Experimental Setup for Determining Ammonia-Salt Adsorption and Desorption Behavior Under Typical Heat Pump Conditions: Experimental Results

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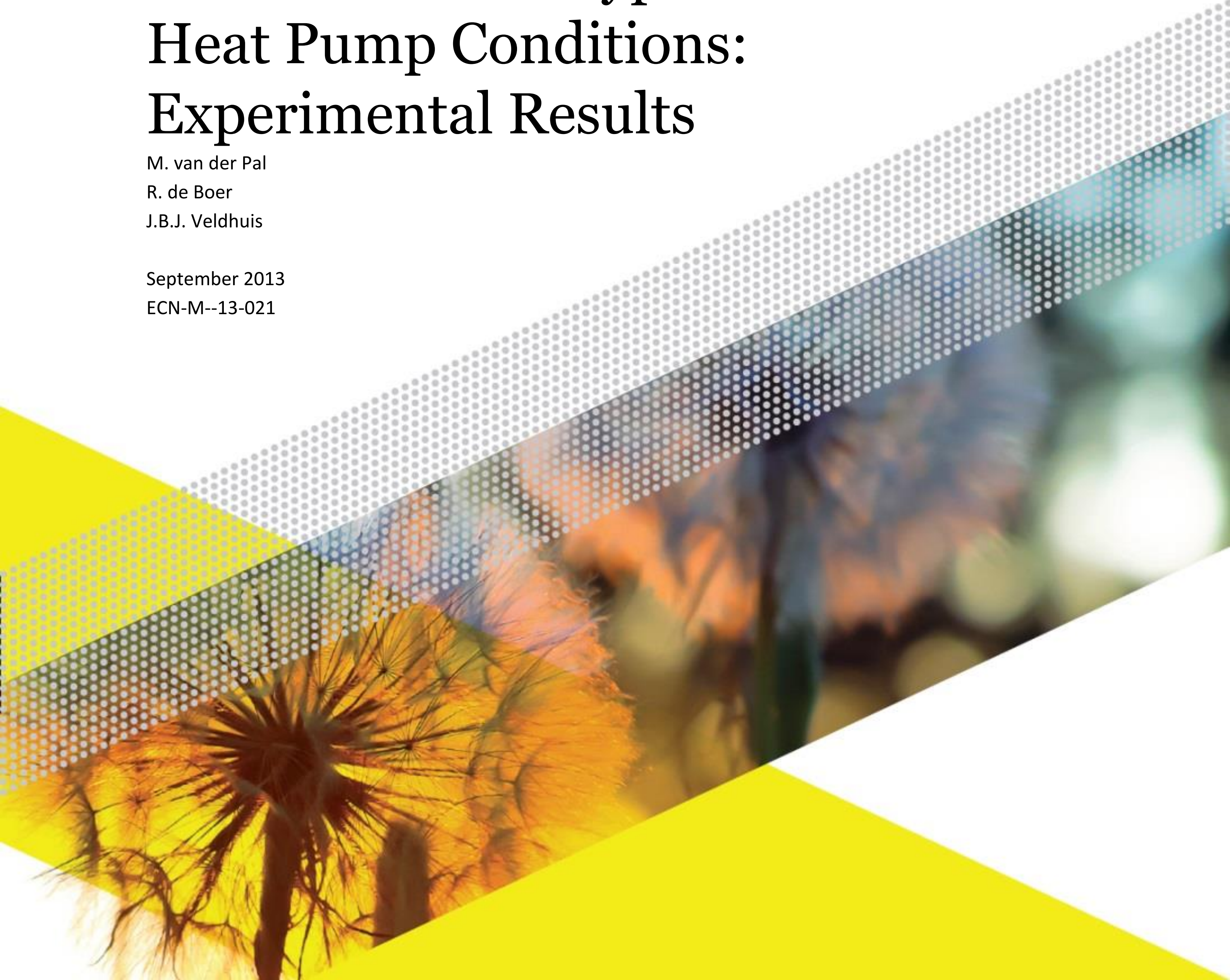

EXPERIMENTAL SETUP FOR DETERMINING AMMONIA-SALT ADSORPTION AND DESORPTION BEHAVIOR UNDER TYPICAL HEAT PUMP CONDITIONS: EXPERIMENTAL RESULTS

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ABSTRACT

For the aim of obtaining a better understanding of the performance of a salt-ammonia sorption reactor/heat exchanger a new test-rig was developed. This test-rig enables the measurement of the performance in adsorption and desorption mode of different sorption reactor designs. It measures the speed of uptake and release of ammonia gas of various salt-ammonia reactions under well-controlled and well-monitored process conditions, similar to the heat pump conditions.

The test-rig measures the ammonia uptake and release under controlled pressure and temperature conditions. Temperatures of the salt reactor can be varied from ambient temperature up to 200°C and the ammonia pressure can be varied between 0.02 to 2 MPa. These conditions can be set independently and repeated at regular time-intervals. Besides NH3-mass-flow meters, pressure and temperature sensors, the setup also contains an endoscope to observe any macroscopic structural changes in the material during uptake and release of ammonia.

