

# Performance of ENG-CaCl<sub>2</sub> reactor for application in thermochemical heat pumps

Michel van der Pal<sup>a,b</sup>, Robert E. Critoph<sup>b</sup>

<sup>a</sup> Energy Research Centre of the Netherlands (ECN), Westerduinweg 3, Petten 1755 LE, The Netherlands

<sup>b</sup> University of Warwick, Library Road, Coventry CV4 7AL, United Kingdom

## Abstract

Thermochemical reactions, such as calcium chloride reacting with ammonia to form calcium chloride complexes, are attractive for application in heat pumps as they produce more heat per kg adsorbed sorbate but also adsorb a considerable higher amount of sorbate per kg of sorbent, compared to adsorbents such as zeolites. These benefits, however, come with together with a number of challenges. Firstly, the salts have poor thermal conductivity so the path from heat exchanger to the sorbent must be limited in order to allow for short cycling times and therefore high power density. Secondly, the salts typically swell and shrink upon (de)sorption, thereby easily losing their contact with the heat exchanger. To overcome these two problems, the salts are often placed in a matrix, such as expanded graphite or zeolites.

This paper shows the performance of a reactor containing approximately 1 kg of CaCl<sub>2</sub> placed in a 1 kg ENG matrix. Its performance in terms of adsorption/desorption rates, heat input and output as a function of temperature and pressure gradients and under typical heat pump and transformer conditions is shown and compared with model calculations. The parameters used in the model calculations have been obtained from literature or independently measured using apparatus such as Rubotherm microbalance and a large temperature jump setup. The results show that material properties measured on small samples do not easily yield a proper description of the sorbent performance on kW-scale reactors. Some suggestions are made to improve future model description and experiments.

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## 1. Introduction

Thermally driven heat pumps and transformers can contribute significantly to reducing our carbon footprint. Various types of thermally driven heat pumps and transformers can be found in literature, each with their own benefits and challenges. In this paper we focus on the development of thermally driven system using thermochemical reactions. These are reactions between a sorbate (e.g. ammonia) and a sorbent (e.g. CaCl<sub>2</sub>) in which heat is released when combined and heat is extracted when separated.

Although considerable amount of research has been done, little or no commercial thermochemical systems are currently available. The main challenge is to achieve stable performance with sufficient high power density to allow for reasonably compact and affordable systems. In the past, ECN has built several prototypes using various heat exchanger designs but each had their own problems preventing further development to a commercial product. After these setbacks, it was decided to develop a unit in which reactor elements could be tested before building an entire reactor and system.

The work presented in this paper takes one of the concepts that was successfully tested in the aforementioned setup and placed it inside a 10kW scale reactor for testing. It describes the performance of a reactor based on CaCl<sub>2</sub> impregnated in ENG. The measurements are subsequently compared to model calculations using thermal conductivity and reaction kinetics data from separate measurements or literature sources.

## 2. Previous work

Fig. 1 shows earlier prototypes of thermochemical heat transformers developed at ECN. The first prototype (left) contained finned tube heat exchanger with a packed bed of salt. Likely due to swelling of the salt the ammonia could not be cycled at sufficient rate. A second prototype was built (middle) where salt was deposited in a metal-foam placed on a sandwich plate through which thermal oil was flowing. This system had two major problems: the first one was the enormous thermal mass of the system, both in the sandwich plates and the flanges/domes and secondly the ammonia uptake was (too) slow, possibly because of too high loading of salts in the metal foam.

A third prototype (right) was developed. This time thermal mass was reduced, using shell-n-tube type heat exchanger with thermal oil on the tube side and plates with aluminium foam on the shell side.

