# Design of a Hybrid Adsorption Compression System: Experimental Results and Model Calculations

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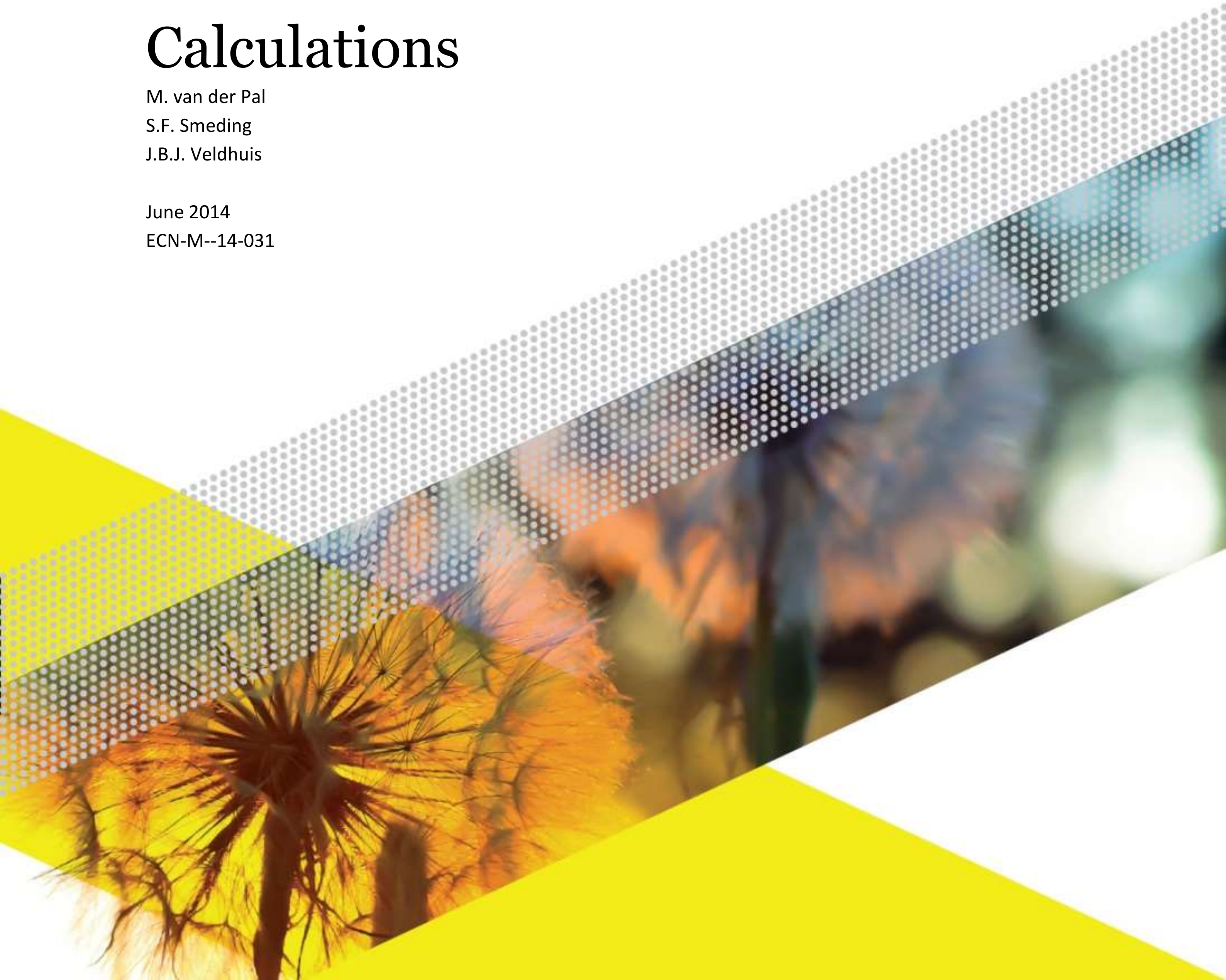

# DESIGN OF A HYBRID ADSORPTION COMPRESSION SYSTEM: EXPERIMENTAL RESULTS AND MODEL CALCULATIONS

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**ABSTRACT**
Hybrid adsorption compression heat pump cycles can be applied to upgrade waste heat to process heat temperatures. Model calculations show a power density of 25 kW $m^{-3}$ can be achieved with a COP on heat of 0.3. By optimizing reactor dimensions, cycle times and by introducing heat and mass recovery options, it is expected this performance can be further improved. The model calculations show good correlation with measured performance at component level but further research is required to improve the model description.

