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Chemical energy storage using reversible solid/gas-reactions (CWS) – results of the research project

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Abstract

Within a four year joint research project the technical feasibility of thermo-chemical heat storage for solar thermal applications and the achievable advantages compared to conventional storage technologies have been investigated. The project, directed to applied research, was divided into a high temperature (> 300°C) and a low temperature part (< 100°C). In the low temperature part the main focus was on the development of a compact seasonal heat store for single or multifamily houses. Concerning high temperature applications thermo-chemical energy stores show high potential for improving energy efficiency of power plants and for recovery of process heat.
The investigations have been carried out by a close cooperation of the Institute of Thermodynamics and Thermal Engineering (ITW) of the University of Stuttgart, specialised for solar thermal heating in the building sector and the Institute of Technical Thermodynamics (ITT) of the German Aerospace Center (DLR) as a specialist on solar thermal power plants.
The project started in 2008 and runs until end of June 2012. This paper will focus on the low temperature part of the project, discuss important experiences and recent experimental results of the project and will report the very latest developments. Moreover the paper will summarise the important improvements achieved for temperature thermo-chemical heat storage. Finally recommendations for future activities will be given.

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1. Introduction

Numerous studies and also many experiences of the last years show that solar thermal is the appropriate technology for raising the fraction of renewable energy in heating sector. For example, the "strategic research agenda" 2030 of the European Solar Thermal Technology Platform /1/ shows that with an accelerated development of the market about 50% of the total heat demand in Europe could be supplied by solar thermal until 2030. This requires beneath the expansion of the installed power of the collectors also sufficient available capacity of heat storage. The realization of a high solar fraction (> 50%) for solar thermal space heating requires an efficient storage technology. In relation to this, alongside improved hot water storages alternative processes become more and more interesting. The thermo-chemical heat storage is an excellent example. This technology abstracts procedures that allow a very efficient way of storing energy for a long period based on adsorption processes or reversible chemical reactions. Within the German research project "chemical heat storage using reversible solid/gas-reactions" (CWS) funded by the Federal Government Department of Economy and Technology (BMWi) the capabilities of the thermo-chemical heat storage and its technical implementation towards low temperature and high temperature application were investigated by the Institute of Thermodynamics and Thermal Engineering (ITW) of the University of Stuttgart and the Institute of Technical Thermodynamics (ITT) of the German Aerospace Center (DLR) /2/. The project was intended for a runtime of 4 years and was divided into the key activities "process design" and "application development". The work of the DLR was orientated towards high temperature applications in the sector up to 400 °C while the investigations of ITW was focused on low temperature applications in the temperature range below 100°C.
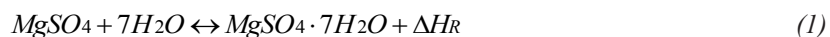
2. Thermo-chemical heat storage

Solar thermal technology aims at contributing a share as high as possible to heat supply. Based on already achieved positive developments of solar space heating it is necessary to advance the systems and make them more compact and cheap. By using thermo-chemical energy storages the research project CWS aims at raising the share of the heat supplied by a solar combi system in an efficient way and at achieving high solar fractions.

The thermo-chemical energy storage is based on utilization of heat of reaction of reversible chemical reactions. For example a chemical compound of type $A - B$ can be split reversibly into the components A and B via adding heat. In this process the added quantity of heat ΔH_R is being converted into the chemical energy of the systems A and B. If the reverse reaction of the products A and B into the lead compound is avoided, the energy stored in chemical bonds can be stored loss-free for an arbitrary duration.

An example for this type of reaction is the dehydration of salt hydrates, for example magnesium sulphate-heptahydrate into magnesium sulphate /3/ as shown in eq. (1). The energy required for the endothermic reaction is provided by the surplus heat of the combi system during summer.

If the salt anhydrate is being stored hermetically sealed, the energetic state can be kept loss-free for an unlimited period of time. This means heat losses only occur during charging the storage respectively discharging of the storage. If at any later time the dried magnesium sulphate gets brought in contact with humidity, the hydration reaction occurs and the quantity of heat added during the dehydration is released at a lower temperature level.

$$MgSO_4 + 7H_2O \leftrightarrow MgSO_4 \cdot 7H_2O + \Delta H_R \qquad (1)$$

3. Developing a thermo-chemical heat storage

Initially, in the beginning of the project a thorough analysis of possible process concepts, operation methods and integration into the conventional solar heating system was carried out. Out of a large spectrum of potential storage materials the most promising were identified and afterwards experimentally analyzed in laboratory scale. A numerous important experiences and results were achieved on the way to the final concept. This article confines itself to describing the final result.

