Salt hydrates as TCM for seasonal heat storage

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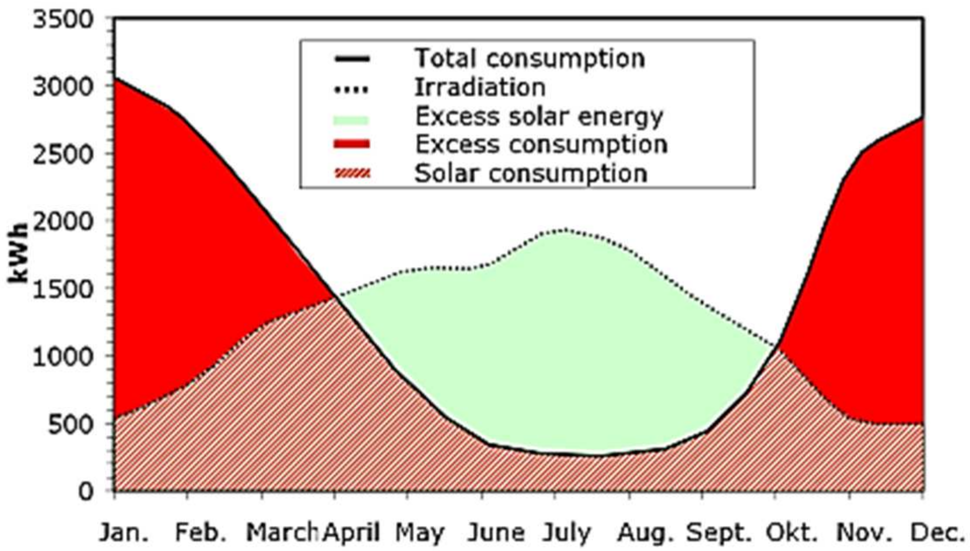
Salt hydrates for seasonal heat storage

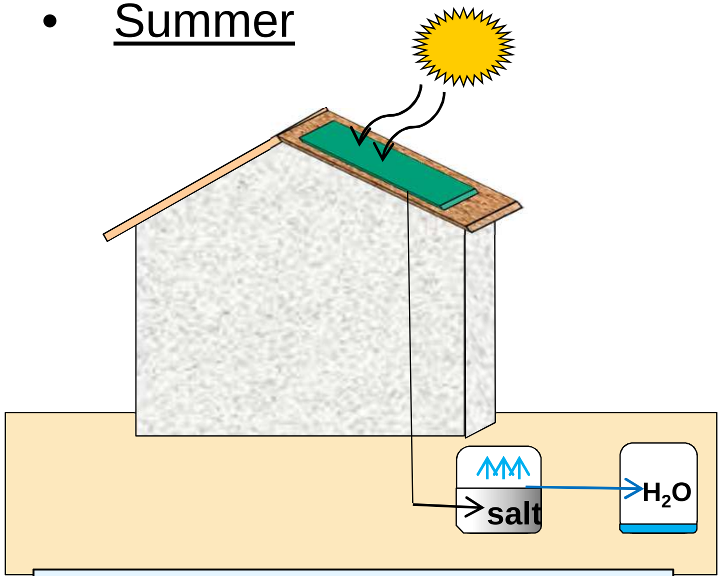


- In the Netherlands : 65 % of the domestic energy consumption (primary energy) is used for space heating and DHW
- Sustainable energy for build environment → solar energy
- Passive house of 110 m^2 with low energy standard → 6 GJ
- Water storage density = 0.25 GJ/m^3 (ΔT=60°C) → water tank > 30-40 m^3

Heat storage with a compact bed of crystalline salt hydrates
High energy density, low cost and eco-friendly materials

Practical conditions for the heat storage

- Summer

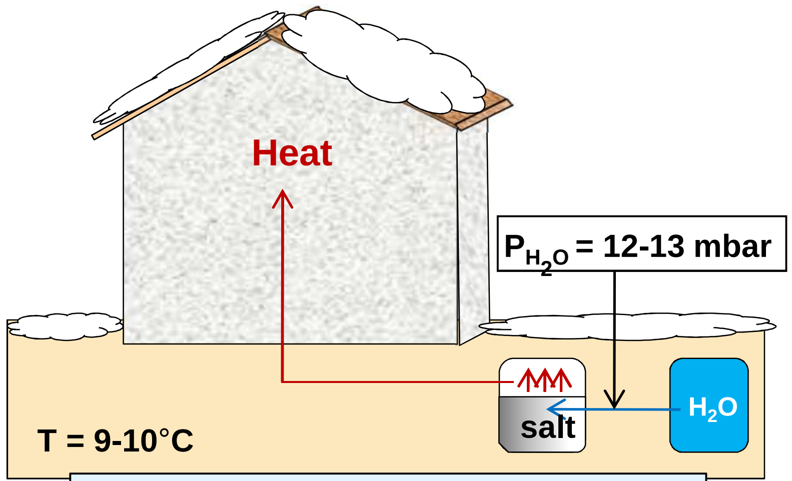


$Salt.nH_2O$ + heat ⟶ Salt + nH_2O

Dehydration @ T < 150°C with

P_{H_2O} = 13 mbar (average seasonal conditions)