**Key words: adsorption, compression, ammonia**

## 1 INTRODUCTION

Figure 1 shows significant amounts of waste heat are available in the range from 70 to 100°C in the Dutch process industry. For upgrading this waste heat to useful process heat temperatures with a temperature lift of at least 50°C, the options are limited: mechanically driven compression heat pumps – if at all available – no longer provide primary energy savings for such temperature lifts whereas heat-driven heat transformer system cannot achieve such a temperature lift for given waste heat temperatures in one stage-operation. By combining the sorption heat transformer cycle with a mechanically-driven compression, a hybrid cycle is created that can upgrade waste heat between 70°C and 100°C with temperature lifts exceeding 50°C and still provide primary energy savings. Earlier studies (van der Pal et al., 2013) have shown such a hybrid adsorption compression system based on ammonia-salt adsorption can be both technical as well as economically feasible.

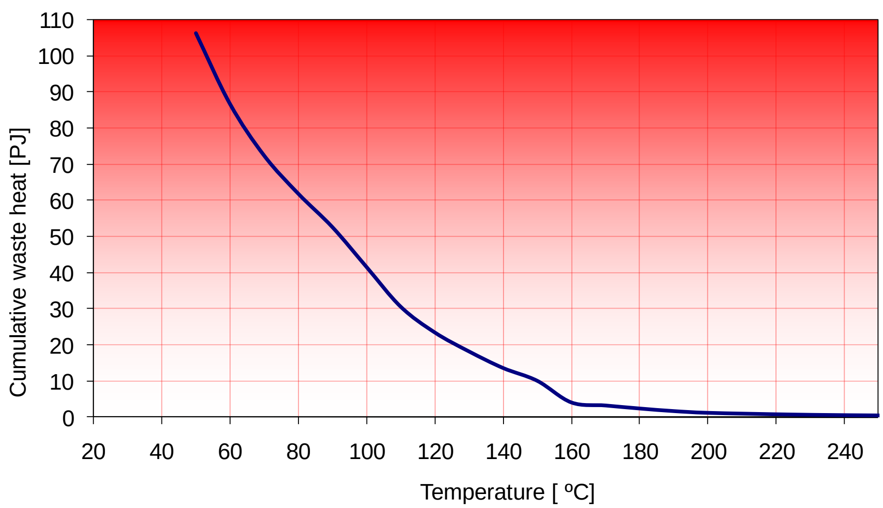


**Figure 1: Amount of waste heat actively disposed in the Dutch refinery and chemical industry as a function of the waste heat temperature.**

This paper describes a transient 2D-model to determine the performance of this hybrid cycle. The model assumptions and input parameters, especially regarding sorbent behavior, have been compared to measurements at component level.

## 2 METHOD

### The hybrid cycle

The thermodynamic cycle is a so-called heat pump type II cycle allowing to upgrade middle temperature waste heat to process heat (discharge phase). Regeneration of the high temperature sorbent is achieved by desorption of the high temperature sorbent at the middle temperature heat whilst keeping the low temperature sorbent at ambient temperature.
In the cycle shown in Figure 2. The compressor is placed in the discharge phase to increase the pressure during discharge and allowing higher pressure on the high temperature sorbent, thereby creating higher process temperatures. Placement of the compressor in the discharge phase is favored over regeneration phase due to the fact that the pressure in this phase is higher and therefore smaller volume flows are required thus smaller and less expensive compressors can be used, and because the work of the compressor on the sorbate yields additional heat at process temperature rather than reducing waste heat demand when the compressor is used in the regeneration phase.
Previous studies (van der Pal et al., 2011) have shown that this cycle is feasible when based on the sorption reaction between $NH_3$ and $MnCl_2$ for the high temperature reaction and the reaction between $NH_3$ and $CaCl_2$ in the low temperature reactor according to the following reversible reactions:

HT salt: $MnCl_2 \cdot 2NH_3 + 4\ NH_3 \leftrightarrow MnCl_2 \cdot 6NH_3$
LT salt: $CaCl_2 \cdot 2NH_3 + 2\ NH_3 \leftrightarrow CaCl_2 \cdot 4NH_3 + 4\ NH_3 \leftrightarrow CaCl_2 \cdot 8NH_3$

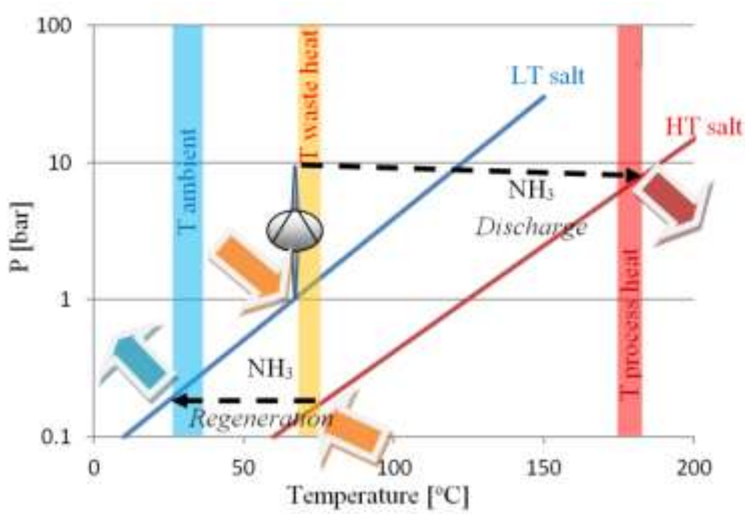


**Figure 2: Schematic representation of the cycle of the hybrid heat pump type II configuration**

### Sorbent reactor design

The reactor geometry that has been examined in this paper is based on the shell-n-tube heat exchanger design. The sorbent is placed inside the tube whereas the heat transporting medium (oil, water or steam) is on the outside of the tube. Such a configuration is schematically shown in Figure 3. The sorbent is immobilized inside the tube using a carrier material (ENG).

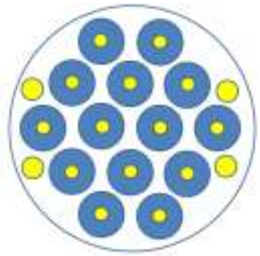

**Figure 3: Schematic representation of lab scale shell-n-tube type reactor with blue the sorbent material and in yellow the open gas volume – allowing the sorbate to flow through the tubes and the white represents the heat transferring medium.**

## Model description

The model is a 2D-transient Matlab model developed at ECN for calculating system performance of sorption system. To reduce calculating time, the reactor geometry has been simplified to a single tube configuration. The dimensions of the tube are adjusted to match the mass of sorbent material and heat transferring medium in the reactor. A radial symmetry has been used with nodes in radial and axial direction.

Figure 4 shows schematically the grid of the model. It contains a primary, one-dimensional grid for the heat transferring medium (e.g. thermal oil). From the difference in enthalpy of the medium leaving and entering this grid the thermal power of the reactor is calculated. The heat can be transferred between the primary and the secondary grid. The secondary grid represents the sorbent material and is two dimensional. It allows to model the conductive transfer of heat through the sorbent and calculates the heat uptake and release due to desorption and adsorption of ammonia by the sorbent. The rate of which the ammonia is released or consumed depends on the local ammonia pressure. This is calculated in a tertiary grid which has an identical spatial distribution as the secondary grid. This grid determines the amount of ammonia resulting from pressure-driven mass flow and reaction-driven uptake/release of ammonia by the sorbent. A quaternary grid connects the ammonia in the tertiary grid to the inner tube of free gas volume and allows ammonia to flow into and out of the reactor.

