SHC 2012

Development of a seasonal thermochemical storage system

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Abstract

In our laboratories, a seasonal thermochemical storage system for dwellings and offices is being designed and developed. Based on a thermochemical sorption reaction, space heating, cooling and generation of domestic hot water will be achieved with up to 100% renewable energy, by using solar energy and waste heat. Development of the reactor and its components (adsorber/desorber, evaporator/condenser) as well as on the active material are described, and indications for further improvement are given. Simulations and experiments yield promising results for further development in demonstrators and field tests of the system set-up, and our newly developed enhanced active material yields promising results exhibiting high storage capacity, good reversibility and ease of use.

1. Introduction

As Europe moves towards low and zero-carbon buildings, challenges arise in the management of building integrated renewable energy technologies. Electricity generating renewable energy sources (RES) have the benefit of electrical connection and financial mechanisms allowing feed-in to the network. Thermal technologies do not have such general interconnectivity and therefore rely on sizing typically meeting 90% of thermal demands in the summer (mainly domestic hot water) in moderate climates. This approach provides little benefit in winter, e.g. for space heating purposes. Moreover, due to the better insulation of the buildings the cooling demand in summer time rises also in the more moderate climates.

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Therefore an obvious approach is that of thermal energy storage that overcomes issues of heat loss, substantially increasing the overall use of RES in buildings throughout the seasons.

Corresponding technologies such as geothermal heat storage in aquifers have been initiated but because of a lack of domestic application in this case they have not sufficiently succeeded so far. The focus is shifting more and more to compact and high energy density thermal storage.

Short term thermal storage systems based on hot water storage, which already exist for a long time and work reliably, cannot be upgraded with regard to seasonal thermal storage (Fig. 1). Compensating seasonal heat-supply and -demand requires storage at the highest energy density possible, e.g. with thermochemical storage systems based on adsorption or absorption principles. These systems, using silica gel, zeolite (both adsorption), or salt hydrates (absorption) embody a high thermal storage-density without the need for thermal insulation measures during storage.

The objective of the present project is to develop, demonstrate and evaluate a compact seasonal storage system based on novel high-density materials that can supply required space-heating, cooling and DHW with up to 100% RES.
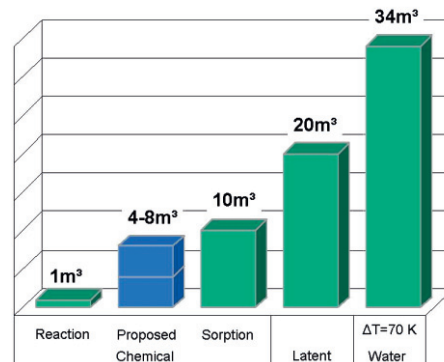

Fig. 1. Volume required to store 6.7 GJ, with the proposed set-up, adapted after [1]

2. Process & technology approach

Delivery of heat on different dedicated temperature levels is one of the key prerequisites of the system. Tailoring to the size of individual dwellings is a second one. The storage system must have a manageable volume comparable with the footprint of a domestic dwelling. Such a tank typically becomes between 4 m^3 and 8 m^3 and has a possibility of being incorporated under for example a garden space. Starting conditions for the dimension of storage materials and capacity will be formulated first, and afterwards a dedicated solar collector for the storage system for specific climate zones will be designed and developed. Next an integrated design for the different components and enhanced thermochemical materials will be developed as well as a design of the storage system and control system. Below, only the development of the thermal store will be discussed.

Design and development are basically an iterative approach. Simulations as well as experimental work are carried out closely together to ensure the transition from an innovative thermal energy storage idea into an effective and marketable technology. Model simulation of these thermally and vapor pressure coupled adsorption/absorption processes in Comsol is solved by using the "Species Transport, Free and

Porous Media Flow and Heat Transfer in Porous Media" model. Matlab is used to model the resulting thermal energy storage and extraction process as well as for the modeling on system level.

Building cutting-edge heat exchangers, optimizing thermal properties, surface area and design for both ad- and desorption and for evaporation and condensation, requires perfect material knowledge and material processing experience. Our groups realize these qualities in a testing environment by interaction of the chemical, thermal-physical and building integration laboratory.

As mentioned, our seasonal thermal storage working principle is based on thermochemical reactions. Therefore, coping with problems such as corrosion, limited physical stability of the active materials, sub-optimal thermal and mass-transport properties, and non-atmospheric pressure levels is indispensable. Initial experiments on development of enhanced active substances to overcome these problems have started in our laboratories, and will be expanded in the near future.

Coupling known mechanisms is not only a question of assembling; all parts depend on each other. This is where we are at the moment: We are at the transition of closing the cycle of adsorption, desorption, condensation, and evaporation into one compact storage system using enhanced thermochemical materials.

