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031 - Chemical and Sorption Storage – Results from IEA-SHC Task 32

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Abstract

Six main groups have studied chemical and sorption storage within IEA-SHC Task 32 “advanced storage concepts for solar and low energy buildings”. Closed and open adsorption systems, two and three phase absorption as well as chemical storage have been studied. The main results of the work are: identification of potentially suitable materials for long term storage of solar heat and publication of material properties; development of new concepts of short and long term storage of solar heat to prototype stage with lab and field tests; development of models for simulation of chemical and sorption storage; simulation of three systems with long term chemical or sorption storage with the Task 32 boundary conditions; and support in the commercialisation of a chemical heat pump with short term thermal storage for solar heating and cooling applications. The main conclusion from the work is that there are a number of promising technologies and materials for seasonal storage of solar heat for single families but that a lot of research is required before it can be become practical and economical.

Keywords: Solar heating, thermal energy storage, sorption, chemical heat storage

1. Introduction

Task 32 of the International Energy Agency’s Solar Heating and Cooling Programme has studied advanced storage concepts for solar and low energy buildings over the period 2004-2007. The Task was split into four subtasks covering the following areas: evaluation and dissemination (A), chemical and sorption storage (B), Phase Change Materials (C) and advanced water storage (D). This paper describes the work performed in Subtask B on chemical and sorption storage, including results from basic research in terms of material and heat transfer characteristics, as well as store and system modelling.

Six groups have been active in this Subtask, as shown in Table 1 below, which also shows the type of technology that the groups have studied. EDF from France have also participated with work on chemical storage towards the end of the Task. The scope, in terms of general system aspects, for Subtask B was the same as that for the whole of Task 32, namely solar heating and cooling systems for residential buildings, principally detached houses for one up to a few families. Buildings with a larger specific heat load (>100 kWh/m^2 for Zurich climate) were not considered. The main focus was to be storage solutions sized to achieve a significant solar fraction. In terms of temperature, the storage solutions have been limited to temperatures < 250°C, with the emphasis on materials suitable up to around 150°C.

The scope in terms of storage concepts included chemical reactions and thermo-chemical storage, which was in practice restricted to sorption processes, both adsorption and absorption. Only one storage solution dealt with in Subtask B has become commercial within the time frame of Task 32, that developed by the Swedish company ClimateWell from Sweden, with over 35 stores/heat pumps having been sold, mostly for solar heating and cooling systems in Spain. A demonstration system of a closed adsorption store was made in the Modestore project, but the materials available for the field test were shown to be not suited for seasonal storage. Three other projects have got as far as design and testing of lab prototypes of sorption stores, and the sixth project was at the stage of material characterisation.

10 reports from the work on chemical and sorption storage are available from Task 32 website at www.iea-shc.org/task32, along with a number of reports on the work on phase change materials, advanced water stores and methods and intercomparisons.

Table 1. Research groups participating in IEA-SHC Task 32's work on sorption and chemical storage.

Group / Project	**Description**
ECN and Univ. Eindhoven, Holland. Compact chemical seasonal storage of solar heat.	Theoretical analysis of suitable chemical reactions in the range 60 - 250°C. Choice of most suitable material and experimental studies of material properties ($MgSO_4.7H_2O$). Simple modelling of the chemical heat store and system simulations with the Task 32 boundary conditions.
SERC, Högskolan Dalarna, Sweden. Evaluation of thermo-chemical accumulator (TCA).	Measurements on a prototype and commercial TCA chemical heat pump, based on a 3-phase closed absorption process, in the lab. Modelling of the process and of the prototype and commercial machines. System simulations for cooling in district heating and solar cooling systems for Swedish and Spanish conditions.
Institut für Solartechnik SPF, Switzerland. Sorption storage.	Solid closed system adsorption process with zeolite or silica gel. Studies of material properties and theoretical analysis. Measurements of heat and mass transfer dynamics.
AEE INTEC, Austria. Modestore (Modular high energy density heat storage).	Design of closed system adsorption heat store with silica gel with all components integrated into one unit. Testing in the lab and in the field. Modelling of the store, design of system and then simulation for full scale domestic seasonal storage for the Task 32 boundary conditions.
ITW, Univ. Stuttgart, Germany. Monosorp.	Initial study of open adsorption system using zeolite. Heat storage and removal from the store utilises the ventilation heat recovery system and moisture in the house. Measurements on prototype heat store in the lab. Modelling of the store and design of system. System simulations of seasonal storage for German conditions as well as the Task 32 boundary conditions.
EMPA, Switzerland. Closed NaOH absorption storage.	Development of closed two-phase absorption process with NaOH. Measurements on a prototype in the lab.

