

Characterisation of a Rotating Adsorber Designed for Thermochemical Heat Storage Processes

Gerald Englmaier¹, Bernhard Zettl¹ and Daniel Lager²

¹ Austria Solar Innovation Center (ASiC), Wels (Austria)

² Austrian Institute of Technology (AIT), Vienna (Austria)

Abstract

The presented experimental study shows the applicability of an open adsorption process with a moving material bed of zeolite grains for aims of room heating and hot water supply of domestic buildings. Based on the idea of continuous-flow adsorption a cylindrical reactor was designed. A prototype was built and integrated in a test rig to study the operation concept for domestic heating and hot water generation. Dehydrated zeolite of the types 4A and 13X were used in form of spherical grains and humidified room air was blown through the rotating bed. Zeolite batches of about 50 kg were able to generate an adsorption heat of up to 43 MJ and temperature shifts of the process air up to 36 K depending on the inlet air water content and the initial state of hydration of the storage materials. A first test series of promising composite materials for the storage process, based on natural zeolite and salt hydrates has been conducted. For the investigated material-reactor combination design-criteria for optimized reaction technology under realistic boundary conditions were found. The collected results of batch runs allow clear statements for further system development and simulation of seasonal heat storage applications.

Key-words: open-sorption process, adsorption, rotating reactor, zeolite, composite material, characterisation

1. Introduction

Sorption heat stores, which utilize the released adsorption heat during hydration of materials, have the potential to be realized as loss free seasonal heat storages to supply hot water and heating for households. Recent studies (like Mette et al., 2012) have examined the possibilities and restrictions of such storage concepts. From the design point of view, in contrast to closed sorption, open sorption has many benefits: free of complex components like condensers, evaporators and water storage reservoirs. Therefore maintenance of system pressure and the process control strategy are less complex (Yu et al, 2013).

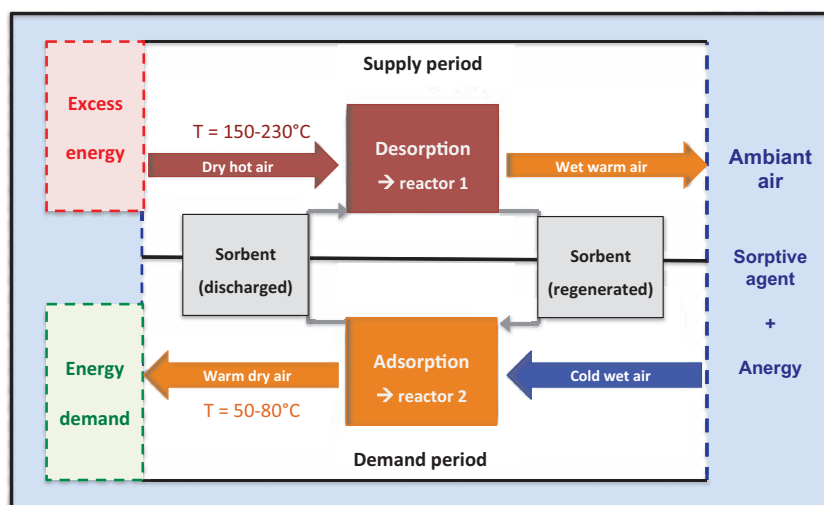


Fig. 1: Operation principle of an open sorption system for domestic applications

Open sorption systems can be potentially realized with modest system components. A process for domestic applications based on the idea of a compact adsorption unit and an external desorption reactor is shown in

Fig. 1. Material regeneration should rely on solar heat and electricity from renewable energy sources in periods of oversupply, therefore appropriate desorption concepts are required. Open adsorption reactors, either fixed or moving beds, are under development to enable continuous heat supply for low temperature applications. Salt-hydrates or mineral-salt composites are said to reach higher storage densities in principle (Posern, 2012). Material and reactor development is necessary to overcome limitations concerning reaction kinetics and material cycling reliability. Therefore a reactor for continuous-flow adsorption, based on a rotating drum containing a moving bed of granulated sorption material was developed. The concept of this adsorber and the effect of the variation of parameters like inlet humidity, air flow and material properties for adsorption has been investigated from Zettl et al., (2014) with commercially available molecular sieves in granular form.

