Experimental setup for determining ammonia-salt adsorption and desorption behaviour under typical heat pump conditions: a description of the setup and experimental results

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EXPERIMENTAL SETUP FOR DETERMINING AMMONIA-SALT ADSORPTION AND DESORPTION BEHAVIOR UNDER TYPICAL HEAT PUMP CONDITIONS: A DESCRIPTION OF THE SETUP AND EXPERIMENTAL RESULTS

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ABSTRACT

Heat-driven heat pumps based on the principle of chemisorption have been researched worldwide. Such research typically focuses either on fundamental materials properties such as sorption isotherms, thermal conductivity and heat of sorption, or on the development and performance of complete systems. Also at ECN the research shows this typical pattern with publications on the fundamental thermodynamic properties on ammonia reactions of lithium chloride and magnesium chloride (Bevers et al., 2006; Bevers et al., 2007) together with results on complete systems (Haije et al., 2007; van der Pal et al., 2009). However, when trying to connect the material properties to the system's performance, for example by using model calculations, various uncertainties on heat exchanger/sorption reactor level remain. These uncertainties, such as reaction kinetics, heat and mass transfer limitations for given specific geometries and conditions but also effects due to repeated sorption, pose a considerable problem for further development, improvement and scaling up of the system.

In order to get a better understanding of the performance of the sorption reactor/heat exchanger design and sorbent bed loading, an experimental setup has been developed. This setup allows measuring the performance of various ammonia-sorbent reactions with various sorption reactor/heat exchanger designs under well-controlled and well-monitored process conditions similar to the heat pump conditions. This setup measures the ammonia uptake and release under well-controlled conditions with temperatures that can be varied from ambient temperature up to 200°C and ammonia pressures that can be varied between 0.02 to 2 MPa. These conditions can be set independently and repeated at regular time-intervals. Besides mass-flow meters, pressure and temperature sensors, the setup also contains an endoscope to observe the macroscopic structural changes in the material during uptake and release of ammonia. After initial testing, the setup is now ready for the first experiments on different heat exchanger designs and sorbent materials. The paper includes a description of the setup and the first experimental results.

1. INTRODUCTION

In The Netherlands more than 100 PJ of heat in the refining and chemical industry is actively disposed of (see *Figure 1*). More than 20 PJ of this heat has a temperature of more than 100°C and can be used in a heat-driven heat pump to upgrade this industrial waste-heat to useful process heat, thereby reducing the industrial primary energy demand.

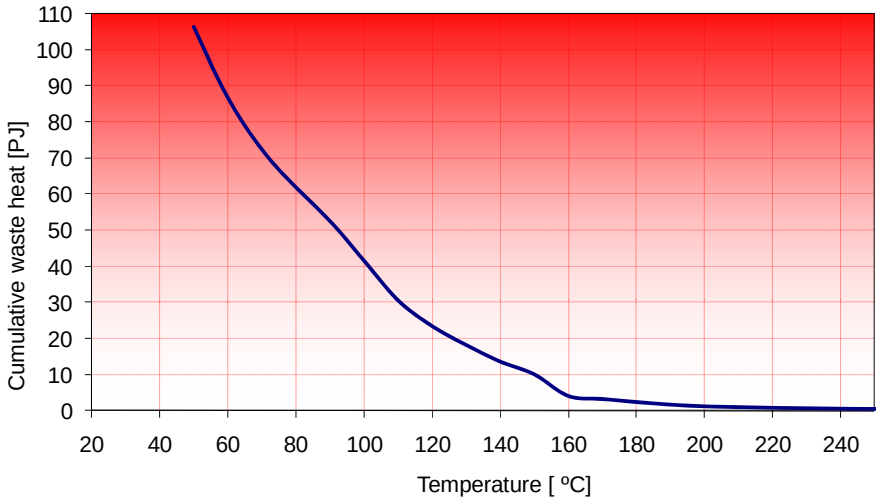

Figure 1. Cumulative waste heat in the refining and chemical industry in the Netherlands. (Spoelstra et al., 2002).