- Winter



Salt + nH_2O ⟶ $Salt.nH_2O$ + heat

Hydration @ ambient temperature

with P_{H_2O} = 13 mbar (borehole)

⇨ Released T > 60°C (space heating & DHW)

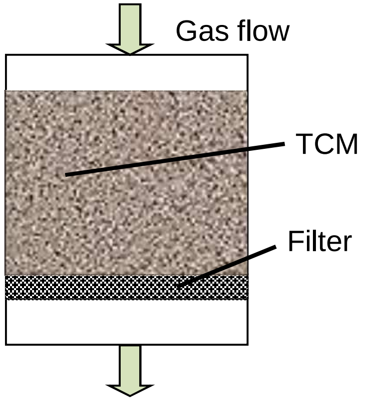
Actual status at ECN

- Screening of materials → selection of two materials

Materials	$MgSO_4 \cdot 7H_2O$	$MgCl_2 \cdot 6H_2O$
Dehydration @ 150°C	**7 → 1**	**6 → 2**
Hydration @ 13 mbar	**1 → 6**	**2 → 6**
Theoretical bed energy density (50% porosity)	**1.10 GJ/m^3**	**0.97 GJ/m^3**

Final heat storage system :

compact bed of 6 m^3



Actual lab tests performed at ECN are performed on a reactor of 20L

Actual status at ECN

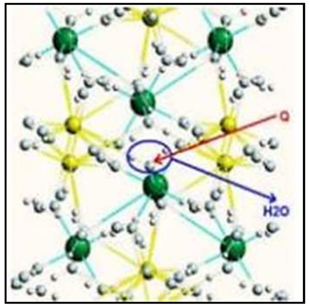
- Experimental results of the selected TCM :

Materials	$MgSO_4 \cdot 7H_2O$	$MgCl_2 \cdot 6H_2O$
Dehydration @ 150°C **Hydration @ 13 mbar**	**7 → 1** 1 → 2	**6 → 2** 2 → 6 + overhydration
Experimental energy density (50% porosity)	**0.4 GJ/m^3**	≈ 1 GJ/m^3
Release of heat	**ΔT = + 6°C**	**ΔT = + 60°C**

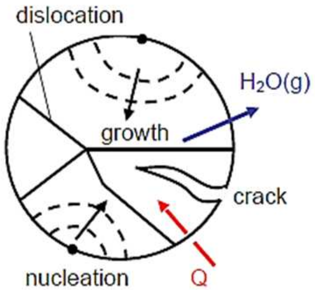
→ A fundamental understanding of the water vapor sorption process is required to improve these materials

Objectives of the project

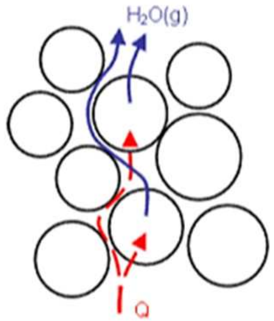
Crystallites



Grains



Powder bed

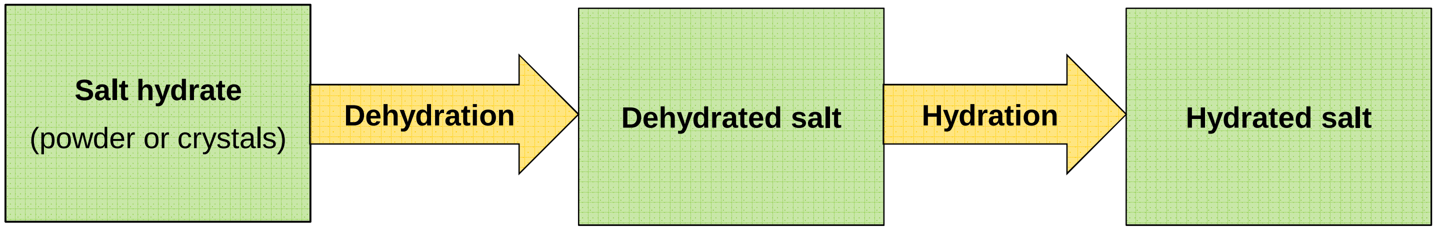


- Characterization of the water vapor sorption process in crystalline salt hydrates under practical conditions :
  - Identification of the reactions of deh./hyd. and definition of their kinetics of reactions
  - Identification of the changes of structure, composition & texture of the material
  - Identification of the heat and water vapor flow
- Improvement of the TCM materials for long term application by means of composite materials or matrix carrier and development at the level of the 6 m^3 reactor

Methodology of research

References : studies of the water vapor sorption on $Li_2SO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$

⇨ Selection of characterization techniques and establishment of experimental protocol

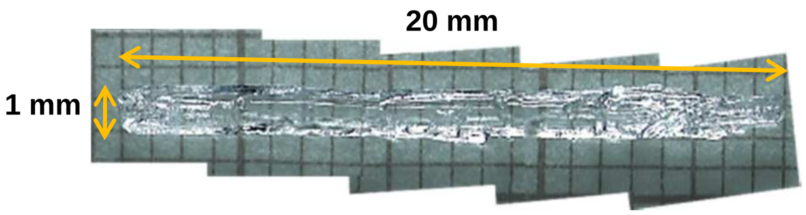


- Identification of the kinetics & reactions enthalpies by Thermal analyses (TGA-DSC)
- Investigations of structure and compositions changes of the material by *in-situ* X-ray diffraction
- Identification of the textural change of the material by microscopic observations on monocrystals

