

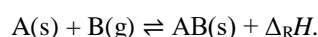
High temperature thermochemical heat transformation based on SrBr₂

Jana Stengler*, Torsten Ascher, Marc Linder

German Aerospace Center (DLR), Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

Abstract

Currently, state of the art working fluids of conventional heat pumps are limited to maximum output temperatures of 140 °C, and thus cannot fulfill the need for high temperature heat pumps in industrial applications. This is why thermochemical reaction systems have come into the focus of interest: they offer the potential of high temperature energy storage and heat transformation, e.g. by making use of the pressure dependency of a gas-solid reaction. These reactions can in general be described by the following equation:



Variation of the pressure of the gaseous reactant B results in a temperature shift of the exothermic reaction. In this way, the exothermic reaction (energy output) can be performed at higher temperatures than the endothermic reaction (energy input). In this contribution, the thermodynamic principle of thermally driven heat transformation and its main difference with respect to conventional or sorption based heat pumps is outlined.

The scope of this work is the potential of the SrBr₂-H₂O system as a possible candidate for thermochemical heat transformation. Constraints for a suitable reactor geometry and the possibility to combine thermal upgrade and thermal energy storage into one system are analyzed. Experimental results from a laboratory scale test reactor (~ 1,000 g) support the proof of concept of heat transformation in the region of 200 °C.

© 2017 Stichting HPC 2017.

Selection and/or peer-review under responsibility of the organizers of the 12th IEA Heat Pump Conference 2017.

Keywords: thermochemical energy storage; heat transformation; salt hydrates; chemical heat pump.

1. Introduction

In chemical process industries, waste heat often occurs in batch production cycles: e.g., if at the end of a batch reaction the end product needs to be cooled before it is discharged from the reactor. Oftentimes, before the start of the next batch run the reactants have to be preheated. In general, not only timely coincidence but also the temperature of the heat supply and heat demand plays a crucial role for the successful reintegration of waste heat. We therefore suggest a thermochemical storage system that allows for both thermal energy storage as well as for heat transformation, i.e. up-lifting of the output temperature during thermal discharging of the energy storage. By using a gas-solid reaction, output temperatures can be tailored perfectly to a specific storage

* Corresponding author. Tel.: +49-711-6862-8238; fax: +49-711-6862-632.

E-mail address: jana.stengler@dlr.de.

application. This presents two major advantages if compared to conventional heat pumps: firstly, thermal energy can temporarily be stored in the form of chemical potential, and, secondly, the range of operating temperatures is significantly higher.

Motivated by this broad range of applications, there is a significant body of research done in particular with respect to material selection. For example, Willers and Groll experimentally demonstrated the concept of heat transformation based on metal hydrides as working materials [1]. Another approach was discussed by Haije et al., who investigated sorption processes based on $\text{MgCl}_2/\text{LiCl}$ and ammonia for heat transformation driven by low temperature waste heat [2]. Trausel et al. focused on salt hydrates for the use of solar thermal energy storage, and reported properties of the most promising candidates for low temperature applications [3]. Amongst others, the decomposition of strontium bromide hexahydrate to its monohydrate was discussed in their study. Besides, the thermochemical reaction system $\text{SrBr}_2\text{-H}_2\text{O}$ was subject to experimental research done by Mauran et al. [4] and Marias et al. [5] for low pressures of water vapor and temperatures up to 80 °C. Both studies investigated the dehydration reaction of the hexahydrate and the rehydration of SrBr_2 monohydrate in a lab-scale reactor setup for the purpose of seasonal storage applications. In the context of waste heat recovery, Esaki and Kobayashi performed a study on the reaction kinetics of the hydration reaction of $\text{SrBr}_2\text{-H}_2\text{O}$ [6].

Nevertheless, the dehydration of $\text{SrBr}_2\text{-H}_2\text{O}$ to the anhydrous SrBr_2 , which takes place at higher water vapor pressures and thus at significantly higher temperatures, has not been discussed for thermochemical energy storage and heat transformation.

