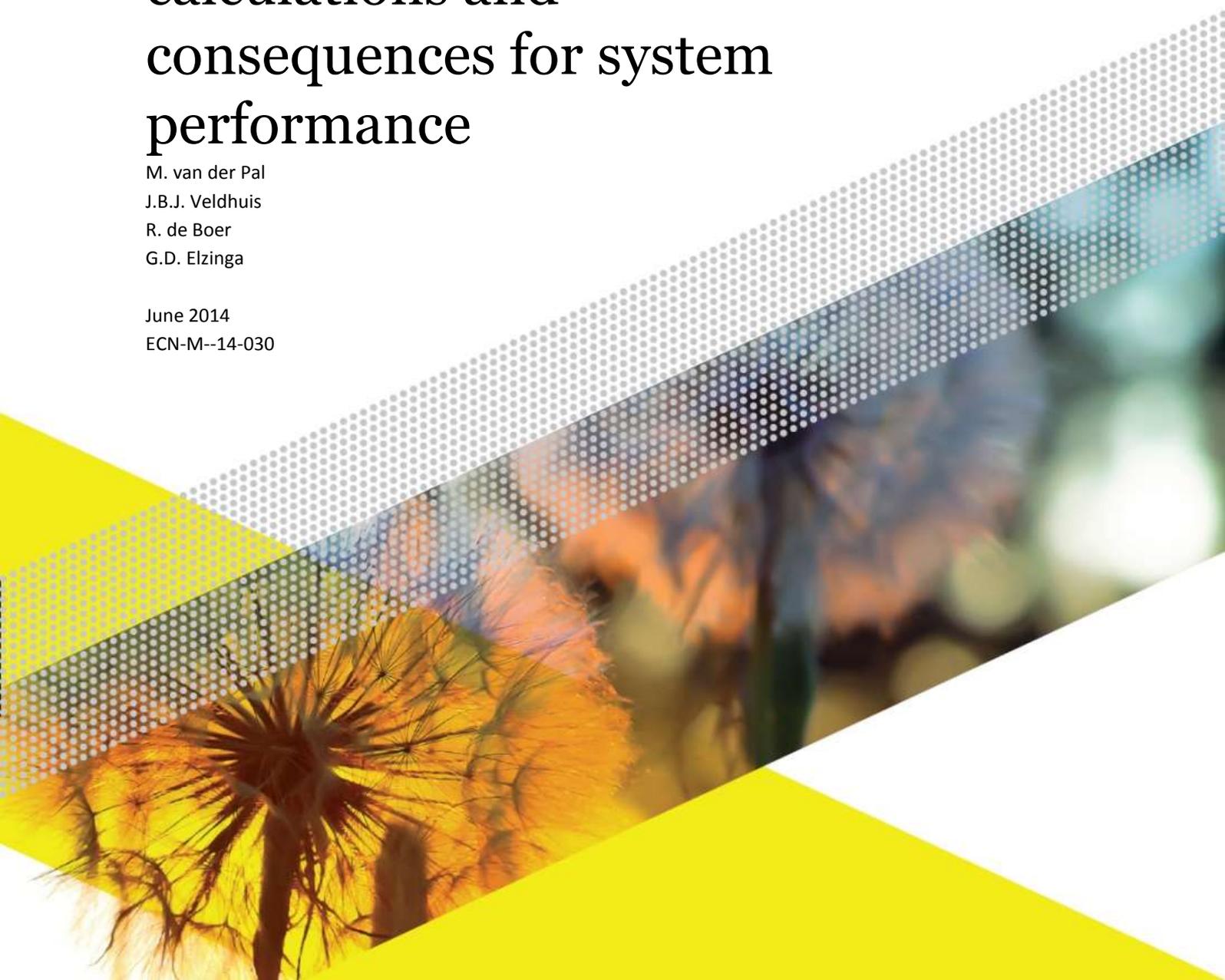


Composite materials for solid sorption heat pumps: measurements, model calculations and consequences for system performance

M. van der Pal
J.B.J. Veldhuis
R. de Boer
G.D. Elzinga

June 2014
ECN-M--14-030



Composite materials for solid sorption heat pumps: measurements, model calculations and consequences for system performance

Michel van der PAL^{1*}, Jakobert VELDHUIS¹, Robert de BOER, Gerard ELZINGA

¹ECN, Energy research Centre of the Netherlands, Thermal Systems Department,
NL-1755 ZG Petten, the Netherlands
Contact Information (+31 88 515 4949, info@ecn.nl)