Preparation of the materials

- Sieving of commercial powder at different PSD → selection of **100-200 μm**
- Synthesis of monocrystals by slow evaporation of saturated solution

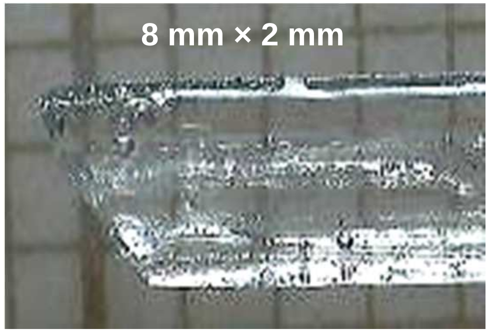
$MgSO_4 \cdot 7H_2O$



Crystal size too small for a good material characterization

→ New experiments in progress

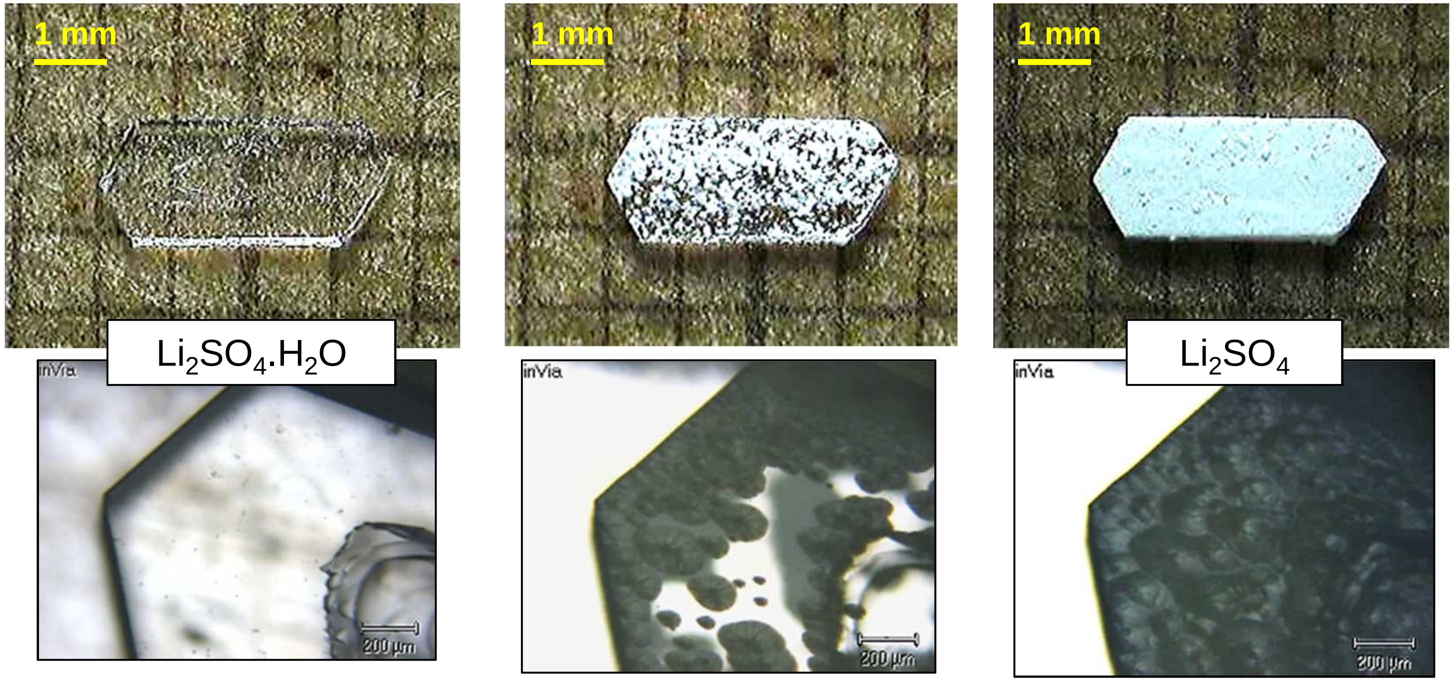
$MgCl_2 \cdot 6H_2O$



→ Investigation of the water vapor sorption process on monocrystal in progress

Investigations on reference materials crystals

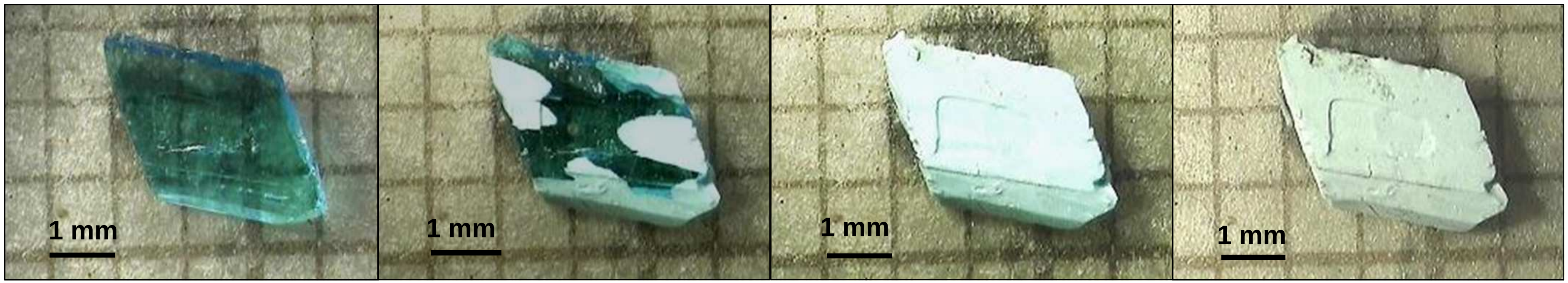
- Textural observations on $\underline{Li_2SO_4 \cdot H_2O}$ monocrystal
  - → homogeneous nucleation and growth processes



