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FAKULTÄT
FÜR MATHEMATIK, INFORMATIK
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Thermochemical storage with salt mixtures

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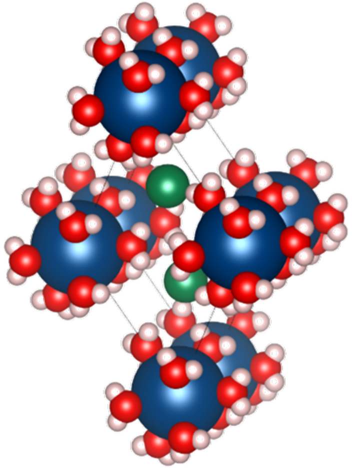
Thermochemical storage materials with salt hydrates

$$M_mX_x{\cdot}n_AH_2O \rightleftharpoons M_mX_x{\cdot}n_BH_2O + (n_A-n_B)H_2O(g)$$

Enthalpy of hydration: typically –(55–65) kJ·mol^{-1} water

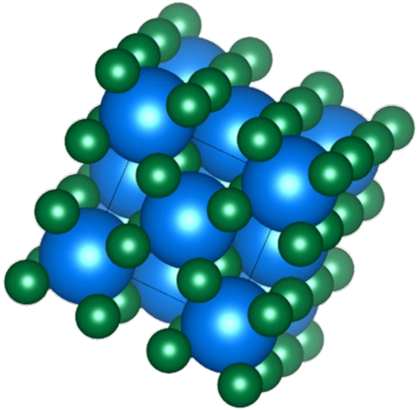


$SrCl_2{\cdot}6H_2O$

(solarthermal)
dehydration

hydration

Heat
(2.5 GJ·m^{-3})



$SrCl_2$

Thermochemical storage materials with salt hydrates

Thermochemically active salts

- Two ions (M, X)
- Three different ions
- Two cations and anions
- More ions

Compound examples

- $Mg_2CaCl_6 \cdot 12H_2O$
- $(M^{I})_2M^{II}(SO_4)_2 \cdot nH_2O$
- $KMgCl_3 \cdot 6H_2O$

.....

Thermochemical storage with salt hydrates

$$M_mX_x \cdot n_AH_2O \rightleftharpoons M_mX_x \cdot n_BH_2O + (n_A - n_B)H_2O(g)$$

Compounds | Additives

- Single salts (binaries)
- Ternary mixtures
- Reciprocal mixtures
- Complex mixtures

Salts @ porous substrates (composites)

Polymers, zeolites, silica, MOFs, activated carbon, clays, cement, …

Binary examples:

- $MgCl_2$, $CaCl_2$, $SrCl_2$, $MgSO_4$, K_2CO_3, ...

Ternary examples:

- $MgCl_2 + MgSO_4$
- $MgCl_2 + CaCl_2$

Reciprocal examples:

- $MgSO_4 + CaCl_2$
- $SrCl_2 + MgSO_4$

Additives

- LiCl (with $Mg(OH)_2$)
- CsF (with K_2CO_3)
- MCl_x (with $SrCl_2$)

.....

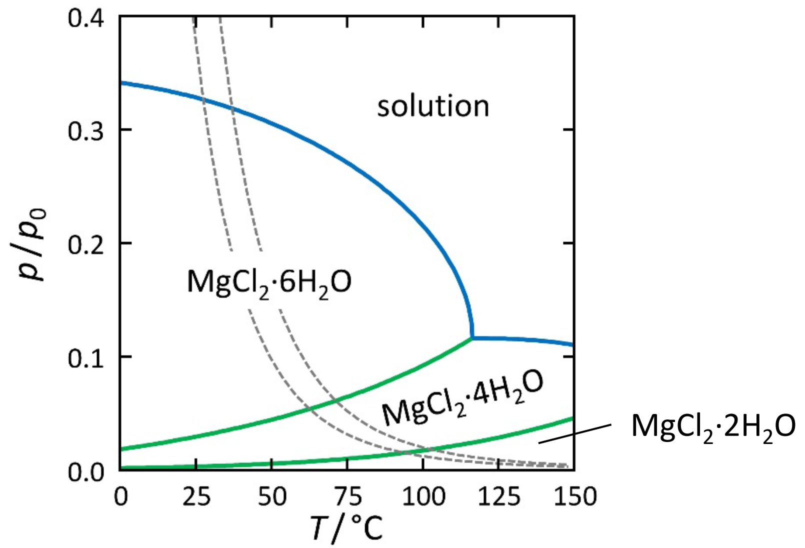
Rammelberg et. al, *Sol. Energ.* **2016**, *136*, 571; Pathak et al., *J. Phys. Chem C* **2017**, *121*, 20576; Kooijman et al., *J. Energ. Storage* **2022**, *55*, 105459

Ryu et al., *Chem. Lett.* **2008**, *37*, 1140–1141; Posern, *Thermochim Acta* **2010**, *502*, 7376; Mazur et al., *Sol. Energ.* **2022**, *252*, 256–266

Why mixtures | additives | compounds?

Issues with salt hydrates as TCM

- Inappropriate thermodynamics
  – too high dehydration temperature
  – too high vapor pressure for hydration
  – liquefaction (deliquescence)
- Inappropriate kinetics
  – dehydration too slow
  – hydration hindered or too slow
- Side reactions
  – hydrolysis
  – reaction with other gases
- Lack of cycle stability
- Limited availability, high cost