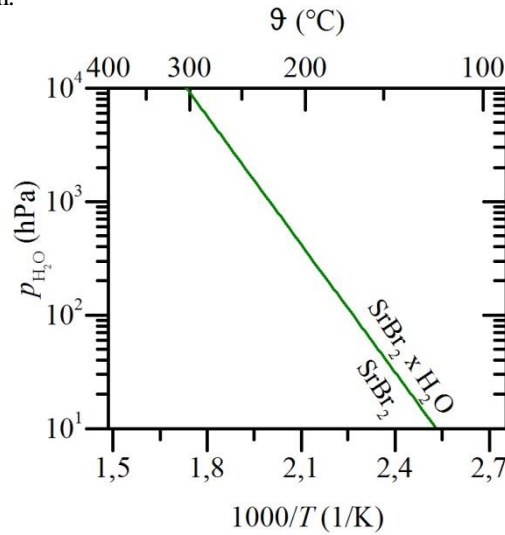
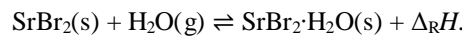


Fig. 1: Van't Hoff phase diagram for $\text{SrBr}_2\text{-H}_2\text{O}$, calculation based on $\Delta_R H = 71,98 \text{ kJ/mol}$ and $\Delta_R S = 143,93 \text{ J/mol} \cdot \text{K}$ [7]

Fig. 1 shows the phase diagram of the thermochemical reaction system $\text{SrBr}_2\text{-H}_2\text{O}$ in a van't Hoff plot. The line depicted in this graph indicates the reversible reaction of strontium bromide anhydrate with water vapor which results in the solid monohydrate form of the inorganic salt:



The phase equilibrium line is calculated from standard enthalpies and entropies of formation [7]. From this data, an operating temperature of roughly 125 °C – 300 °C is found for water vapor pressures of 10 hPa – 10⁴ hPa. It is known from other salt-water systems that under experimental conditions, thermal hysteresis between the dehydration and the hydration reaction can occur, e.g. in the $\text{Na}_2\text{S-H}_2\text{O}$ system as described by De Boer et al. [8]. This means that for a given vapor pressure, the dehydration reaction can only be conducted at a higher temperature than the hydration reaction at the very same pressure. A similar result was obtained in the $\text{CaCl}_2\text{-H}_2\text{O}$ system by Molenda et al. [9]. Taking these considerations into account, we expect similar effects to occur in the $\text{SrBr}_2\text{-H}_2\text{O}$ system. It is therefore necessary to experimentally determine the transition lines for both the hydration and the dehydration reaction, as the reaction thermodynamics dictate the temperature lift that is feasible via heat transformation. In the following, experiments with around 1 kg sample mass tested in a specifically designed reactor-setup are presented and a proof of principle experiment is described.

2. Experimental Setup

The monohydrate samples were pre-dehydrated from hexahydrate (strontium bromide hexahydrate, 99%, CAS 7789-53-9, particle size: 0.2 mm – 1.25 mm) to monohydrate in a furnace at 70 °C by slowly heating up from room temperature. Complete decomposition from hexahydrate to monohydrate was assured by measuring the mass loss. Afterwards, the prepared samples were stored at 110 °C.

The reactor setup consists of two pillow plates that are mounted flat back to flat back. This way, they form a 290 mm x 225 mm x 20 mm space that is filled with 1,050 g of $\text{SrBr}_2 \cdot \text{H}_2\text{O}$. A schematic drawing of the setup is presented in Fig. 2. Metal filters with a mesh size of 5 μm keep the packed bed in position and minimize undesired release of powder into the vapor supply pipework. Still, additional in-line filters are mounted in the tubes with a mesh size of 15 μm . The proposed reactor design offers several advantages regarding experimental handling and investigation of different process parameters:

- Easy access for temperature and pressure sensors
- Broad variation of process parameters: variation of vapor inlet/outlet
- Generic geometry that allows for model validation
- Minimization of heat losses from the packed bed to the ambience.

