Thermally driven ammonia-salt type II heat pump: development and test of a prototype

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Abstract

ECN developed together with Bronswerk Heat Transfer Inc. a thermally driven prototype heat pump that uses ammonia adsorption/desorption on the salts LiCl and $MgCl_2$ for respectively low and high temperature reactor. Measurements on this prototype have been conducted to determine its peak power production, its achievable temperature lift and cyclic stability. The measurements show a peak power production of about 600W with an average output of 300W. Data-analysis suggests that the power output is limited by heat transfer rather than kinetics. The temperature lift that has been shown on the setup is 50ºC, from 130ºC to 180ºC. Cyclic stability test show consistent, reproducible output during for more than 100 cycles.

Contents

List of figures

1. Introduction

Upgrading industrial waste heat over the pinch temperature has great potential for reducing industrial energy use. For small temperature lifts, this can be achieved using (re)compression heat pump systems. For high temperature lifts (over 50ºC), the options are more limited. At ECN, a heat pump has been developed to increase waste heat in the temperature range of 90 to 160ºC with more than 50ºC up to temperatures of 220ºC. This type II thermally driven heat pump is based on absorption and desorption of ammonia onto LiCl, the low-temperature salt and $MgCl_2$, the high temperature salt. This heat-powered cycle is based on the following reactions for charging and discharging of the system:

Charge:	$LiCl{\cdot}1NH_3 + 2\ NH_3$	$\rightarrow LiCl{\cdot}3NH_3 + \text{heat}\ (T_{ambient})$
	$MgCl_2{\cdot}6NH_3 + \text{heat}\ (T_{wasteheat})$	$\rightarrow MgCl_2{\cdot}2NH_3 + 4\ NH_3$
Discharge:	$LiCl{\cdot}3NH_3 + \text{heat}\ (T_{wasteheat})$	$\rightarrow LiCl{\cdot}1NH_3 + 2\ NH_3$
	$MgCl_2{\cdot}2NH_3 + 4\ NH_3$	$\rightarrow MgCl_2{\cdot}6NH_3 + \text{heat}\ (T_{abovepinch})$

The useful, high-temperature heat is released during the discharge phase via adsorption of ammonia by the magnesium chloride. After thorough characterization and validation of the salts' properties and behavior (Bevers et al., 2006; Bevers et al., 2007), a prototype heat pump has been designed, built and tested. The results are presented in this paper.

2. Method and materials

2.1 Prototype design & construction

Earlier proto-types based on ammonia sorption on $LiCl/MgCl_2$ showed poor or limited performance (Haije et al., 2007) due to degradation of the salts, salts escaping from its matrix and poor heat and mass transfer to and from the salts. To avoid these problems, a method was developed to deposit the salts into metal foam, which increases the heat transfer while limiting the degradation and mobility of the salts, and thus maintains proper mass transfer. The final design of the reactors is based on a shell and tube type heat exchanger in which each fin supports a sheet of metal foam containing the salt. Figure 2.1 shows the final design of the reactor with on the left the shell and tube heat exchanger containing 2x80 fins coated with a metal foam, in the middle a picture of the set-up as realized and on the right the fin layout is shown. The two reactors have been constructed and tested by Bronswerk Heat Transfer Inc. After the pressure test at 40 bars, the reactor has been filled with respectively 1.21 and 2.49 kg of LiCl and $MgCl_2$, followed by adding ammonia to each reactor forming respectively $LiCl{\cdot}1NH_3$ and $MgCl_2{\cdot}6NH_3$.