2. Main Results

2.1. Compact Chemical Seasonal Storage of Solar Heat (ECN and TU Eindhoven, Holland)

The main findings of the studies on storage through chemical reactions, as reported by ECN and TU Eindhoven, are the following:

• An extensive theoretical study at ECN [2, 3] indicated magnesium sulphate heptahydrate as potential interesting storage material using the following reversible reaction: $MgSO_4.7H_2O(s)$ + heat ⇔ $MgSO_4(s) + 7H_2O(g)$. The theoretical storage density of the material is 11 times that of water [4].

• Initial characterization experiments reveal that the dehydration of $MgSO_4.7H_2O$ actually proceeds through three steps: first, $MgSO_4.6H_2O$ is formed after releasing one water molecule, in the second step 5.8 water molecules are released and finally $MgSO_4$ is formed in the third step. The second dehydration step is most interesting since it is able to store ~420 kWh/m3 energy (6 times that of water) [4, 5]

• After dehydration, $MgSO_4$ was able to take up water in a single step until $MgSO_4.6H_2O$ was formed. The vapour transport between the particles is the limiting factor for hydration of magnesium sulphate [4, 5]

• The cyclability of the material at hydration temperature of 20°C was very good, however, no water uptake was observed at 40°C, which may be caused by a lower water vapour pressure. Currently, experiments are performed to investigate this observation [4].

• System studies were carried out, indicating that a large increase in solar fraction can be obtained by adding a TCM storage to a solar system with sufficient collector area. Care should be taken to find materials with a good DH (not too low for heating, but also not too high for the solar array). The system performance turned out to be very sensitive to the value of DH. Correspondingly, the system yield was found to decrease significantly if flat-plate collectors were used instead of vacuum tube collectors. [6].

• It was found that the coupling of the TCM system to a water storage tank significantly reduces the power requirements on the TCM reactor [6]. The water tank can then supply the high-power loads, while the TCM tank can afterwards recharge the water tank at a lower power level. Simulations were carried out for the case in which the solar collector system gives priority to the charging of the water tank and uses any excess heat to charge the TCM tank. However, it is now very important that the solar array is large enough to be able to provide significant charging of the TCM tank. For the case of the 15 kWh/m2/a building in Zürich (total load 7.3 GJ for space heating and 10.9 GJ for domestic hot water), it was found that the collector array required to charge a 6.6 GJ TCM storage completely was about 20 m^2 vacuum tube if a TCM material with a DH of 66 kJ/mol of water was used; for higher DH the required collector area increases strongly.

2.2. Closed Three-Phase Absorption (SERC, Högskolan Dalarna, Sweden)

The main findings of the studies on the TCA technology [7], as reported by SERC, are the following:

• In comparison to storage in water, cold storage is more interesting that heat storage, as the available temperature range for water is much lower for cold than for heat. For the commercial machine the storage density for the store (that is also a heat pump) is roughly 5 times greater than that for water for cold whereas it is only 1.5 times greater for heat [4].

• The thermal storage of the TCA is sufficient for small scale solar cooling applications that do not have large night cooling loads. Otherwise additional storage is required. [8].

• The temperature lift for the prototype and commercial heat pump/stores is relatively low and limits the application range to systems with low temperature differences between cold/heat distribution system and the desired temperature of the conditioned space [8].

• LiCl, the salt used in all stores so far, is not suitable for seasonal storage due to its high cost (~3600 €/m^3) [4]. However, the storage density would be approximately 2.7 times that of water for seasonal storage of 1000 kWh.

• A TRNSYS model of process and the controller for commercial machine have been developed [9] and are available from the authors.

• The problems with unwanted crystallisation and non-condensable gases in the storage have been solved and the store has been redesigned for rational production resulting in a reliable process. The technology has been commercialised under the product name ClimateWell 10. The heat pump/store is sold mainly for solar heating and cooling applications in Mediterranean countries.