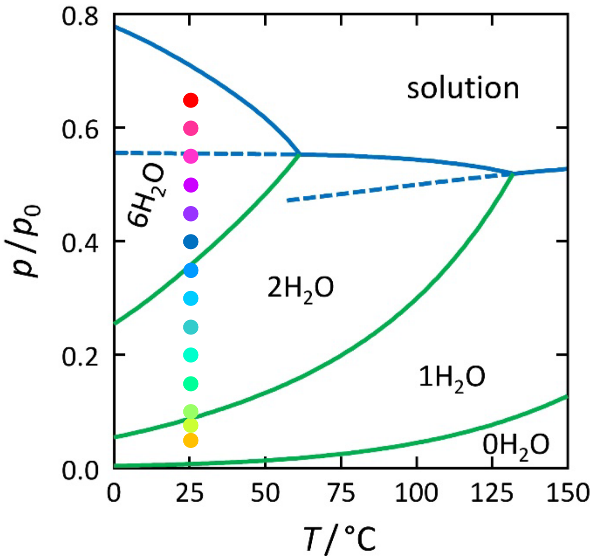


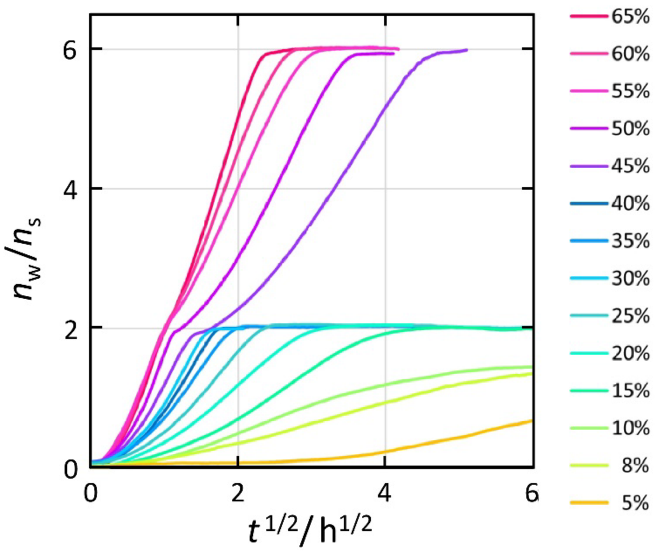
$(x{+}y)\,MgCl_2{\cdot}6H_2O \rightarrow Mg_{x+y}(OH)_{2x}Cl_{2y}{\cdot}(z{-}x)\,H_2O + 2x\,HCl + (5x{+}6y{-}z)\,H_2O$

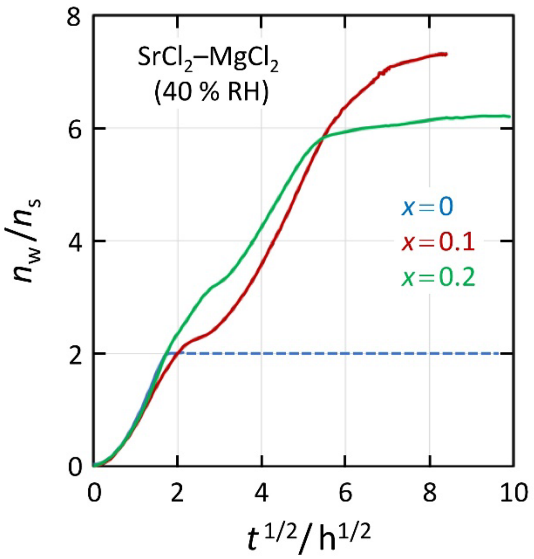
(e.g. $Mg_{21}(OH)_2Cl_{40}{\cdot}16H_2O$)

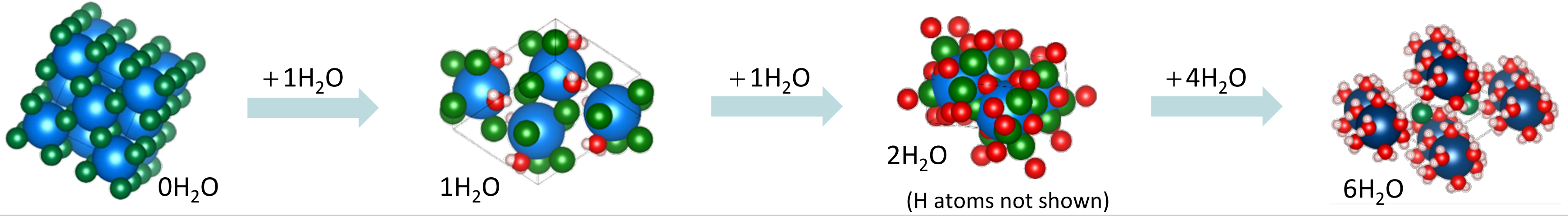
➡ Any improvement with mixtures?

Kinetics of hydration $SrCl_2$





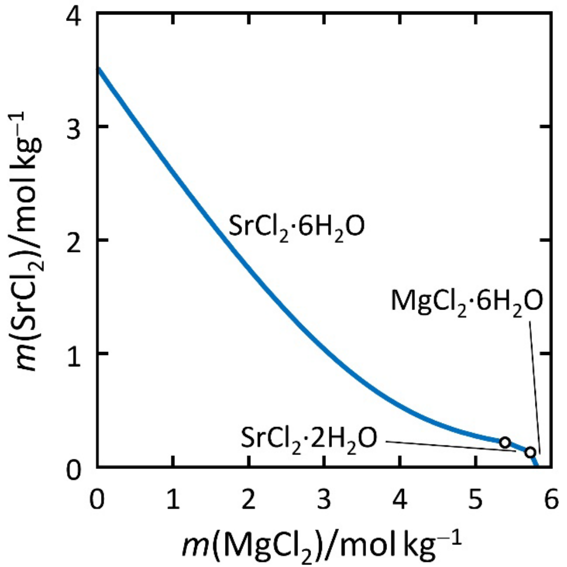


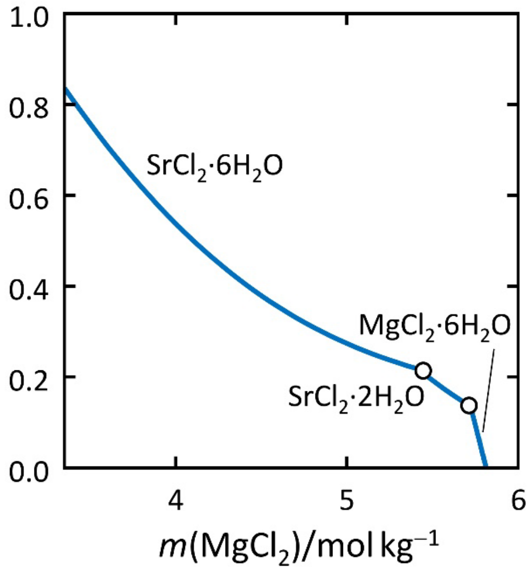


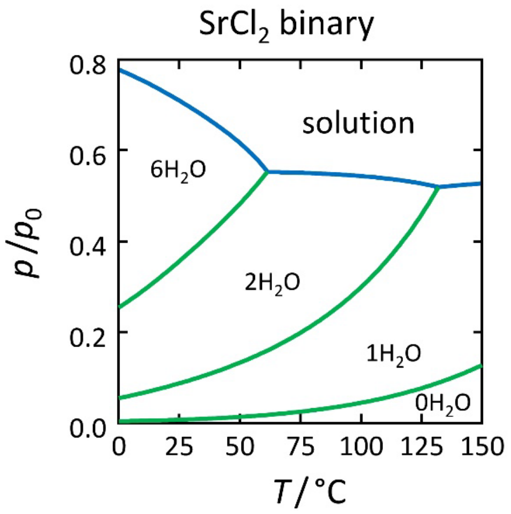
Ternary salt mixtures (solubilities)