Investigations on reference materials crystals

- Textural observations on $\underline{CuSO_4 \cdot 5H_2O}$ monocrystal

  → preferential orientation of the nucleation and growth processes



$CuSO_4.5H_2O$ → $CuSO_4.3H_2O$ → $CuSO_4.H_2O$

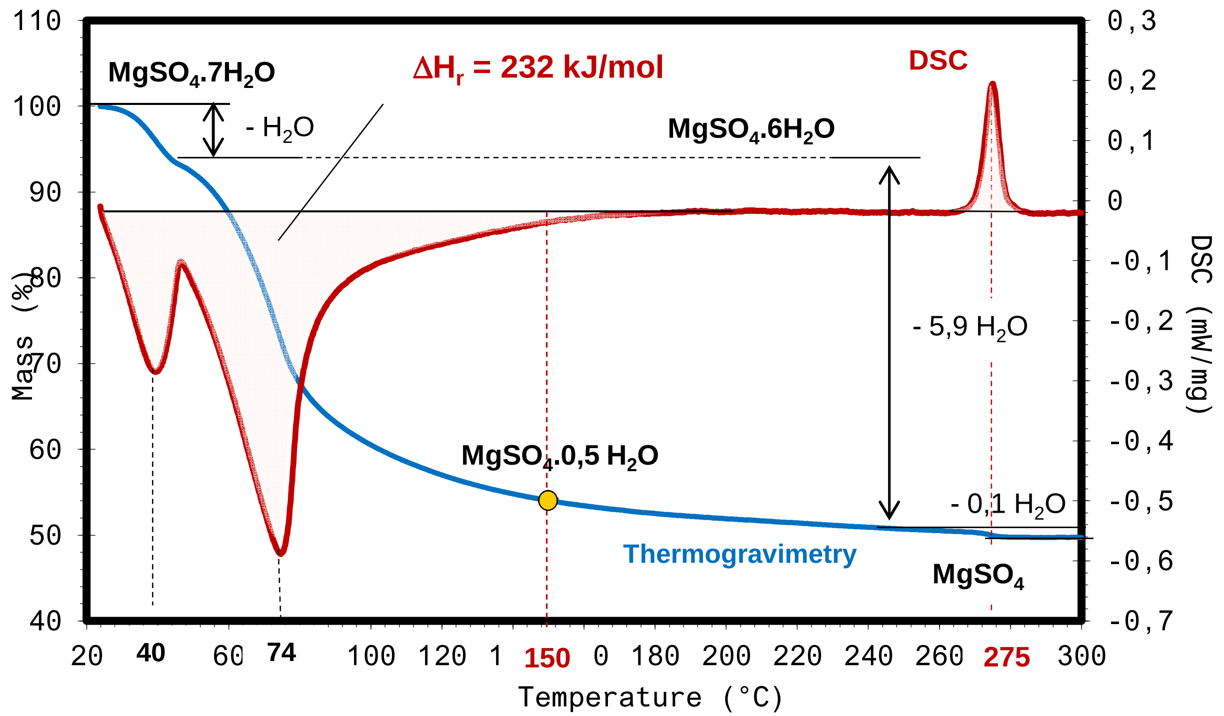
Preferential orientation of the nucleation and growth on one face of the crystal

Increase of cracks with the temperature

Study of $MgSO_4 \cdot 7H_2O$ powder

- Thermal analysis of the dehydration of $MgSO_4 \cdot 7H_2O$

Experimental conditions : $p(H_2O)$ = 13 mbar, ΔT = 30 - 300℃, heating rate = 1℃/min



