ABSORPTION/COMPRESSION CYCLE FOR HIGH TEMPERATURE HEAT PUMPS – SIMULATION MODEL, PROTOTYPE DESIGN AND INITIAL EXPERIMENTAL RESULTS

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Abstract: The objective of this work is to develop a small capacity absorption/compression heat pump system for decentralized industrial heat recovery. By means of the solution cycle, it is intended to reach hot water outlet temperatures above 100°C at moderate pressure levels. Aiming to build up a prototype, different system configurations are investigated, using e.g. variation of the working pair and design boundaries, and solutions for system design problems are researched.

It is shown that heat transfer and pressure drop characteristics, crystallization issues, compressor outlet temperatures and oil-management have to be particularly considered. The results of the simulation model are used as basis for the choice of a working-pair and the system design. Due to limited pressure levels of standard components and limited compressor outlet temperatures a suitable control strategy has to be worked out.

Within this work a prototype was designed and constructed with NH3-LiNO3 as working pair. With the prototype first measurements were realized and the Coefficient of Performance (COP) is determined for different temperature lifts. In this context, tests at different pressure levels and inlet temperatures were carried out.

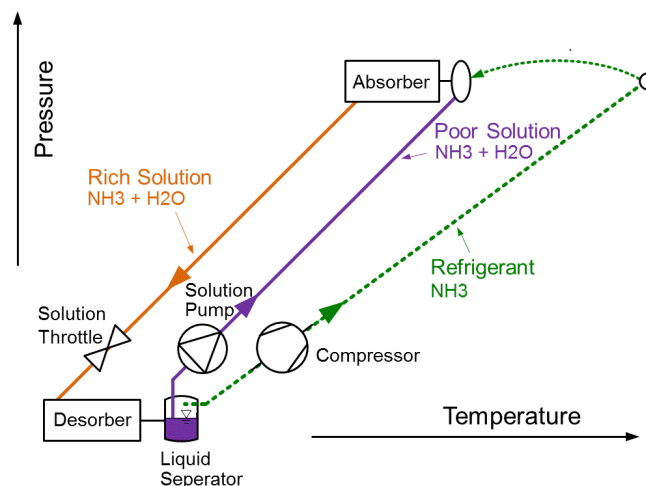**Key Words: absorption compression heat pump, high temperature application, ammonia lithium nitrate**

1   INTRODUCTION

High temperature heat pumps can be used for e.g. industrial heat recovery. Related publications show that the heat demand has a major share of the total end use energy segmented in different temperature levels (e.g. Euroheat & Power 2006). Conventional compression heat pump cycles have to deal with high pressures and high compressor outlet temperatures when used as high temperature heat pump (above 100 °C heat sink outlet temperature). Furthermore, most refrigerants limit the temperature level of condensation because of their critical point. E.g. Zhang et al. (2010) show possible refrigerant mixtures which can be used at high condensation temperature levels with moderate pressure levels and achieve a high Coefficient of Performance (COP) for heating application.

Simulation results for a conventional compression heat pump cycle, based on the refrigerant properties available in EES (Engineering Equation Solver 2013) show which refrigerant can be used up to 105°C condensation temperature. Some of the possible refrigerants are already prohibited for use in heat pumps (R11, R12, R114, R123, R124, R141, R142b, R500, RC318) and most of them have a high Global Warming Potential (GWP). Further, R600 and R600a are highly flammable. Regarding the pressure levels, some of the refrigerants (e.g.

R500, R717, R1234ze) reach a high condensation pressure, hence special equipment would be needed. On the other side R718 (H_2O) has evaporation pressures below atmospheric pressure if evaporation takes place below 100°C. Although R245fa has moderate pressure levels, the GWP_{100a} of 950 has to be considered. Resulting from the simulation, it can be shown that there is a certain market potential for high temperature heat pumps with adequate refrigerant properties.

The concept of the absorption/compression-heat pump cycle (also called "hybrid" heat pump cycle) is known since the late 19th century (Osenbrück 1895). Due to certain technical and economic difficulties the concept couldn't be implemented commercially in large scale until now. In general, the system uses a combination of a vapor-compression heat pump cycle and a liquid solution cycle, shown in figure 1 for the working pair ammonia/water (refrigerant/absorbent).