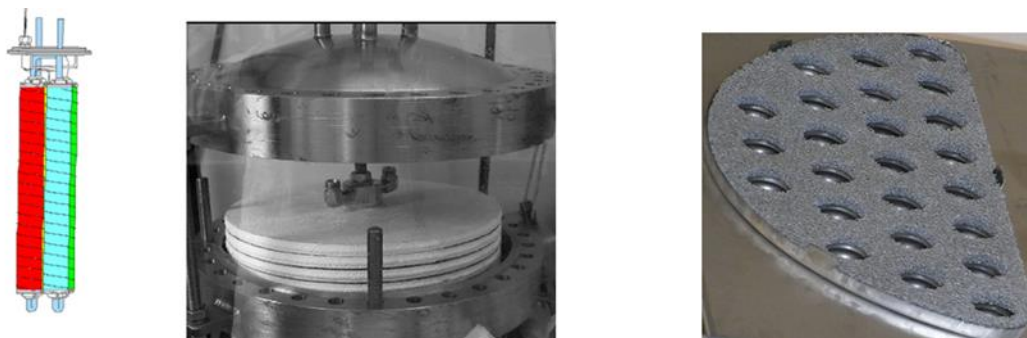


Fig. 1: Earlier thermochemical heat transformer prototypes developed and tested at ECN.

Although the reactors contained about 2.5 and 1.3 kg of salts, LiCl and MgCl<sub>2</sub> respectively, and a volume of several litres, measured power peaked at around 500W. Analysis were unclear about what caused the low power density although recent experiments showed lithium chloride ammonia complex melts at 5 bar ammonia pressure and temperatures above 95°C. This could explain the poor performance as it is the operating conditions of the heat transformer. Also poor thermal heat transfer from the thermal oil to the tubes and fins could have contributed to the poor performance.

In order to allow for more rapid development of heat exchanger types, salt loading methods and cyclic stability, the lab-scale setup has been constructed, see Fig. 2. This setup allows for testing heat exchanger elements rather than having to build entire systems. Results using a similar aluminium foam as used in the previous heat transformer system in combination with calcium chloride showed repeatable results but charging/discharging times still took 30 to 60 minutes, resulting in too low power densities for industrial application.

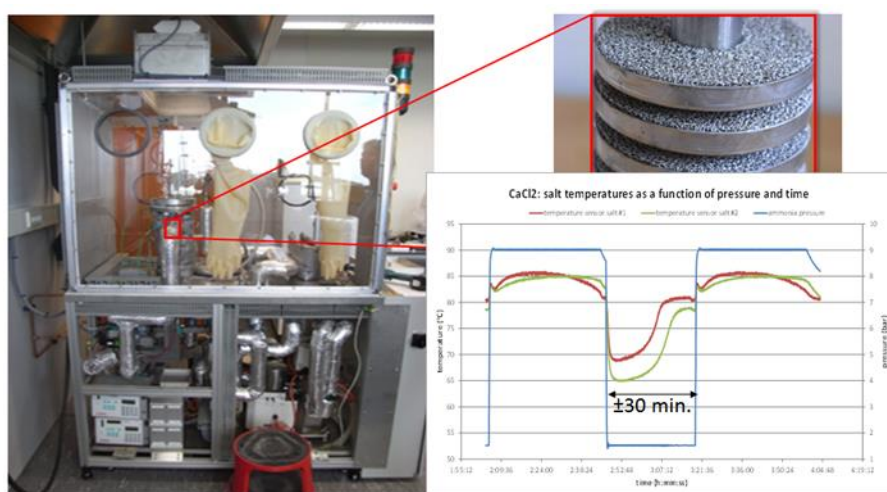


Fig. 2: Lab-scale setup (left), reactor element (top right) and result CaCl<sub>2</sub>(4-8)NH<sub>3</sub> (bottom right).

After these experiments, the concept of a fin containing an aluminium foam with salt was abandoned and replaced by ENG in tube concept with oil/water on the shell side. The results for  $\text{MgCl}_2$  in ENG disks is shown in Fig. 3 similar results are obtained for measurements on  $\text{LiCl}$ ,  $\text{MnCl}_2$ ,  $\text{CaCl}_2$  and  $\text{ZnCl}_2$ . The measurements also showed good cyclic stability for more than 1000 cycles. With half cycle times of less than 600 seconds, application in industrial systems becomes feasible.

