

Properties of salt compounds

Exposé

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1. Background

Materials used for chemical heat storage applications [1, 2] need to possess certain key properties. The most important of those properties are a high heat storage density and an also high cycle stability, which will allow for a compact storage system that can run for several years without requiring an exchange of the storage material within. Further it is aimed to find inexpensive and non-hazardous/-corrosive materials. As salts are cheap and easily available, as well as relatively safe materials to work with and most of them can incorporate water (or other polar reaction partners, such as ammonia or alcohols) into their crystal structure in a reversible chemical reaction, they are of prime interest in the research for suitable materials.

While most basic salts possess the latter properties, and some show promising heat storage densities, they usually need relatively high temperatures for dehydration of $T > 100^\circ\text{C}$. This is a serious limitation, since many thermal processes are based on water as heat transfer fluid and therefore the boiling point of water is limiting the temperature range.

The other main problem is the low cycle stability of the materials. Hydrated salts easily lump together or melt during dehydration, as they have low melting points compared to their anhydrides. Once molten, they rather solidify as an amorphous mass upon cooling than recrystallizing which will hinder the rehydration process.

2. Materials

Chlorides, Sulfates and Bromides of Na, K, Li, Sr, Ca, Mg, Zn, Fe^{2+} , Fe^{3+} or Al are storage material candidates. However Fe^{2+} and Fe^{3+} can cause the development of unwanted byproducts and most Li containing salts are too expensive to be efficient.

Several of those basic salts and their reactions have already been tested, among others by Lyimen-Schwarz and M.D. Lechner [1, 2], Zondag et al. [3] and Ferchaud et al. [4] (ECN) or Kerkes et al. [5] (see table 1) for their thermal decomposition [6] and their use in heat storage applications.

Among the most promising materials concerning their heat storage density are Calcium and Magnesium chlorides but they show low cycle stability and need Temperatures of $T = 100$ to 200°C to be efficient. The low stability is caused by $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ having a low melting point of 29°C [7] and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ decomposing and emitting HCl at temperatures above $T \sim 140^\circ\text{C}$ [2, 3, 4, 6, 8]. Additionally the

magnesium chloride is prone to overhydrating and turning into a gel like substance [3].

Table1 ^[5]: Reversible reactions and temperature intervals for some basic salts as tested by Kerkes et al.

Reaction	Temperature interval [°C]
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \leftrightarrow \text{MgSO}_4 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$	100 – 150
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$	100 – 130
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{CaCl}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$	150 – 200
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \leftrightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$	120 – 160

3. Previously used methods

3.1 Matrix

One way to increase the cycle stability is by impregnating a porous matrix with the chosen storage material [5]. However this results in a decline in heat storage capacity of the battery.

3.2 Pellets and granules

Compressing the storage material into the form of pellets or granules so the material will not lump together or form too thick hydrated layers around the still anhydrate material [5].

3.3 Additives

Adding a second material to reduce the unwanted alterations of the chosen storage material. While sand or zeolites are used to increase the structural support of the material, other additives like graphite or copper are used to increase the thermal conductivity of the battery. [9]

Tests with adding Al_2O_3 to reactions with MgCl_2 did not improve the properties but rather increased the material's alteration. Positive effects were noted in adding Al_2O_3 to CaCl_2 and SrCl_2 systems. [1]

Mechanical mixtures of MgCl_2 - and CaCl_2 -hydrates, showed some promising improvements concerning cycle stability and kinetic properties [10].

4. Hypotheses

Instead of just using additives or mechanical mixtures, it is possible to combine two or more of the basic salts with good heat storage density to a compound. Whether those compounds have better or worse properties than the starting materials depends on their crystal structure.

The higher the symmetry of a crystal structure is the more energy is needed to change it to either hydrated or dehydrated phases. The lower the symmetry, the less stable the material. High energy means high activation temperatures or high pressure of water vapor will be necessary to initiate dehydration or respectively hydration while an instable material may decompose into unwanted byproducts.

This implies that a material suited for high cycle stability and low temperature application needs to have a symmetry that is neither too orderly (as cubic or hexagonal) nor too simple (as monoclinic or triclinic).

A partial exchange of cations or anions in a basic salt by ions with different atomic extent will alter the material's symmetry.

So it should be possible to create mixed salts with precededented properties, predicted by the crystal structure of the expected compound material.

Since such complex salts occur naturally, their crystal structures are well documented in mineralogical databases [11, 12, 13] and can be used as a basis for modeling synthetic salts as well.

As there haven't been any systematic tests with complex salts for heat storage applications in the past, their possible positive or negative properties are unknown as of yet.