2.3. Solid Closed Adsorption Storage (Institut für Solartechnik SPF, Switzerland)

The main findings of the studies on closed adsorption storage, as reported by SPF in Switzerland, are the following:

• The geometrical parameters and the dynamical behaviour of the closed sorption system are strongly related. The available temperature depends on the pressure of the sorbate and the driving force is limited by the external temperature ranges - the low temperature energy source - the mid temperature source/sink and – the high temperature energy source, which is aimed to be a solar collector.

• The measured temperature behaviour as a function of time in the sorbent module and in the sorbate (water) tank is indicating an optimum cycle time in the range 3 to 8 min. The determined power output shows a higher system performance for cooling than for heating because of a higher heat transfer in the evaporation of the sorbate. Regarding the short cycle time and the higher power output for cooling, the adsorption process is more suitable for cooling application of a thermally driven heat pump. At this development level a scaling up to long term storage is doubtful.

• A further understanding of the sorption system will be needed for a maximum power design because it will be determined by the geometric dimension of the system i.e. particle distribution of the sorbent fixed bed in a defined solid sorbent – liquid sorbate material combination.

• In a comparison of the solid adsorption and a the liquid absorption processes the liquid system could be favoured for storage application – exactly because the fluid can be pumped from one storage tank through a reaction zone to an other storage tank.

• Thermal energy storage in a sorption storage system is depending on the available thermal energy sources and sinks. So, the selection of the sorbent – sorbate material combination has to be done under these general conditions, beside of others. With the idea of the reduction of moving parts i.e. pumps in a solid sorption system the power limiting low heat transfer coefficients are leading to a layer structure in the sorption module. But a layer structure applied to a heat exchanger will limit the energy output of the system.

2.4. Modestore (AEE INTEC, Austria)

The main findings of the studies on closed adsorption storage, as reported by AEE INTEC in Austria, are the following:

• A sorption heat store with the material pair silica gel and water was developed, the system was scaled up for use in a single-family house and a first pilot plant was built.

• In this project, it could be shown for the first time that sorption technology for heat storage is technically feasible in a live test. The system concept, as well as the control strategy, have been proven to be functional under real operating conditions.

• The operation of the system was satisfactory and the system concept could be implemented in further systems. It has been shown that sorption storage with the used material combination is technically feasible. However, the temperature lift that can be achieved is only technically useful in a relatively small range of water contents. As long as the silica gel is very dry, the temperature lift is sufficient. But starting at a water content of approximately 13%, the temperature lift is not large enough to compensate for higher losses in heat exchangers, pipes and tanks. That means that the energy density of the material that can be used in a real application is much smaller than both the theoretical one and what has been measured under laboratory conditions. Therefore, a large quantity of material would be necessary which makes sense neither technically nor economically.

- The used material has been chosen because it is manufactured in mass production and therefore inexpensive. Up to now, there are very few research institutes that develop sorption material specifically for heat storage. In most cases, the focus is on heat pumps, cooling machines or gas separation and drying processes. Singular projects have shown that the development of sorption materials for heat storage is technically feasible. So far, these materials have been expensive or for example corrosive.
- A TRNSYS model for the sorption store including the evaporator/condenser heat exchanger has been developed and a TRNSYS deck has been set up for the Task 32 reference conditions.
- For the simulations reported in report B6, a different sorption material has been used to show the possibilities of the store/system concept. The system concept was similar to the one used in the field test system which was using the sorption store only for space heating and not for domestic hot water preparation. This was done because of the low temperature lift of the material pair silica gel / water. The temperature lift of the material chosen for the simulations is much higher. Therefore, domestic hot water preparation would be feasible. But in the simulations, the solar fraction was limited to a value below 100% even for very large storage volumes because of the mentioned system design.