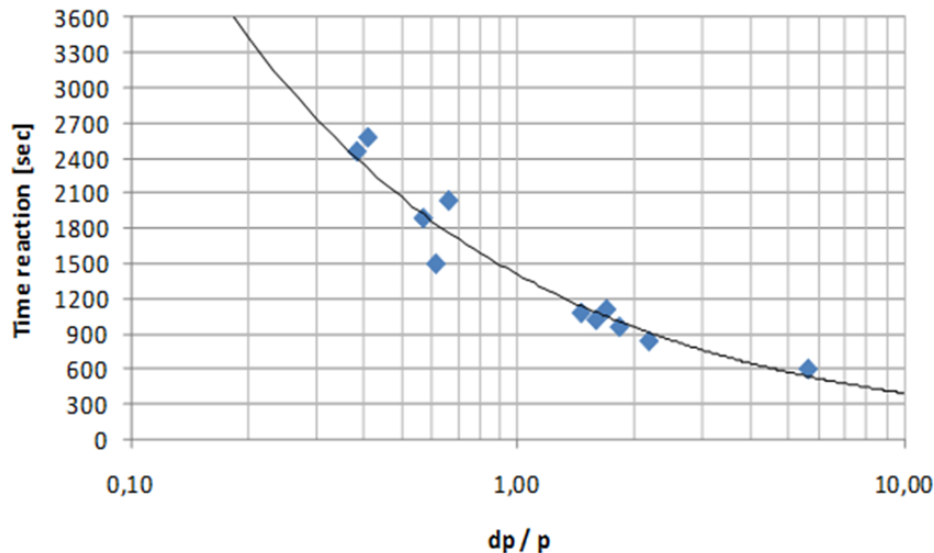


Fig. 3: Lab-scale setup results for reaction time as a function of relative pressure ratio for  $\text{MgCl}_2$  in ENG.

### 3. Experimental setup

At the heart of the experimental setup is a shell-n-tube reactor containing the ENG- $\text{CaCl}_2$  matrix inside of the tubes and a heat transfer fluid on the shell side. The reactor is connected to the so-called ThermXSrig infrastructure that supplies or extract heat as shown in Fig 4. The ammonia is supplied using a shell-n-tube type evaporator and removed using plate heat exchanger type condenser. The reactor, condenser and evaporator can be set a desired temperature using Huber thermostatic baths. The flow of ammonia is controlled by opening the valves between the reactor and the evaporator and condenser. Typically the reactor is varied between two temperatures (and pressures) while the evaporator and condenser are kept at a constant temperature. The latter allows for accurate measurement of heat fluxes to/from the condenser and evaporator. For the equilibrium measurements the connection between the reactor and the evaporator/condenser were closed to maintain the state of the calcium chloride ammonia complex.

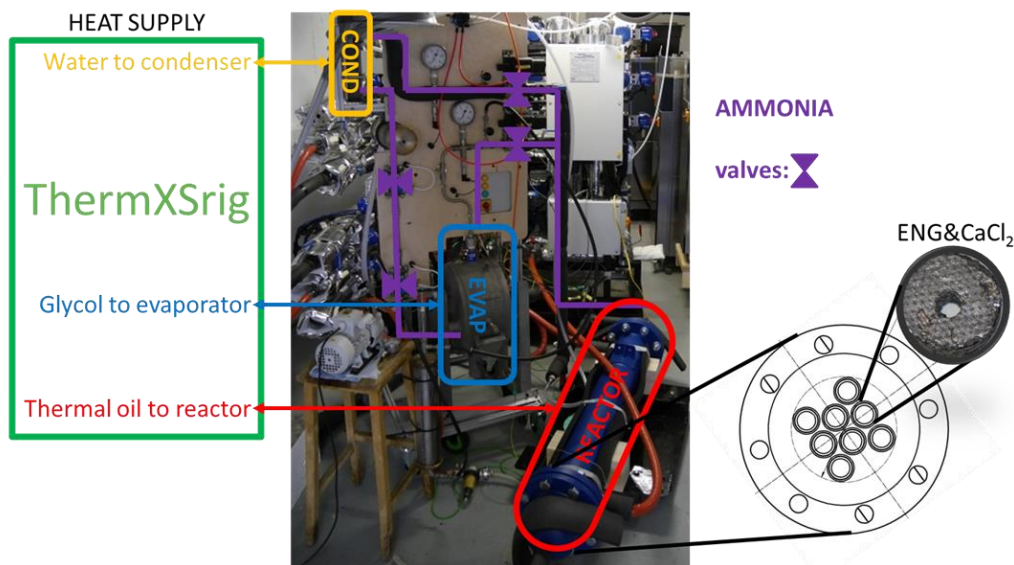


Fig. 4: Reactor filled with ENG- $\text{CaCl}_2$  disks connected to ThermXSrig infrastructure for supplying/extracting heat and ammonia.