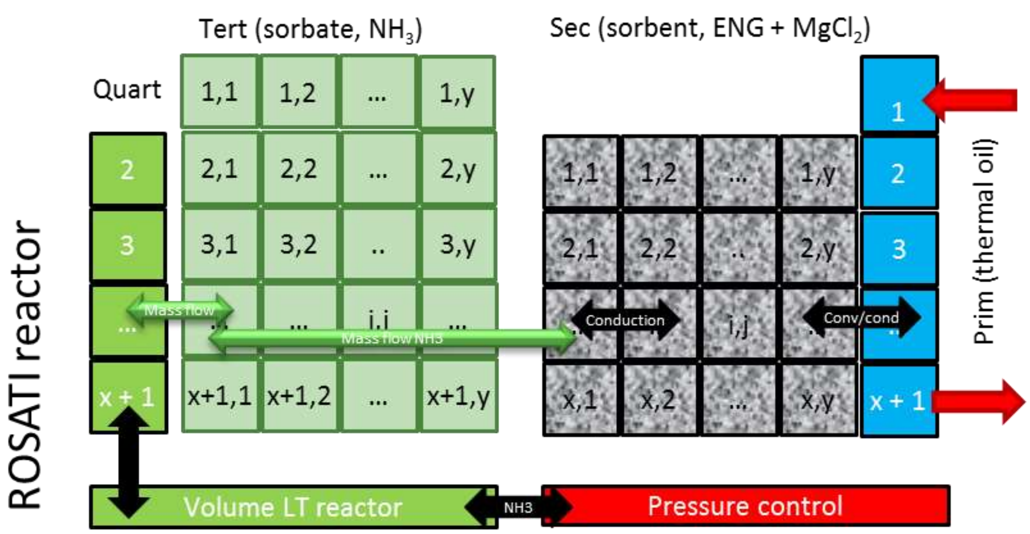


**Figure 4: Definition of the calculation grid of the SOSYMO model.**

For both the LT and HT reactor such a grid is created, each with their own specific properties. A pressure ratio between the two reactors is applied to mimic the effect of a compressor. For simplicity reasons, this ratio is currently a fixed number and only depending on the state of the reactor (discharge or regeneration). More dynamic compressor behavior will be added at a later stage of the model development.

All the calculation grids are coupled to each other using heat and mass balances and heat and mass transfer relations. The heat transfer rate is calculated using the temperature difference, the area and the heat transfer resistance (convection and conduction). Comparable, the mass transfer rate will be calculated using the difference in actual pressure en equilibrium pressure, amount of sorbent and a reactivity factor. The van 't Hoff equation is used to determine the equilibrium pressure from the sorbent temperature and the reaction enthalpy and entropy:

$$P_{eq} = P_0\, e^{\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right)}$$

where:

$P_{eq}$ equilibrium pressure (bar);
$P_0$ reference pressure (bar);
$\Delta S$ entropy (J mol$^{-1}$ K$^{-1}$);
$\Delta H$ enthalpy (J mol$^{-1}$);
$R$ gas constant (8.31 mol J$^{-1}$);
$T$ sorbent temperature (K).

**Model input parameters**

Table 1 shows the main input parameters used to determine the performance of an estimated 1 MW hybrid heat pump system. Such a system consists of two pairs of reactor sets. Each set contains one LT-reactor and one HT-reactor.

The model calculation is conducted for upgrading 100°C waste heat to 150°C process heat with a sink to ambient at 30$^o$C.

**Table 1: Main input parameters for model calculations**

| parameter | unit | LT salt | HT salt |
|---|---|---|---|
| sorbent | | $CaCl_2$ | $MnCl_2$ |
| sorbate | | $NH_3$ | |
| composite material | | ENG | ENG |
| total tube length | m | 4200 | 4200 |
| diameter sorbent (inner/outer) | mm | 8 / 22 | 14 / 22 |
| sorbent mass | kg reactor$^{-1}$ | 374 | 427 |
| gas volume | m$^3$ | 1 | 1 |
| reactivity factor | $kg_{sorbate} kg_{salt}^{-1} s^{-1} Pa^{-1}$ | $2.5 \cdot 10^{-7}$ | $2.5 \cdot 10^{-7}$ |
| number of elements (radial/length) | | 5 / 3 | 5 / 3 |
| convective heat transfer steam | W m$^{-2}$ K$^{-1}$ | 3000 | 3000 |
| temperature (regeneration/discharge) | °C | 30 / 100 | 100 / 150 |
| compressor pressure ratio (regeneration/discharge) | | 1 / 3 | |
| cycle time (regeneration/discharge) | seconds | 900 / 900 | |

**Model verification**

The model has also been verified with measured data. This data is collected using a setup that has been developed at ECN. This setup has been developed to determine the performance of sorption systems at reactor component level, which is very similar to the model, i.e. a tube containing the sorbent material (see Figure 5). This setup allows accurate control of ammonia pressure and the temperature of the heat transferring fluid (i.e. thermal oil). Typically the measurements are isothermal with regular pressure changes or isobaric measurements with temperature changes. The measured data contains the set and measured pressure, the ammonia mass flows in/out of the setup and various temperatures such as the oil temperature in/out and the sorbent temperature(s).