NBS tables : 7→ 1

ΔH_r = 336 kJ/mol

Phase transition not independent

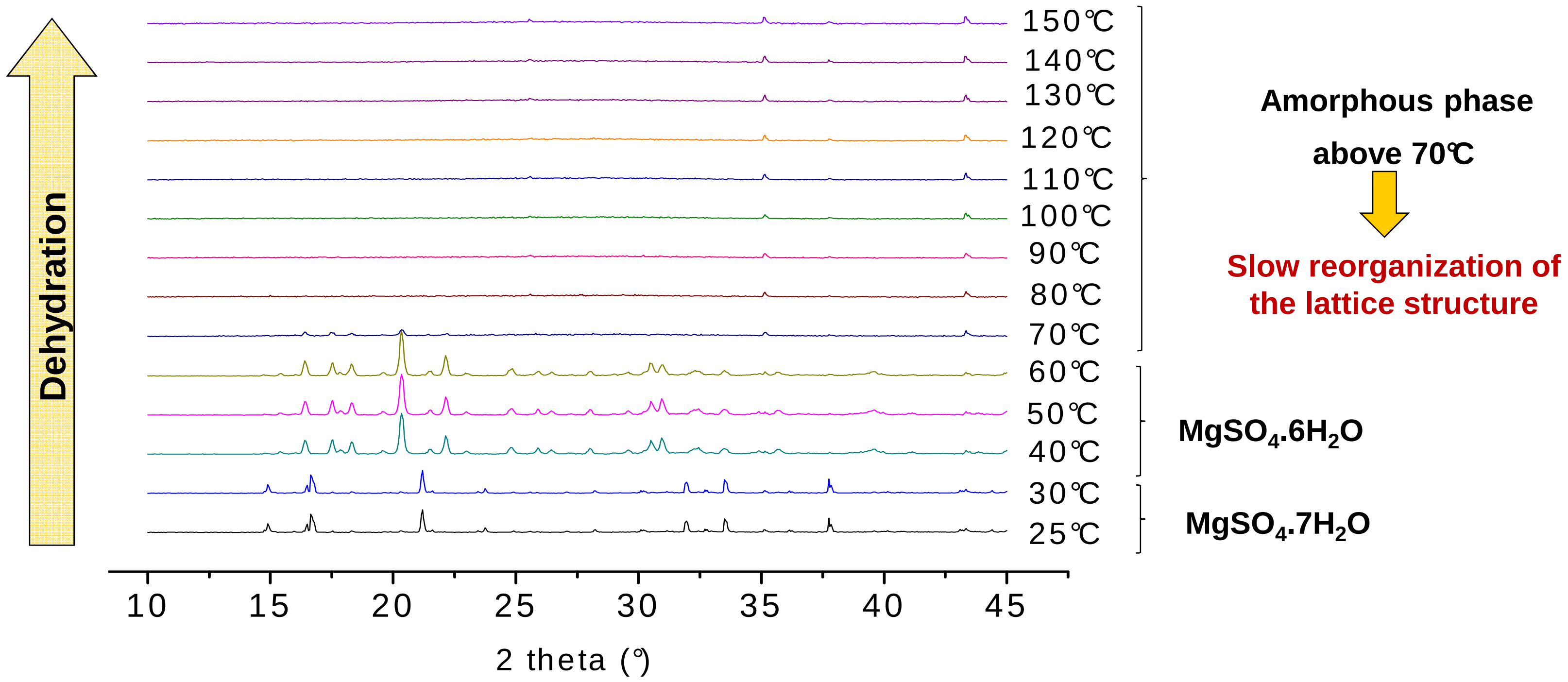
Heating rate too fast

Control of the $p(H_2O)$ uncertain

Study of $MgSO_4 \cdot 7H_2O$ powder

- XRD analyses of the dehydration of $MgSO_4.7H_2O$

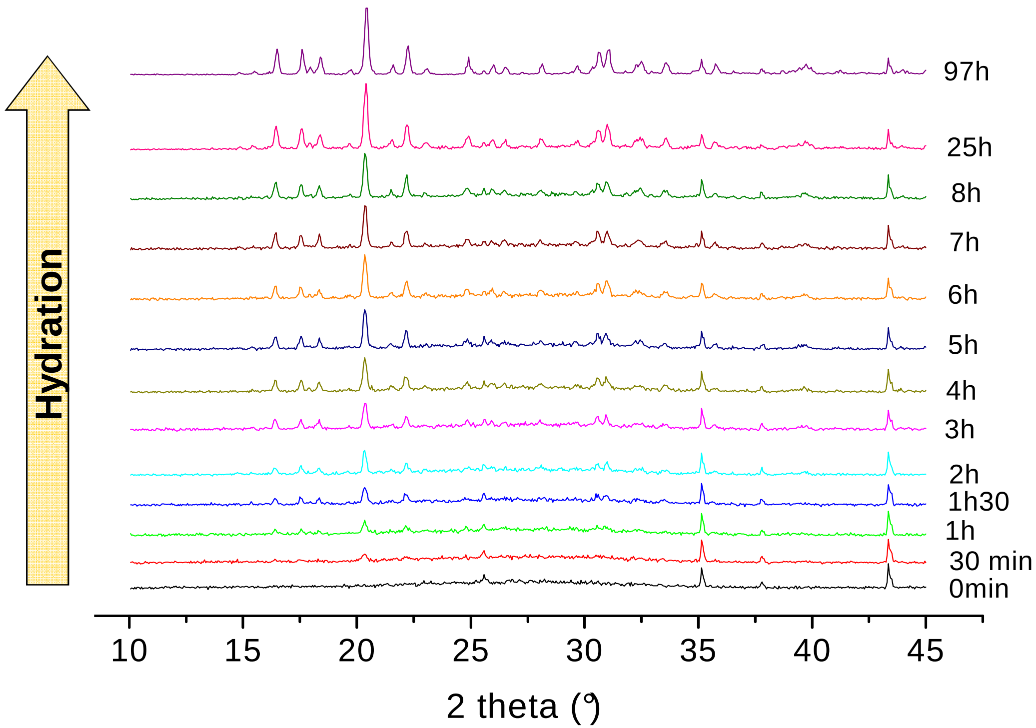
Experimental conditions : $p(H_2O)$ = 13 mbar, ΔT = 25 - 150℃, heating rate = 1℃/min