Figure 1: Absorption-/compression- heat pump cycle

This heat pump process can be used for high application. Due to the use of a working pair instead of pure refrigerant (ammonia), the pressure levels of absorption and desorption can be adjusted by variation of the solution concentration (and are not depending on the temperature level primarily). The following advantages of an absorption/compression-heat pump can be named compared to a vapor-compression heat pump:

- A high heat sink temperature level is possible at moderate pressure levels compared to a vapor-compression heat pump. For example temperatures above 100°C at the heat sink can be reached with a high-pressure level below 20 bar for ammonia/water.
- The heating capacity can be adjusted at constant temperature levels by means of varying the pressure levels or of the solution's concentrations.
- An approximation to the "Lorenz"-process and higher coefficient of performance due to gliding temperatures during absorption and desorption can be reached. If the temperatures of the heat sink and heat source are also gliding during heat transfer, higher exergetic efficiencies are possible (in case of counter-current heat exchangers).
- Bi-generation of heat (Absorber) and cold (Generator) by one heat pump system and one fluid stream used as heat sink and heat source is possible.

Recently, there are increasing research activities related to the "hybrid" heat pump system and some test facilities, but there is only one supplier for industrial application on the market until now. The company "Hybrid Energy AS" (2014) from Norway offers customized absorption/compression-heat pumps starting from min. 100 kW heating capacity, shown in figure 2.

Figure 2: Pictures of two "hybrid" heat pumps by "Hybrid Energy AS"
left: 300 kW, right: 650 kW heating capacity (Nordtvedt 2009)

In the underlying project "HyPump" a "hybrid" heat pump for small scale application (ca. 25 kW) is developed. The test facility should be mainly built up with standardized components like for example plate heat exchanger, to reach low cost and thereby low payback times, resulting in a high market potential.

Within this paper, some investigations and design principles of the cycle design for different ammonia-based working pairs are shown. Furthermore, detailed simulation results for the chosen working pair ammonia - lithium nitrate and selected preliminary experimental results are presented.
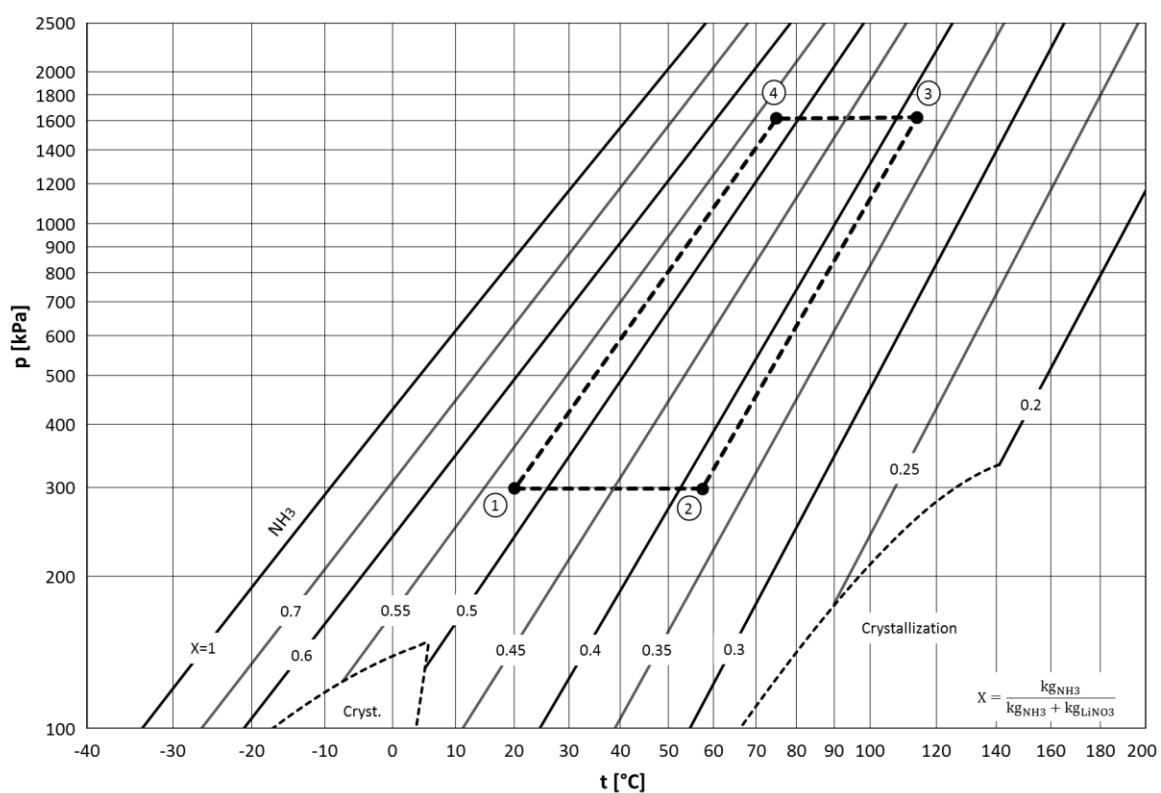

