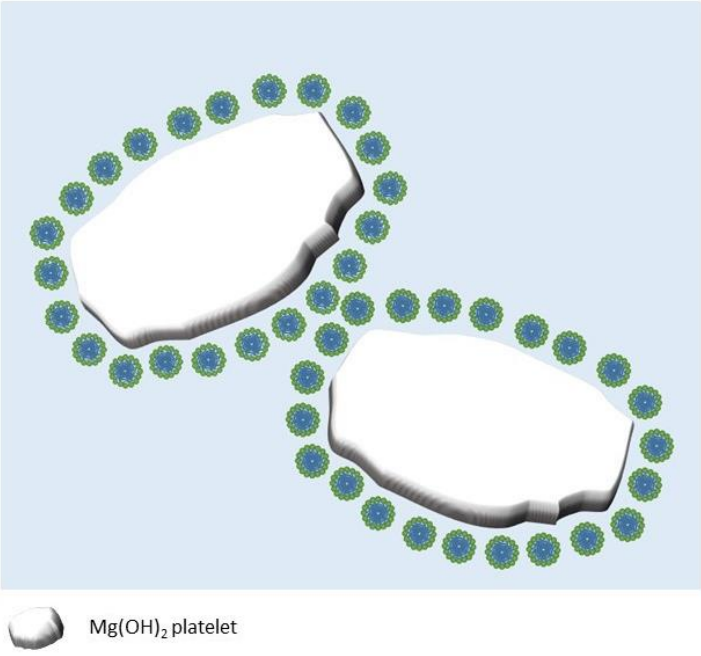
Precipitation in presence of a cationic surfactant (cetyl trimethyl ammonium bromide)

Use of a strong base

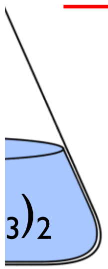


•What we expect:
Larger nuclei, larger p
Smaller surface area

•What we expect:
Smaller nuclei, sma
Larger surface area



Mg(OH)$_2$ platelet

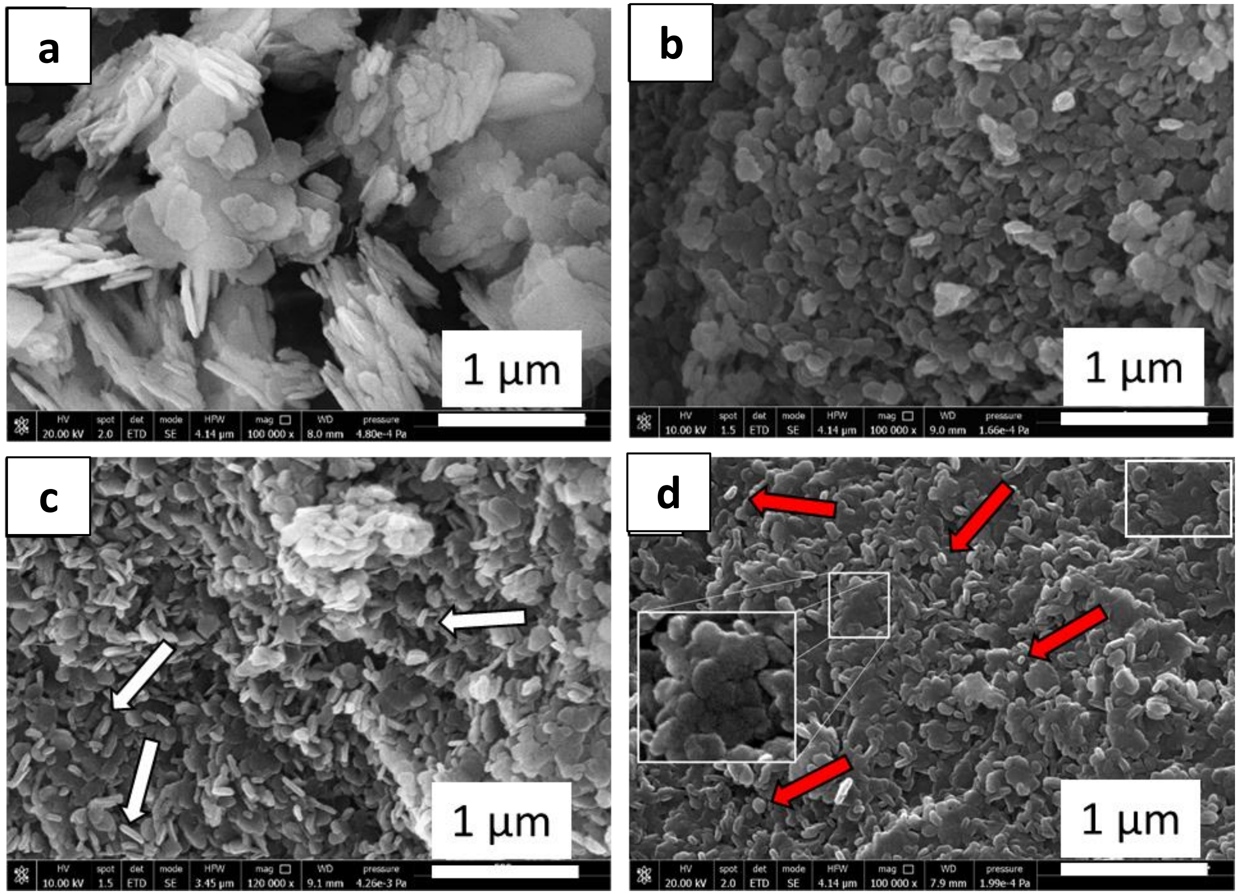


•What we expect
Increase the exposed active phase,
Increase the stored/released heat per volume unit