$SrCl_2$–$MgCl_2$ mixtures

- No influence on hydration phase boundary
- Strong influence on solubility and DRH







Hydration equilibrium:

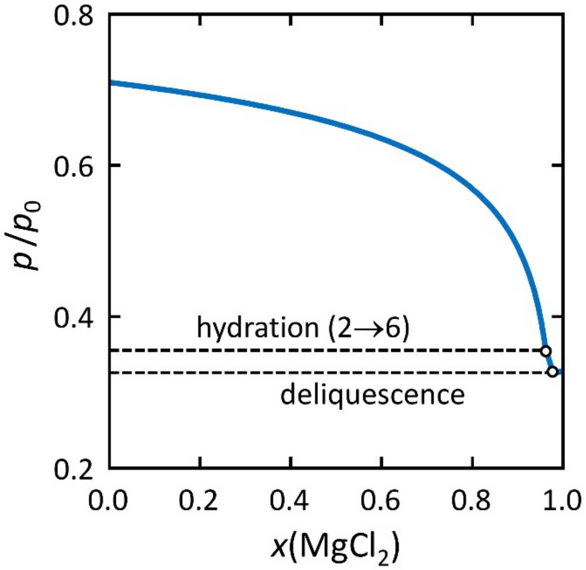
$SrCl_2 \cdot 6H_2O \rightleftharpoons SrCl_2 \cdot 2H_2O + 4H_2O$

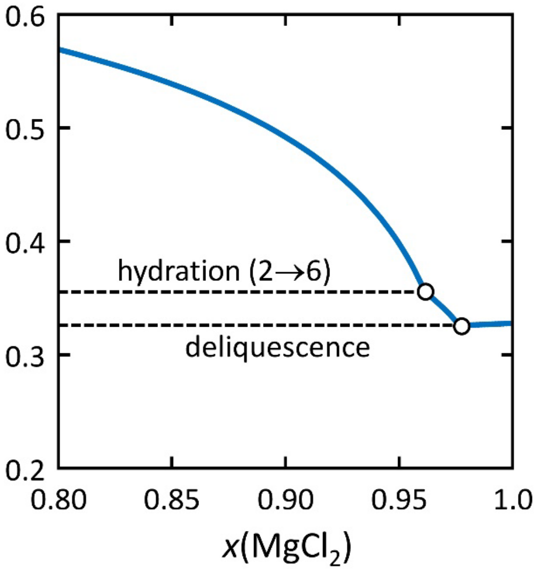
(only depending on water activity)

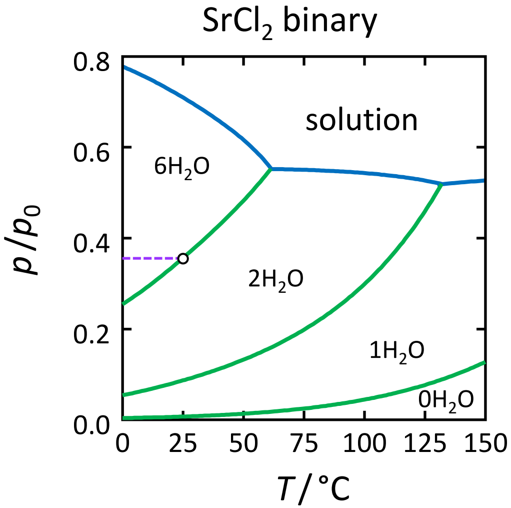
Ternary salt mixtures (deliquescence)

$SrCl_2$–$MgCl_2$ mixtures

- No influence on hydration phase boundary
- Strong influence on solubility and DRH







Hydration equilibrium:

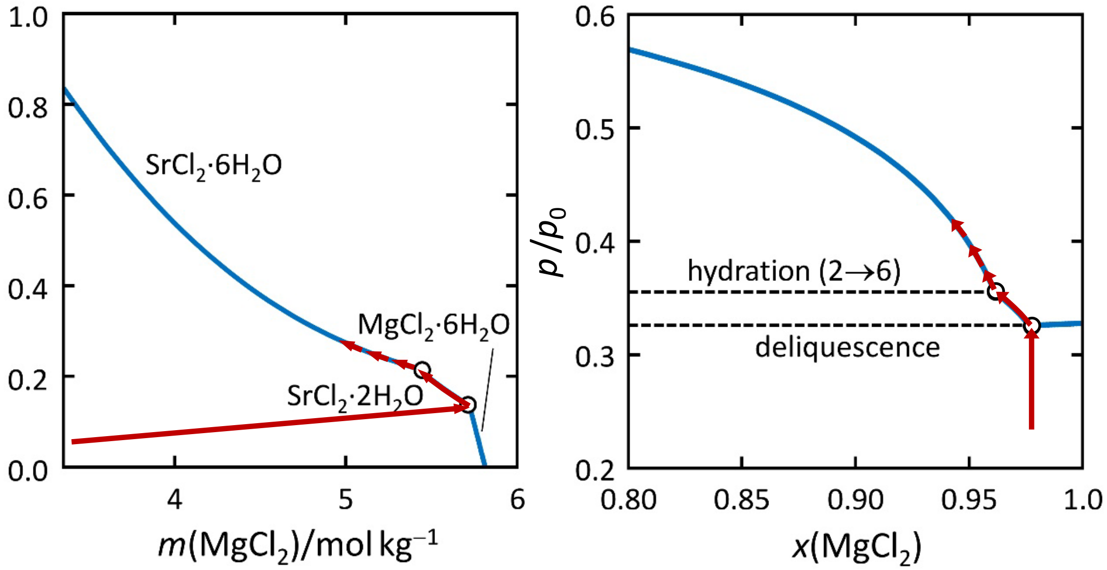
$SrCl_2{\cdot}6H_2O \rightleftharpoons SrCl_2{\cdot}2H_2O + 4H_2O$