* Corresponding Author
tel +31 88 515 4837, vanderpal@ecn.nl

ABSTRACT

The performance of adsorption heat pumps is strongly related to the properties of the used sorbents. Not only the pressure – temperature relations that determine the operating window but also the heat and mass transfer properties, which determine cycling time and hence power density, are of great importance. The use of composite materials, such as sorbent with ENG or metal foams, can greatly enhance the heat and mass transfer of sorbent materials. In this paper various heat and mass transfer properties of ammonia salts in a porous composite material are measured and analyzed. Its consequences in terms of cycle time and power density are discussed in the light of the system's design. The determined heat and mass transfer parameters include adsorption and desorption rates of various ammonia-salts under a range of pressure and temperature conditions, the thermal conductivity of composite materials in relation to their state-of-charge and the long-term stability of the composite material related to the number of adsorption-desorption cycles.

1. INTRODUCTION

Industrial waste heat is available at various temperature levels, ranging from 30°C up to 160°C and more. Re-use of waste heat offers the opportunity for significant energy savings in industrial processes. (Neelis, *et al*, 2007, Pehnt *et al* 2011) Several options exist to re-use waste heat. Direct re-use in the process is of course the first option to consider, but when these process pinch principles are fully implemented, other options need to be considered. Direct re-use on site in neighboring processes is to be considered, storage of heat can be applied in situations where heat supply and heat demand is shifted in time. Heat pumps can be applied to upgrade the temperature level of the waste heat towards levels where it can be re-used. Also the transformation of waste heat to electricity by ORC can be considered, and in some situations the transportation of heat to external customers can offer specific benefits.

The application of heat pumps to upgrade waste heat to useful temperature levels can provide a feasible solution for many industrial processes (Spoelstra *et al*, 2002). It can be integrated in a process without the complexity of interconnections and regulatory matters when heat is to be transferred across process borders. Sorption based heat pump technologies are an interesting class of heat pumps for re-use of waste heat, because their primary energy input is thermal energy. Sorption heat pumps are applied frequently for the production of cooling using (waste) heat as driving energy, and sorption heat pumps can also be applied as heat transformers. Heat transformation, also known as heat pump type II, is a thermally driven heat pump that upgrades heat to higher temperature levels, without significant electrical input normally required by mechanical compression. However, the applicable temperature range of application of existing heat transformers is limited to heat delivery up to 150°C (Berntsson *et al*, 1989)



Thermo-chemical heat transformers, using sorption reactions between a solid salt and ammonia can provide process heat at temperatures above 150°C, (Pal, *et al*, 2009) and can be applied for waste heat higher than 100-130°C (Yu *et al*, 2008). The development of a prototype thermochemical heat transformer is one of the ongoing research activities of ECN's thermal systems group. In previous developments the long term stability of the reactive salts were investigated. Although the reactivity remained constant over more than 100 cycles, it was observed that the mechanical stability still needs improvement. The particle sizes of the reactive salt become smaller when the absorption-desorption reaction is repeated. Previous prototype heat transformer systems used consolidated beds of salts. These beds deteriorated over time, resulting in reduced thermal conductivity, and therefore reduced power output and the fine salt particles moved freely through the system.

This paper addresses the development and test of composite materials for application as stable reactive medium in heat transformers. Creating composite materials is an frequently used method to achieve immobilization of reactive species. Various options for creating composite materials are described in literature, varying from combining the salt with expanded natural graphite (ENG) (Wang *et al* 2010, Han *et al* 1996), carbon fibers (Vasiliev *et al*, 2010) or other materials (Hünemörder, 2002) such as metal foams or inorganic clay (Restuccia *et al*, 2005). An additional advantage of a composite material is that it not only enhances material integrity and thereby enduring performance, it also allows to apply the sorbent in new heat exchanger designs, to create better performing and/or cheaper heat exchangers and reactor designs.

From a literature research on composite material options it was decided to focus on the use of carbon or graphite as a stable matrix structure for the reactive slats. The favorable properties of graphite or carbon based supports is their good thermal and chemical stability, their high porosity, leaving much space for salt incorporation and mass transfer of the gaseous reactant. Also the potential high thermal conductivity, the flexibility in shapes of graphite blocks and the low price make it an attractive support material.

The work described in this paper deals with the synthesis of the composite materials, characterization of the reactivity of the composites, the measurement of thermal conductivity of the composites as well as the multi cycle stability tests. The final activity is dedicated to the characterization of the performance of the composite integrated in a sorbent reactor concept.

2. MATERIALS AND METHODS

This section gives a description of the experimental procedures, measurement equipment and methods used to prepare, characterize and test the composite materials for applicability in solid sorption heat pump systems.