After a review of potential heat pump technologies, a heat pump based on chemisorption of ammonia on salts was selected for further development at ECN. Industrial waste heat with a temperature between 100°C to 150°C can be upgraded to 180°C to 220°C to create medium-pressure steam. The sorption cycle is shown schematically in *Figure 2* with the colored arrows showing the heat flows into (at middle temperature) and out (at ambient and high temperature) of the system. It uses a low temperature and a high temperature sorbent. During the charge phase, the waste heat is used to desorb the sorbate from the high temperature onto the low temperature sorbent. This is achieved by cooling the low temperature sorbent to ambient temperature. During the discharge phase the low temperature sorbent is heated to waste heat temperature. The resulting increase in pressure causes the sorbate to be adsorbed by the high temperature sorbent. This results in an increase of temperature and the high temperature heat can be harvested. After literature searches and testing various sorbents, the following pair of sorption-reactions was found to meet the criteria on sufficient temperature lift, energy density and energy efficiency, best:

$$LiCl \cdot 1NH_3 + 2NH_3 \leftrightarrow LiCl \cdot 3NH_3 + \text{heat}$$
$$MgCl_2 \cdot 2NH_3 + 4\,NH_3 \leftrightarrow MgCl_2 \cdot 6NH_3 + \text{heat}$$

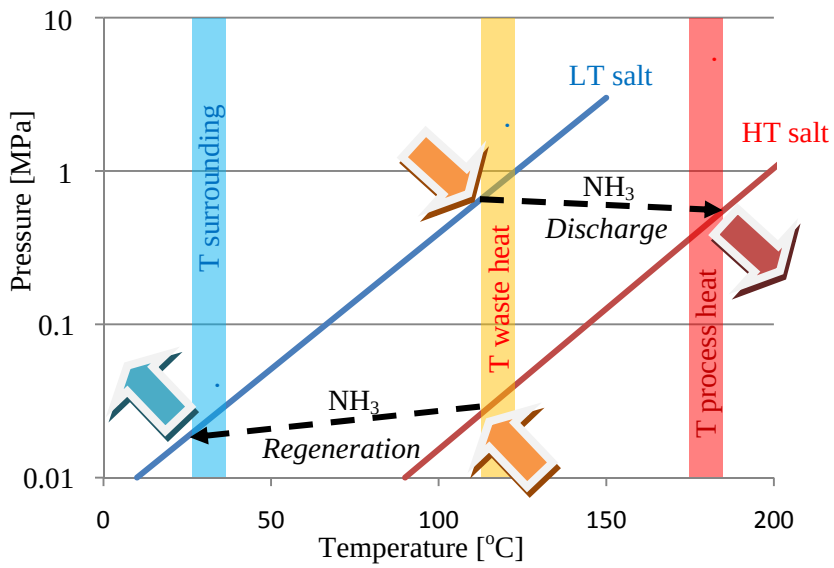

Figure 2. Schematic diagram of a heat-driven heat pump type II for upgrading (industrial) heat to a higher temperature. The blue and red line show the sorption line of respectively low and high temperature sorbent. The colored arrows show heat flows into (at middle temperature) and out (at ambient and high temperature) of the system.

Using these salts, in 2001 a first prototype heat pump was build. It comprised of two reactors, one with the low temperature salt (LiCl) and one reactor containing the high temperature salt ($MgCl_2$). The salts were as solids deposited in a finned-tube heat exchanger as shown in *Figure 3*. Repeated measurements showed decreased activity and soon the system completely failed to transfer any ammonia between the reactors. In 2005, a second prototype heat pump was designed and constructed. A tube-fin heat exchanger was used where the heat exchanging fluids can flow through the hollow fins. The system performed better but had mass transfer related problems.

After thorough testing of the materials (Bevers et al., 2007; van der Pal and Veldhuis, 2010), the third prototype system was constructed. This prototype used a tube-fin heat exchanger with aluminum foam glued on top of the fins in order to keep the sorbents accessible for the ammonia, the (liquid) lithium chloride in place and the heat easily transferred into/out of the reactor (van der Pal et al., 2009).