3. Results & discussion

Initial experiments for thermochemical storage took place on a glass lab-scale zeolite reactor containing copper heat exchangers (for both adsorption/desorption and evaporation/ condensation). A picture of the lab-scale reactor, as well as initial results for static and dynamic unloading of the reactor are given in Fig. 2.

In the first experiment shown (Fig. 2b) a quantity of zeolite was fixed in a heat exchanger surrounded by a water-permeable membrane, and it was brought into contact with a quantity of water vapor at a fixed temperature. Thermocouples and pressure sensors were attached in several places and the experimental situation was monitored throughout. After reaching a thermal equilibrium, the pressure was lowered and the measurement was started. In this particular experiment, evolved heat was not transferred out of the reactor. Maximum temperatures of 85-88 ºC were reached in the reactor bed, but higher values (up to 140 ºC) were reported later as well.
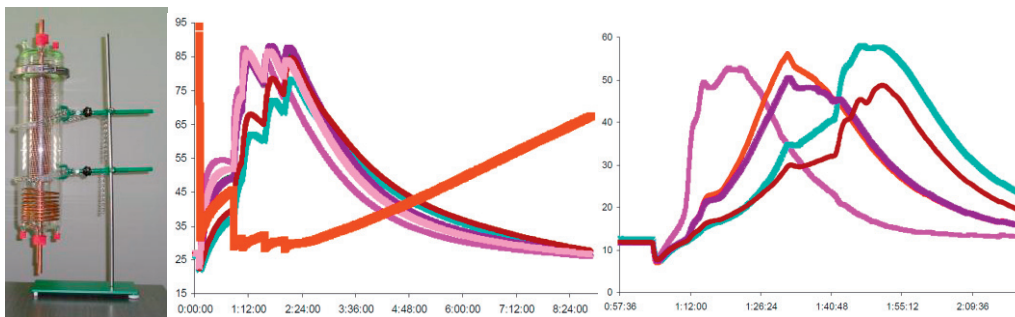

Fig. 2. (a) Lab-scale reactor set-up containing copper heat exchangers; (b) initial results for the static and (c) dynamic unloading of the thermochemical material. Horizontal axes in the graphs display time (h:mm:ss), vertical axes display temperature (ºC) (and pressure (mbar); red curve in (b))

In the second experiment shown (Fig. 2c) a similar experiment was carried out. In this case, the evolved heat was transferred out of the reactor by the heat transfer fluid running through the heat exchanger (water). Maximum temperatures of 55-60 ºC were reached in the reactor bed, while thermal transfer was not perfect by far. In addition, for both experiments long reaction times were measured (hours).

Maximum specific output power was measured to be 164 W/kg active material. Taken all non-optimal issues into account (thermal losses, less-than-optimal thermal conductivity and mass- and heat-transfer), a basic understanding of a generating thermochemical storage system was obtained. In situ regeneration experiments showed that regeneration of the material was in principle possible, but it is clear that care should be taken to use adequate regeneration temperatures and pressures.

Based on the described indicative experiments a thorough investigation was set-up. The development of the adsorber geometries for thermochemical storage compounds was investigated through modeling and experiments. Using Comsol Multiphysics the adsorption of water on different set-ups of zeolite on different heat exchanger surfaces has been modeled. In addition, the results have been verified by experimental measurements.

Three different adsorber geometries are described, and on the basis of the adsorption their water-concentration and temperature change is simulated. Simulations are focused on finding a geometry that shows fast adsorption of the water vapor and is cheap and easily built. The suggested set-up comprises zeolite spheres in glued contact with a copper plate (Fig. 3). Obtaining adequate thermal contact of the zeolite and the heat exchanger, as well as rendering a high surface area combined with a low material usage proved key issues in the development of the adsorber.

Based on the modeling results, the next adsorber set-up consisted of a heat exchanger base of 0.2 mm copper foil, with a water-accessible cross-section of 20 mm x 2 mm and a length of 400 mm.

The following photo and design set-up (Fig. 4) show the development of the experimental reactor, of which the characteristics were fully assessed. The results of the experiments can be found below.
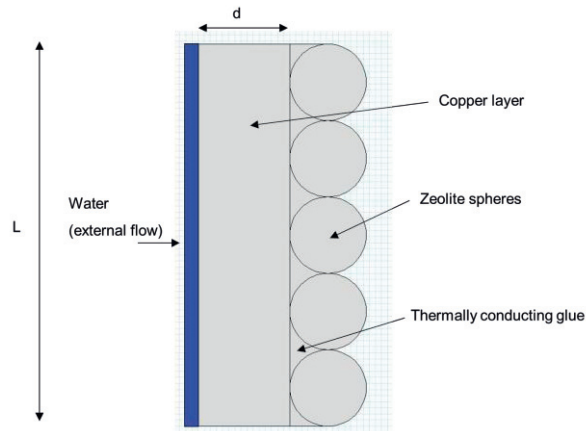

Fig. 3. Copper layer, zeolite material and thermally conducting glue in the modeled set-up

Fig. 4. (a) The real heat exchanger strips after theoretical optimization; (b) the built reactor with heat exchanger strips, evaporator/condenser, and measurement equipment.