2   WORKING PAIR

Within this work, different ammonia-based working pairs are investigated. Due to the reasons listed below ammonia/lithium nitrate (NH3 – LiNO3) has been chosen, hence all further chapters refer to this working pair. Ammonia/lithium nitrate has the following advantages for the cycle design compared to other ammonia-based working pairs:

- While ammonia/water (NH3-H2O) shows a certain amount of water vapor in the resulting gaseous refrigerant, for NH3-LiNO3 and ammonia/sodium thiocyanate (NH3-NaSCN) no evaporation of the solvent is expected.
- No rectification is needed before the compressor inlet. When the working pair NH3-H2O is used most of the water-vapor has to be separated before compression, mainly due to the reasons listed below.
- Standard oil-lubricated NH3-compressors can be used. Most NH3-compressors (because of the materials used) and most compressor lubricants do only accept a certain amount of water-vapor in the refrigerant.
- When operated in 2-stage-compression the refrigerant can be cooled between the two stages, without any condensation of a water-rich solution. Also when oil-lubricated compressors and NH3-H2O are used, a mixture of oil and solution will fall out, which has to be separated, if the continuous oil return has to be guaranteed.
- Regarding the oil separation, standard components can be used and no additional NH3-H2O solution is gathered in the oil separator.

- Due to the comparatively higher risk of crystallization of NH3-NaSCN in the desorber (when operated with low pressure levels and high desorption temperatures, resulting in low ammonia concentration of the solution) this working pair can be ruled out.

Properties for vapor-liquid equilibrium, density, viscosity and heat capacity for NH3 – LiNO3 are published in Libotean et al. (2007) and Libotean et al. (2008), values for thermal conductivity can be taken from Cuenca et al. (2013). Further working pair properties for NH3-LiNO3 not listed in the publications above can be taken from Infante-Ferreira (1984). For the working pair the log(p)/(-1/T)-diagram based on the correlations given by Libotean et al (2007) can be seen in figure 3. The parameter X shows the ration of mass of ammonia to the overall mass of solution. The curves for crystallization at the bottom of the diagram are based on the values given by Infante-Ferreira (1984). The bold dotted line shows an example for the idealized hybrid heat pump solution cycle.

**Figure 3: log(p)/(-1/T)-diagram for the working pair NH3-LiNO3, numbers in circles according to Figure 4**

As a disadvantage, according to the property correlations the calculated viscosity of NH3-LiNO3 is about ten times higher than the viscosity of NH3-H2O at same operating conditions. At low pressure level, low temperature and low ammonia concentration in the saturated mixture, NH3-LiNO3 reaches a dynamic viscosity of up to 10 mPa/s. This certainly has to be considered during the absorption and desorption process and for the dimensioning of heat exchanger areas.

3   CYCLE DESIGN

The developed cycle schema for the working pair ammonia/lithium nitrate (refrigerant/absorbent) and a picture of the built up prototype are shown in Figure 4.

Starting with the refrigerant vapor in the suction line, the vapor gets compressed to high pressure level by the compressors. For high pressure ratios the single stage compression reaches high compressor outlet temperatures. One possibility to limit the compressor out outlet temperature is a two-stage compression cycle design. In the final cycle design shown in Figure 4, a two-stage compression with additional bypass for the low-stage compression has been realized, to make different pressure ratios possible. The swept volume of the high-stage compressor has been chosen according to the expected volume flow after the low-stage compressor.