2.1 Sorbent Composite preparation

The preparation of a salt-graphite composite materials can be made along different synthesis routes. First exploratory trials were made to obtain a quick analysis of feasible approaches. The composite preparation was options explored were

- dry mixing of salt and ENG powder (SGL, type GFG500, GFG50 and GFG5) and then compressing the mixture.
- Dry mixing of solid salt-ammoniacate and ENG powder, compressing of the mixture.
- Compressing ENG powder and then apply wet vacuum impregnation of a salt solution, followed by a drying step
- Compressing of low density ENG powder followed by vacuum impregnation of a salt solution
- Vacuum impregnation of pre-shaped ENG plates. (SGL, Thermophit®)

Variables used in the process are the compression strengths, mixing weight ratios of dry salt and ENG powder, the concentration of the salt solutions for the vacuum impregnation, the porosity of the pre-shaped ENG structures. The salt used in the composite experiments is CaCl₂. This salt is considered representative for other metal-chloride salts, eg. MgCl₂, MnCl₂, and ZnCl₂ in its chemical properties. Composite preparation procedures for CaCl₂ need only to be slightly adapted for the other salts, where CaCl₂ has the benefit of easy and safe handling.



2.2 Sorbent reactivity testing

When a salt is contained within the porous structure, its sorption behavior and reactivity towards ammonia should remain preferably unchanged in comparison its bulk properties. Verification of the reactivity of the composites was done by exposing the dry CaCl_2 to NH_3 gas at 5bar in a pressure vessel. The composite was kept at room temperature and NH_3 gas flow is fed to system. The NH_3 flow is measured and the system is kept pressurized for 2 to 3 hours after the flow has become zero. The weight change of the composite materials is afterwards measured as an indication of the reactivity of the CaCl_2 contained in the graphite matrix. The pressure-temperature condition applied, 5 bara NH_3 and CaCl_2 at room temperature, should result in the formation of $\text{CaCl}_2 \cdot 8\text{NH}_3$. The reaction equilibrium lines for the reactions in the CaCl_2 - NH_3 system are shown below in Figure 1.

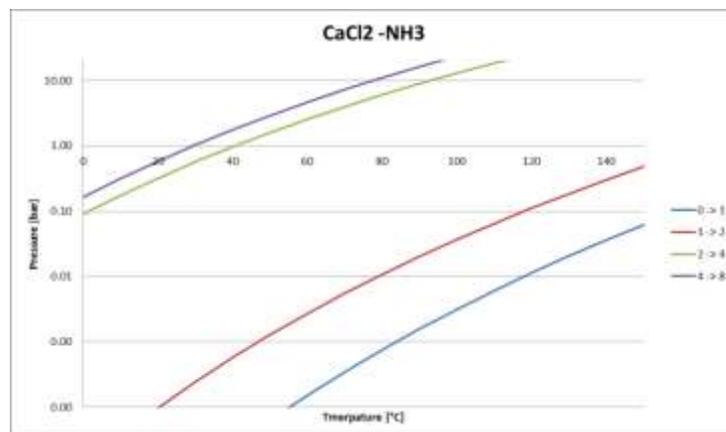


Figure 1: Equilibrium NH_3 vapor pressures as a function of temperature for different reaction equilibria. $4 \rightarrow 8$ is the reaction $\text{CaCl}_2 \cdot 4\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g}) = \text{CaCl}_2 \cdot 8\text{NH}_3(\text{s})$. $2 \rightarrow 4$, $1 \rightarrow 2$ and $0 \rightarrow 1$ correspond to comparable reaction equilibria for the lower ammoniacates of CaCl_2 - NH_3 system

2.3 Thermal conductivity tests

Thermal conductivity has been measured using a Hotdisk© thermal conductivity meter and the results analyzed using a COMSOL model to adjust for specific sample geometries, anisotropic heat transfer coefficients and boundary conditions.

The Hotdisk thermal conductivity meter is based on transient plane thermal conductivity measurement. This consists of measuring the surface-temperature of the sample as a function of time whilst simultaneously supplying a known amount of heat per unit of time to the sample. The supplied power was varied between 100mW to 2W for periods of 1 to 80 seconds. The tests have been carried out using a double-sided measurements, i.e. the sensor was placed between two samples. The samples were clamped 'hand tight' in the Hotdisk sample holder such that no visible deformation of the samples occurred.

The COMSOL model contained two components: the sensor surface and the sample. Boundary conditions: The applied power input was set as boundary condition on the sensor surface whilst the sample boundary conditions where either no heat transfer (sides) or ambient temperature (top of sample). The thermal conductivity for ENG and the sorbent(s) was taken from literature, the density of ENG and the sorbents was based on the results from the sorbent composite preparation. As ENG is an anisotropic material, the thermal conductivity was varied in both axial and radial direction.