Figure 1 shows schematically the integration of the thermo-chemical storage into a solar combi system. The thermo-chemical storage consists of an external reactor in which the chemical reaction takes place, of a separate storage container for hydrated and dehydrated storage material as well as a material transport system. The collector array serves as heat source, which alternatively heats the combi store or supplies the heat needed for dehydrating the storage material. The combi store is especially required because of procedural purposes. The chemical reactor can be designed for a constant heat load and peak demands can be buffered by the combi store. The thermo-chemical heat storage is operated in the two following states.
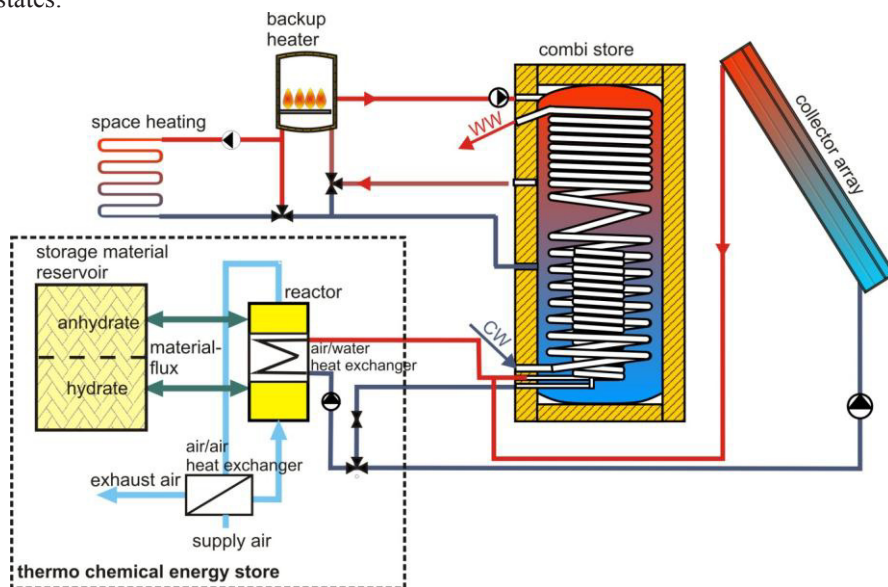

Fig. 1. Schematic illustration of the complete system using the example of a solar thermal combisystem with a thermo-chemical energy storage

Summer: Regeneration of the storage material

During summer months when there is more solar radiation available as needed in order to cover the current heat demand, the regeneration of the storage material is taking place. The collector array supplies the required heat, so that the endothermic reaction for dehydrating the storage material can take place. Therefore an air stream is being heated (until about 180 °C) by an air to water heat exchanger and the hot air is blown through the reactor. Water vapor released during the dehydration is removed by the air stream. The air leaving the reactor is conducted through an air to air heat exchanger in order to preheat the fresh inlet air. Afterwards the air is being conducted to the environment.

Winter: Loading of the storage material

When solar radiation during winter is not sufficient in order to cover the heat load for hot water and space heating directly through the solar system, loading of the combi store happens with help from the thermo-chemical storage. Therefore wet air is sucked in from the environment and conducted through the reactor. Simultaneously regenerated storage material is being conducted to the reactor at which the water vapor which is present in the air hydrates. The released heat of reaction is transported via the air stream to the air to water heat exchanger and afterwards is applied to the combined storage tank by the solar circle. Exhausted air from the air to water heat exchanger is being conducted to the air to air heat exchanger in order to preheat the sucked in air from the environment.