Additionally, process engineering is needed to meet the requirements of defined applications. The characterization of innovative adsorption reactors is necessary to identify typical operation behaviors and to demonstrate advantages over other reactor concepts. The experimental evaluation of the adsorption concept is presented in this paper. The focus is on the adsorption behavior, considering aspects of heating and hot water generation for households.

2. State of technical development

2.1 Reactor design

The reactor was designed as a slowly rotating cylindrical drum to enable a steady mixing of the storage material in order to reach homogeneous temperatures and to avoid over-hydration of the storage material. It is filled with 70 liter of a granular storage material covering a volume fraction of about 80% of the interior. The air is guided through the air treatment unit and then into the storage material bed by passing a sieve, like illustrated in Fig. 2. Humidity is transferred into the storage material while thermal energy is dissipated.

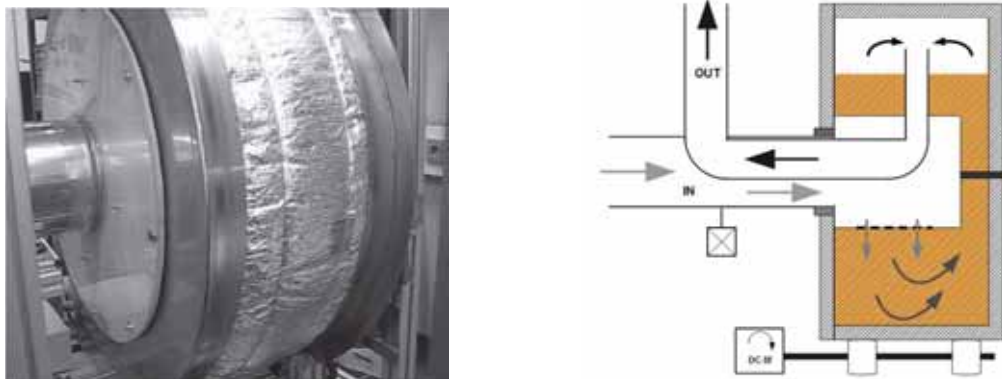


Fig. 2: left: adsorber construction, right: adsorber air flow (schematic)

After passing the material-bed, the air is leaving the reactor through the central pipe of the gas-feed-through transferring the thermal energy out of the reactor. An axial fan drives the airflow (80-160 m³/h). Potential advantages compared to other reactor concepts are: high specific thermal power, very good controllability, low pressure drop inside the reaction bed and high electrical instantaneous coefficient of performance (COP). Important characteristics for adsorption with zeolite 4A are (Zettl et al., 2014):

- Maximum thermal power 1500 W (per 50 kg of storage material)
- Sufficient temperature shift to supply room heating and hot water
- Humidity uptake efficiency is sufficiently high
- Storage capacity compared to the theoretical potential (Fischer, 2009) is about 90 %
- The process can be characterized by using the temperature shift as function of water content of the zeolite and process air water content
- $COP_{el} > 10$ by taking into account the electrical power to drive the adsorption process

2.2 Characterisation of new composite materials

Additionally to the used zeolite products, three different composite materials based on natural zeolite and inorganic salts have been considered for application. Measurements to describe their water uptake and

calorimetric behavior in a thermo-gravimetric/differential-scanning-calorimetric (TG/DSC) measurement system were done. As substrate clinoptilolite was chosen as economic alternative to synthetic zeolite materials. The used impregnated salt mixtures are based on MgSO_4 , MgCl_2 and LiCl as shown in Tab. 1. The set mass fraction of inorganic salts in the composite is based on the work of Posern (2012), where different mass fractions of salts and substrate were already tested and evaluated. This study has shown that higher amounts of salts can cause amongst others a crustification of the surface, which could lead to lower water uptakes.