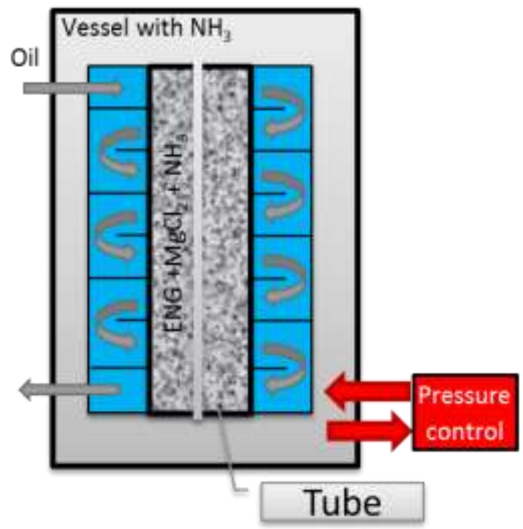


**Figure 5: Schematic view of experimental setup**

## 3 RESULTS MODEL CALCULATIONS

Figure 6 shows the performance of a hybrid heat pump system based on model calculations. The sorbent temperature, the ammonia pressure in the reactor and the amount of ammonia sorbed – expressed as mole fraction of the salt – is given as a function of time. In total three complete heat pump cycles are shown starting with the regeneration phase (t = 0 to 15 minutes). The first cycle is clearly an initial cycle to get to a steady-state condition as the amount of sorbed ammonia has to set which accordingly affects temperature and pressure development.

The following two cycles are much more similar in terms of temperature, pressure and sorbed ammonia. These two cycles have been used to determine overall cycle performance such as power density and COP - where COP is defined as nett useful heat output divided by nett waste heat input. These results can be found in Table 2. The useful heat output per reactor peaks at 1250 kW with an average of 472 during the discharge phase. The resulting overall system performance in terms of power density is 25 kW $m^{-3}$. The waste heat input is 1590 kW, yielding an overall system performance in terms of COP of 0.30.