A likely drawback of the mixed salts could be that usually a compound of two substances has a lower melting point than either of the pure substances. This may lead to unwanted melting of the compound during dehydration. It can be countered by slow heating rates, allowing the water to escape the substance and changing it to a phase with a higher melting point, before the critical temperature is reached.

5. Models

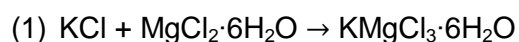
Based on a chosen starting material a mineralogical database can be searched for information about naturally occurring complex minerals, which are based on said starting material and have hydrated phases as well as their crystal structures.

5.1 Example 1: Carnallite

The salt Sylvite ($Pm-3m$) with cubic-disdyakis-dodecahedron crystal class [12] is expected to react only inertly if at all with water.

Bischofite ($C2/m$) with monoclinic-prismatic crystal class [12] is the phase of Magnesium chloride with six hydrates.

The compound of Sylvite and Bischofite is a salt known as Carnallite ($Pnna$) that has an orthorhombic-bipyramidal crystal class [12]. (See Figure 1.)



Aside from the naturally occurring mineral, synthetic variations with the cations Ca, Fe²⁺ or Zn replacing the Mg partially or completely can be created for increasing the field of research.

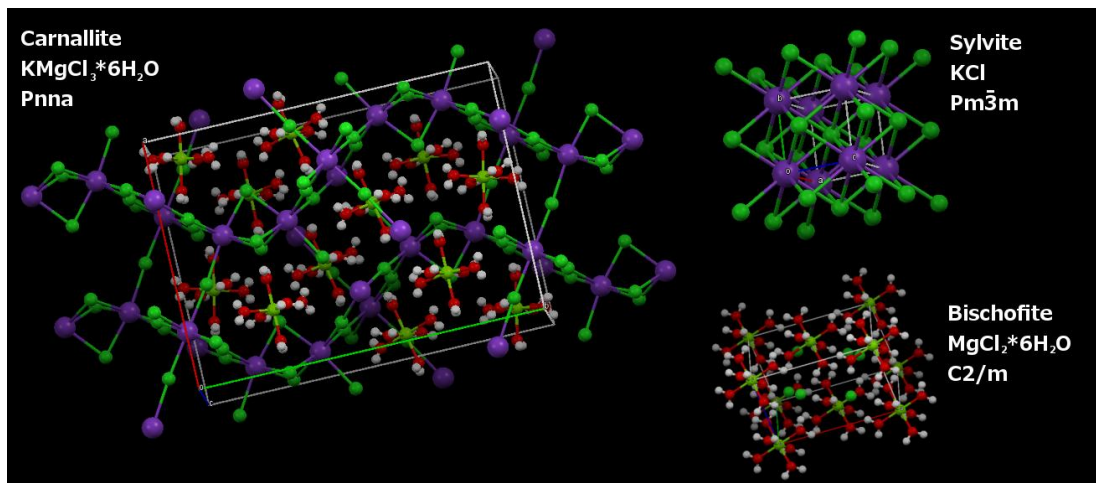
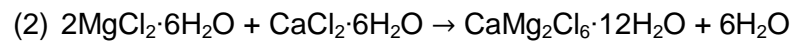


Fig. 1^[11, 14]: The complex salt Carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), resulting from mixing the basic salt components Sylvite (KCl) and Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

5.2 Example 2: Tachyhydrite

Antarcticite ($P3_21$) is a salt with trigonal-trapezohedral crystal class [12].

With the monoclinic-prismatic Bischofite ($C2/m$) it forms the compound Tachyhydrite ($P-3$) which is trigonal-rhombohedral [12].



Like Antarcticite, naturally occurring Tachyhydrite is a deliquescent mineral, which should allow for an easy incorporation or release of water from the crystal structure.

The difference in symmetry between Antarcticite and Tachyhydrite is minimal but higher than that of Bischofite. So the compound needs to be tested whether this symmetry influences its stability at Temperatures of $T > 140^\circ\text{C}$ positively.

6. Research questions

To test the hypotheses, first the modeled salts need to be synthesized. For that the best mixing ratios need to be calculated to support the development of compounds in the product. Those compounds can be either synthetic versions of naturally occurring salts or synthetic materials based on the natural minerals' crystal structures.

The actual composition of the products can be validated by PXRD.

The heat storage capacities as well as the cycle stability can be tested by TGA measurements.

The results of those analyses then have to be compared to the structures, the reactivity and the thermodynamics of the basic salts needed for synthesizing the complex salts, to assess whether there really is a measurable improvement in properties.