2.4 Long term stability tests

The application of a salt composite in a chemical heat pump requires a stable reaction behavior of the composite over approximately 10^5 adsorption-desorption cycles. For an initial analysis of the long term stability of the ENG-salt composite a test is performed. A composite sample is put in a microflow reactor at atmospheric pressure and various gasses can be supplied to the reactor under well controlled flow rates. The reactor and sample temperature can be set and controlled by resistance heating. The reactor volume, containing the composite is first filled and

blown through with NH_3 (8 ml/min) gas for a period of 1 hour, then the NH_3 is replaced by a N_2 gas flow (50 ml/min) for 2 hours. This process is then repeated for 100 cycles. In this sequence the composite can repeatedly adsorb and desorb ammonia. The composite sample is kept at room temperature during the sorption cycles. The difference in flow rate between inlet and outlet of NH_3 is monitored to analyze the amount of NH_3 uptake. The composite sample temperature is also measured during the reactions, and temperature changes are used as a qualitative indication of the occurrence of the absorption and desorption reaction.

The lay-out of the microflow reactor set-up and the quartz reactor are shown in Figure 2

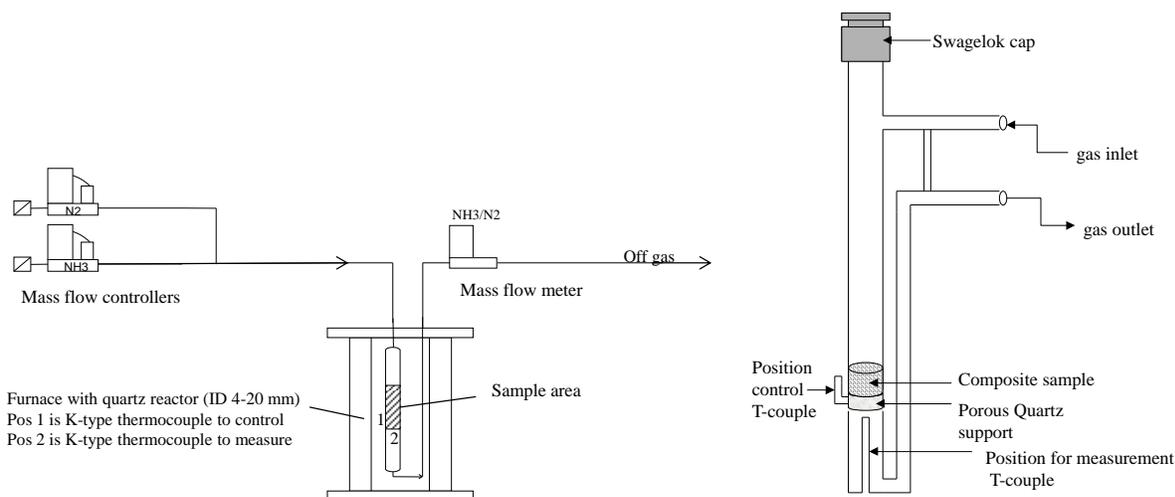


Figure 2: Flow scheme of the microflow reactor setup (left) and details of the quartz reactor (right) .

3. RESULTS AND DISCUSSION

3.1 Sorbent composite preparation and reactivity tests

First preparation method that was applied was based on dry and wet mixing of expanded natural graphite and salt. The mixtures were compressed in a mold with various pressures, from 25 to 200 bar. The composites obtained had densities of 1500 g/cm^3 and even more, and graphite to salt weight ratios in the range of 2 to 1.

The second composite preparation method starts with ENG powder that is compressed to a porous pellet. The pellet was impregnated with a salt solution, and then the solution is slowly removed by a heating step. Various compression strengths were applied to prepare the ENG pellets with porosities ranging from 50 to 20 volume %. The wet impregnation of these pellets resulted in a falling apart of the compacts that were compressed with low compression strengths and low salt uptake and a graphite to salt mass ratio of 4 to 1

The ENG powder used in the above tests had a density of 100 g/dm^3 , which is high in comparison to previous works (HAN *et.al.*1996) The next preparation trails were done using ENG material with a powder density of 10 g/dm^3 (SGL-Sigraflex), so a more porous starting material, to obtain a more porous structure of the compressed graphite matrix material.

Porosities of 88% were obtained in the pellets, by just compressing at low pressure. Even with the low pressure the pellets obtained sufficient mechanical strength to stay intact during the wet impregnation. The ENG pellets obtained in these trials showed strong similarity to commercially available pre-shaped ENG plates. Additional preparation tests were done using the pre-shaped ENG plates of SGL, designated as Thermophit® . The characteristics of the composites obtained by the last two methods are given in the table below.