A "desuperheater" heat exchanger is used to cool the refrigerant at the high stage compressor outlet. This is especially needed to enable oil separation with standard components, when the compressor outlet temperature is high (above 140°C). As a heat sink the hot water after the absorber is used. The heat transfer area can be kept small, when high temperature differences (especially at the pinch point located at the hot water inlet) during heat transfer are accepted.
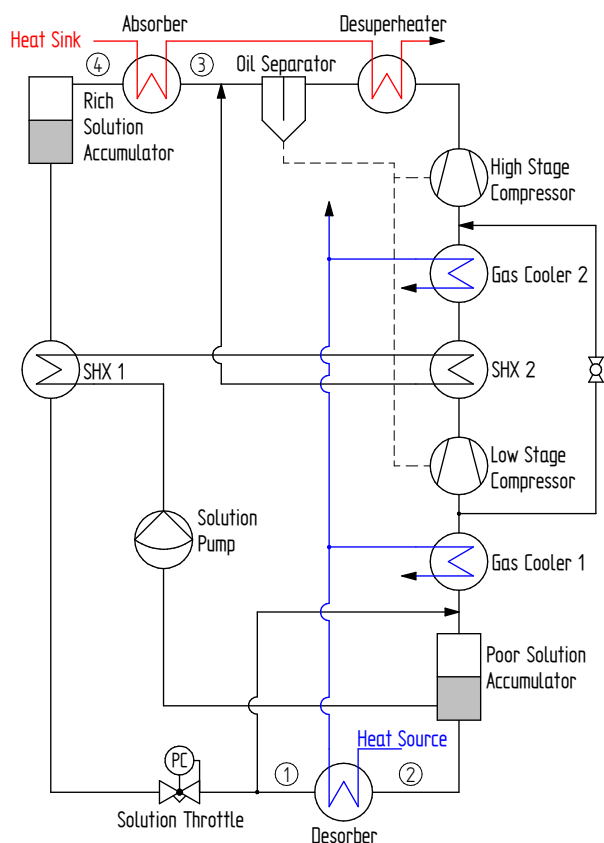
Figure 4: Schematic cycle design of the absorption-/compression heat pump (left) and picture of the prototype (right)

After that, the refrigerant is mixed with and absorbed by the liquid poor solution in the Absorber. During the absorption process the released absorption heat is transferred to the heat sink at high temperature level. The resulting liquid solution concentration, the saturation temperature and the saturation pressure are dependent to each other, hence the pressure

levels can be set by the solution concentration or the circulation ratio (ratio of solution mass flow to refrigerant mass flow).

After the absorber the liquid rich solution gets expanded in the solution throttle. In the following the refrigerant can be desorbed in the desorber heat exchanger at low temperature level and gets separated afterwards. The remaining liquid poor solution is pumped back into the absorber by the solution pump, the separated refrigerant vapor gets sucked by the low stage compressor.

Further gains in performance are expected to be reached by means of an additional solution heat exchanger (SHX 1) in the solution circuit, which transfers heat from the rich solution after the absorber to the poor solution after the desorber. The heat transferred to the poor solution in the solution heat exchanger results in a higher temperature and enthalpy at the absorber inlet and thereby increases the absorber capacity and the COP. The influence of the heat exchanger on COP increases, when the water inlet temperature of the absorber is higher than the water inlet temperature of the desorber or when high circulation ratios (ratio of circulating solution to circulating gaseous ammonia) are set, because in these cases the amount of heat transferred in SHX1 is high.

In order to cool the refrigerant after the low pressure compressor, another solution heat exchanger (SHX 2) is used. Due to the temperature level of the solution, the outlet temperature of the refrigerant can't be cooled below desorber outlet temperature. Therefore a gas cooler heat exchanger (Gas Cooler 2) is installed, which can be fed by the cold water outlet temperature after the desorber, to reach lower refrigerant temperatures at the high stage compressor inlet (and thereby lower compressor outlet temperatures). The possible cooling of the suction gas is limited by the condensation temperature of ammonia at middle pressure level, to avoid liquid slugging in the compressor.

To sustain good phase-distribution in the desorber and to keep the velocity in the inlet line low, the liquid solution and the refrigerant vapor are separated after the solution throttle. The gaseous ammonia is fed to the suction line of the low stage compressor, thereby cooling the ammonia coming from the desorber. Again, an additional gas cooler heat exchanger (Gas Cooler 1) is installed, which can be fed by the cold water outlet temperature after the desorber, to cool the ammonia before the low stage compression. This time the cooling of the suction gas is limited by the condensation temperature of ammonia at low pressure level.

According to the cycle design in Figure 4 all components had to be dimensioned with respect to the desired capacity of the prototype, which is set by the compressors used. In the current project both compressors are provided by the company "Frigopol Kälteanlagen GmbH" (2014), which does offer separating-hood compressor in semi-hermetic design. In consultation with the supplier, the heating capacity of the prototype has been set to about 20 kW at nominal operating conditions (refrigerant mass flow ca. 40 kg/h).