•What we expect:
Smaller nuclei, smaller particle size
Larger surface area

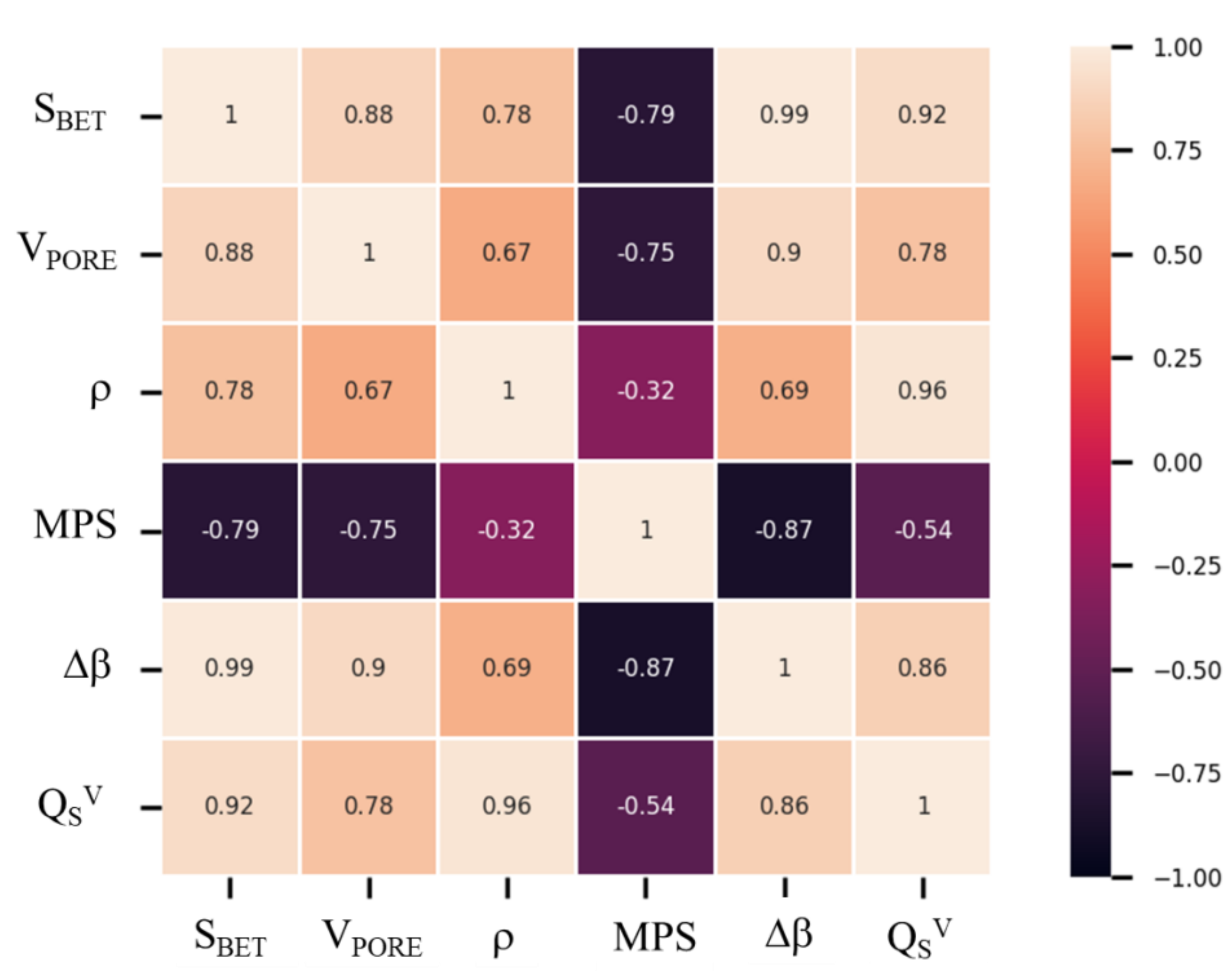
Results & Discussion

Code	Synthesis Procedures	Physical Properties		
		S_{BET} (m^2/g)	V_{PORE} (cm^3/g)	ρ (kg/m^3)
RDP-MH	Reverse deposition precipitation	44.4	0.112	350 ± 5
DP-MH	Deposition precipitation	64.5	0.618	345 ± 6
CTAB-DP-MH	Deposition precipitation in presence of CTAB	85.6	0.735	602 ± 6
N-DP-MH	Deposition precipitation using NaOH as precipitating agent	124.5	0.723	660 ± 4



Scanning electron microscope (SEM) images of (**a**) RDP-MH, (**b**) DP-MH, (**c**) CTAB-DP-MH, (**d**) N-DP-MH samples.