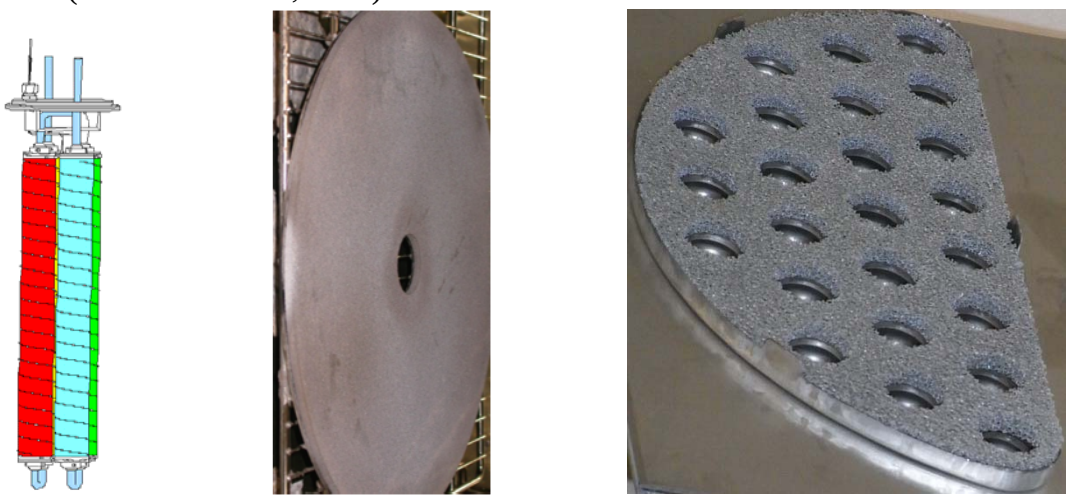

Figure 3. Left: first prototype heat exchanger, a finned tube, middle: second prototype heat exchanger, brazed nickel foam on heat exchanging plate, right: third prototype t heat exchanger, aluminum foam on a fin with tubes with thermal oil to remove/provide heat.

Despite all efforts made in testing cups of aluminum foam, testing the sorbents on a HP-DSC, a Rubotherm magnetic balance, TG-DTA, autoclave and pressure-cells, also this prototype did not yield the expected efficiencies or required power densities. During the analysis of the data, it became apparent that from the prototype-system our questions regarding the causes of the limited performance of this (and previous) prototypes. Seemingly straightforward questions, such as “which of the sorbents was the reaction-rate limiting factor?” and “was the reaction rate limited by heat-transfer or mass-transfer?” could not be answered using the data we collected from this prototype. In order to improve and optimize the system’s design, such basic questions had to be answered.
Therefore the objective of the current research was, prior to building a new prototype system, to gain insight in the limitations and effects related to heat and mass transfer under realistic heat pump conditions for each of the ammonia complexes. The heat transfer was measured on aggregate materials using a Hotdisk transient plane thermal conductivity meter and analyzed using COMSOL software. To determine the effect of the combined heat and mass transfer limitations, a new setup was built which is presented and discussed in this paper.

2. MATERIALS AND METHODS

Experimental Setup

Figure 4 shows a schematic flow diagram of the mass transfer setup. At the heart of this setup is “mini-reactor 1”. In this reactor vessel a small-scale heat exchanger can be placed with a height and diameter of respectively 200 and 60 mm. An endoscope is placed in the reactor to observe the macroscopic structural changes in the material during the sorption reactions, such a swelling, melting and shrinking. *Figure 5* shows a picture and cross-section of the reactor vessel (left) and pictures of the heat exchanger from the endoscope and outside the reactor (right). The heat exchanger is connected to the system using a Swagelok connector and therefore it can easily be removed and/or replaced.
Two Julabo HT-60 thermo-static baths are used to operate the heat exchanger at two different temperature levels, similar to the cyclic heat pump conditions. The temperature of the heat exchanger is monitored using two temperature sensors that are placed on the heat exchanger as well as two temperature sensors that measure the temperature of the thermal oil entering and leaving the heat exchanger. Heat losses from the reactor vessel are reduced by using trace-heating and insulation of the wall. This also prevents condensation of ammonia. The temperatures were measured using Rössel type K thermocouples. The pressure in the reactor vessel is controlled by three Brooks pressure-controllers (PC), one allowing a flow of ammonia into the reactor (adsorption) and two for the flow of ammonia out of the reactor vessel (desorption). Depending on the cycle of the measurement, only one of the three pressure-controllers is active. The set pressure can be varied between 0.02 and 2 MPa and is measured with an accuracy of 0.5% full scale. The subsequent ammonia flows into and out of the reactor are measured using three Brooks mass flow meters (MFM). An orifice is placed to avoid the flow exceeding the measurement range of the flow meters. The maximum mass flow is 250 mg NH_3 per second and is measured with an accuracy of 0.7% of rate and 0.2% of full scale.