With the simulated mass and energy balances calculated with the simulation model (see chapter 4), the heat transfer for all heat exchanger could be estimated and the number of plates for the plate heat exchanger has been set. Due to the high viscosity of NH3-LiNO3 the heat exchanger areas of all solution fed plate heat exchanger has to be comparatively higher than in similar systems operating with NH3-H2O as a working pair.

Further, the system control has been set up for testing at variable operating conditions. In order to allow an operation at changing temperature levels of the heat sink and heat source supply and at the same time limit the low and high pressure level, the amount of ammonia in the system can be varied. During operation the low pressure level can be set by the operator, thereby defining the cycle conditions in dependence to the amount of ammonia in the

system. The heat sink and heat source are supplied by the infrastructure available at the institute. The temperature levels and mass flows of both can be set by the operator.

To adjust the mass flows of gaseous ammonia and solution, both compressors and the solution pump are frequency-controlled. The low stage compressor frequency is therefore set constant, the high stage compressor frequency can be calculated according to the overall pressure ratio, with the condition of same pressure ratios in both compressors. The frequency of the solution pump is controlled by the filling level of the rich solution accumulator, which is intended be constant at about 50% during operation.

4   SIMULATION MODEL

Based on the cycle design according to Figure 4 a simulation model has been set up in EES. The process parameters have been set according to the following boundaries:

- The temperature level of heat sink and heat source have been varied from 40 to 80°C.
- The temperature difference between solution and heat sink at the absorber inlet and the absorber outlet has been set to 10 K.
- The subcooled state of the solution before and after absorption has been set to 3 K below saturation temperature.
- The temperature difference between solution and heat sink at the desorber inlet and the desorber outlet has been set to 7.5 K (compared to the absorption, the temperature difference has its maximum during the desorption, so the inlet and outlet temperature difference can be kept comparatively smaller).
- The efficiency of all other heat exchangers has been set to 0.8 (ratio of heat transferred to the maximal transferable amount of heat).
- High pressure limit: 20 bar (due to components used)
- Low pressure limit: 1.5 bar (due to crystallization)
- Both pressure levels have been set and varied in the simulation.
- The frequency of the low stage compressor has been set to 50 Hz (standard).
- The frequency of the high stage compressor can be calculated and adjusted so that both stages have the same pressure ratio.
- For both compressors the compression efficiency and the volumetric efficiency have been calculated according to measured values transferred by the compressor supplier.
- The frequency of the solution pump can be adjusted according to the mass flow needed. The efficiency has been set to 0.5.

4.1   Simulation Results

Figure 5 shows the maximum compressor outlet temperature ($t_{comp,out}$), the heat sink outlet temperature after the desuperheater ($t_{sink,out}$), the heat source outlet temperature ($t_{source,out}$) after the desorber and the Coefficient of Performance for heating application (COP$_H$, equation (1)) for different heat sink and heat source inlet temperatures ($t_{sink,in}$ / $t_{source,in}$), which are set equal. Further, the low pressure level (p_{low}) has been set constant to 3 bar and the high pressure level (p_{high}) to 12 bar (pressure ratio of 4).

$$COP_H = \frac{\dot{Q}_{Absorber} + \dot{Q}_{Desuperheater}}{\sum P_{electric}} \qquad (1)$$