Type	Clinoptilolite wt. %	MgSO_4 wt. %	MgCl_2 wt. %	LiCl wt. %	H_2O capacity wt. %
Material 1	78	11	11	0	10.84
Material 2	85	7.5	7.5	0	10.03
Material 3	85	10.5	0	4.5	14.65
Clinoptilolite	100	0	0	0	6.5

Tab. 1: Examined materials and water uptake capacity in test conditions

To evaluate heat of condensation, sorption and hydration effects it is necessary to calibrate the sensitivity of the TG/DSC sensor. The calibration and the experiments were measured in a nitrogen atmosphere using Pt-Rh crucibles. A sapphire disc was used as reference standard to evaluate the sensor sensitivity. For humidification of the nitrogen atmosphere a humidity generator was used to enable isobar measurements. Each material was characterized in the first test series at partial water vapor pressure of 20 mbar. This number corresponds to a water vapor content of 13 g/kg dry nitrogen under atmospheric conditions.

The material was wetted in the TG/DSC system at an adsorption temperature of 35 °C until no significant change in mass occurs. Then, by drying with a dry nitrogen gas flow at a temperature of 193 °C the water uptake capacity was determined. Material 3 shows the highest capacity (14.65 wt.%) in the evaluated experiments, the detected consumed heat consumed for drying in the test facility was 487.8 kJ/kg. LiCl is very expensive in comparison to other inorganic salts, so for economical reasons the mass fraction should not be too high. It is necessary to think about how to optimize the amount of LiCl for future investigations.

3. Adsorption process setup

Design criteria for thermochemical adsorption processes based on continuous-flow adsorption rely on the implementation of sufficient humidity supply. This could in principle be realized by evaporation with energy sources from underground or solar thermal equipment operated at rather low temperatures all the year round. Beside active heat supply in an adsorption setup, passive measures have to be considered. The development of thermal power, the humidity uptake efficiency and therefore the adsorption efficiency during the adsorption process strongly depend on the operation conditions. To enable studying the parameters for domestic applications two representative operation modes have been defined and tested with an appropriate test rig in the laboratory. Based on ambient humidity available and temperatures necessary the inlet airstream enters the adsorber either via the room (Fig. 3), where additional water vapor sources are located, or it comes directly from ambience (Fig. 4).

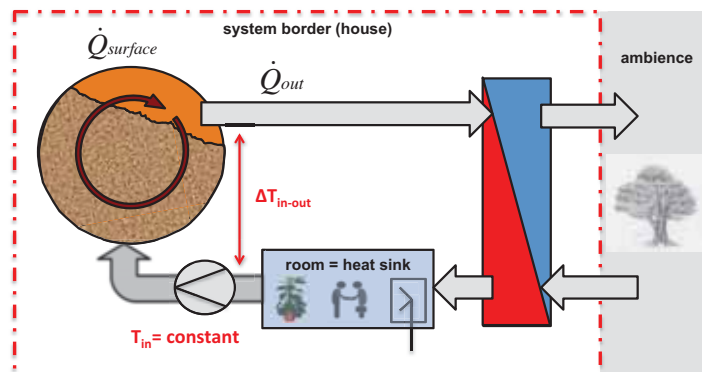


Fig. 3: Domestic heating operation mode (scheme A)