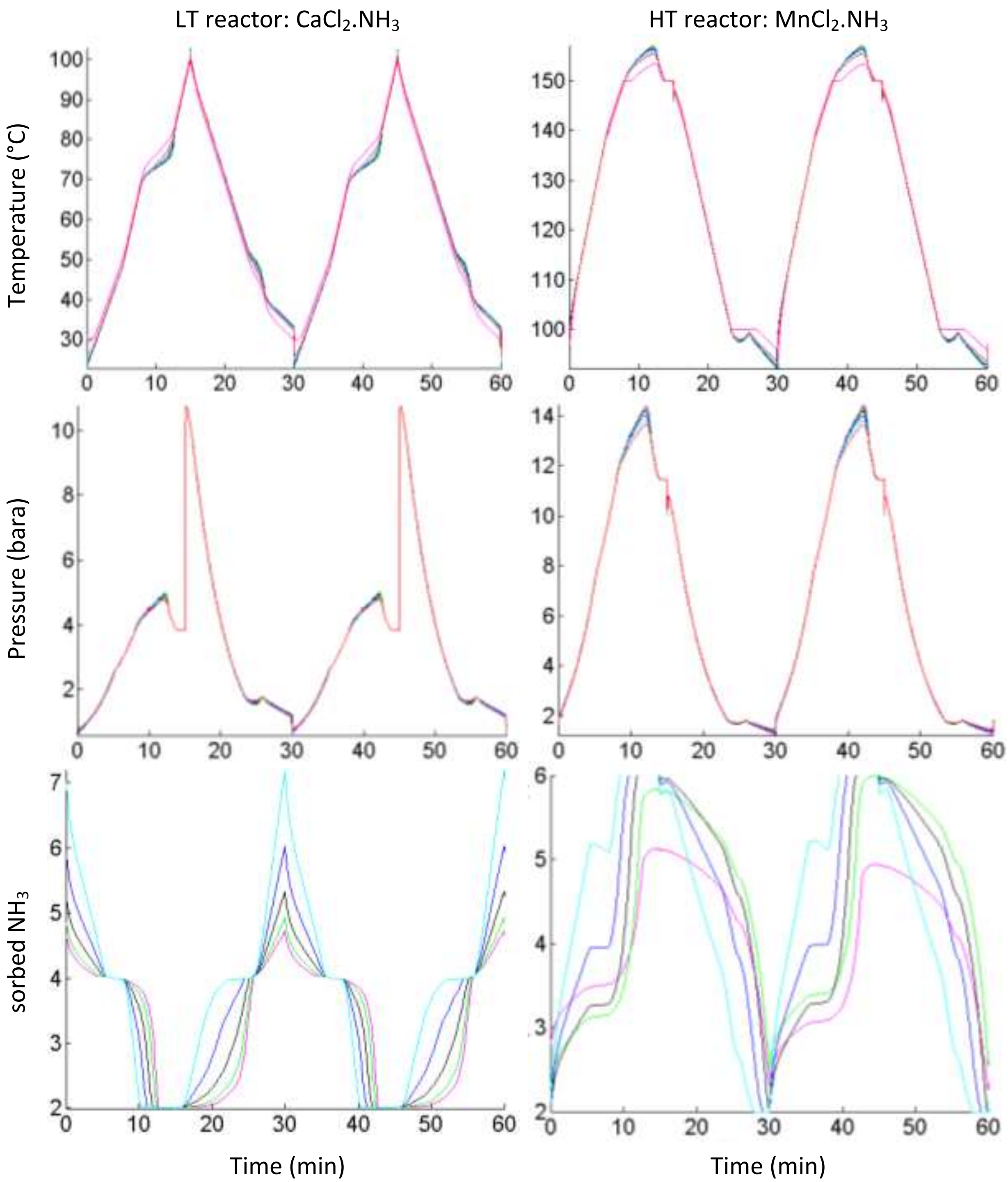


**Figure 6: Model calculations of sorbent temperature, pressure and amount of $NH_3$ sorbed as a function of time for a system with 1 MW heat output**

**Tabel 2: Main model results**

| parameter | unit | value |
|---|---|---|
| reactors | | 4 |
| average power input waste heat | kW per reactor | 1590 |
| useful heat out at process temperature<br>- average power<br>- maximum power | <br>kW per reactor<br>kW per reactor | <br>472<br>1250 |
| period at maximum heat output | seconds | 300 |
| $COP_{heat}$ | heat out/heat in | 0.30 |
| power density | kW $m^{-3}$ | 25 |

## 4 MODEL COMPARED WITH MEASUREMENTS

Figure 7 shows the measured temperature of thermal oil and the measured and model calculated sorbent temperature as a function of time for five discharge and regeneration cycles. It can be observed that the measured sorbent temperature during discharge (high temperature) is 6$^{o}$C lower than the calculated value but the temperatures do follow a similar pattern during the cycle. During the regeneration phase, both temperatures are initially very similar but the measured temperature returns to oil temperature before the end of the cycle whereas the calculated value remains close to the equilibrium temperature. Figure 8 shows the measured and model calculated mass flows as a function of time. The measured mass flow is about 25% smaller than the calculated value during the discharge phase. During the regeneration phase this difference is considerably larger. This is due to the difficulties the setup has in measuring ammonia mass flow at low(er) pressures and should be ignored. Considering the results of both figures, it seems likely that the model overestimated the amount of ammonia sorbed by about 25%. Various explanations can be given, such as inactive sorption sites, pressure-gradients in the sorbent material or uneven sorbent distribution. Nevertheless, further investigation is required to confirm the real cause and further adjust model to describe the occurring processes.