The measured parameters include mass flow of the thermal oil, water and glycol, the temperatures of fluid entering and leaving the reactor, evaporator and condenser and the ammonia pressures in these components. Also a temperature sensor has been inserted in the ENG disks to measure the temperature of the salt-ENG composite. The pressure measurement is accurate to 0.5% F.S. and the thermocouples are within 0.1K accurate compared in relation to the reference temperature. Heat flows to/from the different components are calculated using the mass flows, heat capacity and temperatures. Pressure is measured in the reactor and the condenser and evaporator.

## 4. Results

### 4.1 Equilibrium measurements

Fig. 5 shows the result of the measurement of the (quasi) equilibrium between pressure and temperature by increasing the reactor temperature in steps of 10K whilst the connections to evaporator and condenser remained closed. The right graph shows the measured pressure – temperature relation in comparison with the theoretical correlation based on the Claussius-Clapeyron equation with the  $\Delta S$  and  $\Delta H$  data for the reactions as shown in Table 1. As can be seen from the right graph, the measured data correlates very well with the theoretical P-T relation for the  $\text{CaCl}_2(4-8)\text{NH}_3$  reaction. This means hysteresis is negligible as well that the thermocouple placed in the ENG-salt composite yields a representative value for the salt temperature. For the  $\text{CaCl}_2(4-2)\text{NH}_3$  reaction (not shown) a minor deviation ( $<5\text{K}$ ) is found, likely due to (slow) reaction kinetics.

Table 1. Entropy and enthalpy values for  $\text{CaCl}_2(2-4)\text{NH}_3$  and  $\text{CaCl}_2(4-8)\text{NH}_3$  reactions [1]

	$\text{CaCl}_2(2-4)\text{NH}_3$	$\text{CaCl}_2(4-8)\text{NH}_3$
$\Delta H \text{ (J mol}^{-1}\text{)}$	42100	42100
$\Delta S \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$	134.1	139.0

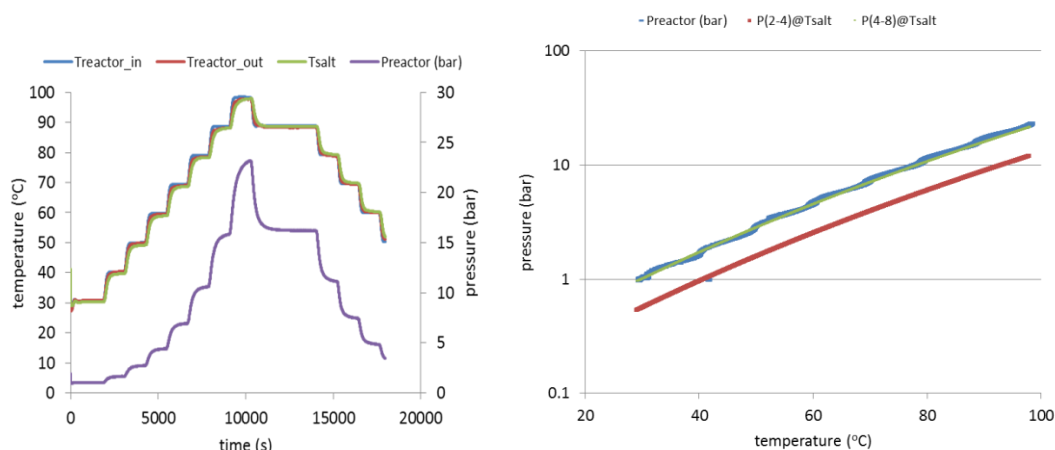


Fig. 5: Left shows the temperature and pressure in the reactor as a function of time, right: P vs T measured and theoretical.