In the first experiment shown for the new reactor set-up with the developed adsorber/desorber heat exchangers (Fig. 4, and Fig. 5a) a quantity of zeolite was brought into contact with a quantity of water vapor at a fixed temperature. Thermocouples and pressure sensors were in place and the experimental situation was monitored throughout. After reaching a thermal equilibrium, the pressure was lowered and the measurement was started. Evolved heat was transferred out of the reactor by means of a water flow through the heat exchanger tubes. Maximum temperatures of 26-28 ºC were reached in the reactor bed, and the experiment was finished within 5 minutes.

In the second experiment shown (Fig. 4b) a similar experiment was carried out, using only two heat-exchanger tubes for better optimization purposes. In this case, the evolved heat was transferred out of the reactor by the heat transfer fluid running through the heat exchanger and the temperature difference (out-in) was recorded. Only moderate temperature differences of ~2 ºC were reached and the total energy gained in the heat exchanger was 6000 J.

In the third experiment shown (Fig. 4c) a similar experiment was carried out using a higher quantity of active material, and additional thermal insulation between the adsorber and the outer reactor surface. In this case, the reaction took much longer to complete (mass transfer resistance inside the active material), but the evolved heat that was transferred out of the reactor by the heat transfer fluid and the temperature difference (out-in) were found to be much higher. Temperature differences of ~9 ºC were reached and the total energy gained in the heat exchanger was 35000 J.
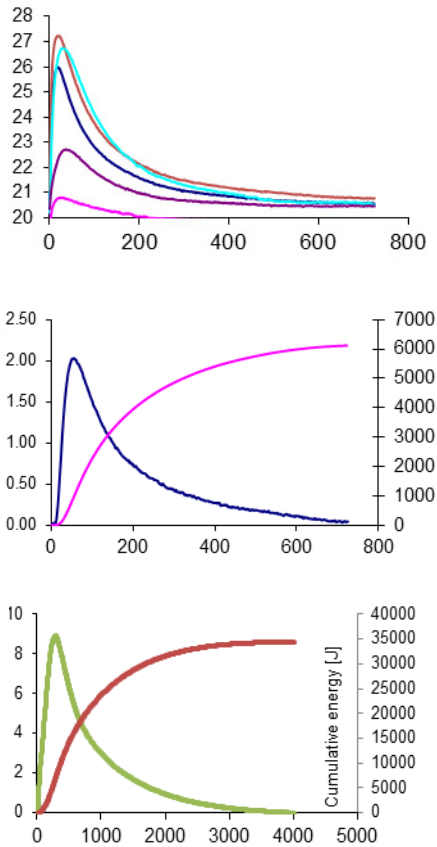
Fig. 5. (a-c) Results for the dynamic unloading of the thermochemical material. Horizontal axes in the graphs display time (s), primary vertical axes display temperature (ºC, (a)), temperature difference (ºC, (b,c)), and secondary vertical axes represent cumulative energy (J). For more extensive information refer to the text.

Maximum specific output power was measured to be 0.60 kW/kg active material in the first 1000 seconds, and it was concluded that the higher output power was delivered due to better thermal contact as well as the faster mass transfer when a single layer of zeolite material was used. Multiple zeolite layers imposed both thermal and mass resistances, thereby diminishing performance. An optimum will have to be found for proper future application. In addition, evaporation of water is crucial for fast reactions and adequate subsequent mass transfer. Static evaporation versus dynamic evaporation experiments show that active dynamic evaporation removes the mass transfer barrier for water vapor altogether (results not shown here).

For future applications, zeolite as used above will likely not be used in commercial reactor systems for small-scale seasonal thermal storages, because of economical (price) and technical reasons (storage volume needed). Therefore, in our labs, research has commenced to enhance certain existing thermochemical materials for more adequate use in thermochemical reactor systems. Downsides of

existing active materials, like fluidization and severe corrosivity, are sought to be minimized as much as possible. A suitable composite material should emerge, having an open structure for good vapor transport, being capable of high loading fraction and therefore still a high storage density, and being flexible, stable and cheap. Initial experiments on such a material (which cannot be further specified as yet in view of IP validaton) are depicted below.