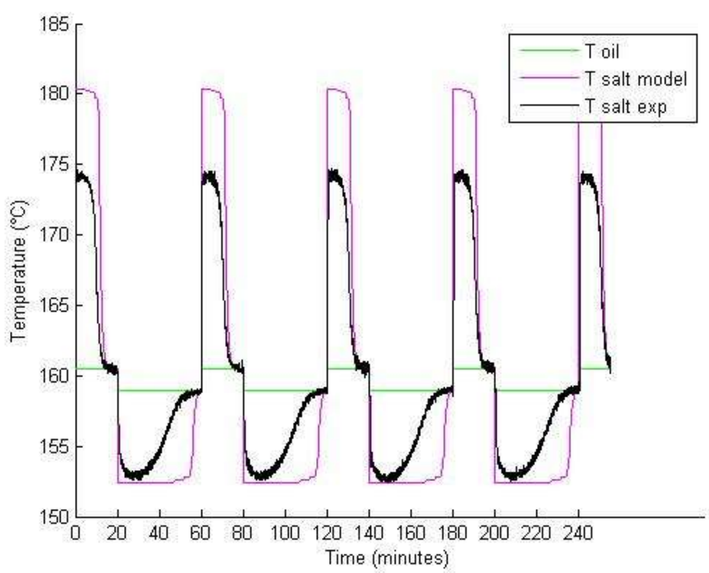


**Figure 7: The relation between temperature of thermal oil (measured = green) and salt (measured = black, calculated = pink) as a function of time.**

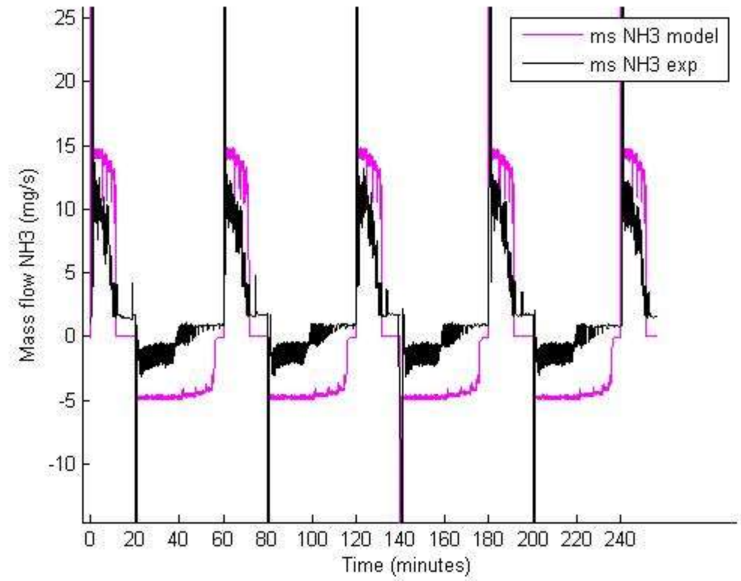


**Figure 8: The measured (black) and calculated (pink) mass flow of $NH_3$ as a function of time.**

## 5 DISCUSSION AND CONCLUSIONS

The transient 2D-model shows a power density of 25 kW $m^{-3}$ and a $COP_{heat}$ of 0.30 for a hybrid adsorption compression heat pump cycle providing 1 MW useful heat output. The calculated performance of the hybrid heat pump system is very reasonable, especially when considering the input parameters have not been optimized for maximum COP and/or power density. By adjusting reactor dimensions, cycle times and by including heat and mass recovery options, it can be expected that the performance can be improved considerably.

Comparison of the model calculations with experimental data shows a good correlation. It seems that the model overestimate of the amount of ammonia sorbed in the measurements by 25%. It is not yet clear whether this is due to experimental errors, such as salt distribution, mass flow measurement deviations, or due to incorrect model assumptions. The latter include the assumed full availability of sorbent sites, the assumed pressure-temperature correlation of the sorbent and the assumed negligible pressure gradients. These aspects will be investigated in future projects.

## REFERENCES

van der Pal, M., A. Wemmers, S. Smeding, K. van den Heuvel (2011): *Study on the performance of hybrid adsorption-compression type II heat pumps based on ammonia salt adsorption*. International Journal of Low-Carbon Technologies, 6[3], pp. 207-211, 2011.

van der Pal, Michel, Anton Wemmers, Simon Smeding, Robert de Boer (2013): *Technical and economical feasibility of the hybrid adsorption compression heat pump concept for industrial applications*. Applied Thermal Engineering, 61[2], pp. 837-840, 2013.

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