Cross-Correlation between $Mg(OH)_2$ Physical, Morphological and Thermochemical Variables



A material with a high surface area, a high pore volume, and a high density could guarantee an optimal conversion and a consequent high stored heat per volume unit.

N-DP-MH has higher density (660 kg/m^3) due to the particular morphology formed by globularly shaped hydroxide particles. This morphological characteristic allows the sample to reach a stored heat per volume unit equal to **684 MJ/m^3**.

<u>This value is one of the highest recorded in the literature for pure magnesium hydroxide</u> and represents a promising result toward the aim of thermochemical energy storage.

Low-/Middle-Temperature Thermochemical Heat Storage

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

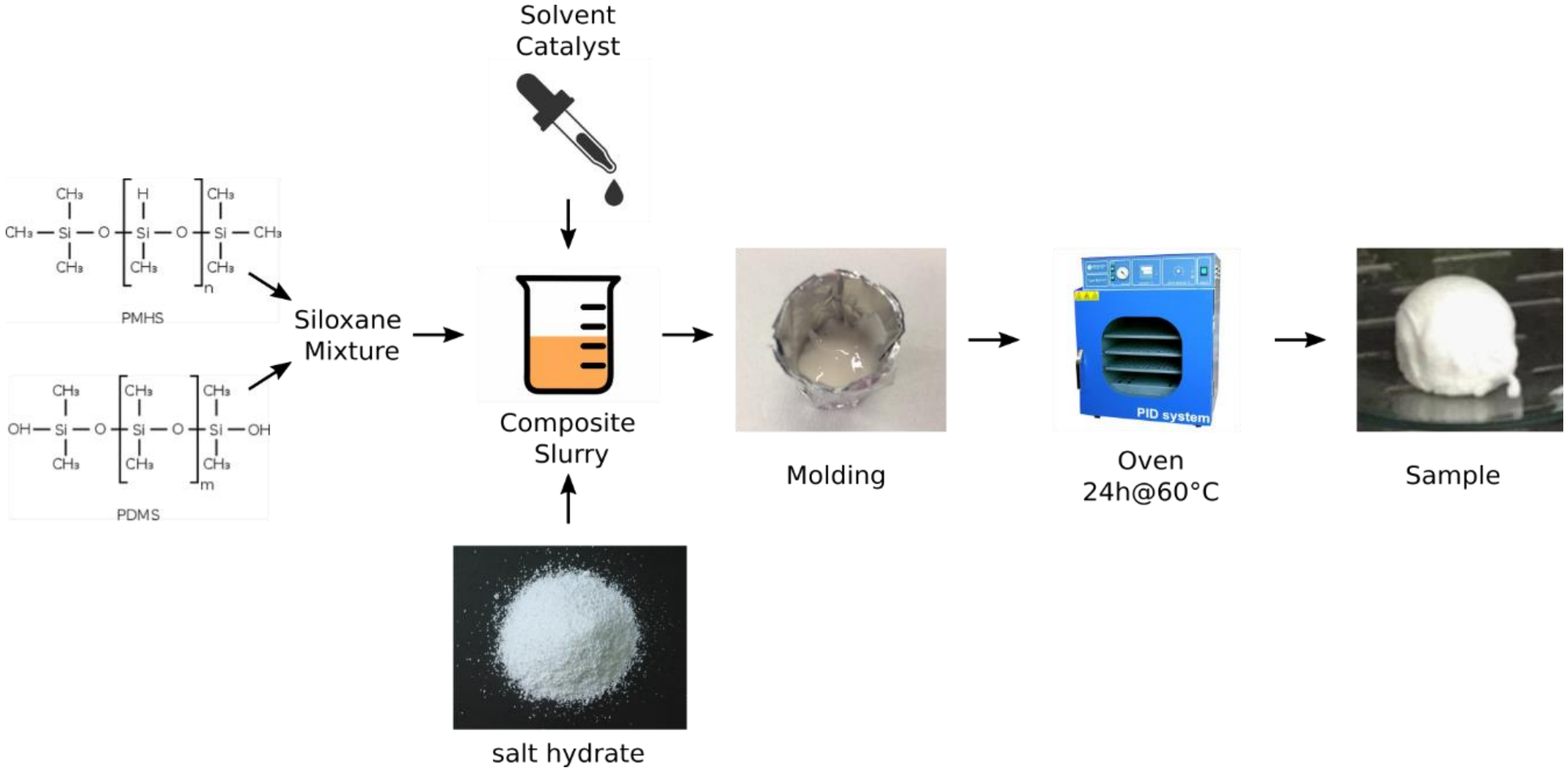
Strategies

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

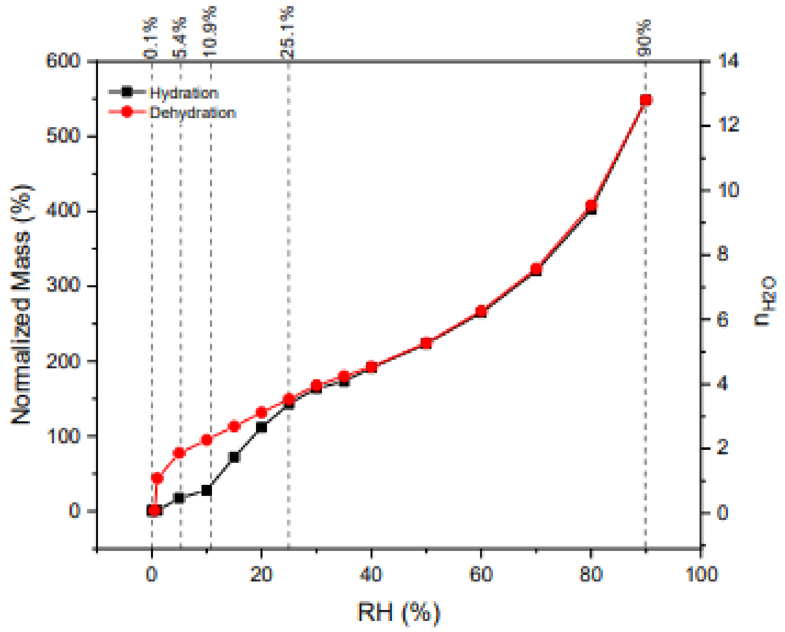
Proof of Concept (1)

Silicone vapor-permeable foam filled with the ISH

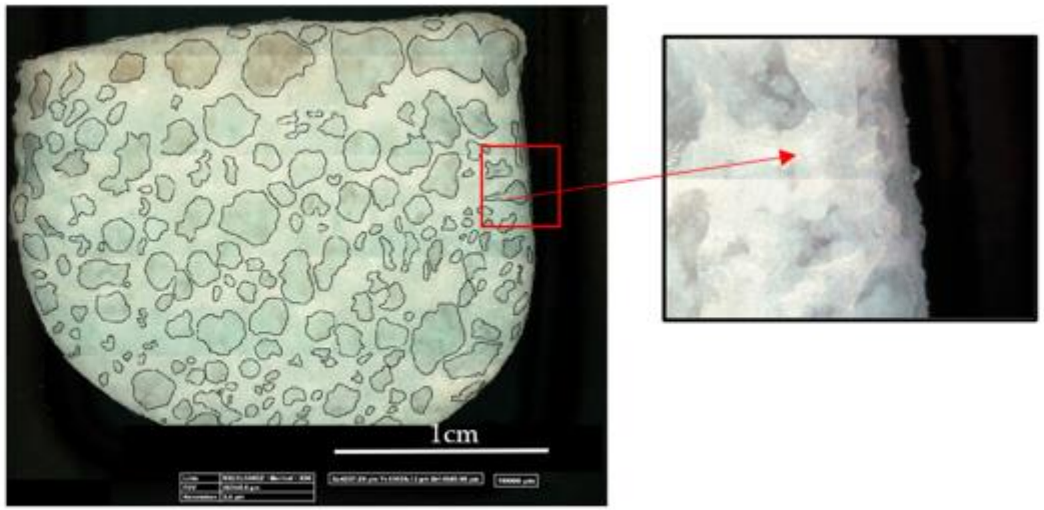
•What we expect:
Confinement of the salt in a matrix to prevent deliquescence-related issue but without inhibiting the vapour flow.