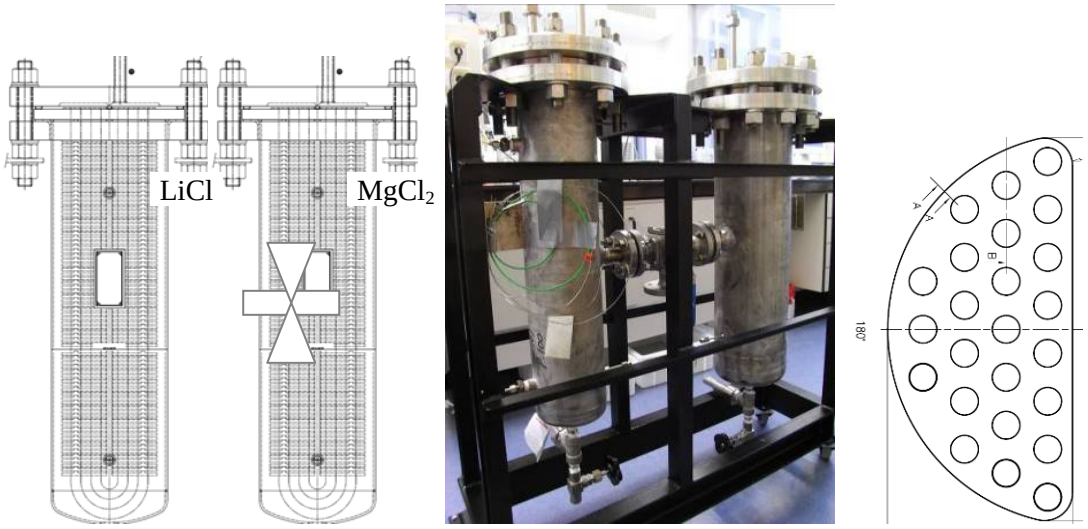

Figure 2.1 *Left: 2-reactor design, middle: picture of experimental setup, right: fin layout*

2.2 Test environment

To test the performance of the ammonia-salt heat pump system, the reactors are connected to a heating&cooling infrastructure. This infrastructure allows heating/cooling at three different temperatures ranging from 20ºC to 200ºC using thermal oil. The maximum, isothermal heating power is about 5 kW while the cooling power is strongly dependent on the temperature level with a maximum cooling power of 2 kW. The infrastructure can automatically switch the reactor between low temperature and medium temperature supply to the LiCl-reactor, and between the medium and high temperature for the $MgCl_2$-reactor.

The power input and output of the reactors is calculated from measured mass flow of the thermal oil and the temperature difference between the oil going in/out of the reactor. The mass flow measurements are conducted with a Coriolis flow meter for the $MgCl_2$-reactor and two turbine flow meters for the LiCl-reactor. For the temperature measurements of the oil, 4 PT100 temperature sensors are used. The $MgCl_2$-reactor contains one temperature sensor that measures

the salt temperature. Furthermore, the pressure difference between the two reactors and the absolute pressure in each reactor is measured.

2.3 Measurement program

The measurement program focused on determining the power output under various conditions and the cyclic stability of the system . To obtain accurate results, the $MgCl_2$-reactor was kept at constant temperatures during the measurement. To determine the temperature lift that could be obtained in a complete cycle, the power input/output of the $MgCl_2$-reactor was measured both at middle temperature (130ºC) and at high temperature (180ºC and 200ºC) whilst the LiCl-reactor was cycled between 20ºC and 80ºC for $MgCl_2$–reactor at 130ºC and between 20ºC and 130ºC for $MgCl_2$-reactor at 180ºC/200ºC. To determine the cyclic stability, 100+ identical cycles were carried out during which the thermal performance and pressures of the system were monitored.

3. Results and discussion

3.1 Pressure and temperatures

Figure 3.1 shows the pressure-temperature relation for formation and decomposition of $LiCl{\cdot}3NH_3$. The pressure follows the expected, on literature (Bevers et al., 2006; Collins and Cameron, 1928; Bonnefoi, 1901) based line. The shown LT temperature is the average, measured temperature of the thermal oil in/out of the reactor. To obtain a better estimate for the actual **salt** temperature, these values have been corrected using the heat input/output and the estimated thermal conductivity of the heat exchanger, resulting in the *LT (T salt calc)* values. The corrected values show a better correlation with the literature values. For low temperatures, there is a deviation from the literature data. This is due to desorption of ammonia from $MgCl_2{\cdot}6NH_3$ setting the pressure. Various other measurements at other temperatures also show good correlation with results from literature. Figure 3.2 and Figure 3.3 show respectively the pressure and the temperatures during the measurement with the $MgCl_2$-reactor at a constant value of 130ºC while the LiCl-reactor is varied in temperature between 20ºC and 80ºC.