Table 1: Results of composite preparations based on ENG support

Graphite type	Sigraflex	Sigraflex	Thermophit	Thermophit	Thermophit	Thermophit
Code	Pres-03	Pres-04	Pres-05	Pres-06	Pres-07	Pres-08
Density [g/cm ³]	0.26	0.25	0.10	0.10	0.19	0.19
Porosity [%]	88	88	95	95	91	91
CaCl ₂ loading [g]	0.48	0.37	0.77	0.47	1.04	0.58
CaCl ₂ /graphite ratio [m/m]	0.62	0.48	2.94	1.67	0.98	0.69
Salt density [kg/m ³]	162	119	287	175	188	130

3.2 Sorbent reactivity

The dry and wet mixing procedure did not result in mechanically stable reactive composites. The composites showed a significant volume expansion upon the uptake of ammonia, leading to loss of mechanical strength. A typical result of the composites obtained in the mixing process is shown in Figure 3.



Figure 3: Picture of the composite obtained in dry mixing procedure, after reaction with NH₃. Top left pellet is graphite without salt.

The weight changes of the composites due to the uptake of NH₃ by the salt were determined directly after releasing the pressure from reactor vessel. The uptake of NH₃ corresponds to compositions in the range of CaCl₂(7.3-7.7)NH₃, indicating that 90% of the salt has reacted. The volume expansion of the salt after uptake of ammonia is too large in these composites to be accommodated by the remaining porosity in the pellet.

The composites obtained with the highly porous ENG matrix (Sigraflex and Thermophit) didn't show significant structural changes after the first reaction with ammonia (Figure 4). The appearance of the composites external structure as well as the external dimensions remained unchanged. The high porosity ENG leaves sufficient internal free volume to accommodate the volume expansion of the salt upon reaction, without changing of the external dimensions. These composites were selected for further testing.



Figure 4: Overview of composites before and after reaction with NH₃

3.3 Thermal conductivity tests

Figure below shows the normalized temperature (temperature divided by power input, in K/Watt) for measurements on ENG with CaCl_2 after NH_3 sorption (left) and COMSOL calculations (right) as a function of time. The measurements show some deviations at the start of the measurements but otherwise a nearly linear increase with log time is observed.

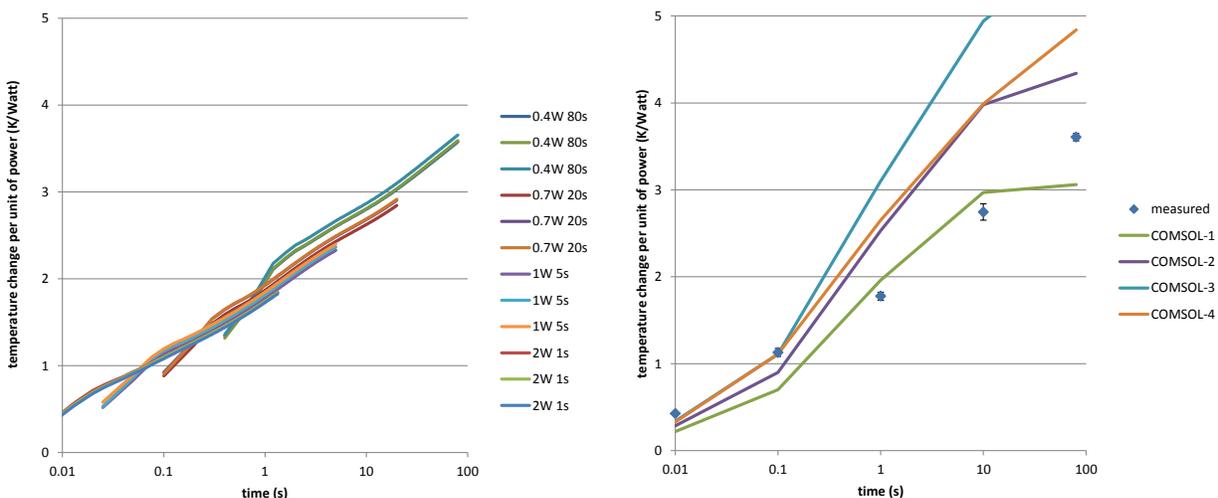


Figure 5: Normalized temperature (K/Watt) versus time (s) for ENG with CaCl_2 after NH_3 sorption. Left: measured values, right average measured values and COMSOL model calculations