### 4.2 Dynamic measurements

Fig. 6 shows an example of a dynamic measurement of the desorption of ammonia from the  $\text{CaCl}_2$ -ENG composite by heating the reactor from 40°C to 130°C with a condenser temperature of 20°C (9 bar  $\text{NH}_3$ ) and a evaporator temperature of 0°C (4 bar  $\text{NH}_3$ ). The blue line shows the salt temperature, which increases from 40°C to 130°C. The green and red lines show the equilibrium temperatures for respectively the  $\text{CaCl}_2(8-4)\text{NH}_3$  and the  $\text{CaCl}_2(4-2)\text{NH}_3$  reaction based on the pressure in the reactor. The purple line shows the power measured on the condenser ( $Q_{\text{cond}}$ ), calculated from the difference in temperature in/out of the condenser and the flowrate of the water.

A rapid increase in salt temperature can be found between 4500 and 5000 seconds. The salt temperature remains near the temperature associated with equilibrium condition for the desorption reaction of  $\text{CaCl}_2(8-4)\text{NH}_3$  whilst the condenser power shows peak power of 1.6 kW. The salt temperature rises further to about 110°C for another 500 seconds after which the condenser power returns to zero, indicating the desorption reaction has finished. At 7000 seconds the reactor and thereby the salt is cooled down again to start adsorption of ammonia again. The temperature profile and the condenser power both indicate a two-step reaction, suggesting a first desorption step of  $\text{CaCl}_2(8-4)\text{NH}_3$  and a second desorption step of  $\text{CaCl}_2(4-2)\text{NH}_3$ .

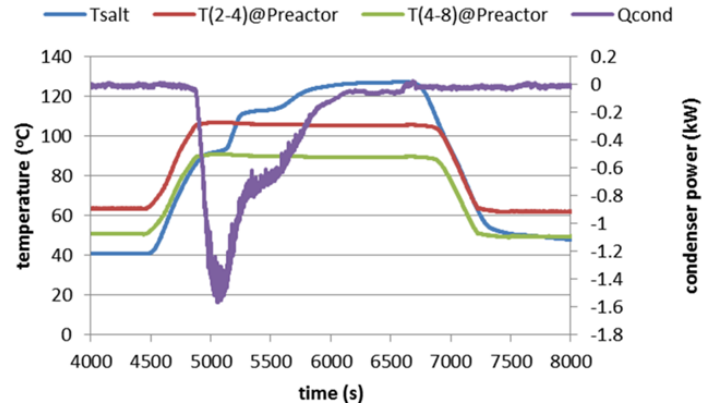


Fig. 6: Dynamic measurement of salt temperature ( $T_{\text{salt}}$ ) and condenser power ( $Q_{\text{cond}}$ ) as a function of time.

#### 4.3 Model calculations

The dynamic measurements as shown in Fig.6 have been modelled using a 1D Matlab model that includes heat transfer resistance from reactor wall to the ENG- $\text{CaCl}_2$  composite, thermal conductivity through the composite and kinetic behaviour of the sorbent. The input parameters are shown in Table 2 and have been obtained from independent measurements or literature sources.

Fig. 7 shows the calculated amount of ammonia desorbed for a range of heat transfer coefficients together with the amount based on measured condenser power. It can be observed that the measured amount of ammonia is about 10% less than the amount that could theoretically be desorbed. It can also be seen that a heat transfer coefficient of  $100 \text{ Wm}^{-2}\text{K}^{-1}$  shows a good correlation with measured data. The temperature profiles from the model calculations have a reasonable correlation with the measured values (left graph of Fig. 8) and a good correlation when a 5-times smaller kinetic rate constant is used for the  $\text{CaCl}_2(4-2)\text{NH}_3$  reaction (right graph of Fig. 9).