Study of $MgSO_4 \cdot 7H_2O$ powder

- XRD analyses of the hydration of dehydrated $MgSO_4 \cdot 7H_2O$

Experimental conditions : $p(H_2O)$ = 13 mbar, ΔT = 150- 25℃, cooling rate = 1℃/min
+ isotherm @ 25℃for 97h



Progressive rehydration of the amorphous phase @ 25℃ starting after 30 min → $MgSO_4 \cdot 6H_2O$

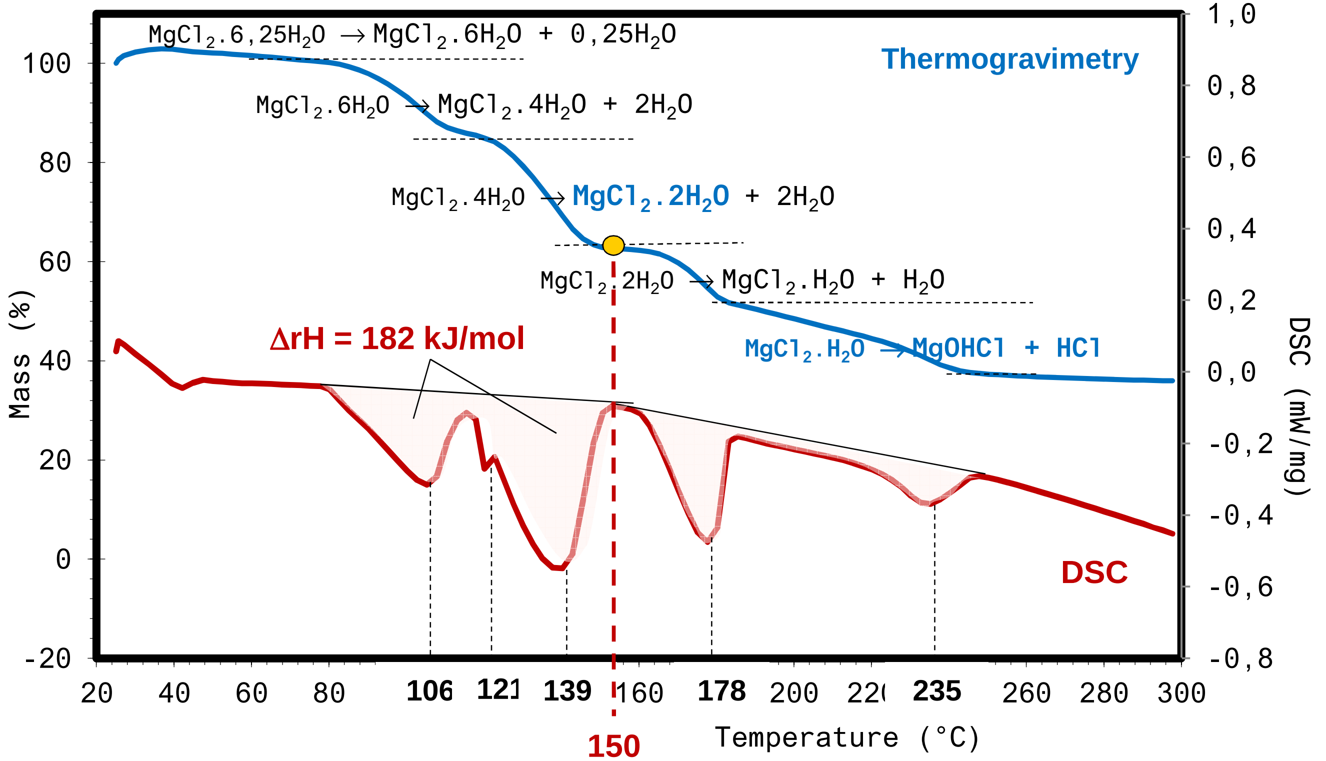
Literature :

Formation of $MgSO_4 \cdot 7H_2O$ for $p(H_2O)$ > 60 mbar

Study of $MgCl_2 \cdot 6H_2O$ powder

- Thermal analysis of the dehydration of $MgCl_2 \cdot 6H_2O$

Experimental conditions : $p(H_2O)$ = 13 mbar, ΔT = 30 - 300°C, heating rate = 1°C/min