Due to higher temperatures of the gaseous ammonia refrigerant and poor solution after desorption, the compressor outlet temperatures rise when the heat source temperature gets higher. In the simulation the temperature after the high stage compressor is slightly higher than after the low stage compressor, which can be explained as following. After the low stage compressor, the ammonia is cooled by the poor solution, coming from the first solution heat exchanger (SHX 1). The temperature of ammonia which can be reached after the heat exchanger is always higher than the temperature after the poor solution accumulator. Therefore, even if the gas coolers are put into operation (assuming that both have equal efficiency), the temperature of gaseous ammonia in the suction line of the high stage compressor is higher than at the inlet of the low stage compressor.
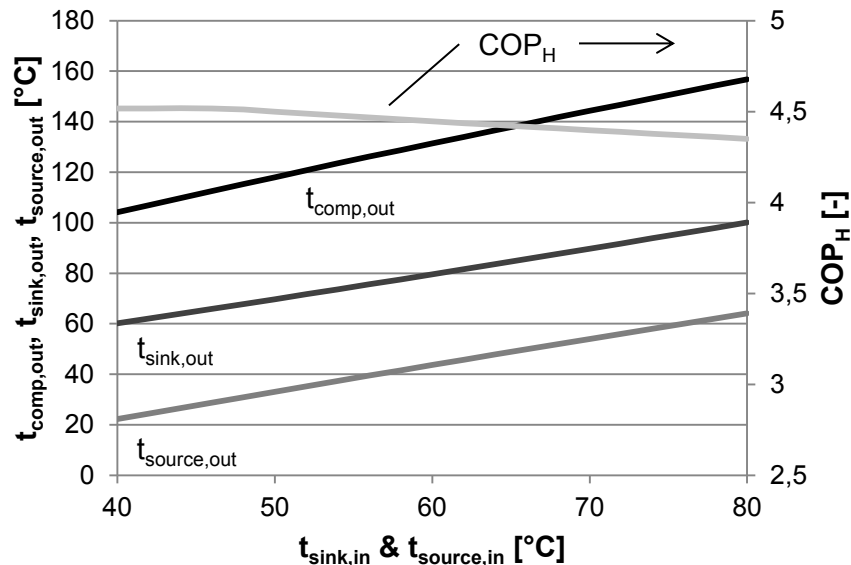
Figure 5: Simulated temperatures and COP_H (p_{low} = 3 bar, p_{high} = 12 bar, equal $t_{sink,in}$ and $t_{source,in}$)

The COP_H slowly decreases when the heat sink and heat source temperature increases. This can be explained by increasing exergy losses in the solution heat exchanger, resulting from lower ammonia concentration differences of the rich and poor solution (in dependence to the rising temperature level) and thereby increasing circulation ratios. With the circulation ratio also the amount of non-transferable heat in SHX1 (at constant efficiency) increases and thereby the absorber heat capacity is reduced. For example at 40°C heat sink and heat source inlet temperature the outlet concentration after the absorber (rich solution) is ca. 0.58 and after the desorber (poor solution) 0.475, while at 80°C it is 0.41 and 0.355 respectively, resulting in higher solution mass flows compared to the refrigerant mass flow.

The heat sink outlet temperature increases almost with the same amount as the inlet temperature. The maximum difference of heat source outlet temperature and inlet temperature occurs at low inlet temperatures, due to the highest difference of concentration of poor and rich solution, which results in low temperatures and high qualities of the solution after the solution throttle.

In Figure 6 the low pressure level has been set constant to 3 bar and the high pressure level to 18 bar. Compared to Figure 5 (p_{high} = 12 bar) the compressor outlet temperature is higher, resulting from the higher pressure ratio. The COP_H is lower than in Figure 5, due to the higher electric power input compared to the heating capacity of the cycle, due to the higher pressure ratio.

At the same time the temperature difference between inlet and outlet of the heat sink at the absorber and the heat source at the desorber increases. The saturated condition at the

absorber inlet is at higher temperatures, thus at the outlet a higher concentration can be reached, due to the increased pressure level of the absorption process, (while the saturated conditions after the desorber do not change compared to the conditions in Figure 5). This results in an increasing concentration difference between rich and poor solution and thereby the temperature at the absorber inlet gets higher (while simultaneously the solution temperature after the solution throttle gets lower). It can be seen, that with heat sink inlet temperatures above 65°C the cycle can reach outlet temperatures above 100°C after the desuperheater.
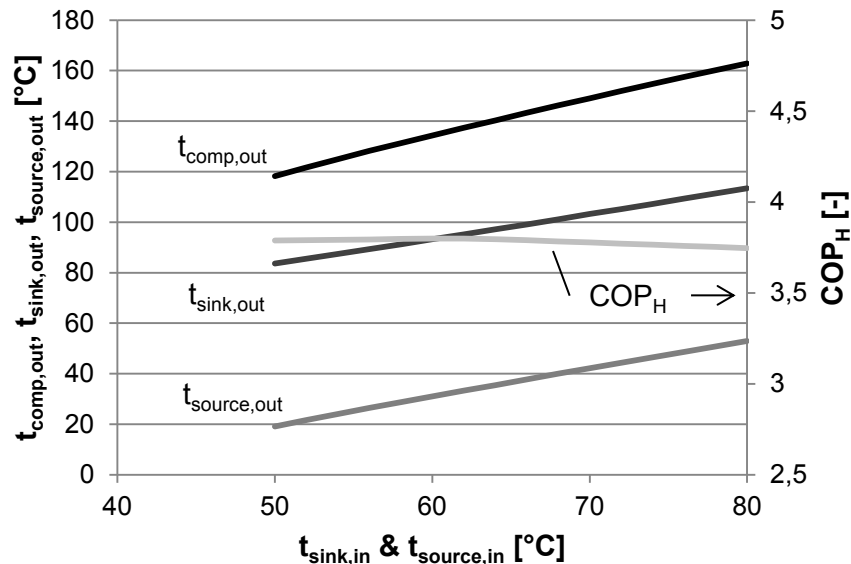
Figure 6: Simulated temperatures and COP_H (p_{low} = 3 bar, p_{high} = 18 bar, equal $t_{sink,in}$ and $t_{source,in}$)