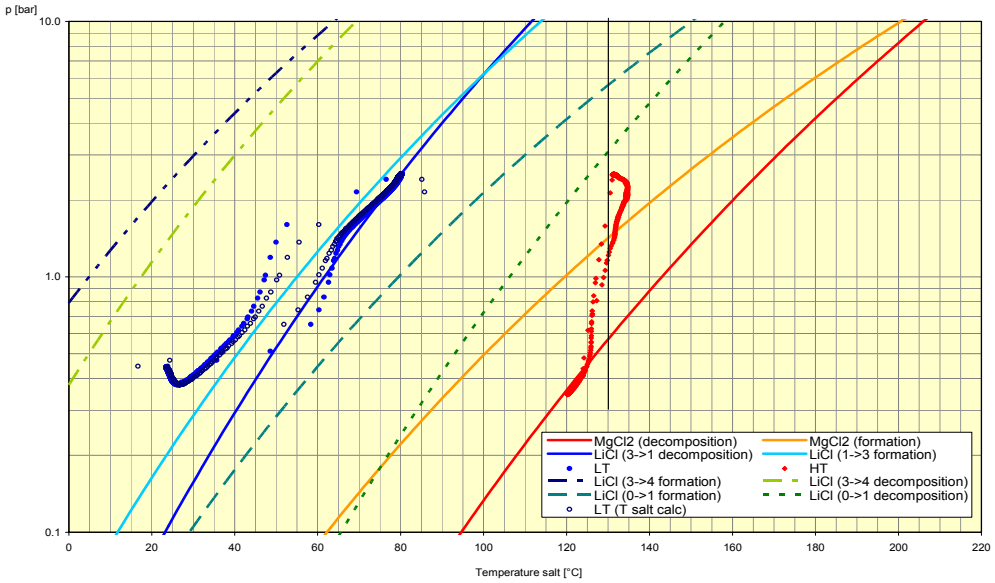

Figure 3.1 *Pressure-temperature correlations for the decomposition/formation of $LiCl{\cdot}3NH_3$ between 20 and 80ºC with the $MgCl_2$-reactor at 130ºC. Lines show on literature based values*

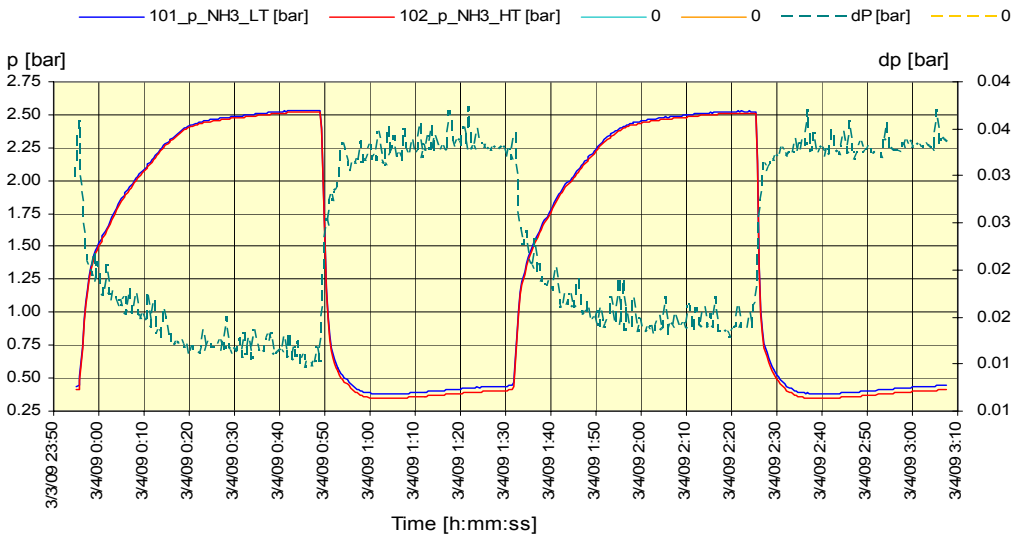

Figure 3.2 *Pressure (left) and pressure-difference (right) as a function of time*