The right figure shows the temperature relation calculated in COMSOL from four sets of radial/axial thermal conductivities, 8/2.5 W/mK (COMSOL-1), 8/1.5 W/mK (COMSOL-2), 8/1 W/mK (COMSOL-3) and 16/1 W/mK (COMSOL-4) as a function of time together with the average, measured values. The results for COMSOL-1 are a good match with the measured values for the first 10 seconds. After this period, the model shows a significantly reduced increase of temperature whereas the measured values still increase after 10 seconds. This could be due to thermal resistance at the top of the sample which is assumed negligible in the COMSOL model. The other COMSOL-calculations show considerably higher temperatures even though the shape is somewhat more similar to the measurements. Therefore a radial thermal conductivity of 8 W/mK seems reasonable as an first estimate for approximating the heat pump performance.

3.4 Long term stability testing

The 100 cycles sorption-desorption tests were performed using ENG pellets with a diameter of 10 mm and height of 10 mm and 95% porosity. Pellets were loaded with CaCl_2 (wet impregnation) to a weight ratio of 2 (low charge) and 4 (high charge) of CaCl_2 to carbon. Both samples were tested over 100 cycles in the microflow setup. The results for the low charged composite are provided below.

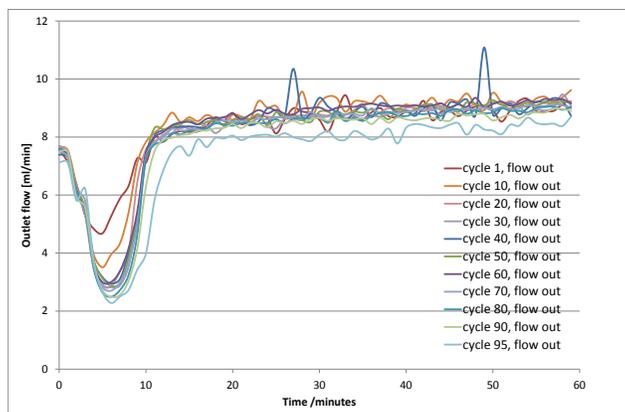


Figure 6: NH₃ outlet flow profile in time during adsorption of NH₃ on the composite plotted as function of the cycle number

The NH₃ flow rate at the outlet of the reactor was measured continuously during the absorption step, see Figure 6. The outlet flow of NH₃ during the first 10 minutes of the absorption is reduced compared to the inlet flow. After 20 minutes the outlet flow equals the inlet flow rate of about 9 ml/min. This reduction of flow rate is caused by the uptake of NH₃ in the composite by the CaCl₂. The initial uptake in cycle 1 and cycle 10 is lower than the uptake reached at cycle 20, after which the NH₃ flow profile remains fairly constant in the following cycles.

The amount of ammonia retained by the composite was calculated and the result indicated a molar ratio of CaCl₂:NH₃ of 1:2, indicating that the expected equilibrium reaction of $\text{CaCl}_2 \cdot 2\text{NH}_3(\text{s}) + 2\text{NH}_3(\text{g}) = \text{CaCl}_2 \cdot 4\text{NH}_3(\text{s})$ is repeatedly taking place.

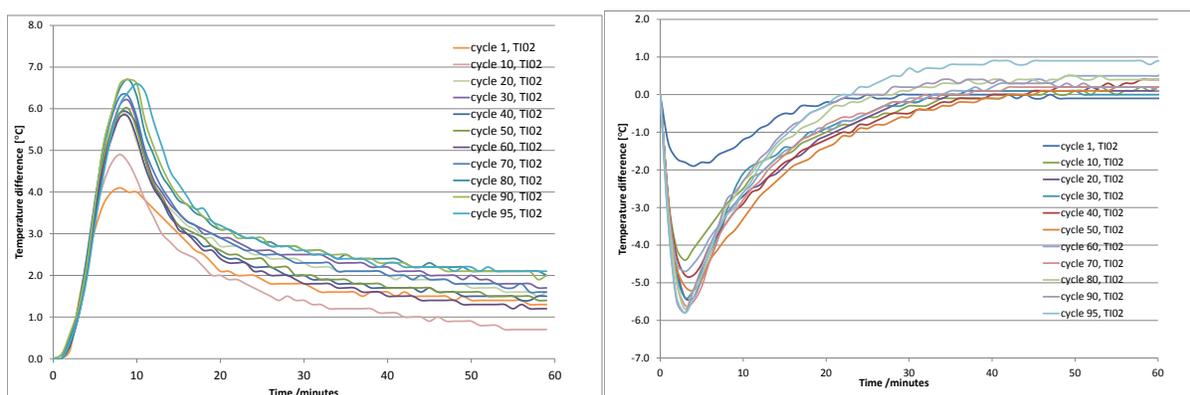


Figure 7: Temperature change in time for the repeating absorption (left) and desorption cycles