(only depending on water activity)

Ternary salt mixtures (without compound formation)

$SrCl_2$–$MgCl_2$ mixtures

- No influence on hydration phase boundary
- Strong influence on solubility and DRH



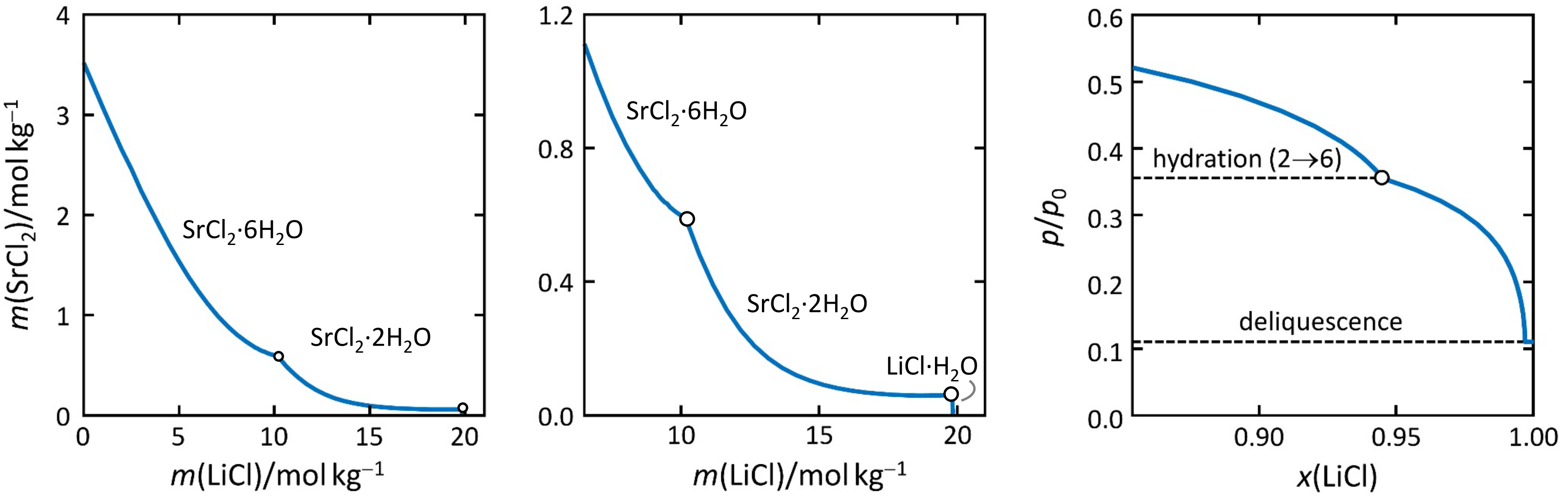
Deliquescence (32.6 % RH)
– dissolution of $MgCl_2 \cdot 6H_2O$
– partial dissolution of $SrCl_2 \cdot 2H_2O$

Hydration (35.4 % RH)
– through solution mechanism (dissolution → crystallization)

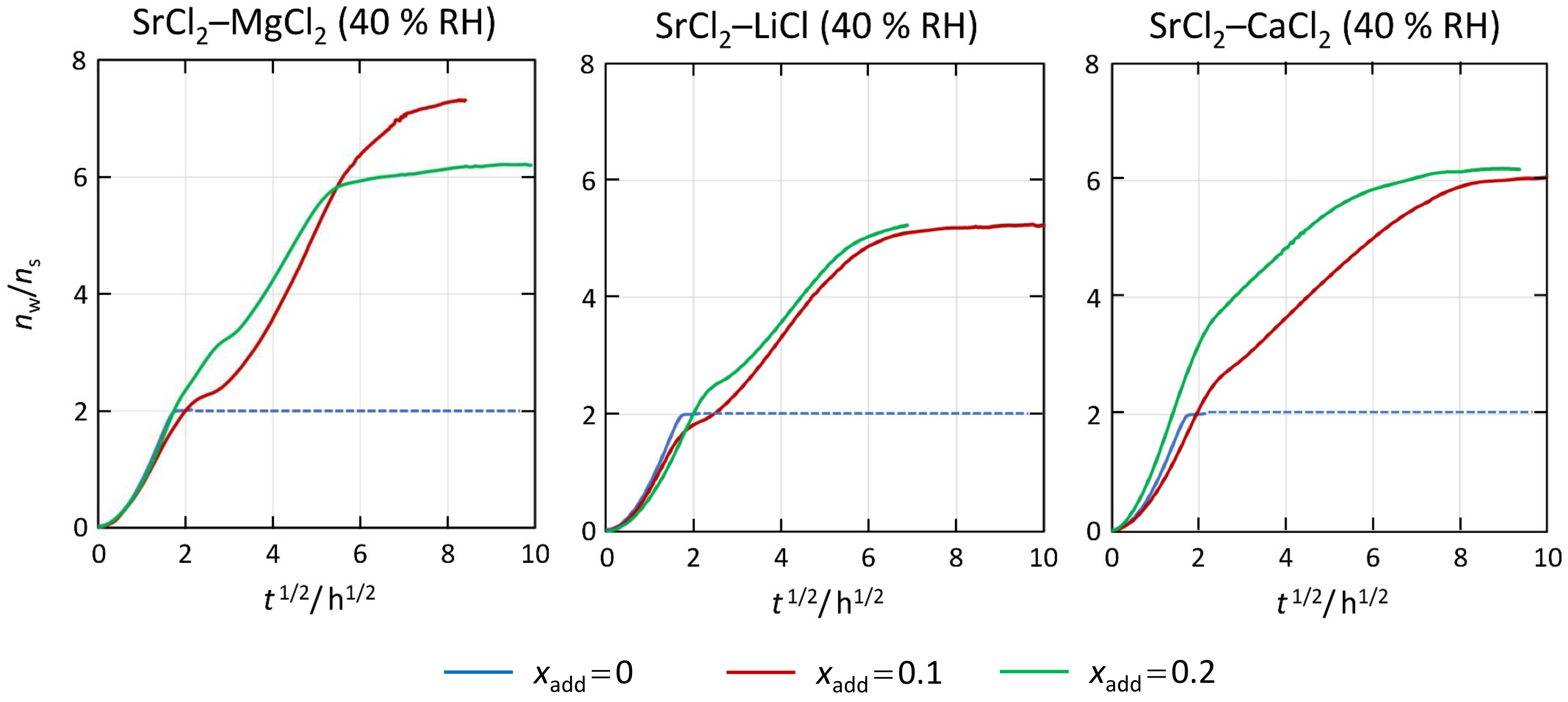
Dilution (>35.4 % RH)
– dissolution of $SrCl_2 \cdot 6H_2O$
– condensation of water vapor