2.5. Monosorp (ITW, Univ. Stuttgart, Germany)

The main findings of the studies on open adsorption storage designed for seasonal storage of solar heat, as reported by ITW in Germany, are the following:

- An effective sorption storage integrated in a conventional mechanical ventilation system has been developed in the Institute of Thermodynamics and Thermal Engineering (ITW), University of Stuttgart and was theoretical and experimental investigated
- For the first time, highly filled zeolite honeycomb structures made by extrusion of zeolite powder using thermoplastic polymers as plasticising aid and binder are used as adsorbent. Honeycomb structures have decisive advantages compared with fixed beds of spheres or other shaped bodies. They show excellent adsorption kinetics and generate low pressure losses along the process length. In open cycle processes low pressure drop is important to minimise the electric power consumption of the fans.
- Theoretical analysis has been carried out. Special attention has been given to precisely incorporate the appropriate physical and chemical processes that occur during adsorption and desorption, into the theoretical model; this will then reflect the proper performance of the proposed sorption system under real practical conditions.
- Simulation of the space heating for a residential building based on sorption storage was carried out using TRNSYS. The sorption process was evaluated using a 1-D two-phase model with heat- and mass-balance in a separate numerical routine.
- A prototype sorption storage tank integrated into a commercially available residential heating system has been built at ITW. The system has been scaled to achieve short cycles on a weekly basis, so that the system could be tested under varying conditions.
- Theoretical analysis shows that, compared to the adsorption period, the desorption process is more sensitive to several input parameters.
- Experiments have been carried out that demonstrate the technical feasibility of the proposed system under real operating condition. The experimental results concerning the thermal behaviour of the adsorption/desorption process and the achieved heat storage capacity are in good agreement with the theoretical analyses. Furthermore it has been shown that the solar thermal desorption

under transient conditions using high performance CPC collectors performs well. Special attention was given to achieve the necessary high desorption temperature of 180°C inside the sorption store.

2.6. Two-Phase Closed Absorption Storage (EMPA, Switzerland)

The main findings of the studies on closed adsorption storage, as reported by EMPA in Switzerland, are the following:

- The heat capacity of the NaOH storage (2 stages) compared to a water storage is about 3 times better for domestic hot water (DHW) and about 6 times better for heating purposes (heating floor). The calculations are made for a building located in central Europe.
- The heat capacity of a one stage (one process unit per storage) system especially for DHW is insufficient. The above specified heat capacity is only given with a second stage.
- The storage is intended to be charged with solar energy with no auxiliary heater. To avoid too big storage volumes, the buildings must be built in low energy standard like "Passive House" or "Minergie" (Swiss standard).
- NaOH – lye as sorbent has a good cost benefit ratio. NaOH is a by-product of the PVC production and costs only about 250€/m³. The estimated volume of NaOH – lye for a passive house is about 5 m³. This figure depends strongly on the climate and the used solar collector area.
- The separation of the process units and the tanks into independent modules, leads to a simple control strategy. In the process unit, there are only small amounts of mass of the chemical process involved. This allows continuous operation.

3. Intercomparison of Storage Technology

The storage concepts have been compared in a number of different aspects including storage density, cost for materials, temperature requirements as well as system simulation results (for three of the concepts) with the same boundary conditions [11]. Data from lab testing of prototypes [4] and estimations of storage size for 70 and 1000 kWh storage capacity showed the following:

- The storage density for cold (based on total system volume), when compared to water, is more favourable than for heat. For the ClimateWell 10 commercial heat pump/store, the storage density for cold is 4.7 that of water whereas for heat it is only 1.2 times greater. This is due to the fact that the temperature range available for water storage for cold is smaller (~10°C) than for heat (~60°C).
- For short term heat storage, the best technologies have an energy density 2 – 2.5 times that of water. This is relatively low due to the space required for reactors and condenser/evaporator in addition to the store. In addition all of the storage systems have irreversibilities in the processes themselves during charge and discharge resulting in lower store efficiencies.
- For longer term storage (1000 kWh) the energy density for the TCA technology and NaOH storage systems is nearly three times that of water, for Monosorp twice and for $MgSO_4.7H_2O$ 2.5. In addition, once the sensible heat from the solution has been lost (or at best recovered), the energy can be stored indefinitely, a significant advantage compared to water.
- In terms of material cost, all materials are expensive compared to water. However, NaOH, is significantly less expensive than the other materials reported: zeolite, LiCl, silica gel, $MgSO_4.7H_2O$ and zeolite 13X. The cost for the whole storage system has not been estimated here. For the ClimateWell 10, the projected cost is ~8000€ for a heat pump system consisting of two units in parallel, with a total heat storage capacity of 70 kWh.