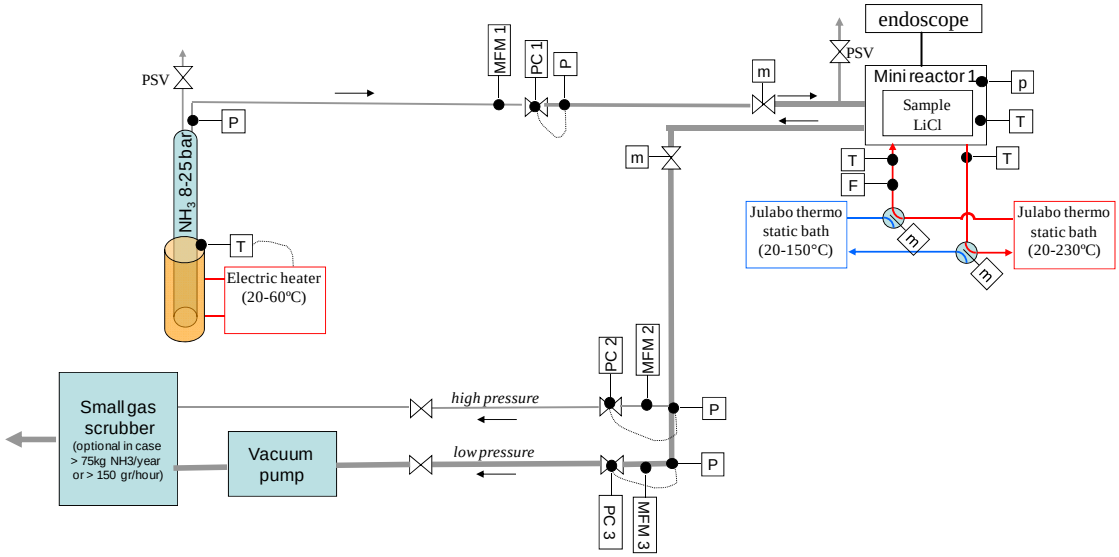

Figure 4. Schematic flow diagram of the mass transfer setup. Ammonia is supplied from a (heated) bottle shown on the left of the diagram. The heat exchanger containing the sorbent is placed in the reactor marked with "Mini reactor 1".

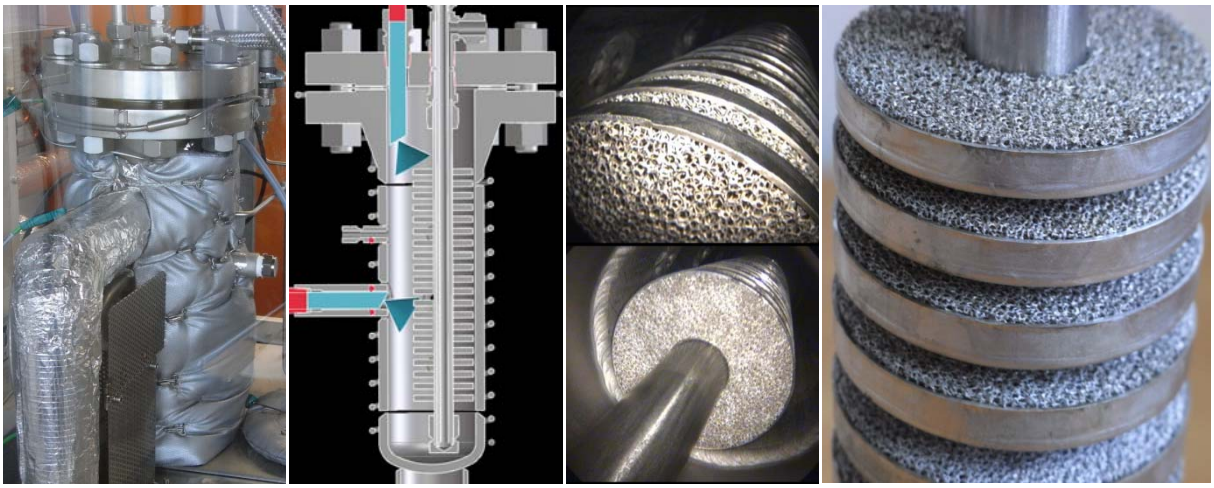

Figure 5. Left: A picture and a schematic cross-section of the reactor vessel (blue arrows show endoscope positions). Right: The inside view of the reactor vessel with heat exchanger from the endoscope and a picture of the heat exchanger outside of the reactor.

Measurement

Using the pressure controllers and the thermo-static baths the conditions similar to heat pump conditions can be created. Because the setup is still under development, only a limited number of measurements have been conducted so far. The measurement presented in this paper was conducted on the heat exchanger filled with lithium chloride as shown in *Figure 5*. Because previous measurements on the high pressure DSC showed that repeated cycling between LiCl(1-3)NH3 increases the amount of sorbent reacting with ammonia (van der Pal and Veldhuis, 2010), the lithium chloride was repeatedly (10+ cycles) exposed to high (and low) pressures of ammonia to repeatedly form $LiCl{\cdot}3NH_3$.

The conditions at the start of the measurement shown here, 0.02 MPa NH_3 and 50°C, are such that $LiCl{\cdot}1NH_3$ is present. During the measurement, the temperature of the oil entering the inner tube of the heat exchanger was kept at 50°C whilst increasing the ammonia pressure on the outside of the heat exchanger was set to 0.54 MPa. The mass flow of ammonia entering

the reactor as well as the temperature of the salt and the oil in/out of the heat exchanger were measured together with the pressure in the reactor. From these parameters some first calculations could be made.