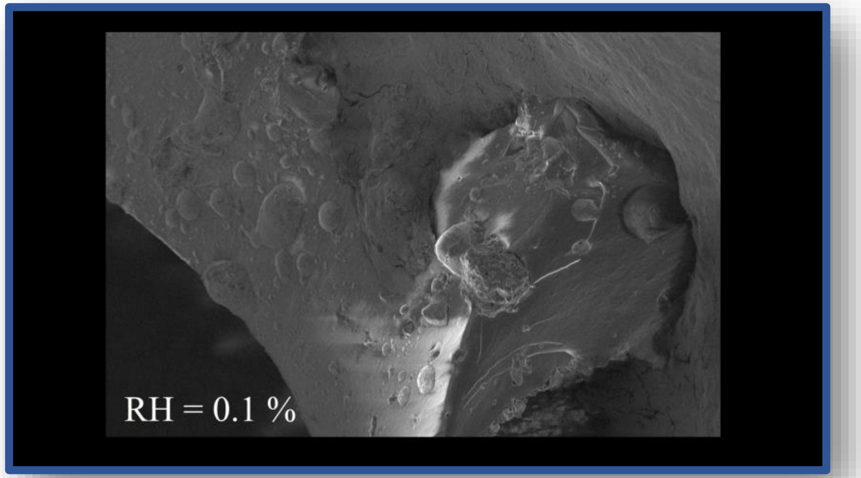
Results & Discussion

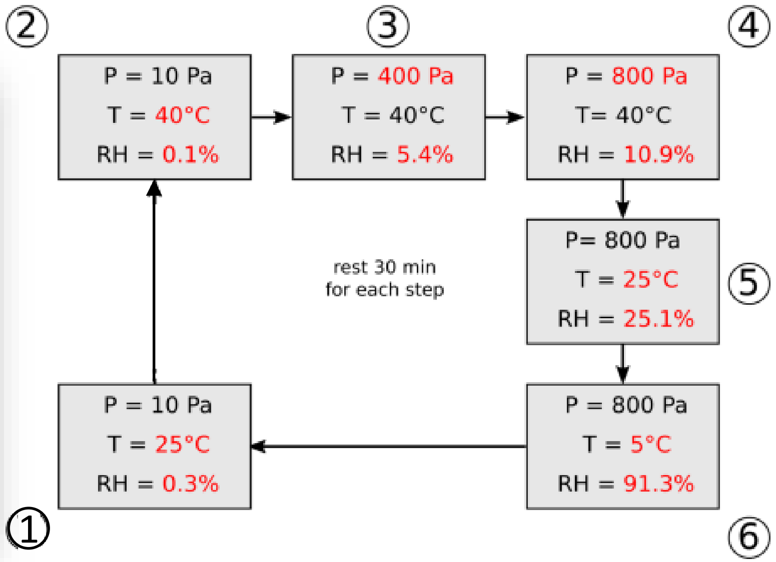


A hysteresis is observable in the RH range of 0–25% above this RH value, the hydration and dehydration profiles almost perfectly overlapped.



open and closed porosities





Sample	L-100	L-60
Salt content [wt.%]	100	60
Sorption enthalpy [J/g]	4500	3150
Foam Density [kg/m³]	-	657
Volumetric energy density [GJ/m³]	2.7	2.1

Proof of Concept (2)

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

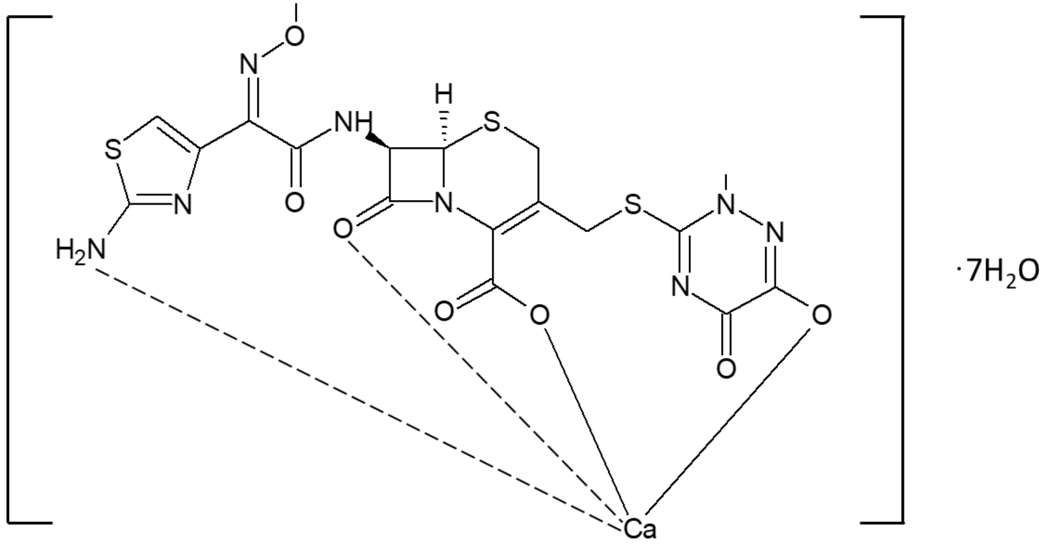
- **low water solubility**,
- **tendency to coordinate a high number of water molecules**
- **stability under operating conditions**.

What we expect:

Higher resistance towards deliquescence

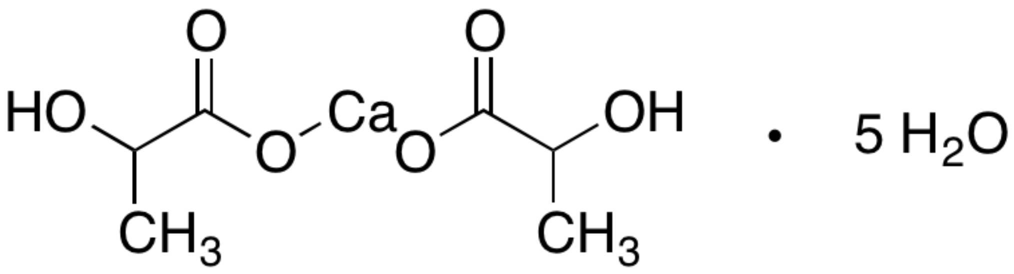
Less agglomeration

Higher cyclability



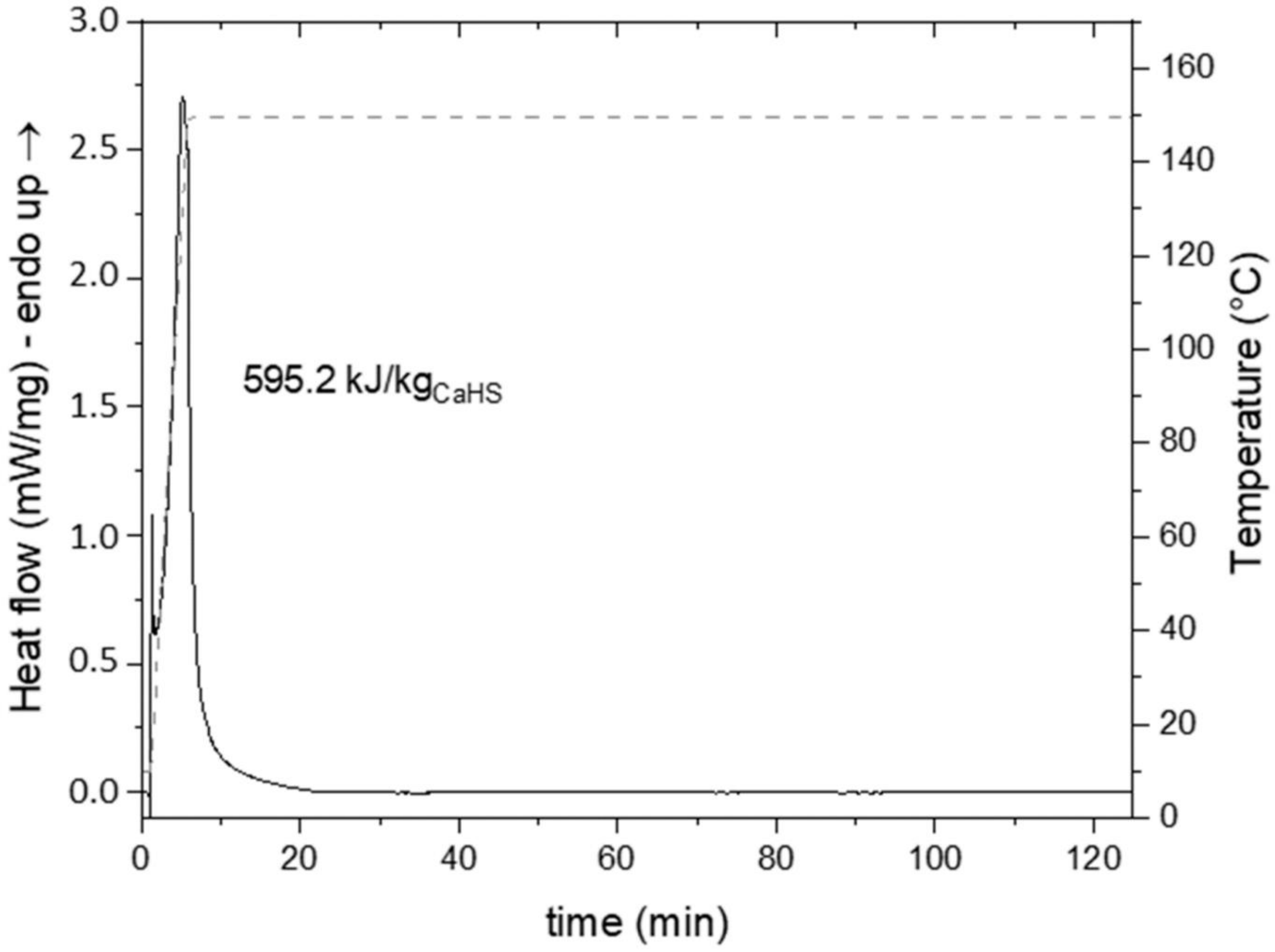
Model compound investigated:

1) Calcium ceftriaxone heptahydrate (CaCf)
2) Calcium Lactate Pentahydrate (CaLP)