Material transportation

For the described process, besides a chemical reactor a material transportation system and a storage material reservoir are required. Figure 2 shows schematically the concept of the material transport. The storage material moves from the storage tank through the reactor driven by gravity from top to bottom. At the reactor exit there is a control device which handles the mass flow. After exiting the reactor the material gets into a daily reservoir. From here the material is transported back into the storage tank once a day. Therefore a vacuum suction device is used. In the pilot plant a vacuum exhauster is used which has an electrical power consumption of about 1600 W corresponding to a hauling capacity of one ton per hour. Assuming a material energy storage density of 250 kWh/t the electrical power consumption is about 13 W_{el} per kW_{therm}.
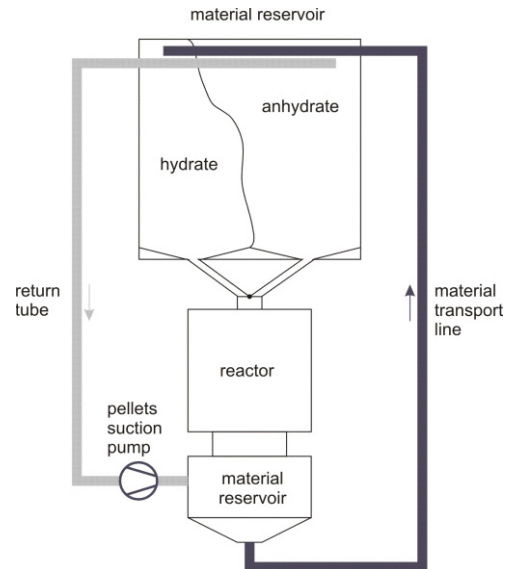

Fig. 2. Concept of the material transport

3.1. Developed CWS-reactor design

The reactor developed in context of the project is designed as a discontinuous operated cross flow reactor /4/. In regular intervals a part of the material in the bottom section of the reactor is discharged and the reactor is filled with new material from the top. The conduction of the air as cross flow towards the material offers technical and energetic advantages in terms of low pressure drop by means of short flow paths, local separation of material supply/removal from the air supply/removal, a simple filling and emptying of the reactor and an approximately steady-state operation with a constant power output.

Figure 3 schematically shows the reactor. It consists of two chambers, one chamber to load the material and one chamber to regenerate it. Both chambers are separated by an air to water heat exchanger. While loading the material (exothermic reaction to release heat of reaction; fig. left) the "reaction chamber" is being filled with regenerated storage material and the "regeneration chamber" is empty. Moist air is being conducted to the reactor. The heat of reaction released via the exothermic reaction is being conducted to the air to water heat exchanger by the air flow. After the heat exchange the air is being transported through the empty "regeneration chamber" out of the reactor.

While regenerating the material (endothermic reaction to insert heat of reaction, fig. right) the "regeneration chamber" is being filled with material and the "reaction chamber" is empty. The air is being transported through the reaction chamber, heated up to the regeneration temperature by the air to water

heat exchanger and transported into the regeneration chamber. Afterwards the moisture saturated air is transported out of the reactor.
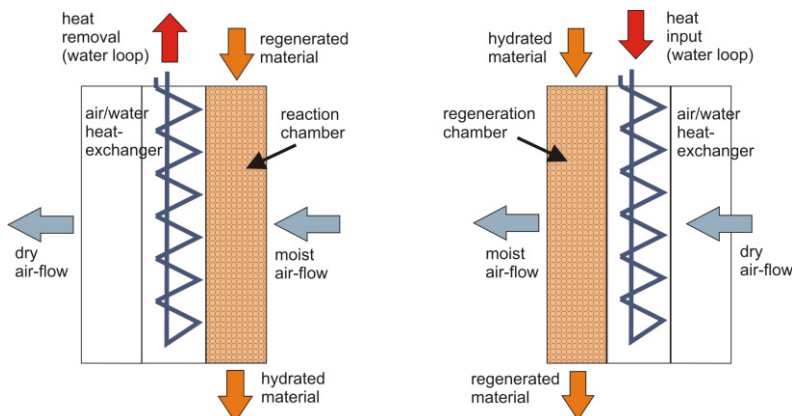

Fig. 3. Schematic of the reactor design

The laboratory reactor has a capacity of 20 liters, the flow cross-section for the air stream is 0.25 m² (W x B) with a flow length of L = 80 mm. During the reaction the material is filled into the reactor from the top and moves through the reactor driven by gravity. Using the shutter at the material outlet the material flow in the reactor can be set to a very low flow-rate (in average $\leq$ 5 kg/h, if necessary interval operation). A diagonal fan supplies the air volume flow with a flow rate of 180 m³/h. Due to the low pressure drop of $\Delta p = 85 Pa$ it is possible to use a fan with a nominal power consumption of about $P_{el} = 20W$.