LiCl additive

- Very high solubility of LiCl
- Hydrate pair LiCl–LiCl·H_2O
- Very low deliquescence humidity



Kinetics with hygroscopic additives



Heat balance and storage density ($SrCl_2$–$MgCl_2$)

Binary system

1. $SrCl_2 + 2H_2O \rightarrow SrCl_2{\cdot}2H_2O$
2. $SrCl_2{\cdot}2H_2O + 4H_2O \rightarrow SrCl_2{\cdot}6H_2O$

Enthalpy of hydration

$\Delta_{hyd}H_{0\rightarrow2} = -125.4$ kJ mol^{-1} (-62.7 kJ mol^{-1} H_2O)

$\Delta_{hyd}H_{2\rightarrow6} = -218.9$ kJ mol^{-1} (-54.7 kJ mol^{-1} H_2O)

Ternary

3. $MgCl_2{\cdot}2H_2O + 4H_2O \rightarrow MgCl_2{\cdot}6H_2O$
4. $H_2O(g) \rightarrow H_2O(l)$
5. $MgCl_2{\cdot}6H_2O \rightarrow Mg^{2+}(aq) + 2Cl^-(aq) + 6H_2O$
6. $SrCl_2{\cdot}2H_2O \rightarrow Sr^{2+}(aq) + 2Cl^-(aq) + 2H_2O$
7. $SrCl_2{\cdot}6H_2O \rightarrow Sr^{2+}(aq) + 2Cl^-(aq) + 6H_2O$

Enthalpies:

$\Delta_{hyd}H_{2\rightarrow6} = -252.0$ kJ mol^{-1} (-63.0 kJ mol^{-1} H_2O)

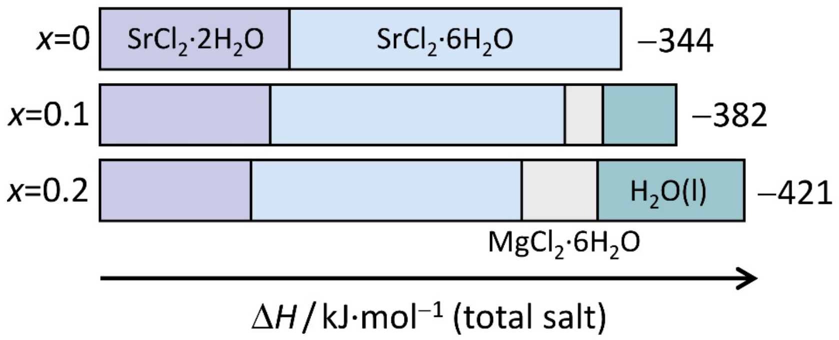
$\Delta_{con}H_{g\rightarrow l} = -44.0$ kJ mol^{-1}

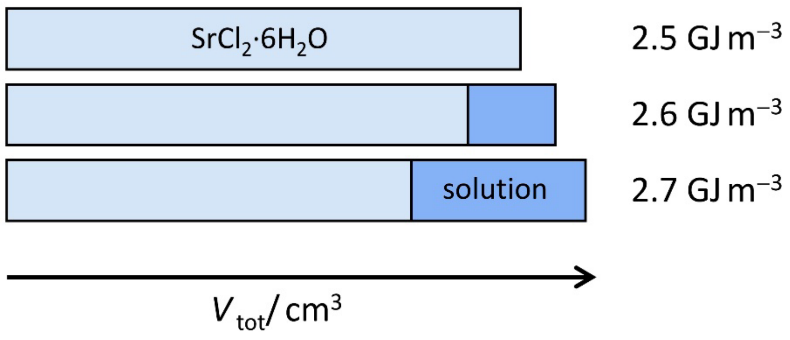
$\Delta_{sol}H_{MC6} = +6.0$ kJ mol^{-1}

$\Delta_{sol}H_{SrC6} = -13.8$ kJ mol^{-1}

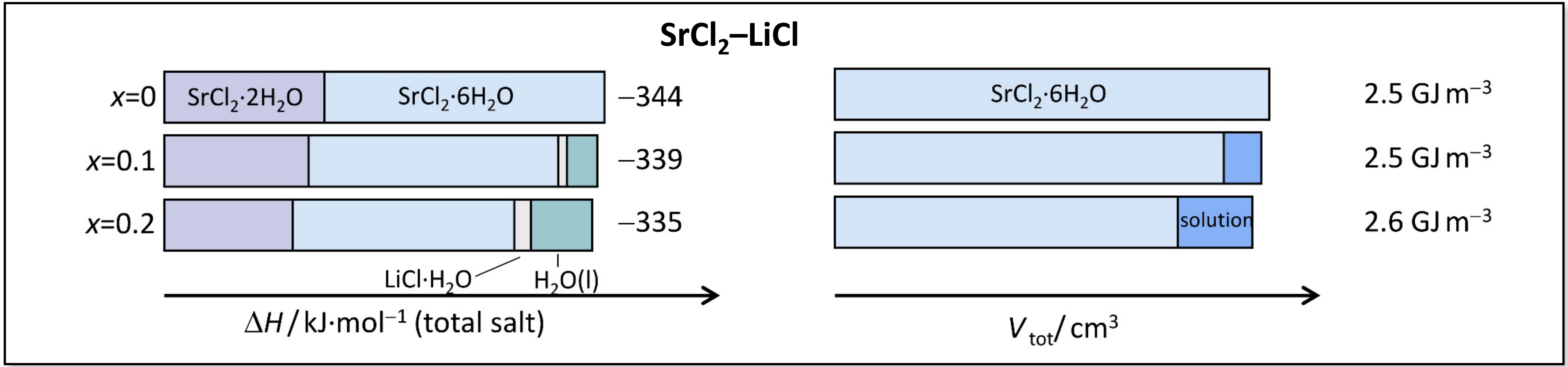
$\Delta_{sol}H_{SrC6} = +28.7$ kJ mol^{-1}

