Effective integration and full use of the potential yield of renewable energy is required to realize an energy neutral society. A compact solution for thermal energy storage in the existing building stock is a key priority to make such a step. Potential solutions are thermo chemical materials, with very high energy densities, hence giving the possibility for small "heat batteries". The seasonal heat needed for one household could be stored in not more than several cubic meters of such high energy density materials. One option for storing heat is the hydration/dehydration reaction of salt crystals\[1\]. Such reactions are reversible and hence, like a battery, the process can be repeated. Moreover the process can be fine tuned on the basis of the vapor pressure of the hydrating solvent. As the reaction only takes place by a hydrating solvent these batteries could store heat almost loss-free, unlike other systems in use nowadays (like phase change materials or water baskets\[2\]). A schematic diagram of a heat battery is given in figure 1.

Like any electric battery, the reversibility of the heat exchange process in such a heat battery by hydration declines in time, and at this moment the degradation is not understood well\[3\]. Nowadays solutions show an additional disadvantage i.e. the slow hydration/dehydration rate of crystals\[4\]. Heat is released to slow in response to the demand. Here we have chosen to look at a well known salt: sodium sulfate (Na2SO4). The anhydrous salt is called Thenardite (Na2SO4 (s)) where the hydrated salt with 10 water molecules Na2SO4.10H2O is called Mirabilite.

In this study we are focusing on two main questions:

- How is water transport through the crystal in the hydration/dehydration process?
- What are the changes in crystal structure in relation to the decline of the storage process?

We use specially adapted Nuclear Magnetic Resonance (NMR) to measure hydrogen distributions in salt crystals during de-/hydration experiments. As an example figure 2 shows the dehydration process as measured for a large single crystal. In this case, the sample is isolated and water can only be exchanged at the top of the crystal, where dry air with a relative humidity of 0% is flowing. As can be seen from the start, the dehydration process is almost homogeneous throughout the sample, which is about 30 mm in length in this case. This homogeneous drying indicates extremely fast water redistribution throughout the crystal. In this case the process, and hence the heat released, is limited by the boundary conditions.

In order to get a better understanding of the dehydration process throughout the crystal we performed additional Rontgen diffraction (XRD) experiments in order to study the crystal structure changes during dehydration.
As an example the signal contribution of the Mirabilite phase is plotted against the Thenardite phase as a function of the dehydration process (figure 3).

An almost linear relation is found, i.e., the transition of Mirabilite into Thenardite is one-to-one. Complementary information of the process is found using another technique, Raman spectroscopy, which gives information on the vibration of the sulphate in a crystal structure. When the results of Raman measurements are plotted in the same figure 3, a different picture emerges. The Raman measurements show that the Mirabilite phase disappears first and, subsequently, the Thenardite phase comes up slowly. Obviously, at intermolecular scale the transition is direct (XRD), but at intramolecular scale the transition occurs through an intermediate state (Raman). Most probably during the Mirabilite-Thenardite transition the vibrations are affected as related to the degree of hydration. This may introduce a route to understand the decline in reversibility in storage systems. Infrared spectroscopy is expected to give complementary information on this process.

Our goal is to combine such information to understand de-/hydration process in relation to water transport and crystal structure changes. This lays a foundation for choosing optimum salt crystal sizes for a heat battery. In the next steps, our dehydration studies will also address salt complexes with different types of water inside [5]. This will outline our path toward the next generation of compact and stable, long lasting heat batteries.

REFERENCES