During wintertime the ambient air humidity is generally low and large variations are occurring depending on the weather situation. In energy efficient buildings the ambient air enters the room pre-heated via the heat exchanger of a ventilation system. Then the water vapor content rises due to sources like plants, bathrooms and occupants. To increase comfort, additional sprayers might be installed to realize at least 40 percent of relative humidity in houses. With a room temperature of 22 °C a water vapor content of 7 g per kg dry air is resulting. So the reactor inlet air is at constant temperature and rather stable humidity conditions. The resulting air temperature shift at the reactor is used for domestic heating. For example, the warm reactor outlet air can be used to preheat ambient air via a big sized heat exchanger. Then a rather dry and cool exhausted airstream is resulting, so the specific air enthalpy is close to ambient air. The driving heat flux for domestic heating ($\dot{Q}_{out}$) depends on the temperature shift between inlet and outlet airstream (ΔT_{in-out}). Assuming that the reactor is situated in a dwelling, also convective heat losses via the reactor surface ($\dot{Q}_{surface}$) contribute directly to heating. For the reactor prototype the convective heat losses were correlated to the laboratory room temperature.

For hot water generation outlet temperatures greater than 50 °C are necessary. On the one hand, high specific inlet air humidity (>12 g/kg) in combination with good sorption material properties are necessary to realise high temperature shifts. On the other hand, heat recovery from the outlet air stream to the inlet air stream is possible. Thus, moderate temperature shifts, resulting from lower specific air inlet humidity, can potentially lead to high material bed temperatures in the reactor and sufficient high air outlet temperatures are resulting. Based on this idea, a second process setup with a well-insulated reaction drum (see Fig. 4) is necessary.

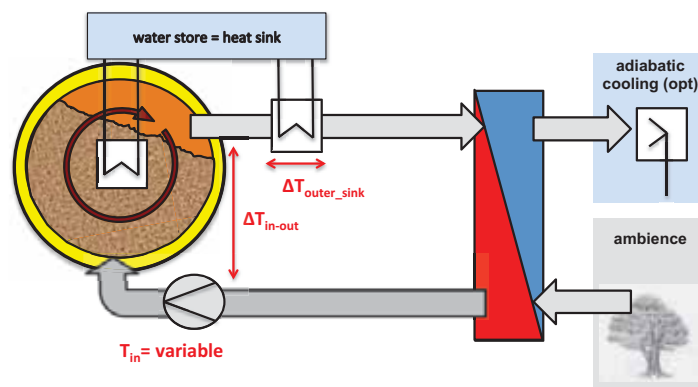


Fig. 4: Hot water operation mode (scheme B)

A stratified water store could be heated via a heat exchanger inside the reaction drum and/or in the outlet air pipework. A control system would be necessary to act on varying reactor temperatures during a full batch run. In contrast to operation scheme A, active heat recovery leads to variable reactor inlet temperatures and the temperature shift between inlet and outlet airstream is reduced by the inner heat sink and drops partially at the outer heat sink. During summertime the rather dry exhausted air could additionally be used for adiabatic cooling purposes. The laboratory scheme B was realized with an air-to-air heat exchanger, which represents both, a heat sink and heat recovery unit. To represent a heat exchanger inside a well-insulated reaction drum in a first approach, the convective heat losses via the reactor surface imply the second heat sink.

Batches of zeolite 4A and zeolite 13X in spheres with a diameter from 1.6 mm to 2.5 mm were used as sorption material. The dry bulk density is 730 kg/m³ for 4A, and 645 kg/m³ for 13 X. Batch masses over 50 kg, depending on the initial water content, were resulting. The amount of water was evaluated by weighing (0.03 kg max. absolute error) and comparing the material weight to that of very dry (1-2 % water after heating to 300 °C) or wetted material (containing max. 21-22 % water – according to producer information). Therefore all water content data can be given with a max. absolute error of 0.8 %. Dehydration of the material took place in a conventional drying oven at atmospheric pressure.

The reactor prototype is equipped with several sensors: temperature in/out (NTC-sensors), moisture content in/out (capacitive sensors), and air-out flow rate (impeller-anemometer). To measure the temperatures of the moving material bed and the rotating drum wall, wireless data-logging sensors (20 mm diameter) were used.