3.1.1. Numerical analysis of the reactor design

In order to analyze the reaction behavior including the material flow, a 2-dimensional numerical model of the reactor was setup with the simulation software COMSOL Multiphysics. Following simplifications were met:

The material flow has a constant vertical velocity over the reactor height and length. Heat losses of the reactor to the environment are not regarded. A schematic illustration of the reactor modeled in the simulation software is shown in figure 4 (left). The geometric shape of the reactor correlates to the actual laboratory reactor (H x L = 0.5 x 0.08 m²).

The following shown results represent exemplarily a steady-state operation of the reactor with typical boundary conditions of transitional months of spring and autumn. The ambient temperature is $\vartheta = 10°C$ with a relative humidity of $\varphi = 80\%$ ($6.2 g_{H2O} / kg_{dry\_air}$). The air, preheated by the air to air heat exchanger, enters the reactor with a temperature of $\vartheta = 35°C$. The air volume flow is $\dot{V}_{air} = 180 m³/h$. The material enters the reactor with a load of $x_{p,in} = 12 g_{H2O} / kg_{adsorbent}$. This initial load results from the defined boundary conditions for the material regeneration (material regeneration at a temperature of $\vartheta = 180°C$ and an humidity of $x_{air} = 6...12 g_{H2O} / kg_{dry\_air}$). The storage material enters the reactor at room temperature ($\vartheta = 25°C$) with a mass flow rate of $\dot{m}_p = 5 kg/h$.

Figure 4 presents the results of the simulation, which show the load distribution (middle) and the temperature distribution (right). The load of the material shows a sharp edge between reacted (top right, blue) and unreacted material (bottom left, red). According to this the temperature in the reactor settles in, with maximum temperature in the top area of the reactor. The highest achieved increase of temperature in

the reactor is $\Delta T = 25K$. The average increase of temperature of the air flow is $\Delta \overline{T}_{air} = 19K$. So, an increase of temperature of $\Delta T_{min} = 15K$ is realized, which is sufficient for a low temperature heating circle. For these calculations an effective power of $\dot{Q}_{air} = 0.92kW$ was transported out of the reactor. By increasing the air stream, the power output can be increased appropriately.
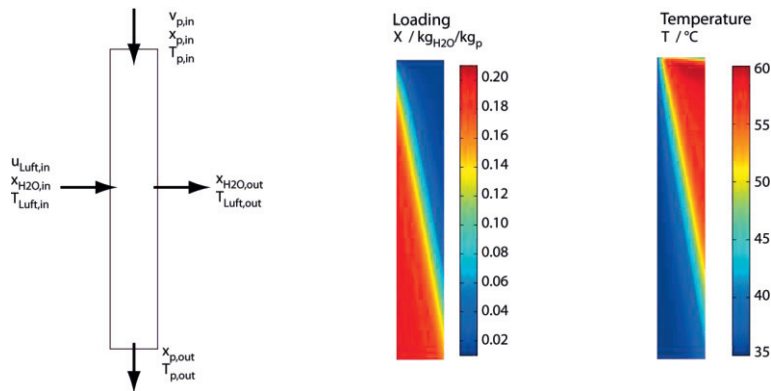

Fig. 4. Schematic of the reactor as depicted in the simulation software (left), results of the simulation: load distribution of the material (middle) and temperature distribution in the reactor (right)

The average load of the material exiting the reactor is $x_p = 190g / kg$ which is about 95 % of the maximum load. The average temperature of material exiting the reactor is $T_{p,out} = 36°C$ which is just one Kelvin above the inlet temperature of the air. Hence only a very small share of the energy released in the reactor becomes lost via the material exiting the reactor (22 W respectively 2%).

The results of the simulations already show the essential advantages of the cross flow:

- Low pressure drop over the packed bed, a fan with low power consumption can be used
- Material has almost equilibrium load at the reactor outlet
- Almost the entire released heat of reaction is transported out of the reactor via the air stream
- Increase of temperature also with a low humidity (for instance ambient humidity during transitional months) applicable for technical use

3.1.2. Experimental analysis of the reactor design

In terms of experimental testing of the reactor concept a test facility was built. Figure 5 shows the schematic build-up of the test reactor. The left figure shows the routing of the air flow. The air flow carries out the heat transport and the water vapor transport from and towards the reactor. An important part of the air circle is the air to air heat exchanger. The air exiting the process preheats the entering air. This minimizes the heat loosed to the environment (thermal power loss) via the air flow and increases the share of useful heat.