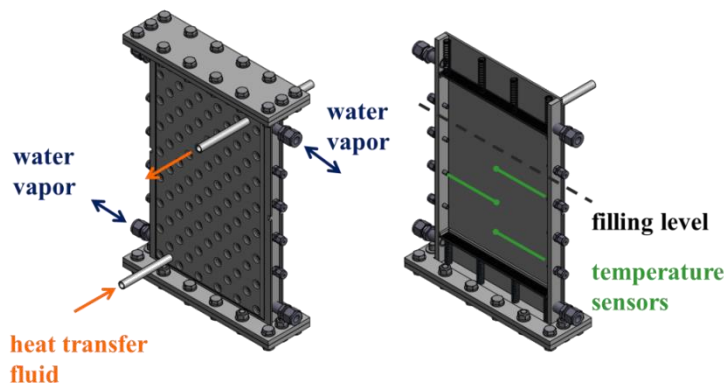


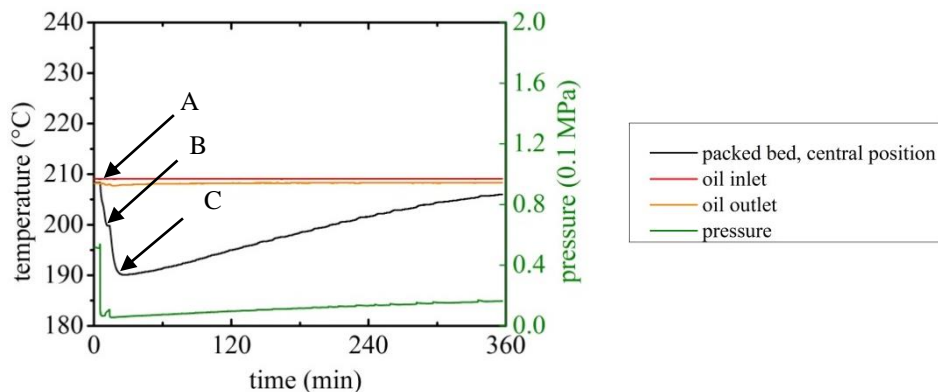
Fig. 2: Pillow plate reactor design

In the experiments presented, the reaction chamber is equipped with several resistance thermometers type Pt100 to monitor the temperature during dehydration (thermal charging) and hydration (thermal discharging) in a central, lower, and upper position within the packed bed. A pressure sensor is mounted in the tube that connects the reactor to a tube bundle heat exchanger which serves as condenser and evaporator. The setup is evacuated before the start of experiments. The setpoint temperature of the condenser/evaporator defines the vapor pressure that is depicted on the ordinate in Fig. 1. To ensure isothermal boundary conditions, the flow rate of heat transfer fluid (thermal oil) that tempers the pillow plates is set to 2 kg/min. Before the start of each run, the reactor is preheated until steady conditions are reached. Thermal charging and discharging is then induced by vapor pressure reduction or, respectively, by vapor supply at a higher pressure. In the presented series of experiments, there are two connecting pipelines between the pressurizer (evaporator/condenser) and the reaction chamber: one enters the reactor at the top, the other one is connected to the chamber below the porous bed. Both connections are opened almost simultaneously within a matter of seconds in order to realize a consistent supply of reaction gas. The same goes for disconnecting the pressurizer from the reactor at the end of an experiment. In ongoing work, the reaction gas supply is limited to either one connection in order to identify potential limitations of gas distribution within the packed bed.

3. Results

3.1. Thermal charging (dehydration)

Before the start of the dehydration reaction, the packed bed is heated to 210 °C. The oil temperature is kept at



a constant value throughout the experiment. By setting the condenser temperature to 34 °C, the vapor pressure is adjusted to 53 hPa. As soon as the condenser is connected to the reactor, the endothermic reaction starts. In Fig. 3, the temporal trend of the temperature at a central position within the porous bed as well as the oil's inlet and outlet temperature are shown. In addition, the pressure measured in the lower connecting vapor pipeline is depicted on the second axis.

Fig. 3: Dehydration experiment with 34 °C condensation temperature

When the reactor is connected to the condenser at the start of the experiment (A), the pressure drops to roughly 65 hPa and the salt temperature falls to 200 °C. Shortly after the start of the experiment (B), inert gas that emerged from the packed bed reactor is removed from the condenser with a vacuum pump. Otherwise, the inert gases would block the heat transfer area and thus decrease the condenser's performance. During the evacuation process which takes two minutes, the connecting pipelines to the reactor are temporarily closed.