4. Experimental results

The demonstration of typical characteristics for the investigated material-reactor combination enables clear statements for system requirements. To illustrate the adsorption behavior for a wide range of material hydration states in Fig. 5 and Fig. 6, zeolite 4A and zeolite 13X was used in very dry state with an initial water content of 2.5 %. The development of specific air-outlet humidity and reactor temperatures using both operation modes (results for scheme B are presented in Fig. 7), have been investigated on batches of zeolite 4A with initial water contents of 6 %.

The humidity of the air is indicated as water vapor content or specific humidity (x), which is defined as the mass-ratio of water vapor to the mass ratio of dry air.

4.1 Domestic heating operation mode (scheme A)

All runs have been carried out with a constant flow rate of about 140 m³/h. The heat-up time results in dependence of the initial water content of the sorption material (sorbent), the water vapor content (sorptive agent) and the temperature of the inlet airstream. Fig. 5 gives an overview about the heat transfer mechanisms at the reactor. Heat from adsorption is set free in the material bed. The red dotted line represents the course of the adsorption heat transfer rate. In the first hour the material and the drum body are heated up via internal heat transfer (purple dotted line) until the maximum material bed temperature is reached. The peak of reactor heat transfer rate (black line, 1500 W after 1.2 hours) which results from the airstream and the drum surface heat transfer rate (orange dotted line) is damped and occurs some minutes after the reactor is fully heated up, then the drum surface heat transfer rate is at maximum. As we can see from Fig. 7 in steady state operation (both modes) the temperature difference between material temperature and outlet air decreases slowly.

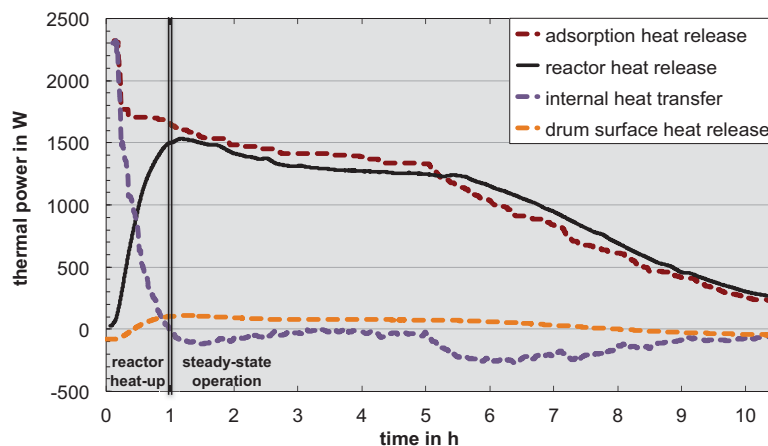


Fig. 5: Development of heat transfer and thermal power generated with a constant reactor inlet temperature (operation scheme A) for zeolite 4A

The behavior of reactor heat release in Fig. 5 (black line) and Fig. 6b (blue line) is indicated for the same batch of zeolite 4A. The specific adsorption heat (red dotted line in Fig. 6b) is very high at the beginning of the run. Thus, the fast initial rise of temperature is associated with a strong hygroscopic effect of the synthetic zeolite material, caused by adsorption in micropores. Therefore, for fast heat-up the sorbent should be at low initial water content. This enables high heating rates of the reactor body material and the storage material. The rather slow temperature decrease over several hours in steady state operation is connected to a slow decrease of differential heat release of the material.