A thermostat was built in to function as heat source and heat sink. It works in a temperature area from 5 to 150 °C and is run with thermal oil as heat carrier. As the regeneration temperature of 180 °C is to reach, an additional electrical heater in the bottom area of the reactor on the air to oil side of the heat exchanger is built in.

The material enters the reactor from the top and moves through it driven by gravity. Air enters the reactor from lateral through special designed air ducts. During the exothermic reaction the heat of reaction is transferred via the air to oil heat exchanger to the oil circle and towards to the heat sink.

The air flow in the test facility is run in opposite direction during the endothermic reaction (when regenerating). While in the actual system a solar cycle is providing the heat, here it is supplied by the thermostat and heat is transferred via the oil to air heat exchanger to the air flow. Water vapor released during the dehydration reaction is transported out of the reactor by the air flow.
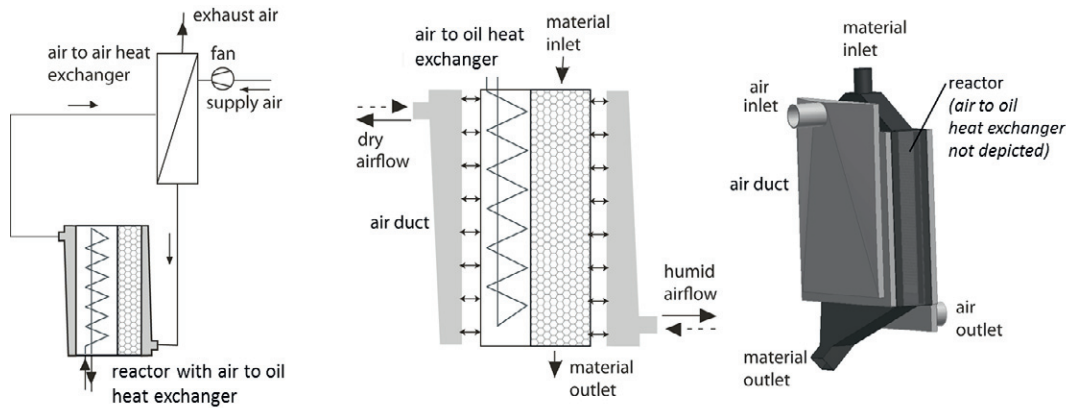

Fig. 5. Left: Schematic of the air flow. Middle and right: schematic reactor design

To test the new reactor concepts first experiments were carried out using zeolite 13X as storage material. In figure 6 a complete adsorption without material exchange is depicted. During this experiment following inward flow conditions were existent: Inlet temperature air $T_{air,in} \approx 23°C$, mass flow air $\dot{m}_{air} = 88kg/h$, relative humidity $\varphi \approx 40\%$, inlet temperature oil $T_{hx,in} \approx 24°C$, mass flow oil $\dot{m}_{oil} = 98kg/h$. The entering air is preheated by the air to air heat exchanger to about 28 °C. Afterwards an increase of temperature of about 30 K is achieved during the adsorption. The air exits the adsorption bed with a temperature of about 58 °C. This matches a heat output of about 750 W.

Approximately 60 % of the heat is transferred to the oil circle and about 37 % become lost as heat loss due to the currently not yet insulated reactor. The air exits the reactor with a temperature of about 33 °C. In the downstream air to air heat exchanger, preheating of the supply air takes place, which chills the out going air to about 24°C. So the exhaust air is only approx. 1 K warmer than the supply air and the heat loss adds up to only 3 %. This means a very high level of utilization of the adsorption enthalpy will be achieved with an appropriate insulation.