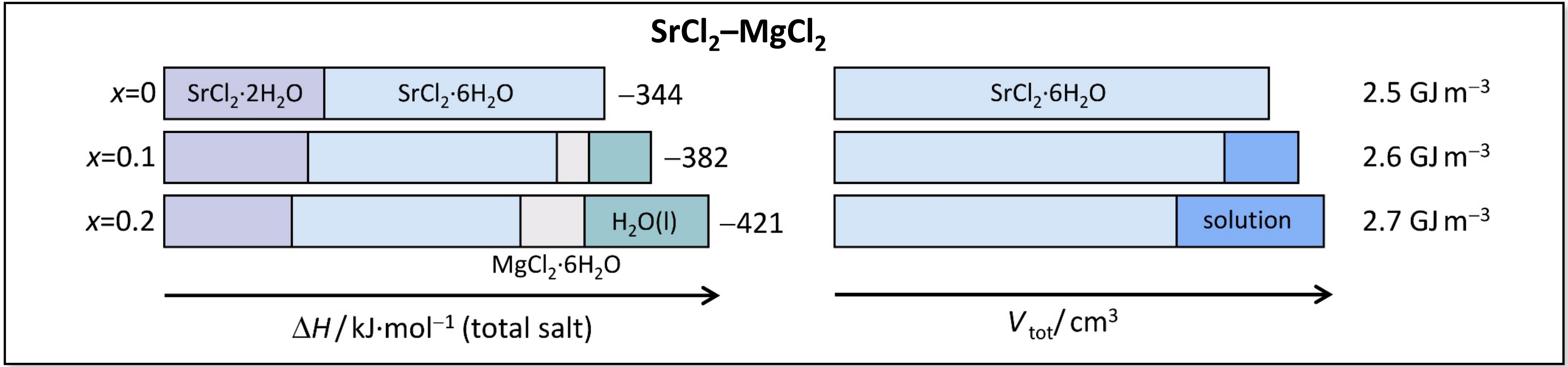
} negligible





Heat balance and storage density with additives

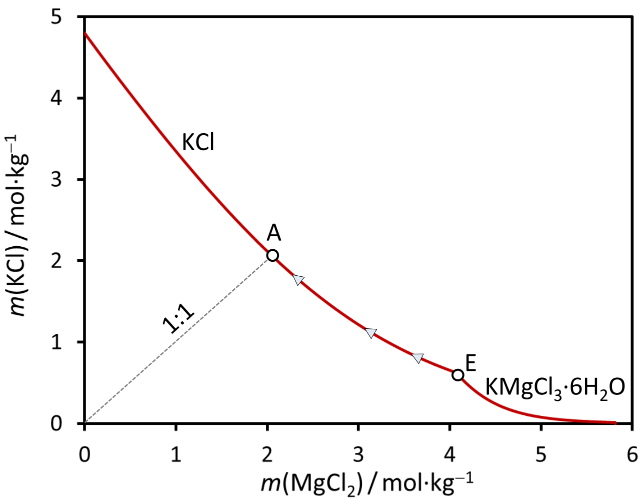


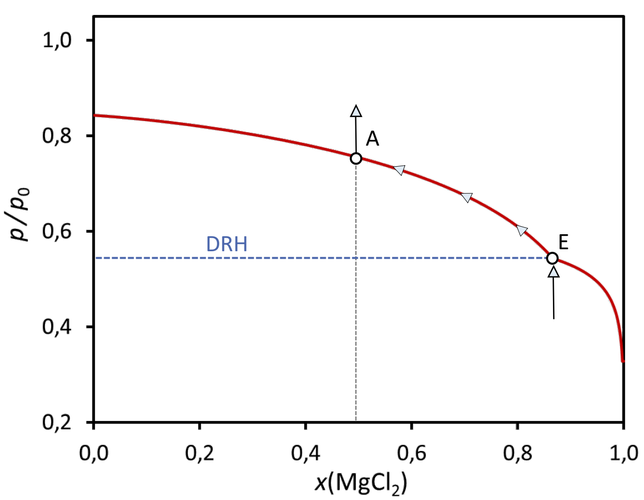


Ternary mixtures with compound formation – carnallite

Carnallite ($KMgCl_3 \cdot 6H_2O$)

- is a natural mineral in evaporite deposits
- is an industrial waste product in lithium processing
- is formally, considered as a mixture of a TCM ($MgCl_2$) and a thermochemically inactive additive (KCl)
- is incongruently soluble





Dehydration and decomposition of double salts

Deliquescence and decomposition of incongruently soluble double salt

Double salt ⇌ single salt + saturated solution

$$KMgCl_3{\cdot}6H_2O(s) \rightleftharpoons x\,KCl(s) + Mg^{2+}(aq) + (1-x)\,K^+(aq) + (3-x)\,Cl^-(aq)$$

Dehydration of double salt

Double salt ⇌ lower hydrated states

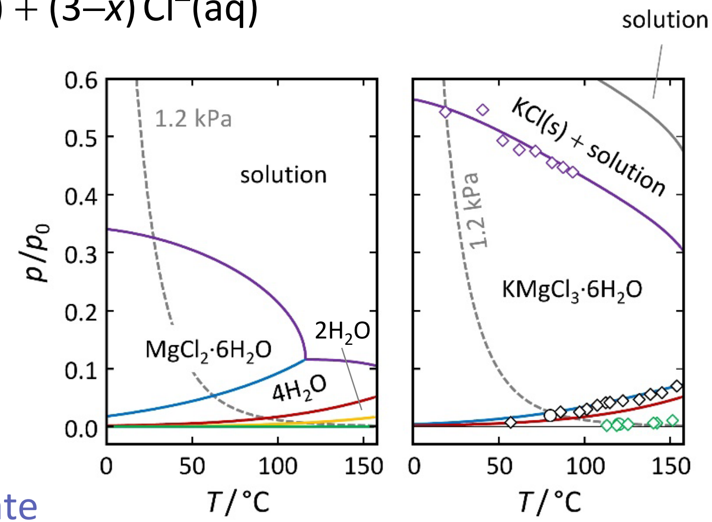
$$KMgCl_3{\cdot}6H_2O(s) \rightleftharpoons KMgCl_3{\cdot}2H_2O(s) + 4H_2O(g)$$