Mass balance

By integrating the mass flow in time, the total amount of ammonia in the reactor has been calculated. Using the measured gas temperature, free gas volume in the reactor and the gas pressure, the amount of ammonia in the gas phase is calculated. The difference between the total amount of ammonia in the reactor and the amount in the gas phase yields the amount of ammonia adsorbed to the sorbent.

$$m_{total}(t) = \int_0^t J(t)\, dt$$

$$m_{free}(t) = N \cdot \frac{P(t) \cdot V}{R \cdot T(t)}$$

$$m_{sorbed}(t) = m_{total}(t) - m_{free}(t)$$

where:

$m_{free}(t)$	amount of ammonia in the reactor in the gas-phase (g);
$m_{sorbed}(t)$	amount of ammonia sorbed by the sorbent at time t
$m_{total}(t)$	total amount of ammonia in reactor at time t (g);
t	time (s);
$J(t)$	mass flow at time t (g s^{-1});
N	molar weight of ammonia (g mol^{-1})
$P(t)$	pressure of the ammonia gas in the reactor at time t (Pa);
R	gas constant;
$T(t)$	temperature of the ammonia gas in the reactor at time t (K);
V	volume in reactor occupied by ammonia in the gas phase (m^3);

Energy balance

The amount of heat generated is equal to the sorption enthalpy multiplied by the amount adsorbed.

$$Q_{sorbed}(t) = \Delta Hsorption \cdot m_{sorbed}(t)$$

$$Q_{loss}(t) = \int_0^t U dt$$

$$Q_{sensible}(t) = M_{reactor} \cdot (< T_{reactor}(t) > - < T_{reactor}(t = 0) >)$$

where:

$Q_{sorbed}(t)$	amount of generated heat due to adsorption of ammonia at time t (J);
$Q_{loss}(t)$	amount of heat lost to ambient at time t (J);
$Q_{sensible}(t)$	amount of heat stored in reactor as sensible heat (J);
$M_{reactor}$	thermal mass of reactor ($J \cdot K^{-1}$);
U	heat loss factor ($J \cdot s^{-1}$);
$<T_{reactor}(t)>$	average reactor temperature at time t (K);
$\Delta H_{sorption}$	sorption enthalpy ($J \cdot g^{-1}$);

The amount of heat lost to ambient is well known for steady-state conditions but will likely vary under transient conditions, due to (spatial) variations in temperature as well as induced gas flows and changed thermal conductivity due to pressure variations. However, for this measurement, the heat loss (per unit of time) has been assumed constant. The thermal mass of

the reactor has been assumed constant. This is an approximation because the thermal mass changes with the in-flux and adsorption of ammonia to the lithium chloride. The effect on its total thermal mass, however, is small compared to the uncertainties in the average temperature of the reactor. This temperature can only be estimated from the measured salt temperature and oil temperature.
The heat generated by sorption of ammonia can only be transferred to the environment and/or as added sensible heat of the reactor. Therefore the overall energy balance yields:

$$Q_{sorbed}(t) = Q_{loss}(t) + Q_{sensible}(t)$$

3. RESULTS

Figure 6 shows the pressure on the sorbent-side of the reactor and temperature of the oil leaving the reactor and of the sorbent as a function of time. The pressure is 0.01 MPa at the start of the measurement and increases rapidly after 10.45. The slow response of the pressure controller is clearly visible in the overshoot to 0.7 MPa and the subsequent undershoot to 0.48 MPa. The oil temperature (green line) rises in 1.5 minute after increasing the ammonia pressure from its initial temperature setting of 50°C to a value of 65°C. Five minutes later the temperature returned to its initial value. The salt temperature increases within two minutes to 105°C and slowly returns to its initial value.