In Fig. 6a, DSC results for our enhanced thermochemical material are given (with DSC results for $CaCl_2$ as a reference in the same scale). It can be seen that although the energy contents is somewhat lower than that of $CaCl_2$ (~50%), a large response is obtained on dehydration upon temperature increase. In Fig. 6b, the mass is plotted against the temperature for different heating cycles of a single sample of enhanced material. It shows that maximum water content in the enhanced material is approximately 40% w/w, and also that the hydration/dehydration reactions are reversible and occur with almost no hysteresis. In addition, no deterioration of the enhanced material could be found, even upon multiple loading and unloading cycles. The material stays present as a solid throughout the measurements, even at elevated temperatures. Furthermore, temperatures at which dehydration takes place can be very well used in thermal storage systems based on normal solar collectors, as the maximum dehydration temperature is situated around 100 ºC. In future publications, the full research on these enhanced materials will be elaborated upon, and a thermal storage reactor based on these new materials will be presented then as well.
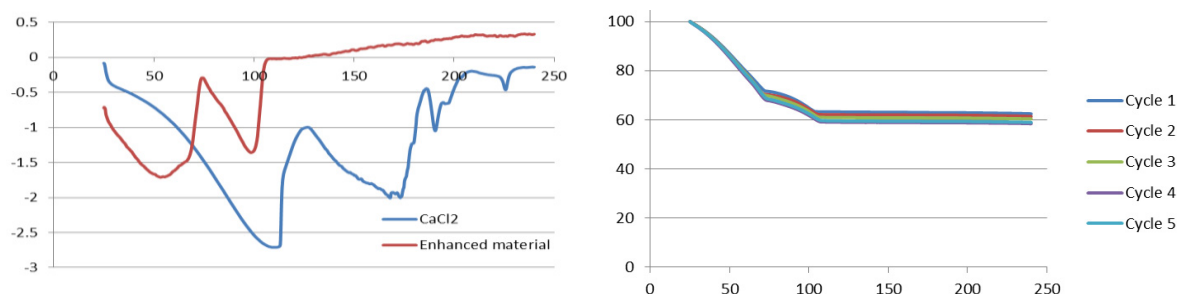

Fig. 6. (a) Results for the DSC measurements of the enhanced thermochemical material and $CaCl_2$; (b) results of multiple TGA cycles of one sample of enhanced material. Horizontal axes in the graphs display temperature (ºC), vertical axes display normalized applied power (W/g, (a)) and mass (%, (b)). For more extensive information refer to the text.

4. Conclusions

Experimental and modeling work showed good initial behavior of a lab-scale vacuum-based thermochemical storage unit. Although suffering from thermal losses and less-than-optimal heat exchange, adequate loading and unloading cycles were shown. Based on these results improved heat exchangers and an improved reactor set-up were designed and developed with good results. High output power (0.60 kW/kg active material) and short reaction times (5 minutes) were obtained, due to improved thermal and mass transport. A total energy yield of 60% of the theoretical value was reached, giving room for further improvement. It was found that especially the rate of evaporation proved crucial for fast and adequate unloading of the reactor volume. Furthermore, initial experiments on novel enhanced active materials for thermochemical storages look promising; a new material has been indicatively assessed, showing good thermal behavior and adequate cycling ability. In addition, temperature ranges are suitable for use in a thermal storage system in combination with solar collectors.

The current project has the ambition to come up with almost market-ready compact thermal energy storage solutions based on novel materials. The cooperation between industry, research and academia enables dedicated knowledge and product development, demonstrated under market conditions. Use of

advanced compact thermal storage systems will significantly increase after wide-spread dissemination of the obtained results from the current project. Subsequently, renewables, like solar energy, will more effectively be used to cover the existing needs for energy in the built environment.

5. Future developments

Ongoing theoretical and experimental research aims for better overall thermal storage systems. In all developments, the price/performance ratio is kept in mind. Based on the obtained results from the laboratory proof-of-principle (high output temperatures, theoretical storage capacity of 0.5-0.8 GJ/m^3, and efficiency of up to 75%), the first proof-of-concept systems are going to be finished and evaluated later this year. They will contain an optimized reactor volume, optimized heat exchangers for ad- and desorption, and optimized evaporator/condenser for use with adsorption materials, as well as the first indications for use with our enhanced active material. Simultaneously, field tests and concepts of building integration of a modular thermochemical seasonal storage system will be prepared.

To improve the future market up-take, specific tasks on business models, market strategies and other non-technical issues will be carried out. Demonstration of the prototypes and subsequent dissemination of the findings and results will likely lead to wide-spread application of seasonal thermal energy storage in the built environment.

Acknowledgements

References

[1] Pinel, P, Cruickshank, CA, Beausoleil-Morrison, I, Wills, A. A review of available methods for seasonal storage of solar thermal energy in residential applications. *Ren Sust Energy Rev*, 2011;**15**:3341–59. from: Hadorn., JC. Advantage storage concepts for active solar energy. *IEA SHC Task 32*; 2003-2007. In: Eurosun – 1st international conference on solar heating, cooling and buildings. 2008.