$$KMgCl_3{\cdot}2H_2O(s) \rightleftharpoons KMgCl_3 + 2H_2O(g)$$

Decomposition and dehydration

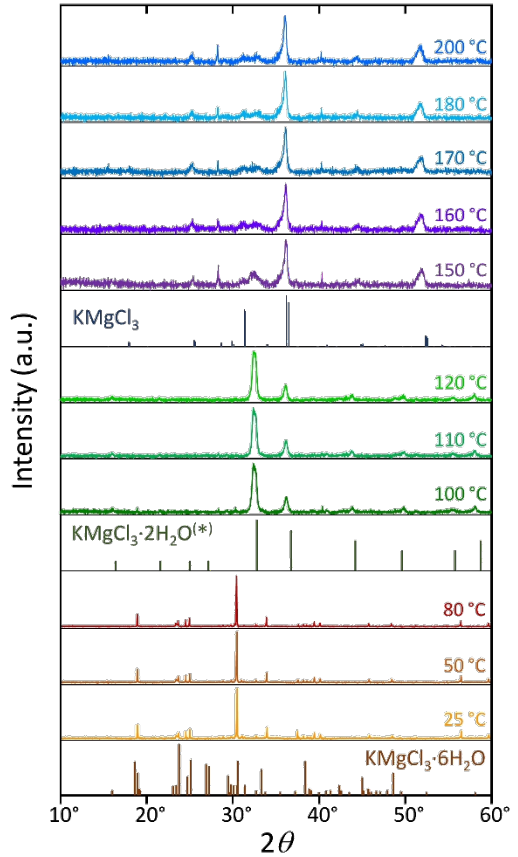
Double salt ⇌ 2 single salts in lower hydrated state

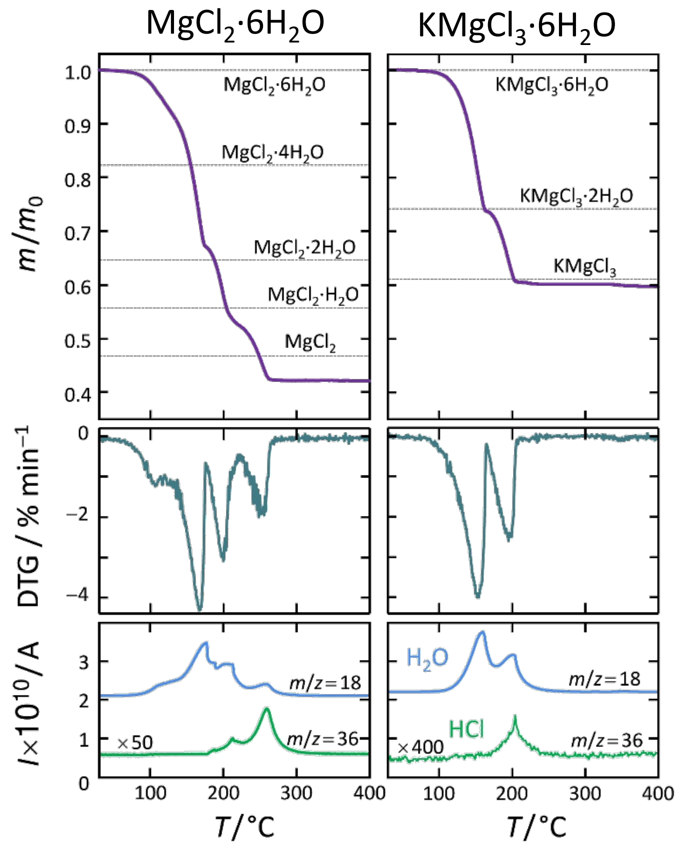
$$KMgCl_3{\cdot}6H_2O(s) \rightleftharpoons KCl(s) + MgCl_2{\cdot}2H_2O(s) + 4H_2O(g)$$

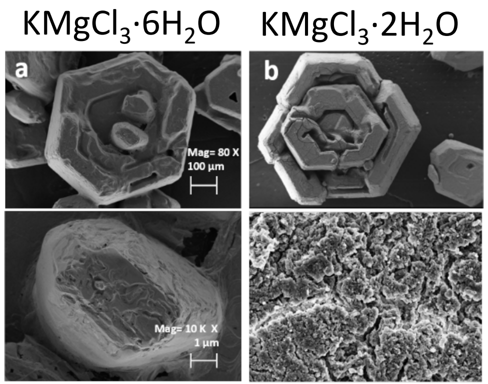


➡ both reactions possible

Dehydration vs. decomposition







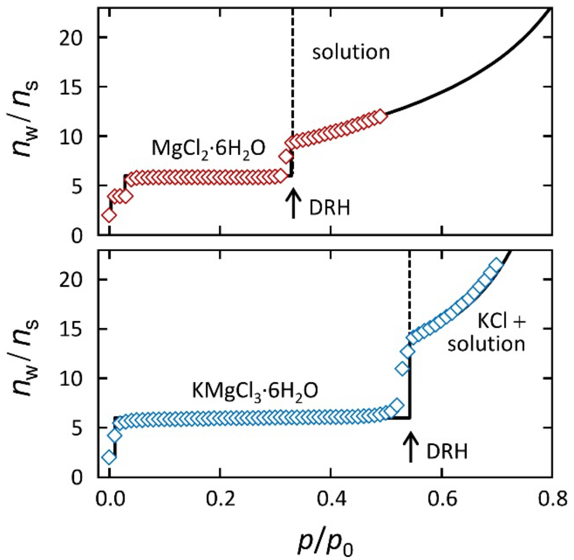
- Less prone to hydrolysis
- No reflexes from either KCl or $MgCl_2 \cdot nH_2O$
  ➡ no decomposition!
- Dehydration at 100 °C
- High deliquescence RH