Figure 7 shows a regeneration test in the reactor without material exchange and without using the additional electrical heater. The test aims at determining the achievable temperature by using the oil to air heat exchanger only. The test duration was 140 minutes. Due to a prior experiment the initial temperature of the reactor was 90 °C. Given are the oil temperatures   at the inlet and the outlet of the oil to air heat exchanger, the air temperatures   at the inlet and the outlet of the air to air heat exchanger and also the reaction bed temperatures   of the top, middle and bottom area of the reactor.
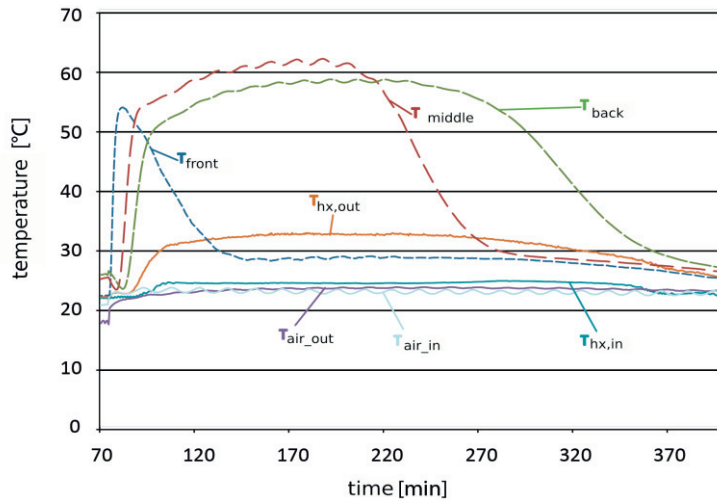
Fig. 6. Adsorption test without exchange of material. Depicted is the progress over time of the temperatures of the air (T_{air}), oil (T_{hx}), as well as adsorption bed ($T_{front, middle, back}$)

The results show that with a maximum oil inlet temperature of 150 °C a bed temperature of 130 °C was achieved. Thereby the distribution of the temperature is very uniform which concludes a homogeneous flow over the reactor cross section. After about 20 minutes the power output of the air to oil heat exchanger is almost constant with a power of 1.8 kW. The specific power loss which is transported out of the reactor averaged over the test duration is approximately 195 W which correlates with approx. 11 % of the heating power.

Further tests aim at moving from a steady-state to a quasi-continuous operation of the regeneration. With aid of the electrical heater, regeneration temperatures of 180 °C shall be made possible.
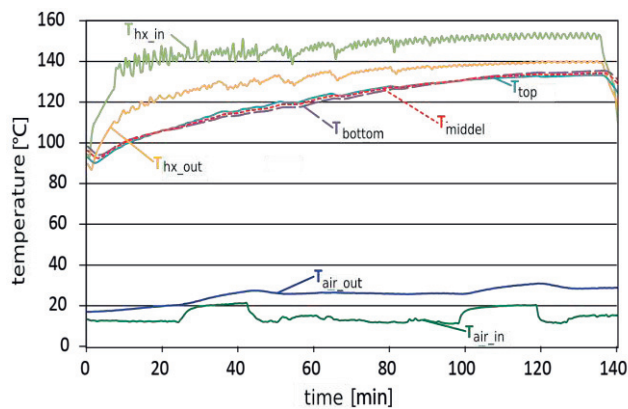

Fig. 7. Regeneration test without exchange of material and without using the additional electrical heater. Air temperature (T_a), oil temperature in the heat exchanger (T_{hx}), as well as reaction bed temperature middle (T_{bed})

3.2. Thermal performance

After the performance of the reactor design was determined and tested in the numerical and experimental analysis, the thermal performance of the complete system was analyzed based on annual simulations in TRNSYS /5/. Derived from the detailed numerical analysis a simplified reactor model of the thermo-chemical heat storage was developed for TRNSYS and implemented. The substantial properties and the characteristics of the reaction, which the model is based on, correlate to these of calcium chloride ($CaCl_2$) and zeolite. The material is characterized by a high storage density of 250 kWh/m³ and a high heat of reaction. Due to the required high regeneration temperature CPC-evacuated tube collector were used for the simulation.

In order to determine the heat demand and the temporal thermal load two building types were analyzed. Both buildings have a living area of 128 m², a 45 ° inclined and south orientated roof and a window area of 10 m² in the southern façade. For the type EnEV the building was insulated according to the current German regulation with a annual heating demand of 9090 kWh for space heating. For the type KfW40 the heating demand was reduced by 50 % which correlates to a heating demand of about 35 kWh/m². The heat demand for hot water preparation is 2945 kWh per year in both cases.