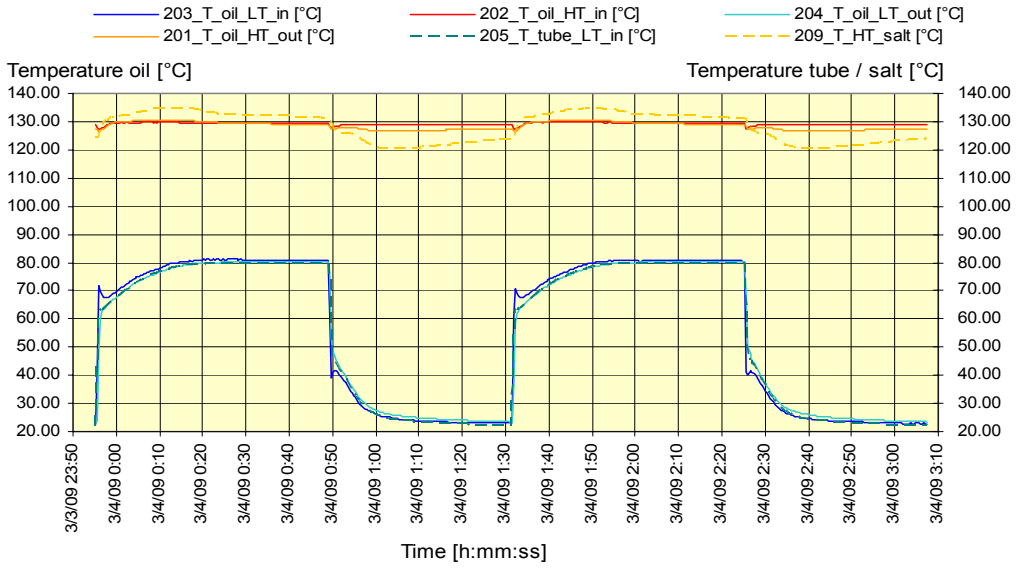

Figure 3.3 *Temperature of thermal oil in/out of LiCl-reactor (LT) and $MgCl_2$-reactor (HT)*

3.2 Power input/output

Figure 3.4 shows the resulting power input/output of the reactors. Because the power input/output of the LT is dominated by the energy required for heating/cooling of the LT reactor between 20ºC and 80ºC, it is of limited value for determining the generated sorption power. The HT reactor remains isothermal during the measurement, so its thermal mass has no direct effect on the measured heat input/output and therefore it is more suitable to determine the amount of generated/consumed heat caused by respectively adsorption and desorption of ammonia. After correcting the heat input/put for the (continuous) heat loss of the reactor to the environment, which has been determined in a separate measurement with no sorption reaction, the total amounts of heat supplied and extracted are during the measurement are nearly identical. The net, peak power input/output is about 600W with an *average* heat input/output of about 300W. These values are considerably lower than expected from model calculations.

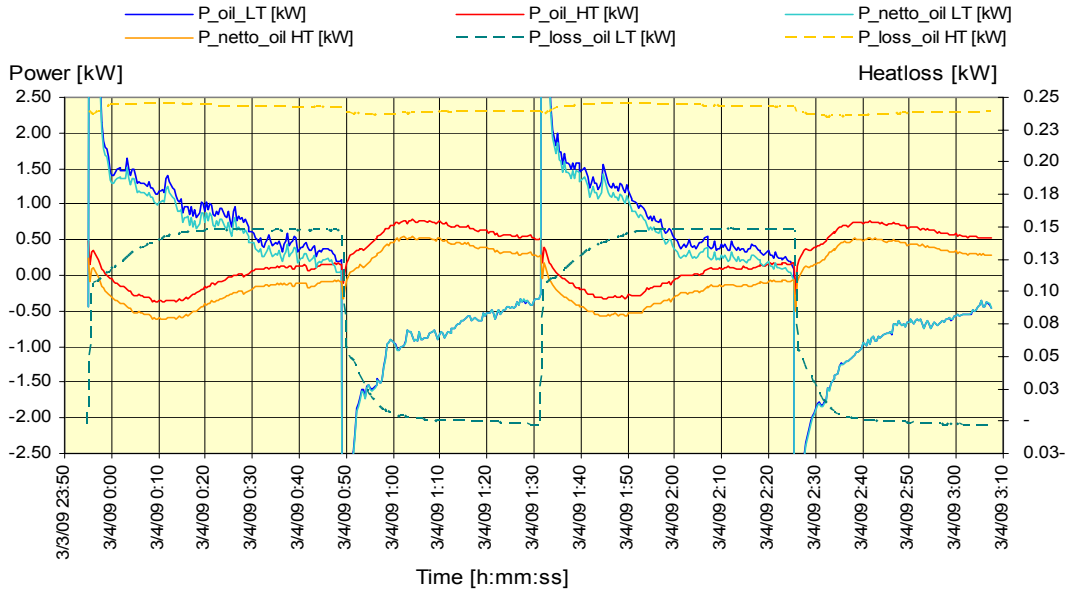

Figure 3.4 *Heat input and output of LiCl-reactor (LT) and $MgCl_2$-reactor (HT), with and without correcting for heat losses*