The fractional energy savings (Fsav,th) of three systems, based on system simulations are shown in Fig.2. FSC´ [13] is a quantity that reflects the theoretical amount of energy a system with given boundary conditions can save, if it is 100% efficient from solar to heat delivery. It is dependent on the amount of radiation incident on the collector, and thus collector size, orientation and slope, and heat demand. It is also dependent on storage capacity. Systems with a large storage capacity compared to the load can have an FSC´ value larger than 1, while systems with small heat capacity have a maximum FSC´value of near 1. The curves show that the performance of the AEE Intec closed adsorption system and that of the ECN chemical storage system are fairly similar, if the storage size of the ECN system is similar to that of the AEE Intec system. A larger storage size gives improved savings. The ITW Monosorp open adsorption system achieves significantly greater savings compared to the others. This is partly due to the fact that the collector is slightly better, but also because the system uses a ventilation heat recovery system that is not in the other systems. This means that the Monosorp system in practice has a smaller space heating load than the other systems, which automatically results in greater savings without affecting the FSC´value.

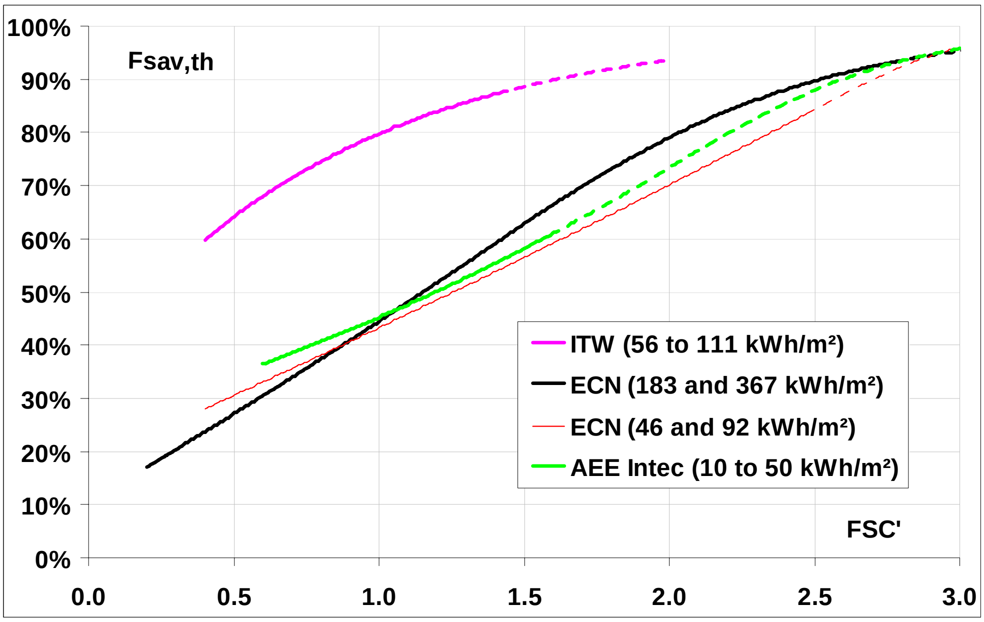

Fig. 2. FSC´ characteristic curves derived from simulations for three chemical and sorption systems [12].

It must be pointed out that these simulation results are for systems in different stages of development, using models with different degrees of detail. The curves are also trendlines for a number of points, with dotted sections being extrapolations.

4. Conclusions and Suggestions for Future Work

The work of Subtask B has shown that there are promising chemical and sorption storage solutions that should be further developed and tested at least in field trials. One concept has gone from prototype to commercialisation in the time period of Task 32, where short term storage for both heat and cold is utilised. The work has also shown that current materials are a limitation for the processes that have been studied, both for short and long term storage. Simulation models have been developed and used for system simulations. These show that high fractional energy savings are possible using seasonal storage for single family houses. Economics have not been considered.

The following areas are suggested for future work in the field:

• Research in materials for seasonal storage. This is required for closed three-phase absorption, open and closed adsorption as well as chemical reactions. The current materials are either too expensive, do not have the correct properties, or have not yet been shown to work in prototypes with realistic boundary conditions. Fundamental materials research is needed to get a better understanding of the physicochemical mechanisms.