When different temperatures for heat source and heat sink are given, the system behavior changes basically. In Figure 7 some simulation results are shown for operating conditions, where the heat sink inlet temperature is 20 K higher than the heat source inlet temperature. For the simulation the low pressure level has been set constant (3 bar) and the high pressure level is varied.
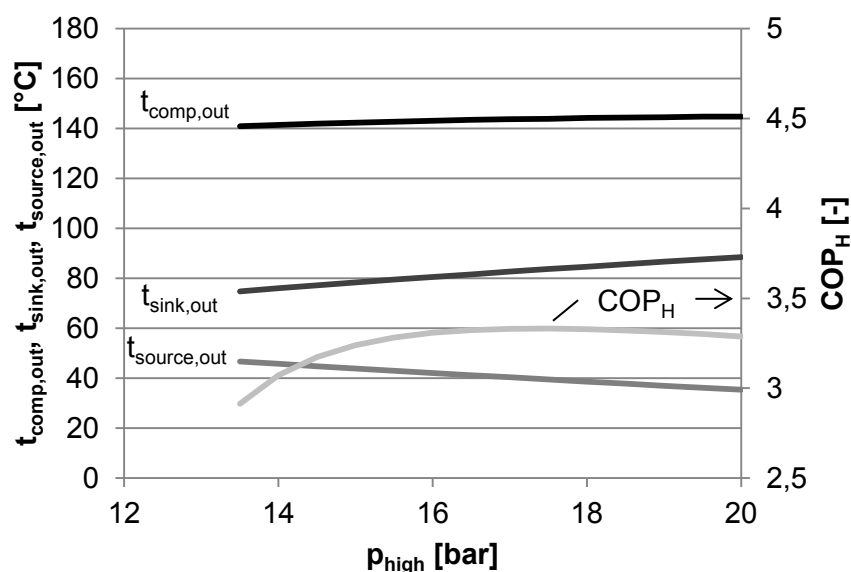
Figure 7: Simulated temperatures and COP_H (p_{low} = 3 bar, $t_{sink,in}$ = 70°C, $t_{source,in}$ = 50°C)

The maximum compressor outlet temperature hardly changes (ca. 140°C), even if the pressure ratio increases. This can be explained by the lower heat source outlet temperature after the desorber, which influences the temperature level of the gaseous ammonia in the suction line. With increased pressure ratio the temperature difference from inlet to outlet of heat source and heat sink gets higher, as explained in context to Figure 6. However, both differences are noticeable lower compared to the operating conditions with same inlet temperatures of heat sink and heat source. This can be explained by the comparatively higher circulation ratio of solution to gaseous refrigerant to maintain the absorption and desorption process according to the saturated conditions and ammonia concentrations reached at the absorber and desorber outlet.

The COP_H decreases when the temperature difference between the heat sink and heat source inlet increases, also due to the higher circulation ratio. In Figure 7 a maximum of COP_H can be achieved at a certain pressure ratio. For operating conditions with lower high pressure level the circulation ratio increases drastically, for operating conditions with higher pressure levels, the electric power consumption gets comparatively higher than the resulting heating capacity, because of the pressure ratio. This even exceeds the positive influence of decreasing circulation ratios at higher pressure ratios.

5   EXPERIMENTAL RESULTS

So far, with the prototype, shown in Figure 4, first experimental results have been measured at medium temperature levels of heat source and heat sink. In further steps the temperature level and refrigerant mass flow, which determines the heat capacity, will be varied.

In Table 2 the main values for two different "Operating Conditions" (OC) are listed. OC1 and OC2 are operated with two-stage compression and for both only gas cooler 2 (see Figure 4) has been used. The uncertainty of measurement for the measured and derived values has been evaluated according to the given accuracies of the measurement equipment taken from the data sheets (converted into standard deviation σ) and Gaussian error propagation. Further uncertainties (e.g. method of measurement) are not considered.