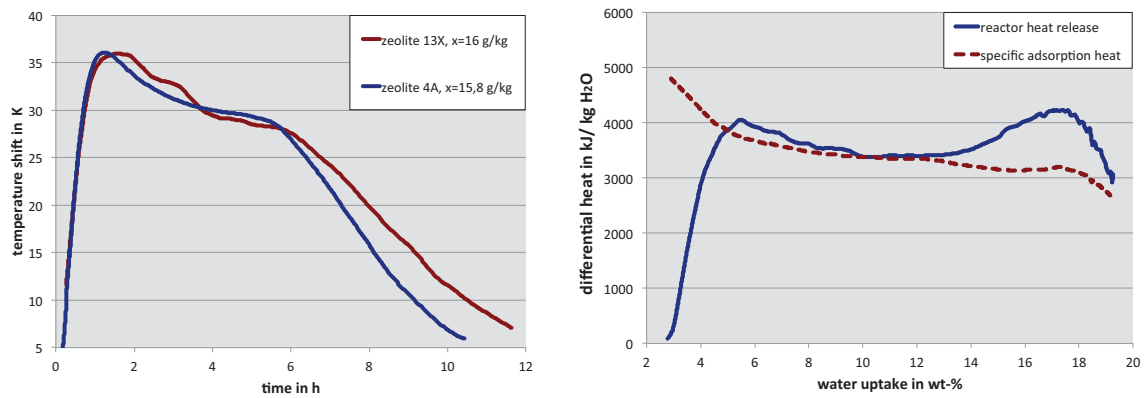


Fig. 6: (a) Temperature shift ΔT between air inlet and outlet (left side), (b) development of adsorption heat and reactor heat release for Zeolite 4A (right side)

The two lines in Fig. 6a represent zeolite 4A and 13X both in nearly dehydrated state at the beginning (initial water content 2.5 %) and exposed to relative high specific air humidity ($x_{in} = 16$ g/kg). Both materials reach comparable maximum temperature shifts of 36 K. The characteristic temperature plateaus between the second and sixth hour occurring imply a balance between adsorption heat and heat transfer from the reactor. Because the air is a heat transfer medium and contains the water vapor, a specific development for each inlet humidity value results, depending on the initial water content of the sorbent. Besides the reactor temperature, the heat storage capacity of the material is the most interesting value for storage applications. The total released heat during the whole batch run (10.5 hours) was calculated by integration of the thermal release rate over time. The test with zeolite 4A generated 38 MJ of thermal energy and 43 MJ were reached with 13X-zeolite. This means a specific enthalpy release of 740 kJ/kg for zeolite 4A and 870 kJ/kg for zeolite 13X, which has a lower material density. During the first phase the specific adsorption heat (Fig. 6b) can reach up to 6 MJ/kg-H₂O. After a certain amount of water was adsorbed (5.5 % - after one hour of operation time), the maximum material temperature was reached. It is worth mentioning that the differential heat generation (blue line) is increasing towards the end. The reason for this effect is the remarkable contribution (up to 300 W) of internal stored sensible heat to the heat transfer in the second half of the operation period.

4.2 Hot water operation mode (scheme B)

The comparison of the temperature measurement developments between the two operation modes (see chapter 3) has shown less difference between material temperature and air outlet temperature by using heat recovery (Fig. 7). During the last operation hours a high share of water vapor uptake takes place in the wider pores of the zeolite material. Therefore, the hygroscopic property of the sorbent decreases, this is associated with a drop of specific adsorption heat to about 3 MJ/kg-H₂O (Fig. 6b). This means that the outlet air water vapor content (blue dotted line) and therefore the humidity uptake efficiency of the material bed decreases with a constant slope over time. The slope is increasing referring to the state of hydration in the material.

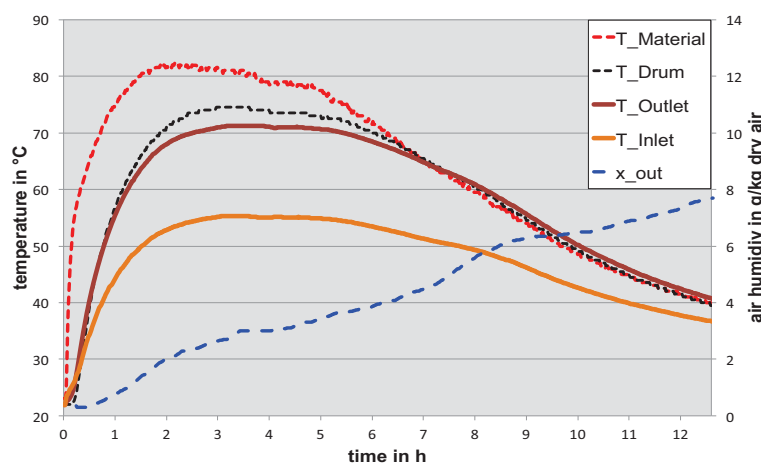


Figure 7: Development of Temperatures and outlet air humidity with variable inlet temperatures (operation scheme B)