As a result, the temperature in the packed bed stays at a constant value and the pressure in the reactor slightly increases within this short period of time, as water vapor continues to slowly escape from the dehydrating salt. When condensation is allowed to continue by re-opening the connecting pipe, the temperature reaches a minimum value of 190 °C (C). We assume that this temperature represents a kind of equilibrium of the dehydration reaction of $\text{SrBr}_2 \cdot \text{H}_2\text{O}$ at a vapor pressure of 65 hPa: in this stage, the thermal energy that is transported to the reaction zone is equal to the thermal energy that is "consumed" by the endothermic reaction. Since the heat transfer through the bed is currently not optimized, this minimum temperature might be higher in case of advanced reactor concepts with improved power density. After reaching its minimum, the temperature starts to rise again as the dehydration reaction continues, and approaches the oil temperature when the endothermic reaction comes to an end. All in all, the thermal charging process takes more than six hours. During the experiment, the pressure constantly increases. We contribute that to air intake from the ambient.

3.2. Thermal discharging (rehydration)

For preparing the hydration experiment, the evaporator temperature is set to 90 °C. This corresponds to a vapor pressure of 700 hPa. Again, the packed bed is preheated to 210 °C, but this time, an exothermic reaction and hence a temperature lift within the salt bed is expected. The resulting pressure and temperature profiles are plotted in Fig. 4. When the vapor is supplied to the reactor chamber, the reaction immediately starts (A).

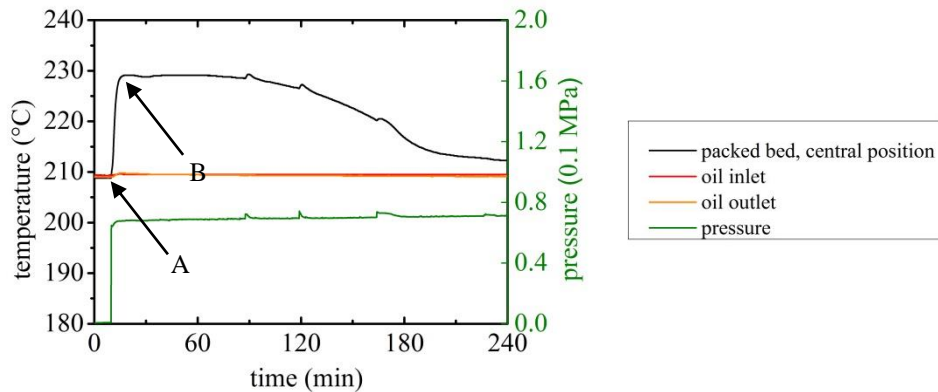


Fig. 4: Hydration experiment with 90 °C evaporation temperature

Within a couple of minutes, the temperature in the middle of the packed bed reaches a maximum of 229 °C (B). We assume this to be the equilibrium reaction temperature that corresponds to a vapor pressure of 714 hPa, which is recorded by the pressure sensor at that time. The temperature stays at a roughly constant temperature for one hour before it slowly converges towards the oil temperature when the reaction reaches full yield. In comparison to the charging run described above, thermal discharging consumes considerably less time. Since the temperature difference between the reaction temperature and the oil temperature is roughly the same, we contribute the slow dehydration reaction to non-condensable gases within the system. This would be in accordance to the different temperature evolutions within the bed. Whereas the hydration reaction temperature

remains at a constant value for roughly one hour, the dehydration temperature increases constantly. This aspect is currently further analyzed.

The most important conclusion of these finding is the following: charging and discharging of the thermochemical energy storage based on the $\text{SrBr}_2\text{-H}_2\text{O}$ system is possible without changing the inlet temperature of the heat transfer fluid. Both experiments are conducted with an oil inlet temperature of 210 °C. This is impossible e.g. for thermal energy storage based on a phase change material (PCM). In contrast to the reaction temperature of a thermochemical system, the melting point of a PCM cannot be altered. Vapor pressure variation is the driving force for the storage reaction temperature adaption of the thermochemical material (TCM). Concluded from the hydration experiment presented above, 90 °C waste heat from industrial processes could be used to upgrade process heat from 210 °C to roundabout 225 °C, given that the reactor concept is optimized regarding thermal power performance. This waste heat-driven process operates in a temperature range that exceeds the operating point of a conventional heat pump by far. Furthermore, thermochemical heat transformation does not require high-grade auxiliary power such as electrical energy.