The observed change in temperature of the samples during the repeated absorption and desorption cycles is shown in Figure 7. The temperatures are plotted as the temperature difference compared to the starting temperature for the respective absorption and desorption cycle. For the absorption cycles the temperature pattern corresponds to the change in NH₃ flow. When NH₃ is absorbed, the temperature rises in the first 10 minutes, and then the sample slowly cools down to ambient temperature. In the desorption situation, the reactor is flushed with N₂ at 50 ml/min, and this gives a temperature decrease of the sample due to the heat of desorption taken from the sample. The desorption process also gives fairly constant temperature profiles after the 20th cycle.

The sample with the high charge of CaCl₂ showed comparable results for the temperature profiles and for the NH₃ outlet flow. The larger amount of CaCl₂ gave slightly longer reaction times and slightly higher temperature difference. The calculated amount of NH₃ retained by this sample also was in the molar ratio of 1:2 for CaCl₂: NH₃.

A picture of the samples before and after the 100 cycle tests is shown in Figure 8. The results for the composite show that the height of the composite is increased after 100 cycles and that this increase is higher for the sample

having the highest CaCl_2 content. Although the change in external volume is significant after 100 cycles the samples are still intact and don't show segregation of the salt in the ENG. The picture shows that in the samples after 100 cycles an increase occurs in the number of cracks over the height of the samples. In the current test setup the samples can freely expand in the height, which is observed in the experiment. When using the composite in a reaction compartment where the room for expansion is limited, it can be expected that the composite external dimensions remain unchanged.

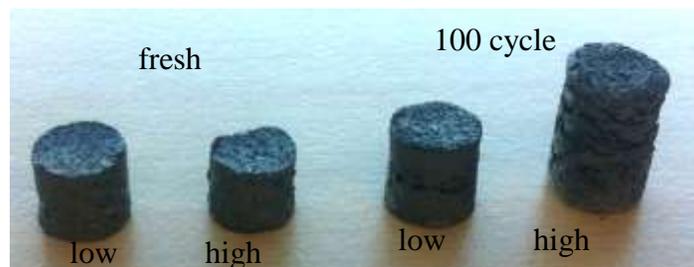


Figure 8: Picture of fresh composite samples and after 100 sorption-desorption cycles. From left to right: fresh sample of low CaCl_2 charge, fresh sample high CaCl_2 charge, low CaCl_2 charge after 100 cycles, high CaCl_2 charge after 100 cycles.

4. SORPTION HEAT PUMP PERFORMANCE CALCULATION

By combining the results of the above measurements, a first estimate of the performance of a sorption heat pump in terms of efficiency, cycle times and power density was made. Application of the composite material in a sorption heat pump type II for upgrading waste heat at 130°C to process heat at 190°C was assumed. The used sorbents were lithium chloride and magnesium chloride. Their thermodynamic properties were taken from literature (Bever, 2006, Bever 2007).

Based on their thermodynamic properties, the discharge and regeneration pressures were chosen such that temperature difference to ambient and waste heat (for regeneration) and waste heat and process heat (for discharge) were equal. For given conditions (ambient is 20°C), this temperature difference is about 13°C . Using this temperature difference as the driving force for the sorption reactions, the sorption heat, based on ENG-sorbent ratio and densities, the typical surface and length the sorption heat has to travel through and the thermal conductivity of the composite material, the regeneration and discharge cycle times were calculated. The heat pump efficiency (COP) is calculated from the net amount of heat at process heat temperature, i.e. the sorption heat of the high temperature salt (MgCl_2) minus the sensible heat to increase the reactor, the sorbent, the ENG and the sorbate from waste heat temperature to process heat temperature divided by the total amount of sorption heat and sensible heat for discharge and regeneration. The power density has been determined by dividing the net amount of heat at process heat temperature by the volume of the reactor and the sum of cycle times for discharge and regeneration.

Results for a 1" tubes filled with ENG-composite show a COP of 0.38, a power density of 419 kW/m^3 with cycle times of less than 400 seconds. Please bear in mind that these numbers do not include all the effects occurring in the process of the sorption heat pump, some of which that can be negative such as (poor) kinetics, mass-transfer limitations, additional heat losses and necessary release/uptake of ammonia to account for increase/decrease in pressure prior to discharge/regeneration, and some of which are positive such as optimized tube material, thickness and diameter, maximized salt concentration, heat and mass recovery and optimized cycle times. Some of these effects will be tested in future measurements.