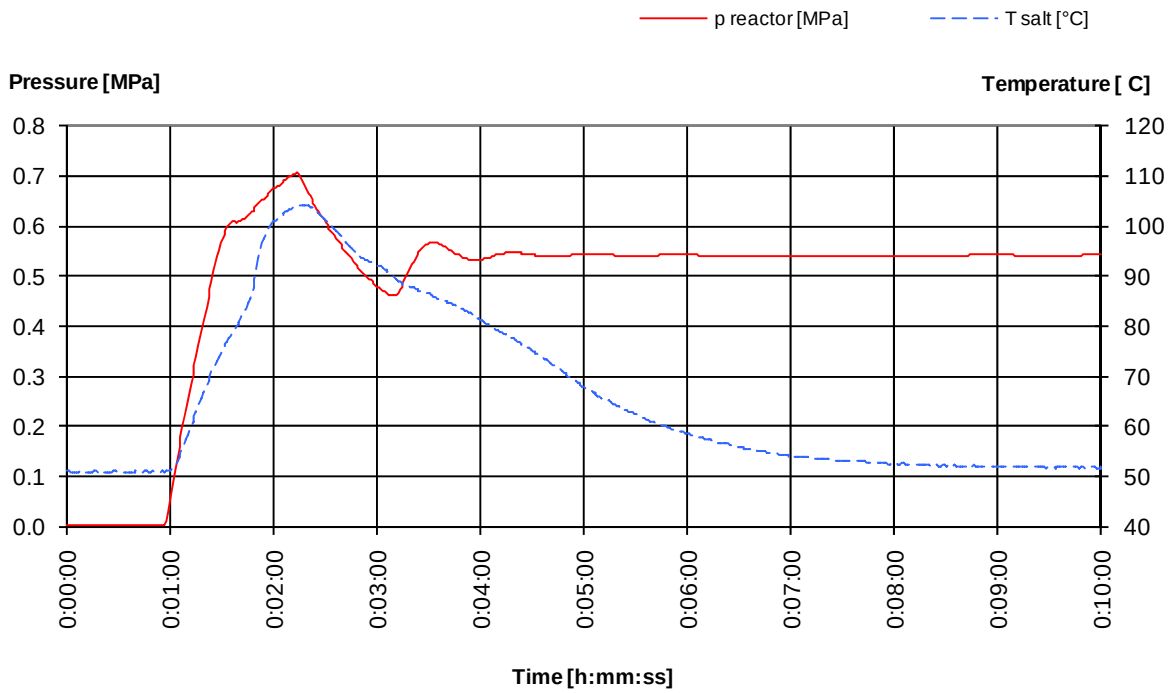

Figure 6. Pressure and temperature of the sorbent as a function of time.

Figure 7 shows the mass balance as a function of time. A total amount of 20 grams of ammonia was added to the reactor vessel. About 80% of the ammonia was adsorbed by the sorbent, the remaining 20% filled the free volume of the reactor. The amount of adsorbed ammonia equals 36% of the amount that could theoretically be adsorbed by the sorbent if all lithium chloride reacted.

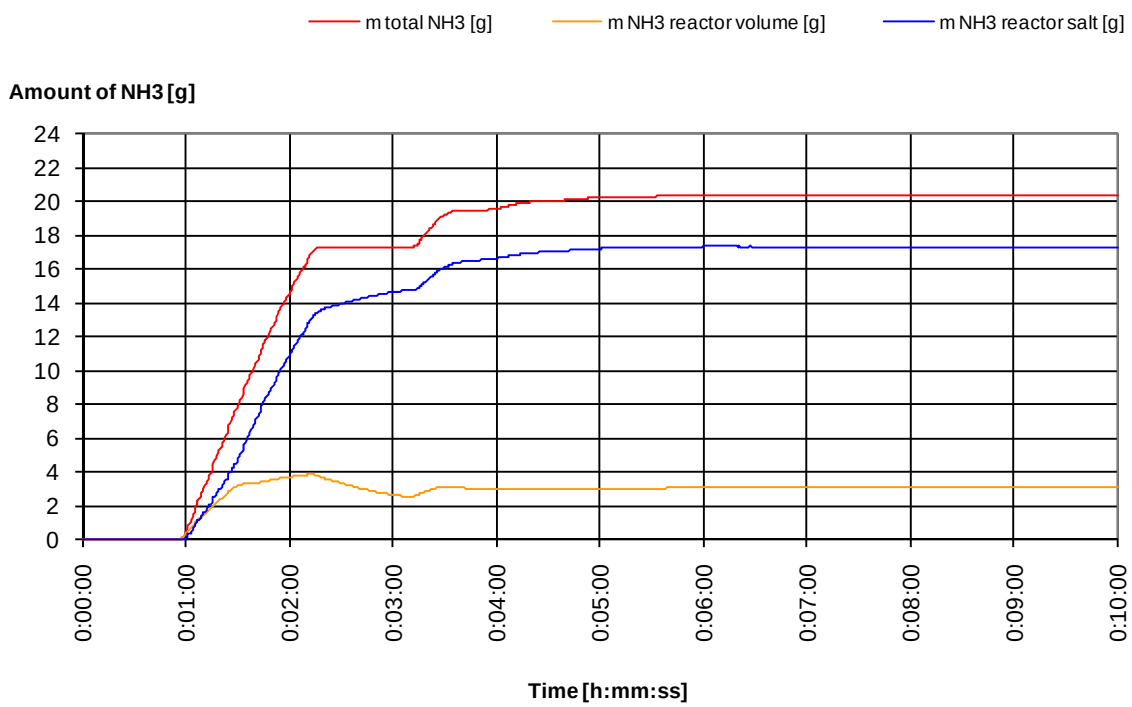

Figure 7. Total, adsorbed and free amount of ammonia in reactor as a function of time.