3.3. Influence of the preheat temperature

A broad set of operating parameters was experimentally investigated. In the following, the impact of the temperature gradient between the heat transfer fluid and the reaction temperature during the exothermic hydration reaction will be discussed. Fig. 5 and Fig. 6 both show the discharge experiment with an evaporation temperature of 69 °C or a correspondent vapor pressure of 300 mbar, but with a different preheat temperature. The experiment depicted in Fig. 5 was conducted with an oil temperature of 170 °C, whereas the experiment presented in Fig. 6 was performed with 150 °C hot oil. Consequently, the temperature lift is significantly higher in Fig. 6. Still, the maximum temperatures show satisfying agreement, although a slightly higher equilibrium temperature is observed for the starting temperature of 150 °C.

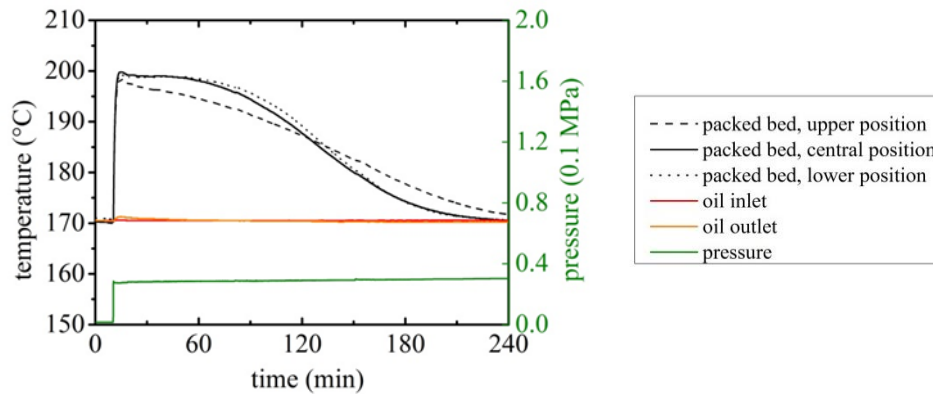


Fig. 5. Hydration experiment with 69 °C evaporation temperature and 170 °C oil temperature

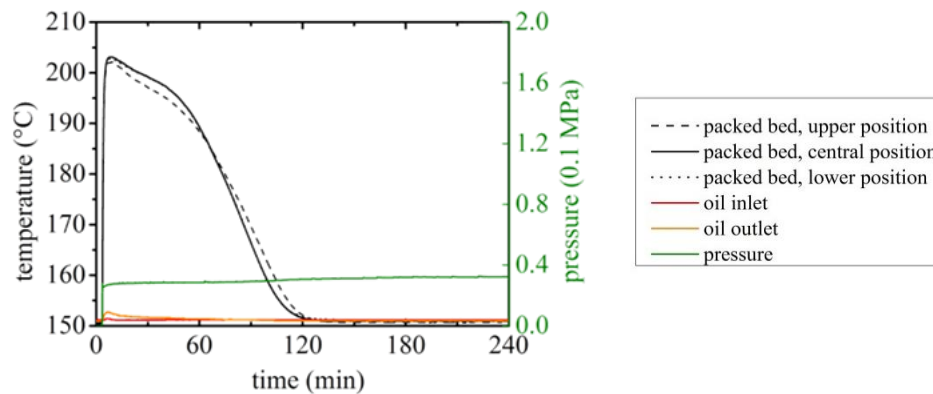


Fig. 6. Hydration experiment with 69 °C evaporation temperature and 150 °C oil temperature

In contrast, the temperature profiles over the course of the hydration experiment show a significant difference: Decreasing the starting temperature by 20 K allows completing the discharging process within half of the time that was needed before. We assume that this is caused by improved heat transfer from the solid bed to the oil due

to the larger temperature difference. Besides that, the increased distance to thermodynamic equilibrium conditions might additionally accelerate the reaction kinetics.