NBS tables : 6→ 2

ΔrH = 252 kJ/mol

Phase transition not independent

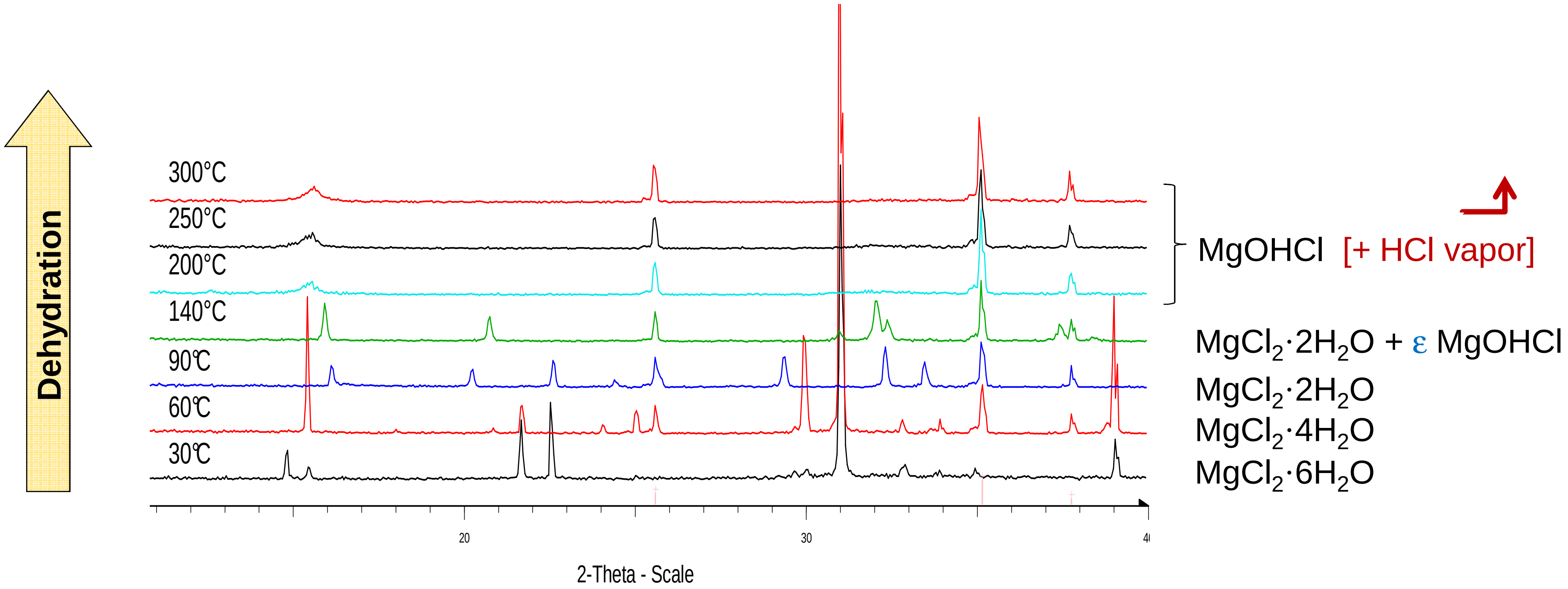
Same conclusions as for $MgSO_4.7H_2O$

→ heating rate too fast, $p(H_2O)$ not well controlled

Study of $MgCl_2 \cdot 6H_2O$ powder

- XRD analyses of the dehydration of $MgCl_2 \cdot 6H_2O$

Experimental conditions : p(H_2O) = 13 mbar, ΔT = 30 - 300°C, heating rate = 1°C/min



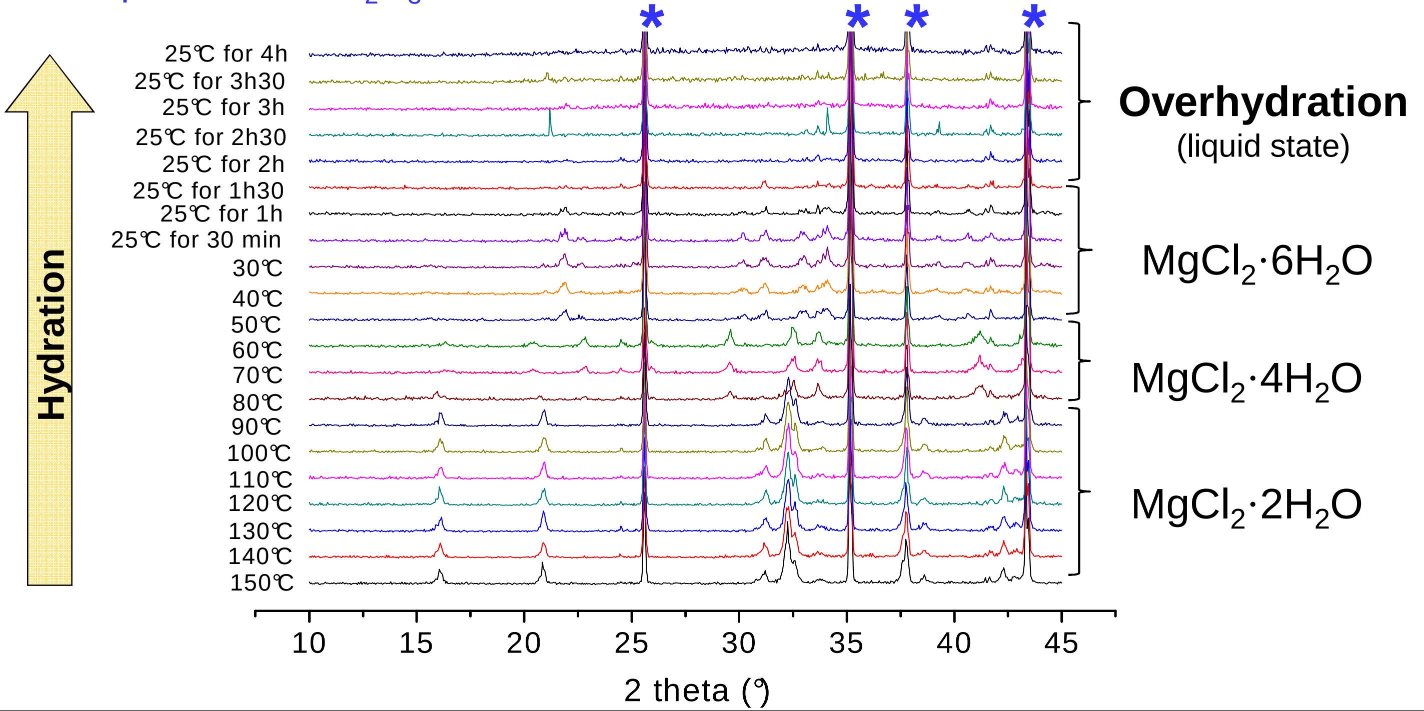
Limitation of dehydration process @ 130°C