5. CONCLUSIONS

The preparation of CaCl_2 -graphite composites using different expanded natural graphite qualities resulted in a recipe to obtain reactive and mechanically stable composite. Key issue in the recipe is the density of the starting material of ENG. Good results were obtained both with low density ENG powder, compressed to low density pellets, and also with pre-shaped plates of ENG. These ENG structures could be impregnated by a CaCl_2 solution, followed by a drying step. Comparable preparation steps can be applied using other chloride salt solutions. The obtained CaCl_2 -

ENG composites kept their reactivity with ammonia to obtain their equilibrium ammoniated state of the salt, and remained mechanically stable for over 100 cycles of sorption and desorption. The radial thermal conductivity of the ENG composite was estimated at 8 W/mK, comparable to the original ENG material. A first estimate of the performance of a sorption heat transformer, based on the salt densities, the thermal conductivity and the pressure-temperature relations, showed sufficiently high COP and power density to pursue further development of a heat pump type II for upgrading industrial waste heat to process heat based on ENG composite materials.

NOMENCLATURE

ENG Expanded Natural Graphite (-)

REFERENCES

- Berntsson, K.M., Berntsson, T., Franck, P.-A., Holmberg, P., Wallin, E., 1989, *Heat transformers in industrial processes*, Caddet Analytes series No.2.
- Beyers, E.R.T., Oonk, H.A.J., Haije, W.G., van Ekeren, P.J., 2007, Investigation of thermodynamic properties of magnesium chloride amines by HPDSC and TG For application in a high-lift high-temperature chemical heat pump, *Journal of Thermal Analysis and Calorimetry*, vol 90:3 p 923-929
- Beyers, E.R.T.; van Ekeren, P.J.; Haije, W.G.; Oonk, H.A.J. 2006, Thermodynamic Properties of Lithium Chloride Ammonia complexes for Application in a High-Lift High Temperature Chemical Heat Pump, *Journal of Thermal Analysis and Calorimetry*, vol 8:3 p 825-832
- Han, J.H., Cho, K.W., Lee, K.-H., Kim, H., (1996) Heat and mass transfer characteristics of graphite salt blocks in chemical heat pumps, *Proceedings of the international sorption heat pump conference*, 1996. p. 135-147.
- Hünemörder, W., (2002) Entwicklung und simulation einer mobile trockenen absorptionkälteanlage unter bneutzung vo Motorabwaerme, *Thesis DKV*, Stuttgart.
- Neelis, M., Patel, M., Blok, K., Haije, W.G., Bach, P.W., 2007, Approximation of theoretical energy-saving potentials for the petrochemical industry using energy balances for 68 key processes, *Energy* 32, p. 1104–1123
- Pal, M. van der; Boer, R. de; Veldhuis, J.B.J.; Smeding, S.F., 2009, Thermally driven ammonia-salt type II heat pump: development and test of a prototype, *Proc. Int. Heat Powered Cycles conference*, Berlin
- Pehnt, M., Bödeker, J., Arens, M., Jochem, E., Idrissova, F., 2011, Industrial waste heat – tapping into a neglected efficiency potential, *Energy Efficiency First, Proceedings ECEEE summer study 2011*, p. 691-700
- Restuccia, G., Freni, A., Russo, F., Vasta, S. 2005, Experimental investigation of a solid adsorption chiller based on a heat exchanger coated with hydrophobic zeolite, *Appl. Therm. Eng.* 25, p 1419-1428
- Spoelstra, S., Haije, W.G., Dijkstra, J.W. 2002, Techno-economic feasibility of high temperature high-lift chemical heat pumps for upgrading industrial waste heat. *Appl. Therm. Eng.* 22 p.1619–1630
- Vasiliev V.V., Filatova O.S., Tsitovich A.P., 2010, Application of sorption heat pumps for increasing of new power sources efficiency, *Archives of Thermodynamics* Vol. 31 No. 2, p.21–43
- Wang R.Z., Xia Z.Z., Wang L.W., Lu Z.S., Li S.L., Li T.X., Wu J.Y., He, S., 2010, Heat transfer design in adsorption refrigeration systems for efficient use of low grade thermal energy, *Proceedings of the 14th International Heat Transfer Conference IHTC14*, Washington, ASME
- Yu, Y.Q., Zhang, P., Wu, J.Y., Wang, R.Z., 2008, Energy upgrading by solid-gas reaction heat transformer: A critical review, *Renewable and Sustainable Energy Reviews* 12 p.1302–1324

ACKNOWLEDGEMENT

TKI-ISPT, the Dutch Institute for Sustainable Process Technology is gratefully acknowledged for their financial support to the work described in this paper.



ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ecn.nl
www.ecn.nl