• The numerical modelling of the heat and mass transfer processes in thermochemical materials is still very basic. Model improvement will result in new tools to better understand the dynamic behaviour of the materials processes and assist the material development in this field.

• For short term storage, research is required to find suitable materials and operational conditions that give a suitable temperature lift for cooling and heating together with sufficiently high energy density for storage. The cost of the material is not as important as for seasonal storage, but it is still an important factor.

• Studies on sources of low grade heat for heat pumping using closed processes. The sorption (and chemical reaction) processes studied in this Subtask, all use water. This needs to be evaporated before it is recombined with the active substance. This energy has to be either extremely low cost or free, and additionally has come from a heat source of at least ~5°C.

• The Monosorp concept is very promising and is suited for a full scale field test. However, at present their is no commercial method for extruding the zeolite monoliths required in the store.

• Seasonal stores are not charged once and then discharged. During autumn and spring there are periods with both charging and discharging. The store operates at different temperatures for these two states. More study is required to understand how best to recover the sensible heat during these changes in store temperature and whether it is best to segment the store so that only smaller portions undergo these changes.

References

[1] Hadorn, J.-C., ed. Thermal Energy Storage for Solar and Low Energy Buildings .- State of the Art. 2005, Lleida University: Lleida, Spain. ISBN: 84-8409-877-X.

[2] Visscher, K., Veldhuis, J.B.J., Oonk, H.A.J., Van Ekeren, P.J. and Blok, J.G. Compacte chemische seizoensopslag van zonnewarmte, 2004, ECN report C04074.

[3] Bales, C., et al. IEA-SHC Task 32 report: Project Report B2 of Subtask B: Thermal Properties of Materials for Thermo-chemical Storage of Solar Heat, IEA-SHC, Paris, France.www.iea-shc.org. 2005.

[4] Bales, C., et al. IEA-SHC Task 32 report: Project Report B4 of Subtask B: Laboratory Tests of Chemical Reactions and Prototypes Sorption Storage Units, IEA-SHC, Paris, France.www.iea-shc.org. 2008

[5] Herbert Zondag, Martijn van Essen, Zeming He, Roelof Schuitema, Wim van Helden, Characterization of $MgSO_4$ for thermochemical storage in Second International Renewable Energy Storage Conference (IRES II), 2007, Bonn, Germany.

[6] Zondag, H. IEA-SHC Task 32 report: Project Report B6.1 of Subtask B: Simulation report - System: ECN TCM model, IEA-SHC, Paris, France.www.iea-shc.org. 2008

[7] Bales, C. and S. Nordlander, TCA EVALUATION - Lab Measurements, Modelling and System Simulations. 2005, SERC, Högskolan Dalarna: Borlänge, Sweden. ISRN DU-SERC--91—SE. www.serc.se.

[8] Bales, C. Solar Cooling and Storage with the Thermo-Chemical Accumulator. in Eurosun 2006. 2006. Glasgow, UK.

[9] Bales, C., et al. IEA-SHC Task 32 report: Project Report B5 of Subtask B: Store Models for Chemical and Sorption Storage Units, IEA-SHC, Paris, France.www.iea-shc.org. 2008

[10] Bales, C., et al. IEA-SHC Task 32 report: Project Report B7 of Subtask B: Final report of Subtask B "Chemical and Sorption Storage" - The overview, IEA-SHC, Paris, France.www.iea-shc.org. 2008

[11] Heimrath, R. and M. Haller IEA-SHC Task 32 report: Project Report A2 of Subtask A: The Reference Heating System, the Template Solar System of Task 32, IEA-SHC, Paris, France.www.iea-shc.org. 2007

[12] Letz, T., et al. IEA-SHC Task 32 report: Project Report A3 of Subtask A: Performances of solar combisystems with advanced storage concepts, IEA-SHC, Paris, France.www.iea-shc.org. 2007

[13] Letz, T., et al. IEA-SHC Task 32 report: Project Report A1 of Subtask A: The extended FSC procedure for large storage capacity, IEA-SHC, Paris, France.www.iea-shc.org. 2007.