Study of $MgCl_2·6H_2O$ powder

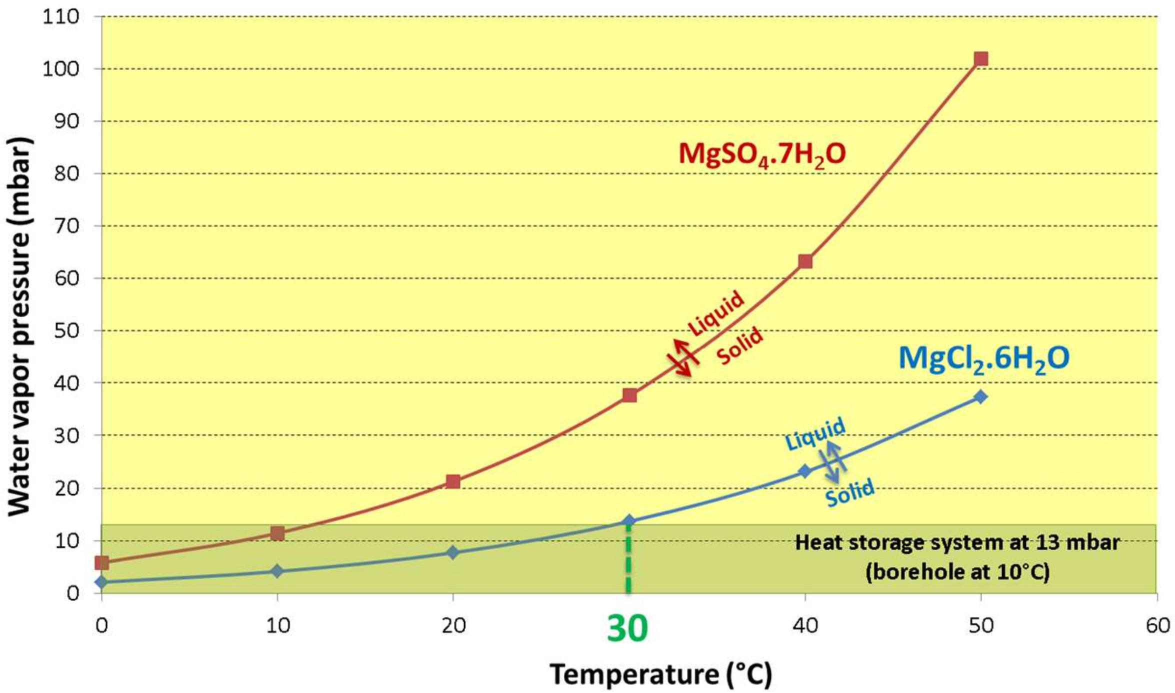
- XRD analyses of the <u>hydration of $MgCl_2·6H_2O$ dehydrated @ 150°C</u>

Experimental conditions : $p(H_2O)$ = 13 mbar, ΔT = 150- 25℃, cooling rate = 1℃/min
+ isotherm @ 25℃for 4h

*sample holder in Al_2O_3



Study of $MgCl_2.6H_2O$ powder



At 13 mbar, $MgCl_2.6H_2O$ stable for a temperature <u>above 30℃</u>

Conclusions

- Summary of the results obtained on TCM

Materials	Dehydration @ 150 ℃ / 13 mbar	Hydration @ 25 ℃ / 13 mbar
$MgSO_4.7H_2O$	Formation of an amorphous phase with the composition $MgSO_4 \cdot 0.5H_2O$	Slow rehydration starting after 30 min to form $MgSO_4 \cdot 6H_2O$ phase, total rehydration after 97h
$MgCl_2.6H_2O$	Temperature max **130℃** to limit the formation of HCl vapor → formation of $MgCl_2 \cdot 2H_2O$	Faster hydration than sulfates Rehydration should take place with a temperature above **30℃**

- Kinetic study : Enthalpy values lower than the theoretical values and the phase transitions are not independent

→ **Heating rate too fast, control of the $p(H_2O)$ is uncertain**

Perspectives

- Reproduction of the thermal analyses under better controlled p(H_2O) and lower heating rate
- Perform similar characterizations on TCM storage materials as the ones made on the reference materials (Li/Cu hydrates)
- Improving the TCM storage materials by using composite materials or add carrier materials
- Development of TCM storage materials at the level of the 6 m^3 reactor

Thanks for your attention !