3.3 Fraction salt used

Using the adsorption enthalpy value measured in HP-DSC measurements (42 kJ/mole NH_3) and the amount of heat generated/consumed, the amount of ammonia adsorbed/desorbed has been calculated. Together with the amount of $MgCl_2$ in the reactor, (the variation in) the fraction $MgCl_2 \cdot 6NH_3$ during the cycle can be calculated. This is shown in Figure 3.5. Note that the starting point of the curve is arbitrary provided the fraction of $MgCl_2 \cdot 6NH_3$ remains between 0% and 100% at any point. Figure 3.5 shows that about 40% of the $MgCl_2 \cdot 2NH_3$ adsorbed ammonia to form $MgCl_2 \cdot 6NH_3$ per adsorption cycle. From Figure 3.4 is can be observed that at the moment of switching between adsorption and desorption, there is still a significant amount of power produced, indicating that the sorption reaction was not finished at the end of the cycle. Thus by increasing the cycle times, the fraction of salt used in the reaction can be increased.

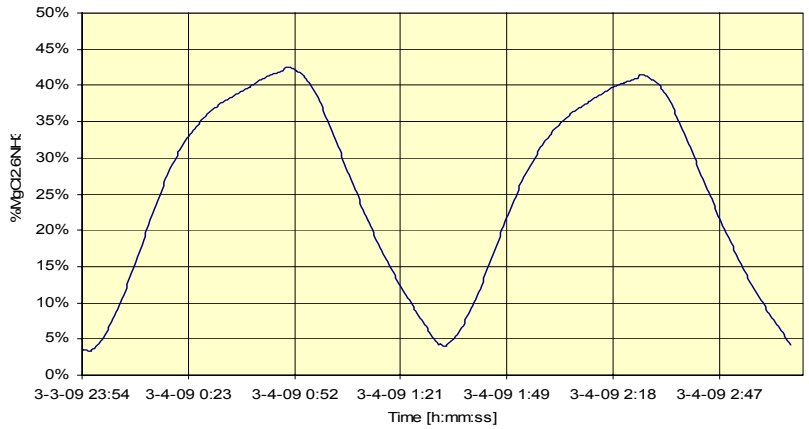

Figure 3.5 *The estimated fraction of $MgCl_2$ in the reactor as $MgCl_2 \cdot 6NH_3$ as a function of time*

3.4 Prototype limitations

Based on previous results it is clear that a cycling time of nearly 1 hour is insufficient to finish the sorption reaction and to use the entire amount of available salt. To determine the rate-limiting factor, two probable causes were considered: limited heat transfer and limited kinetics. It has been assumed that heat transfer limitations will show a proportional correlation between produced heat and the temperature gradient over the reaction bed. To determine the temperature gradient, it is assumed kinetics is fast and therefore the measured pressure equals the equilibrium pressure on the salt. Using the entropy and enthalpy data for the sorption reaction, the salt temperature is calculated. ΔT is the difference between the salt temperature and the average temperature of the thermal oil. For kinetics limitations, heat transfer is assumed fast and the reaction rate assumed proportional with pressure gradient, which is calculated as the difference between the measured pressure and the equilibrium pressure at average thermal oil temperature. Figure 3.6 shows the relation between ΔP, ΔT and the power consumption during regeneration of $MgCl_2$(6-2)NH_3. From the figure and the estimated linear fit, it can be observed that the correlation between temperature difference and power seems to yield an almost zero power consumption when there is no temperature difference. For the pressure difference, also a linear correlation can be observed. However, there is a large offset in pressure difference at zero power consumption indicating that whilst still driving power (ΔP) remains, no sorption occurs. This might indicate regeneration of MgCl2(6-2)NH_3 is limited by heat transfer rather than kinetics. Based on the found correlation between ΔT and power consumption, the thermal conductivity of the metal foam with salt matrix has been estimated, yielding a value of 0.5 W/mK, which seems significantly smaller than literature values. Further examination of the data and additional experiments must yield more information on this topic.