For a better assessment of the results the identical solar thermal system was simulated using a hot water storage instead of the thermo-chemical storage. Figure 8 shows the achieved annual energy saving f_{sav} over different collector areas. Additionally, the particular corresponding storage capacity is given. The storage capacity was chosen so that the collector area exactly suffices to regenerate the thermo-chemical storage material during one summer.
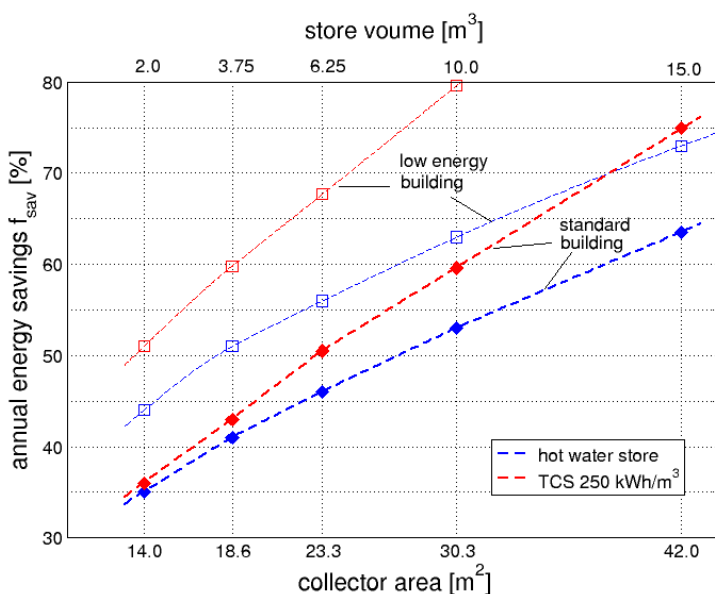

Fig. 8. Comparison of the annual energy savings of identical solar thermal systems with hot water storage respectively with thermo-chemical storage (CWS)

The simulations show that a solar system with a thermo-chemical heat storage with a capacity of 6.25 m³ and 23 m² vacuum tube collectors achieves an energy saving of 50 % for the EnEV-house.

Additionally raising the collector area and the storage capacity leads to almost linear rising energy savings. This is a great difference to hot water storages where losses occur. The difference becomes even clearer when comparing the needed size of the system. If there is to achieve a annual energy saving of f_{sav}=75 %, the CWS-system requires a storage tank of a volume of 8 m³ and a collector area of 27 m².

In the contrast, the water based system requires a storage tank capacity of 15 m³ and a collector area of 43 m² to achieve the same proportional saving of f_{sav} = 75 %.
Two effects become clear: The higher volumetric storage capacity does not correlate one-to-one with a decrease of the volume of the storage but leads to a remarkable decrease of required collector area.

4. Conclusion

The presented research activities and results show that thermo-chemical storages have a great potential for solar thermal heating systems. The high storage density and the low heat losses over a long duration are leading to high solar fraction with comparatively moderate sizes of storage and collector area. Despite the low amount of loading and unloading cycles the efficiency of the storage is high. This is demonstrated via a high storage efficiency which is close to the efficiency of a short-term storages with a high amount of cycles.

The process developed within the research project CWS was numerically and experimentally analyzed. The procedural feasibility and energetic advantages compared to conventional hot water stores were demonstrated. In relation to a hot water store the technical effort is higher due to the procedure. The energetic advantages of clearly higher energy savings with simultaneously smaller and presumably also cheaper systems justify the technical effort. Further research is necessary in order of utilize the shown potentials. Especially the reactor design as well as the implementation into the complete system has a need for further research. Substantial progress was made in the area of storage materials. Several reaction systems were analyzed and efficient and low-priced storage materials were tested. From the economical point of view an important condition for seasonal heat storage is the use of low-cost storage materials with a high energy storage density. Composite materials based on low-cost carrier materials are conceivable. A price of 0.5 €/kg seems realizable /6/. There is a development of national and international interdisciplinary research that already has achieved remarkable goals. This is also because thermo-chemical heat storage is becoming more and more interesting for a broad spectrum of applications besides solar thermal (such as current regulated cogeneration plants up to e-mobility).

Considering that thermo-chemical heat storage is still in the beginning of its development and that a remarkable increase of performance and a decrease of cost are achievable it becomes clear that there will be new application areas and a high benefit for solar thermal.
It is intended to even further advance the development of the sector of thermo-chemical heat storage and to realize a demonstration system in a following project.

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