About CaCf

Heat Storage Capacity



ΔH_r = 595 kJ/kg

Energy density = 278 kWh/m^3

Operating Temperature range: 20-150°C

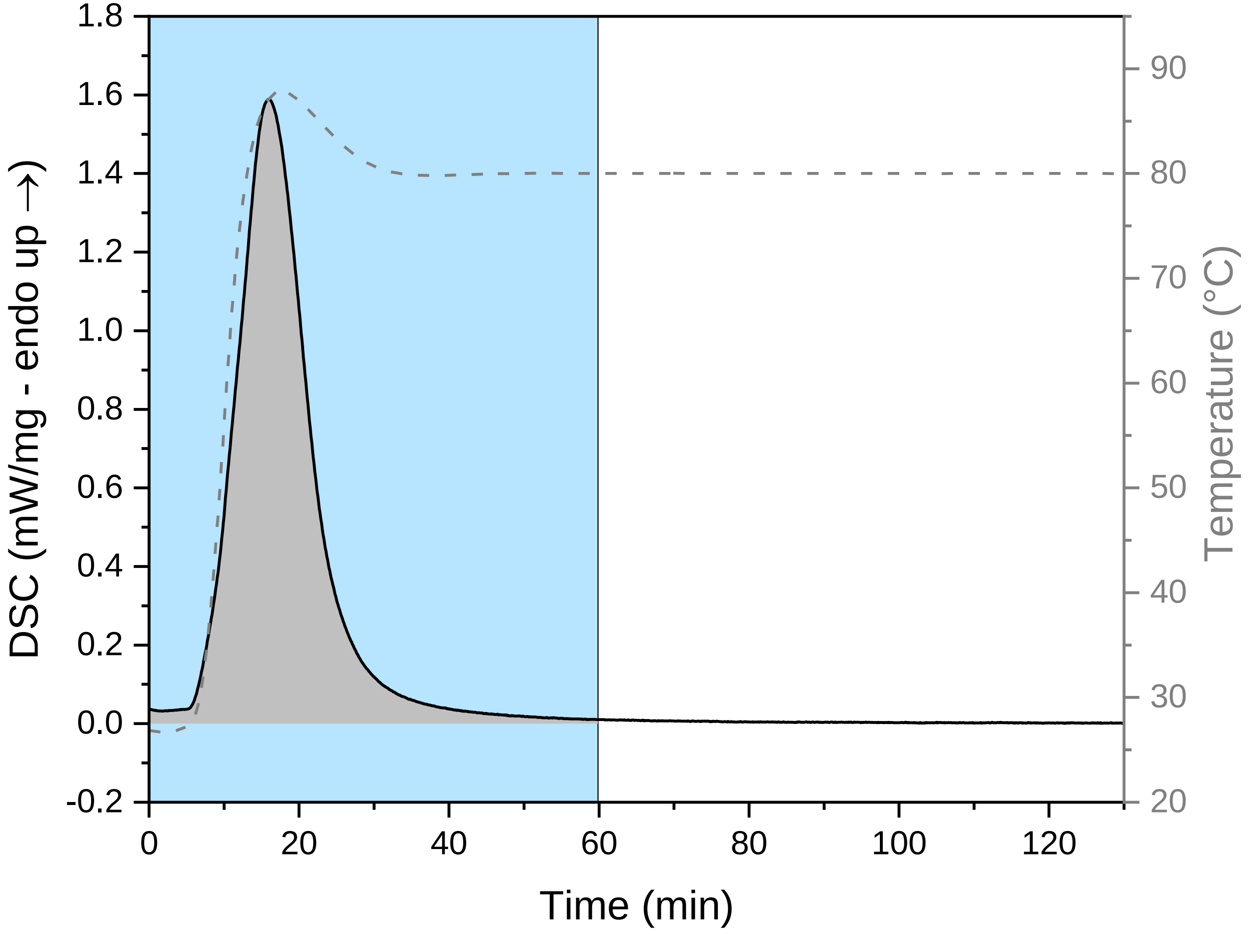
Advantages:

- No observed deliquescence at RH 100% and 22 °C
- Environmentally safe
- Non-corrosive