(*) Serowy & Tittel, *Freiberger Forschungshefte A* **1959**, *128*, 1–88

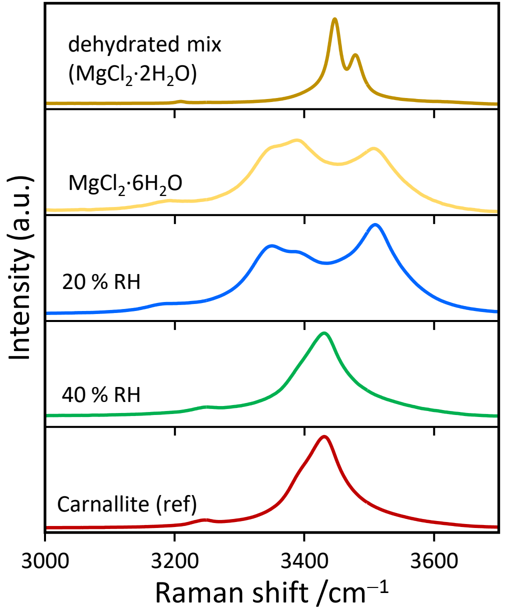
Hydration reactions

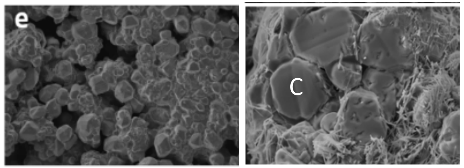
Experiments with dehydrated

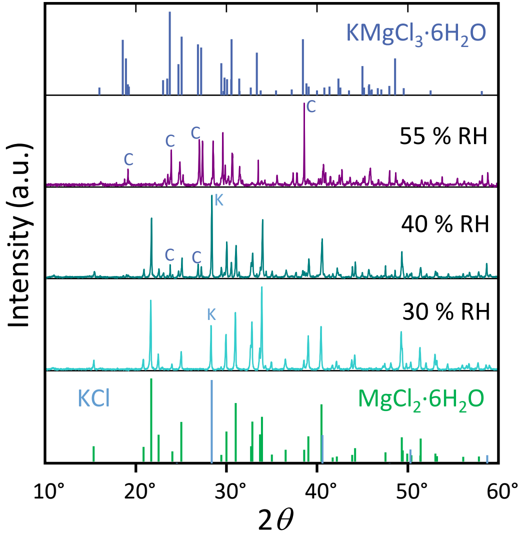
- bischofite ($MgCl_2 \cdot 2H_2O$)
- carnallite ($KMgCl_3 \cdot 2H_2O$)
- physical mixture ($KCl + MgCl_2 \cdot 2H_2O$)



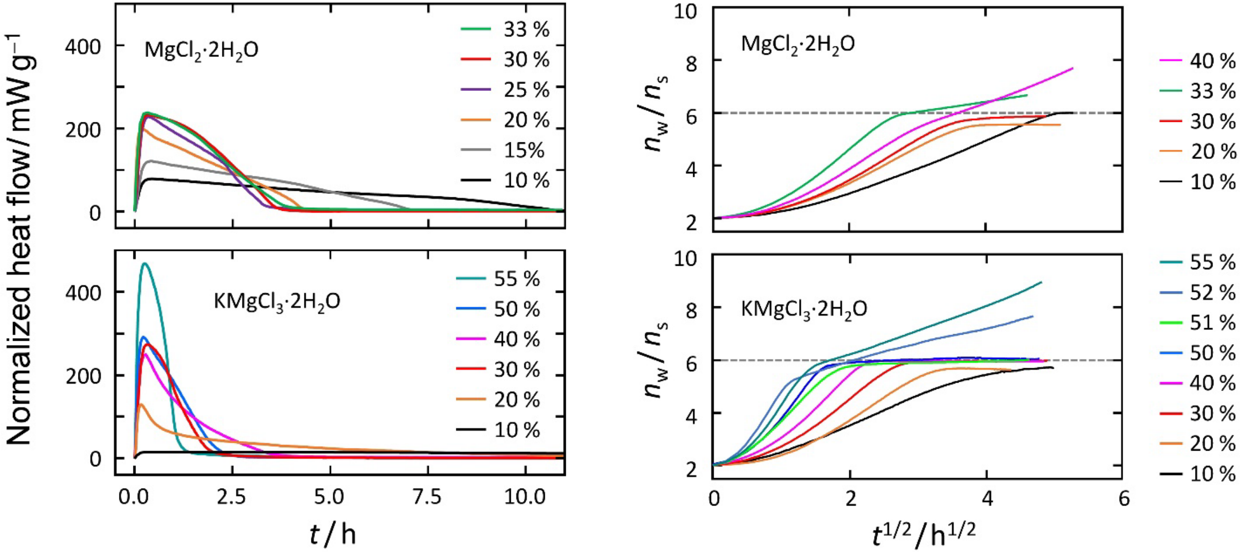
Physical mixture
($KCl + MgCl_2 \cdot H_2O$)







Kinetics of hydration



- Hydration of $KMgCl_3{\cdot}2H_2O$ at higher rate than $MgCl_2{\cdot}2H_2O$
- Slight reduction of theoretical storage density ($\text{carnallite}: 1.52\ GJ{\cdot}m^{-3}$, $MgCl_2{\cdot}6H_2O: 1.97\ GJ{\cdot}m^{-3}$)

Carnallite vs. magnesium chloride

Carnallite

- High DRH, no liquefaction
  (55 % RH vs. 30 % RH for $MgCl_2 \cdot 6H_2O$)
- Very low dehydration temperature
  (100 °C sufficient to reach the dihydrate)
- Much less prone to hydrolysis
  (than magnesium chloride)
- Very low vapor pressure for hydration reaction
  (<0.3 mbar @20 °C)
- Very good hydration kinetics
  (faster than $MgCl_2 \cdot H_2O$)
- Available as by-product of lithium production
- Lower, yet reasonably high storage density
  (carnallite: 1.52 $GJ \cdot m^{-3}$, $MgCl_2 \cdot 6H_2O$: 1.97 $GJ \cdot m^{-3}$)

About 25–30 t carnallite per t Li_2CO_3

Conclusions

- TCM may be improved by hygroscopic additives
  (faster hydration kinetics)
- Heat balance is more complicated
  (no significant loss in storage density)
- Mixing ratio needs to be optimized
  (liquid volume, fast reaction, storage density)
- Double salts as new class of TCMs
  with entirely different properties
- Carnallite is a very promising new material
  – easy dehydration to the dihydrate ($KMgCl_3 \cdot 2H_2O$)
  – rapid re-hydration at very low vapor pressure
  – no liquefaction, no hydrolysis
  – still high storage density (23 % less than $MgCl_2 \cdot 6H_2O$)