Figure 8 shows the energy production due to the reaction and the temperature variation in the oil. The blue line shows the energy balance in kJ. This is the difference between the total amount of heat produced by adsorption of ammonia, calculated from the mass flow and sorption enthalpy, and the amount of heat dissipated by the thermal oil, calculated from the temperature difference and flow rate of oil. The peak in sorption power (490W) is reached within the first four minutes of the measurement. The energy balance seems to fit well, being only slightly higher at the end of the measurement compared to the start. This suggests no undesired effects such as leakage of ammonia or large heat-losses to the ambient occur.

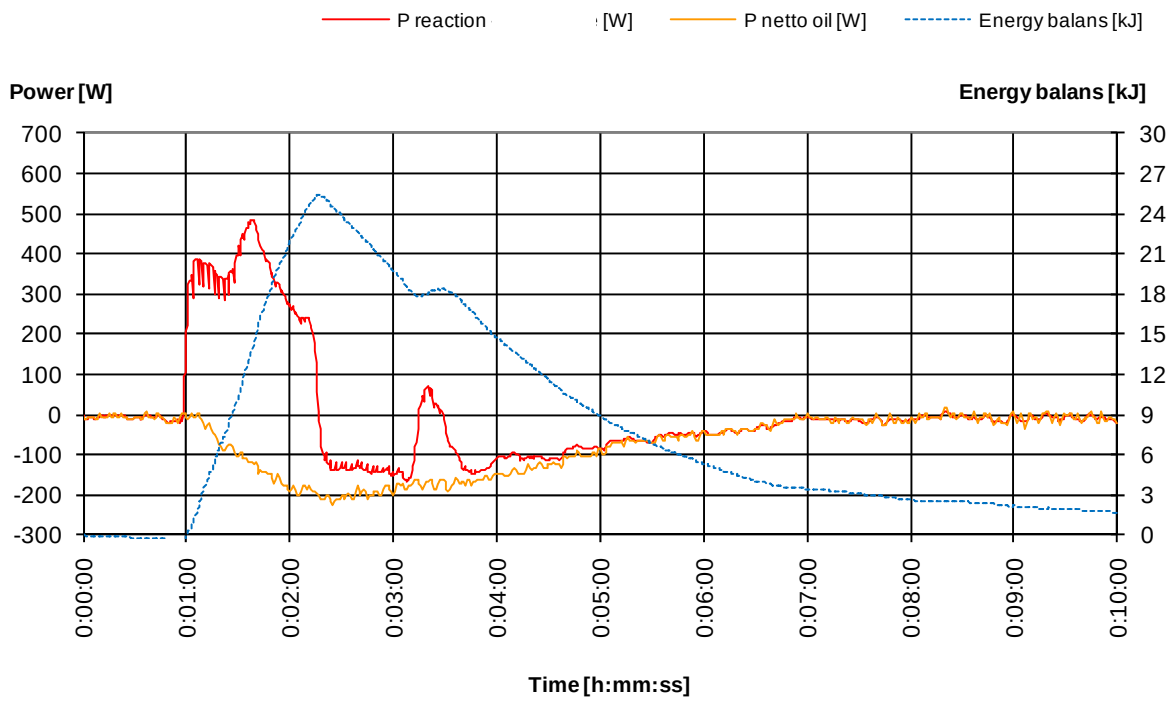

Figure 8. Measured powers and energy balance as a function of time.

Figure 9 shows the pressure-temperature relation. The blue and purple line show respectively the formation and the decomposition line of $LiCl{\cdot}3NH_3$.The yellow dots show the measured salt-temperature as a function of the measured pressure. The arrows show the development of the pressure-temperature relation in time. From the figure it can be observed that the pressure and temperature conditions prior to the pressure step (to 0.7 MPa) $LiCl{\cdot}1NH_3$ is the stable phase whilst the conditions after the pressure step would favour the formation of $LiCl{\cdot}3NH_3$ ammonia complex. For a small period, the salt temperature closely follows the theoretical pressure-temperature relation. This indicates the salt responds quickly to the changing conditions. This response indicates that the reaction rate under these conditions exceed the rate at which heat is transferred from the sorbent to the thermal oil.
Using the endoscope it was observed that a liquid phase was formed under the high pressure conditions. This is in line with observations conducted earlier on lithium chloride ammonia complexes (van der Pal and Veldhuis, 2010).