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

About CaLP

Heat Storage Capacity



ΔH_r = 1021 kJ/kg

Energy density = 425 kWh/m^3

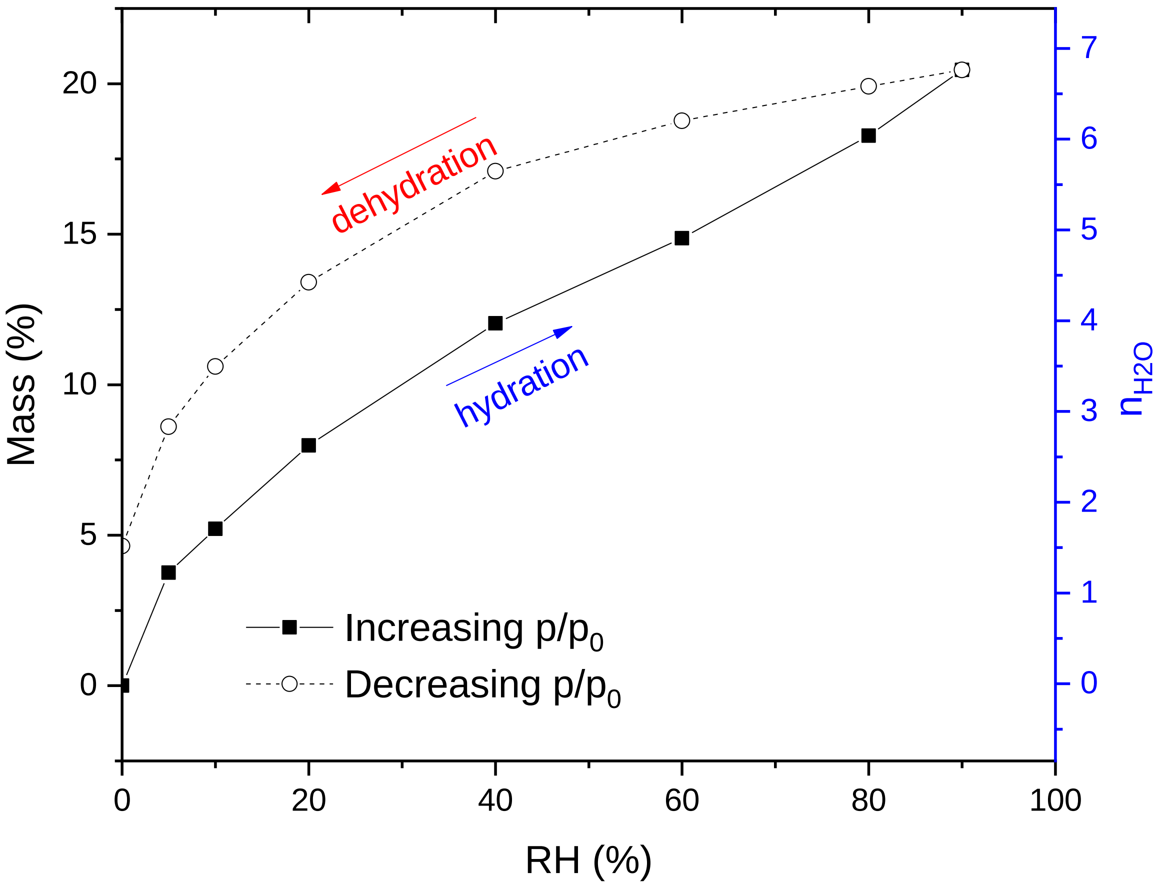
Operating Temperature range: 20-120°C

Advantages:

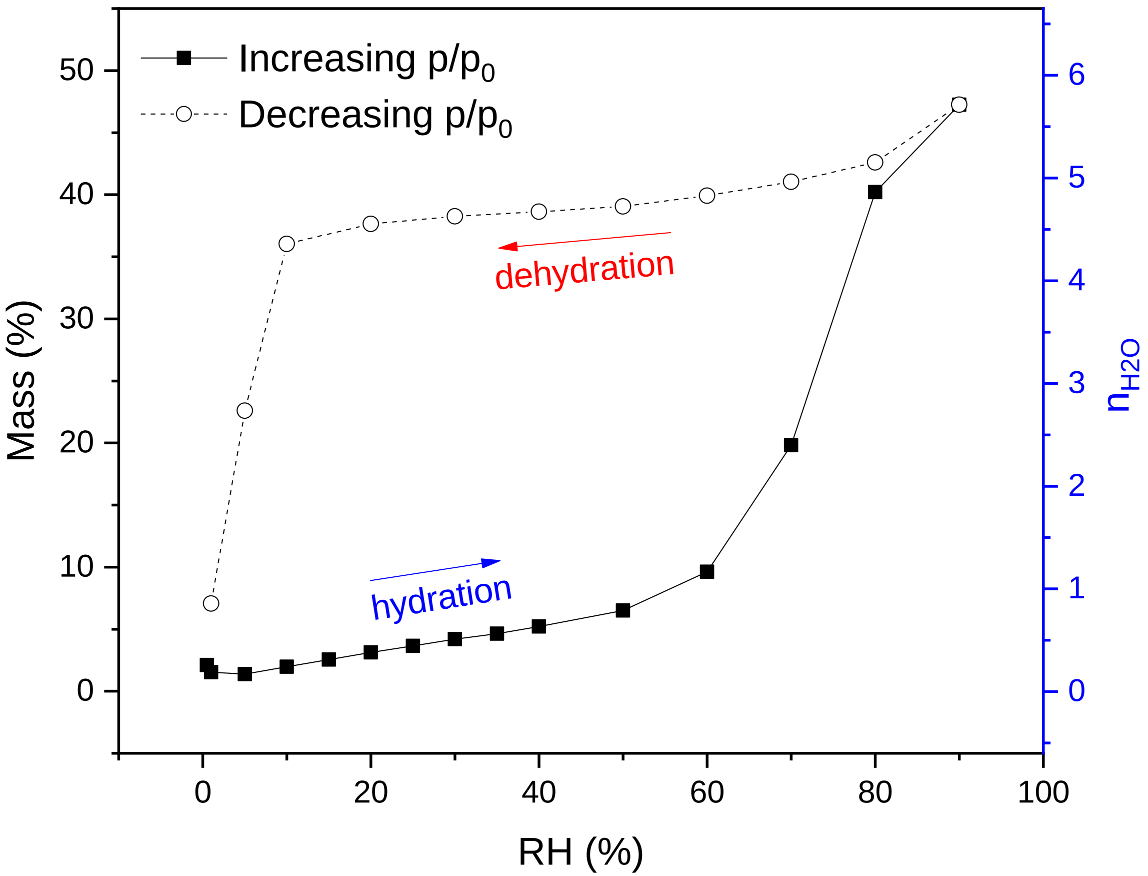
- Large enthalpy change
- No observed deliquescence at RH 100% and 22 °C
- Inexpensive
- Environmentally safe
- Non-corrosive
- Large availability

Comparison of Ca-based Organic Salt Hydrates

CaCf



CaLP



Comparison of Ca-based Organic Salt Hydrates with ISH

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

Università degli Studi di Messina
DIPARTIMENTO DI INGEGNERIA

TREES-MAT: Staff












7 Faculty Members

1 Secretary

1 Technician

7 Ph.D. Researchers

2 Fellowship Researchers

3 Graduate/Undergraduate Students

Technology and Research on Energy, Environment and Safety MATerials

Acknowledgments

This project has recived fundings from…..

Thank you!

Università degli Studi di Messina

DIPARTIMENTO DI INGEGNERIA

Contact: lcalabrese@unime.it

SORPTION FRIENDS III

Mission Innovation Heating and Cooling – Sorption Heat Pump Systems

Sorption Friends III

1st to 4th May 2023 Taormina ME, Italy