Table 2. Main input parameters for the Matlab model calculations

parameter	value	Source
Thermal conductivity ENG	$6 \text{ Wm}^{-1}\text{K}^{-1}$	Data SGL Carbon
Heat transfer coefficient oil to ENG	$50/100/200 \text{ Wm}^{-2}\text{K}^{-1}$	estimated range according to literature
Kinetic rate constant $\text{CaCl}_2(8-4)\text{NH}_3$	$0.04 \text{ s}^{-1}$	[2]
Kinetic rate constant $\text{CaCl}_2(4-2)\text{NH}_3$	$0.04 \text{ s}^{-1}$	[2]

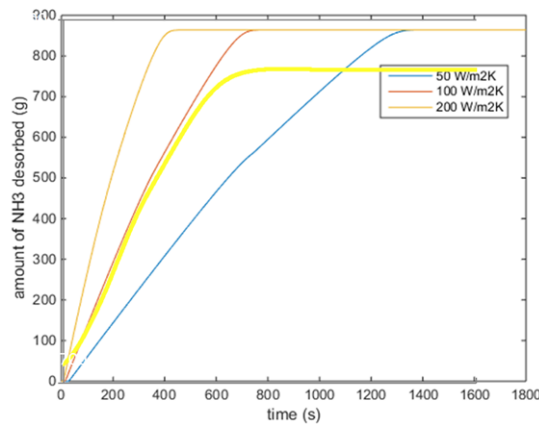


Fig. 7: Amount of ammonia desorbed measured (yellow bold line) and based on model calculations using heat transfer coefficients of respectively 50, 100 and  $200 \text{ Wm}^{-2}\text{K}^{-1}$  as a function of time.



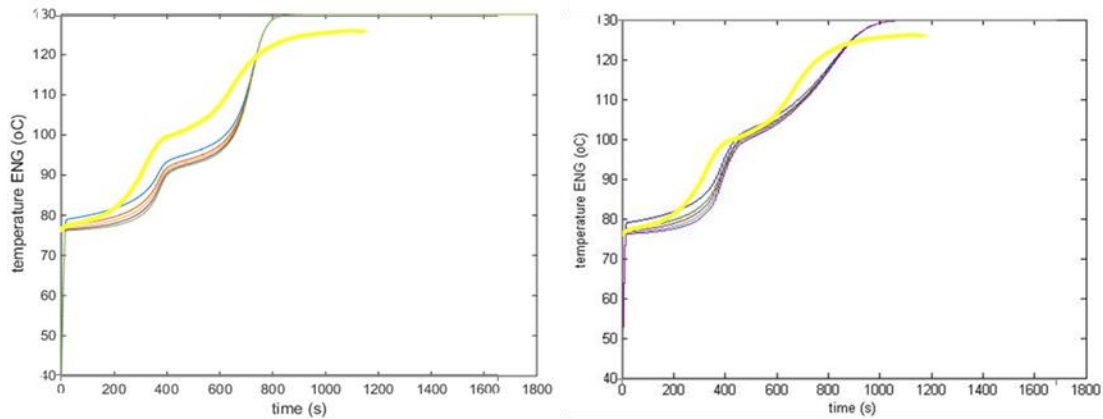


Fig. 8: Model calculations with original (left) and a 5-times reduced (right) reaction kinetics for the  $\text{CaCl}_2(4-2)\text{NH}_3$  reaction and assuming  $100 \text{ Wm}^{-2}\text{K}^{-1}$  heat transfer coefficient for both cases.

## 5. Discussion and conclusions

Results show good correlation between measurements and model calculations. The fit can be improved by applying a lower reaction kinetic constant for the  $\text{CaCl}_2(2-4)\text{NH}_3$  reaction. The reduced reaction rate seems to be confirmed in the equilibrium measurements where a slight difference is found between measured P-T relation and the reported equilibrium line. This is contradicting the large temperature jump measurements conducted on  $\text{CaCl}_2$  by Jegede [2] that showed equal kinetic rate constants for both reactions.

The (de)sorption rates shown in this paper seem to be limited by the heat transfer from the heat transfer fluid (thermal oil) to the ENG- $\text{CaCl}_2$  composite. The value for the thermal contact resistance lies in the lower range of what would be expected for the transfer of thermal oil to a steel tube. However, it cannot be excluded that also heat transfer from the tube to the ENG- $\text{CaCl}_2$  composite is limiting the sorption rates. It is therefore recommended to repeat the experiments presented in this paper using a heat transfer fluid with better thermal conductivity properties. Water would qualify as such a fluid.

## Acknowledgements

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## References

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