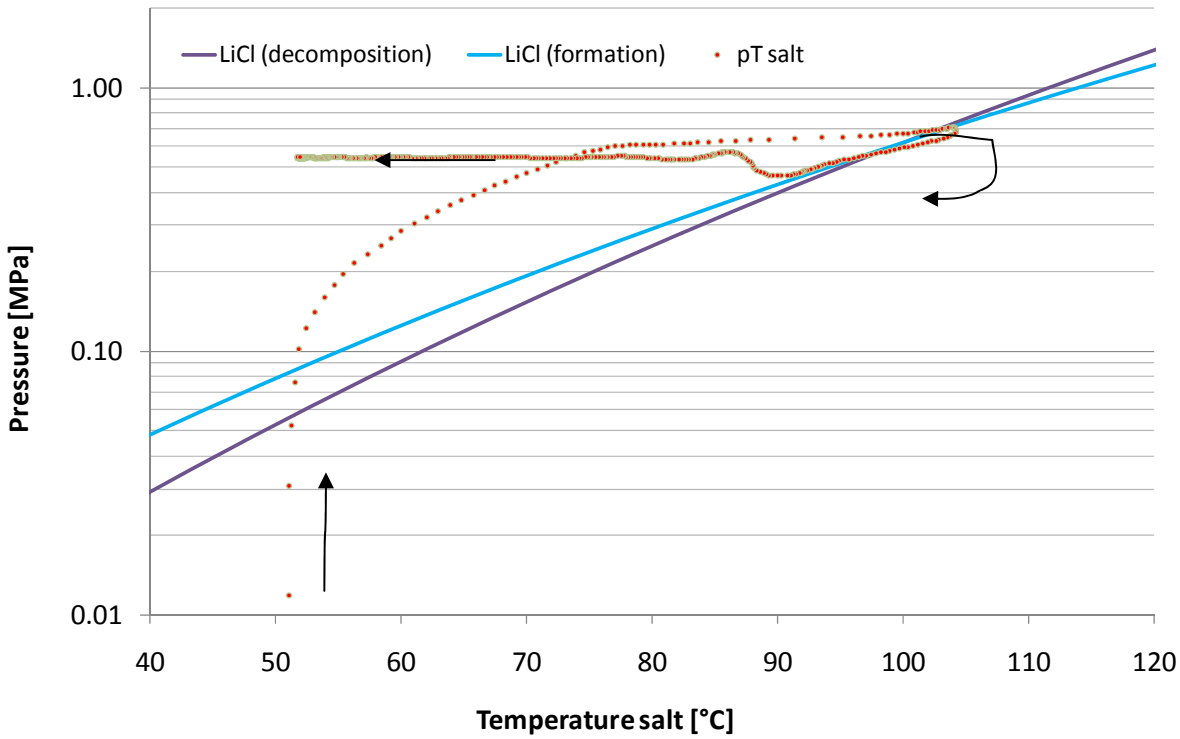

Figure 9. PT-diagram shows the measured pressure as a function of salt temperature together with the formation/decomposition equilibrium lines for $LiCl(1\text{-}3)NH_3$.The arrows shows how the temperature and pressure changed in time.

4. DISCUSSION AND CONCLUSIONS

A setup for measuring the performance of sorbent in a heat exchanger under heat pump conditions have been developed and succesfull tested. The first measurements show rapid adsorption of ammonia by lithium chloride. Within four minutes all ammonia is adsorbed with maximum power output is measured less than a minute from the rise in pressure. Although this suggests that lithium chloride reacts quickly enough for application in a heat transformer, the driving forces (i.e. pressure and temperature gradients) in the final application will be considerably smaller. Another point that needs to be addressed is the amount of ammonia adsorbed. From the mass balance can be observed that a bit more than 17 grams (= 1 mole) of ammonia is adsorbed. The reactor contains 60 grams (= 1.4 mole) of LiCl, capable of adsorbing 2.8 mole of ammonia to form $LiCl{\cdot}3NH_3$ from $LiCl{\cdot}1NH_3$, this means only 36% of

the theoretically available amount of ammonia is adsorbed. Earlier high pressure DSC experiments (van der Pal and Veldhuis, 2010) have shown this fraction can reach 80% but only after repeated adsorption. Further measurements are required to determine the long-term capacity.

Despite all uncertainties and limitations of these first measurements, the results are promising for the application of LiCl in the heat pump type II application. The sorbent reacts quickly and follows the theoretical temperature-pressure relation. Further measurements with different sorbents (e.g. $MgCl_2$) and different reactor types should give good insight in the properties of the sorbents and their behaviour in combination with various heat exchanger designs. This should reduce the uncertainties concerning the performance that can be expected when scaling up from sorbent to prototype heat pump type II.

The setup still has some minor problems, such as the overshoot of the pressure controller. However, it has shown it is possible to measure mass- and heat flows and they show a good correlation. Using the endoscope, it is possible to observe macroscopic structural changes in the material.

ACKNOWLEDGEMENT

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