Furthermore, the graphs also show the temperature profiles at different locations within the reactive bed. In both experiments, the temperature sensors mounted in the lower part and in the central part of the powdery bed show almost perfect agreement. Even though the water vapor has to cover twice the distance to reach the inner core of the filling, no effect of mass transfer limitations is observed at a pressure level of 300 hPa. On the contrary, the temperature sensor mounted in the upper position records a delay in time and, furthermore, lower absolute temperatures. As the vapor transport distance is even shorter compared to the lower sensor position, we assume this deviation to be caused by macroscopic inhomogeneity in the upper part of the packed bed. After conducting 11 charging/discharging-cycles, we observed that the SrBr_2 particles agglomerate and form a fixed structure. These phenomena and the resulting change of the particle size distribution are subject of the ongoing work.

4. Conclusions

Both charging and discharging the $\text{SrBr}_2\text{-H}_2\text{O}$ based thermochemical system with a heat transfer fluid temperature of 210 °C was experimentally demonstrated. It is shown that the temperature within the packed bed decreases by 20 K during dehydration and increases by 20 K during hydration. To alter the reaction temperature, the vapor pressure was set to 700 hPa (~ 90 °C). This clearly outlines the potential for thermal energy storage without “temperature gradients” by means of thermochemical reactions. Moreover, by slightly increasing the reaction gas pressure, this technology has the potential for heat transformation with a temperature lift of more than 50 K in the temperature range of around 200 °C. Further work will include the reduction of the charging temperature, i.e. the temperature of the heat transfer fluid during the dehydration process to further increase the potential temperature lift. To achieve this, options for improving heat and mass transfer will be studied. Additionally, above mentioned open points will be addressed by combining simulation and experimental methods.

Acknowledgements

The authors gratefully acknowledge the financial support from the German “Bundesministerium für Wirtschaft und Energie” (BMWi, Federal Ministry for Economic Affairs and Energy).

References

- [1] Willers, E., Groll, M., 1999. Two-stage metal hydride heat transformer. *International Journal of Hydrogen Energy*, 24, p. 269–276.
- [2] Haije, W. G., Veldhuis, J. B. J., Smeding, S. F., Grisel, R. J. H., 2007. Solid/vapour sorption heat transformer: Design and performance. *Applied Thermal Engineering*, 27(8-9), p. 1371–1376.
- [3] Trausel, F., De Jong, A. J., Cuypers, R., 2014. A review on the properties of salt hydrates for thermochemical storage. *Energy Procedia*, 48, p. 447–452.
- [4] Mauran, S., Lahmidi, H., Goetz, V., 2008. Solar heating and cooling by a thermochemical process. First experiments of a prototype storing 60 kW h by a solid/gas reaction. *Solar Energy*, 82, p. 623–636.
- [5] Marias, F., Neveu, P., Tanguy, G., Papillon, P., 2014. Thermodynamic analysis and experimental study of solid/gas reactor operating in open mode. *Energy*, 66, p. 757–765.
- [6] Esaki, T., Kobayashi, N., 2016. Reaction Rate Characteristics of SrBr_2 Hydration System for Chemical Heat Pump Cooling Mode. *Journal of Materials Science and Chemical Engineering*, 4, p. 106–115.
- [7] Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., 1982. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. *Journal of Physical and Chemical Reference Data* 11, Supplement No. 2.
- [8] De Boer, R., Haije, W. G., Veldhuis, J. B. J., 2002. Determination of structural, thermodynamic and phase properties in the $\text{Na}_2\text{S-H}_2\text{O}$ system for application in a chemical heat pump. *Thermochimica Acta* 395, p. 3–19.

- [9] Molenda, M., Stengler, J., Linder, M., Woerner, A., 2013. Reversible hydration behavior of CaCl_2 at high H_2O partial pressures for thermochemical energy storage. *Thermochimica Acta* 560, p. 76–81.