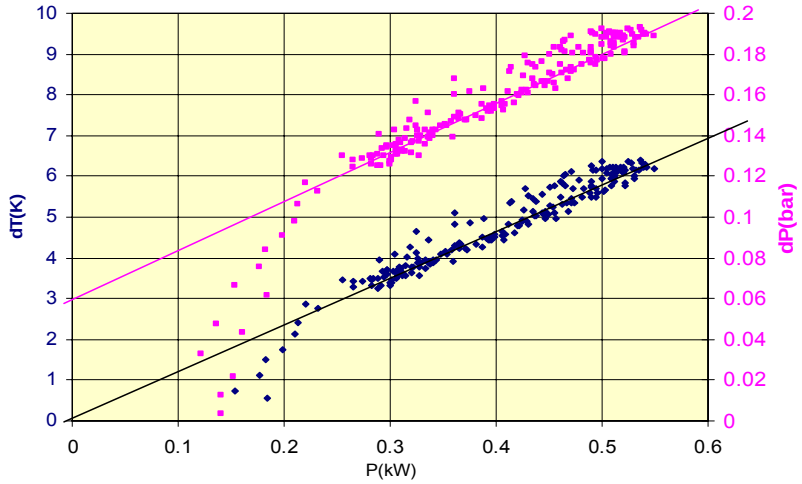

Figure 3.6 *Power consumption during regeneration HT versus temperature difference (left axis) and pressure difference (right axis)*

3.5 Temperature lift

Similar measurements were conducted with the $MgCl_2$-reactor at 180ºC and 200ºC whilst LiCl was cycling between 20ºC and 130ºC. From the results of these and previous measurements, a cycle with a temperature lift from 130ºC to 180ºC/200ºC, i.e. a lift of 50ºC/70ºC, is possible. When calculating the overall coefficient of performance of the system, defined as the net heat output (after subtracting heat required to warm up the $MgCl_2$-reactor) at high temperature divided by the net heat input at middle temperature, yields, due to large amounts of thermal mass (35 kJ/K and 65 kJ/K for $MgCl_2$ and LiCl-reactor respectively), a value close to zero.

3.6 Cyclic stability

Figure 3.7 shows the temperature difference between the oil flow temperature in/out of the $MgCl_2$-reactor for the start and the end of the 100+ cycles measurement. The heat input/output is proportional to this temperature difference and because the figure shows the patterns are similar throughout the entire measurement, it can be concluded that heat production/consumption is similar for the throughout the measurement and thus the system has a stable performance for at least 100+cycles.

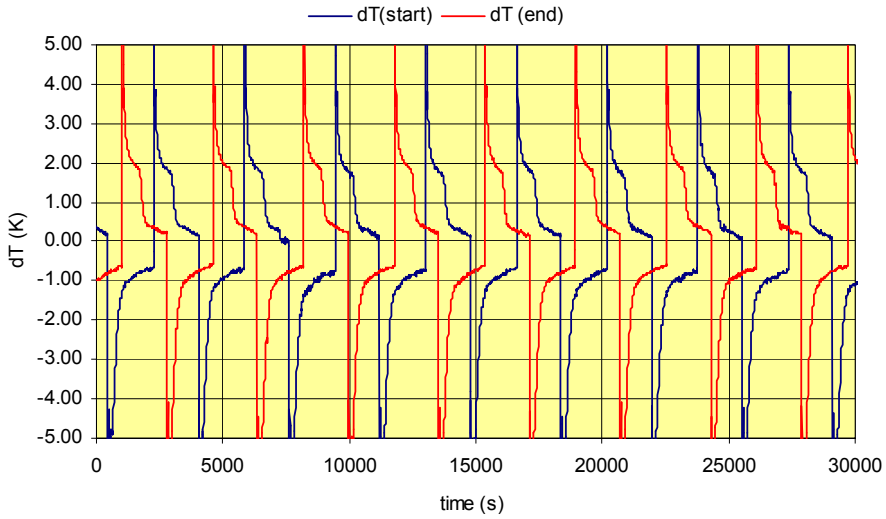

Figure 3.7 *Temperature difference between flow in/out of the $MgCl_2$-reactor at the beginning (blue) and end (red) of 100+ cycles under same temperature conditions*

4. Conclusions

The measurements show that a cycle with a resulting temperature lift of 50ºC and even 70ºC is achievable and power input and output has been measured under all conditions of such a cycle. The regeneration of $MgCl_2$ (6-2)NH_3 seems limited by heat transfer. The system delivers a stable performance for more than 100 cycles.

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