During the batch run in Fig. 7 ($x_{in} = 9.5$ g/kg) the peak load reached 850 W at 3 hours of operation, when the outlet air temperature (brown line) and the drum temperature (black dotted line) reached their maximum. Heat was set free for more than 12 hours. The inlet temperature (orange line) rose up to 55 °C, while the ambient temperature was kept stable at 23 °C. Higher loads lead to a decrease of inlet air temperatures, and then all temperatures are shifted downwards. Heat-up could be realized faster by disconnecting the load at the beginning of the run. Starting from the sixth hour the temperatures of the material bed (red dotted line), the drum and the outlet air are close together. Because there is also a heat transfer between material and the wireless data logging sensors, the surface temperature of the material grains is assumed to be slightly higher as the measured material temperature, especially during the cooling-down of the reactor.

5. Discussion

The high specific heat transfer rates resulting from water vapor adsorption in zeolites enable heat supply for domestic applications with a compact rotating adsorber unit. Measurements have shown that heating and hot water generation can be realized with an appropriate operation set-up. While temperatures for heating of energy efficient buildings could be achieved with a setup regarding to operation scheme A hot water generation requires additional measures like active humidification (see Zettl et al., 2014) or heat-up of the adsorber inlet airstream by means of operation scheme B. The material bed temperature and therefore the reactor outlet air temperature could be raised significantly by heat recovery from outlet airstream to inlet airstream.

If reaction kinetics of novel materials like salt impregnated zeolites can compete with commercially available molecular sieves in a rotating adsorber, then thermochemical adsorption processes can enable domestic applications. The retarded adsorption behavior of thermochemical material could be eventually compensated by heat recovery from a batch based continuous flow adsorption to reach sufficient reactor temperature. This has to be proofed in test runs with the experimental setup presented in this paper. On the contrary a decline in water vapor uptake rate, apart from the development of differential heat release in sorbents, which is connected to state of material hydration, means always a decrease of the reactor heat release rate. Then the energy efficiency ratio of heat released and electricity needed for the adsorption process with heat recovery is lower, because pressure losses and therefore energy consumption of a fan, caused by the airflow through the material bulk, will remain constant in the continuous flow reaction.

For practical reasons several operation modes should be combined, regarding the development of heat transfer during a batch run. In general, fast reactor heat-up can be achieved by heat recovery from the outlet airstream, while high reactor heat release rates are resulting from high inlet humidity and the direct use of the power from the outlet air. At the end of a batch run the reactor is cooling down because of low differential heat release from adsorption. Then the outlet air temperature should be close to the material temperature by the support of heat recovery. The utilization of adsorption heat at lower material temperature, during advanced hydration of the sorbent, is necessary to achieve high specific energy storage potential of the sorbents over the whole sorption cycle. Therefore an appropriate controller is a clear system requirement for a hybrid domestic system for heating and hot water generation.

The theoretical values for adsorption enthalpies of several zeolite materials in dependence of the adsorption temperature have been evaluated by caloric measurements (Fischer, 2009). Although the peak adsorption temperature in a rotating reactor can differ from operation mode to operation mode, the adsorption enthalpy achieved with batch runs of the same initial conditions did not change significantly when the material bed was cooled down to a comparable end temperature. This means most of the sensitive heat stored in the reactor was set free.

6. Acknowledgement

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7. References

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