Parameters shown in Table 2 are the refrigerant mass flow ($\dot{m}_{NH3}$), the poor solution mass flow ($\dot{m}_{pso}$), the low pressure level (p_{low}), the high pressure level (p_{high}), temperatures (t), volume flows ($\dot{V}$) and calculated heat capacities ($\dot{Q}$) of the heat sink and the heat source (note: heat capacity values include desuperheater and gas coolers), the total electric input for compressors and solution pump (P_{el}) and the COP_H, calculated according to equation (1).

The volume flows of heat sink and heat source have not been adjusted for maximized temperature differences from inlet to outlet at the absorber and desorber during operation. Instead, high volume flows have been set for test reasons. Hence the heat sink and heat source outlet temperatures listed in Table 2 cannot be compared with the values shown in chapter 4.

Compared to the simulation results (compare chapter 4) the measured COP_H is lower than expected. This can primarily be explained by a higher electric power consumption of the system (compressors and solution pump including frequency converters) than expected. Secondly, heat losses to the ambient, especially of the compressors, have not been considered in the simulation model. As a result, the measurements show that the compressor outlet temperature is lower than expected. Considering these observations the significant COP difference between simulation and experiment can be explained.

Table 2: Experimental data (incl. uncertainties) for two different operating conditions

		OC 1	OC 2
Remark:		two stage, only Gas Cooler 2	two stage, only Gas Cooler 2
$\dot{m}_{NH3}$	kg/h	35.93 ±0.15	36.29 ±0.19
$\dot{m}_{pso}$	kg/h	179.1 ±0.4	149.0 ±0.4
p_{low}	bar	2.95 ±0.06	3.00 ±0.06
p_{high}	bar	15.07 ±0.14	18.22 ±0.14
$\dot{V}_{sink}$	l/h	1145 ±20	1105 ±19
$t_{sink,in}$	°C	45.06 ±0.14	50.01 ±0.14
$t_{sink,out}$	°C	56.61 ±0.15	62.43 ±0.16
$\dot{Q}_{sink}$	kW	15.13 ±0.38	15.65 ±0.38
$\dot{V}_{source}$	l/h	1090 ±19	1083 ±19
$t_{source,in}$	°C	45.01 ±0.14	50.02 ±0.14
$t_{source,out}$	°C	34.45 ±0.13	39.07 ±0.13
$\dot{Q}_{source}$	kW	12.88 ±0.33	13.20 ±0.35
P_{el}	kW	5.89 ±0.02	6.35 ±0.03
COP_H	-	2.70 ±0.12	2.67 ±0.13

Further the absorption and desorption process can be evaluated in detail. The measured temperature difference between solution and heat sink/heat source at medium temperature level has been higher than assumed in the simulation model. Hence the absorber capacity decreases, because of the higher temperature difference at the solution outlet, and the circulation ratio increases, because of the lower ammonia concentration difference between poor and rich solution resulting from the saturated conditions after absorption and desorption. Finally, the measured values show a slightly higher circulation ratio than expected at the operating conditions, even if the higher temperature differences in absorber and desorber are considered, which also decreases the COP_H. The reason has to be investigated in further steps.

6   CONCLUSION

This paper shows the design of an absorption/compression heat pump that can be used for high temperature application. Furthermore a detailed simulation model, cycle design considerations and first experimental results with the working pair ammonia/lithium nitrate are shown.

Major advantages of the absorption/compression heat pump cycle are the adjustable pressure level in dependence to the concentration and the temperature glide of the solution in the absorber and desorber. Important problems that can be named are the high compressor outlet temperatures and the oil separation before the solution cycle, if oil-lubricated ammonia compressors are used. The working pair ammonia/lithium nitrate was chosen because of the expected pure ammonia gaseous phase in contrast to the water vapor occurring with the working pair ammonia/water.

With the resulting cycle design a simulation model of the absorption/compression heat pump has been set up. The results of the simulation are used to forecast operating conditions, e.g. the compressor outlet temperatures, to design a system control for operation and to evaluate the cycle performance at different operating conditions.

With the prototype first steady-state measurements have been carried out at a medium temperature level. In further steps the operating conditions will be varied and the measured values will be used to evaluate and modify the simulation model.

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ACKNOWLEDGEMENTS