The goal of the experiments should be to find a heat storage material with excellent properties by optimizing the synthesis processes and if possible, to detect a reliable correlation between those desired properties and the materials' crystal structures to facilitate future research for other heat storage materials.

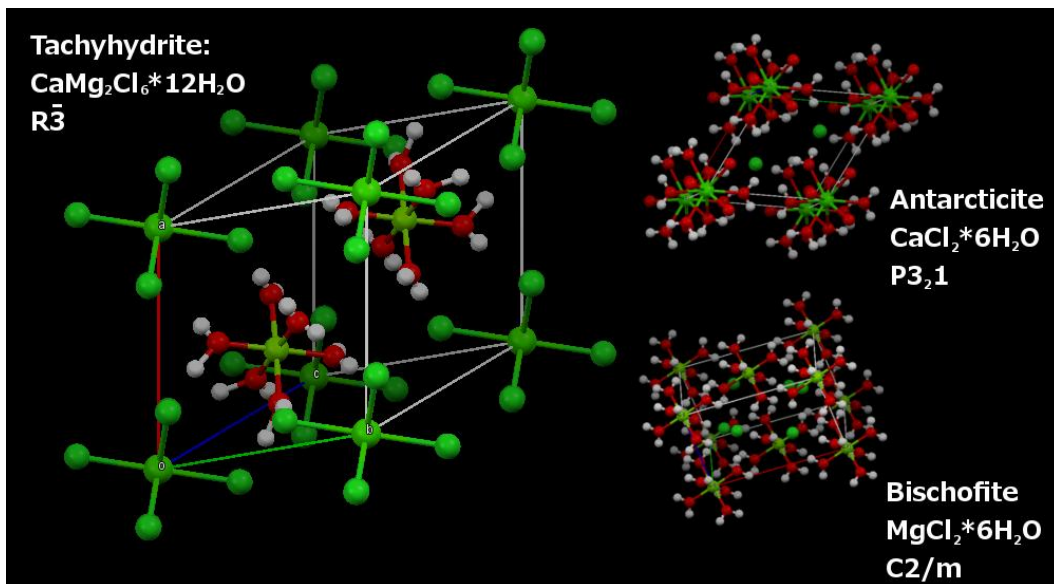


Fig. 2^[11, 14]: The complex salt Tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$), resulting from mixing the basic salt components Antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) and Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

7. References

- [1] Z. Iyimen-Schwarz, *Energiespeicherung durch chemische Reaktionen*, (1983)
- [2] Z. Iyimen-Schwarz and M.D. Lechner, *Energiespeicherung durch chemische Reaktionen. I. DSC-Messungen zur Quantitativen Verfolgung der Enthalpieänderungen von Speicherstoffen für die Hin- und Rückreaktion*, *Thermochimica acta*, 68 (1983), 349-361
- [3] H. A. Zondag et al., *Applications of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ for thermochemical seasonal solar heat storage*, (2010), ECN-M-10-094
- [4] C. J. Ferchaud et al., *Seasonal Sorption Heat Storage – Research On Thermochemical Materials And Storage Performance*, (2012), ECN-M-12-070
- [5] H. Kerskes et al., *Thermochemische Energiespeicher*, *Chemie Ingenieur Technik* (2011), 83, No. 11, 2014–2026
- [6] K. Sugimoto, R. E. Dinnebier and J. C. Hanson, *Structures of three dehydration products of bischofite from in situ synchrotron powder diffraction data ($\text{MgCl}_2 \cdot n\text{H}_2\text{O}$; $n = 1, 2, 4$)*, *Acta Crystallographica Section B, Structural Science*, (2007)
- [7] I. Behunek, T. Bachorec, and P. Fiala, *Properties and Numerical Simulation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PhaseChange*, *Piers Online*, vol. 2, No. 6, (2006)

[8] B.B. Bosse, M.H. Khundkar, *Dehydration of Magnesium Chloride Hexahydrate*, J. Ind. Chem. Soc., 14 (1951) 171.

[9] Opel et al., *Thermochemical Storage Materials Research – TGA/DSC-Hydration Studies*, Proceedings of the International Conference for Sustainable Energy Storage (IC-SES), 21.02.-24.02.2011, Belfast, GB, (2011)

[10] H. U. Rammelberg et al., *An Optimization Of Salt Hydrates For Thermochemical Heat Storage*, Paper No. IMPRES 2013-117, (2013)

[11] Crystallography Open Database, <http://www.crystallography.net/search.html#>

[12] Mineralogy Database, <http://webmineral.com/>

[13] ATHENA, <http://athena.unige.ch/athena/mineral/search.html>

[14] Created with Mercury 3.1, <http://www.ccdc.cam.ac.uk/mercury/#>