Measurements so far have shown a liquid phase of $LiCl^{\cdot}3NH_3$ at pressures of 0.5 MPa and temperatures exceeding 90^oC. Voilent foaming is observed at 120^oC resulting in salt losses. A correlation was determined between the reaction rate of $MgCl_2(2\text{-}6)NH_3$ and the relative pressure gradient yielding a reaction time of about 1500 seconds for a relative pressure difference of 1. Multiple sorption cycles of the $CaCl_2(2\text{-}4)NH_3$ reaction, showed a reduced activity from 85% of the theoretical maximum sorbed mass at the first sorption cycle, to 15% after 300+ cycles.

Keywords: Chemical heat pump, performance testing, finned foam tube reactor

1. INTRODUCTION

Heat-driven heat pumps based on the principle of chemisorption have been researched worldwide for cooling and heating purposes. Such research typically focuses either on fundamental materials properties such as sorption isotherms, thermal conductivity and heat of sorption, or on the development and performance of complete systems. The research at ECN also shows this typical pattern with publications on the fundamental thermodynamic properties on ammonia reactions of lithium chloride and magnesium chloride ([1],[2] and[3]) together with results on complete systems ([4],[5]). However, when trying to connect the material properties to the system's performance, for example by using model calculations, various uncertainties on heat exchanger/sorption reactor level remain. These uncertainties, such as reaction kinetics, heat and mass transfer limitations for given specific geometries and conditions but also effects due to repeated sorption, formation of dust particles, pose a considerable problem for further development, improvement and scaling up of the system.

Various and diverse systems are using the sorption of a gas to a solid for, for example, separation or thermal effects [6],[7]. Heat and mass transfer are critical items in these systems. Performance is an intricate interplay between sorbate, sorbent, heat conducting surfaces of the reactor and mass transport limitations.

On a system level the overall performance is readily determined. Discrimination of the performance in terms of thermal conductivity, pressure drop or reaction kinetics is difficult to discern. On the other hand, analytical material performance measurements that determine specific material characteristics do not give a straightforward answer for the optimization of the reactor design.

In order to get a better understanding of the performance of the sorption reactor/heat exchanger design and sorbent bed loading, an experimental setup has been developed. This setup allows measuring the performance of various ammonia-sorbent reactions with various sorption reactor/heat exchanger designs under well-controlled and well-monitored process conditions similar to the heat pump conditions.

This paper describes the set-up of the apparatus and first results. The results are illustrated with experiments with lithium chloride, magnesium chloride and calcium chloride as sorbent and with ammonia as sorbate in one type of finned tube reactor.

2. EXPERIMENTAL SETUP

Figure 1 shows a schematic flow diagram of the mass transfer setup that we named “ROSATI”. At the heart of this setup is “mini-reactor 1”. In this reactor vessel a small-scale (finned) heat exchanger can be placed (Figure 2). The shown finned heat exchanger has a tube diameter of 16 mm, containing 20 fins with 50 mm diameter and a fin thickness of 5 mm of aluminum foam and a fin spacing of 8 mm. An endoscope is placed in the reactor to observe the macroscopic structural changes in the material during the sorption reactions, such a swelling, melting and shrinking. The heat exchanger is connected to the system using a Swagelok connector and therefore it can easily be removed and/or replaced

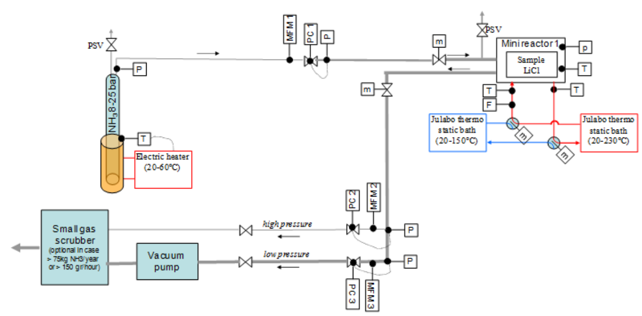

Figure 1. Schematic flow diagram of the mass transfer setup. Ammonia is supplied from a (heated) bottle shown on the left of the diagram. The heat exchanger containing the sorbent is placed in the reactor vessel marked with "Mini reactor 1".

Two Julabo HT-60 thermostatic baths are used to operate the heat exchanger at two different temperature levels, similar to the cyclic heat pump conditions. The temperature of the heat exchanger is monitored using two temperature sensors that are placed on the heat exchanger as well as two temperature sensors that measure the temperature of the thermal oil entering and leaving the heat exchanger. Heat losses from the reactor vessel are reduced by using trace-heating and insulation of the wall. This also prevents condensation of ammonia. The temperatures were measured using type K thermocouples. The pressure in the reactor vessel is controlled by three pneumatic operated valves and pressure-controllers. The inlet circuit allows a measured flow of ammonia into the reactor (adsorption). The outlet circuit is divided into a high pressure and a low pressure part, that are operated consecutively. The high pressure part has also a Coriolis mass-flow meter and a control valve and the ammonia is blow off into a vent. The low pressure part has a thermal mass flow meter and controlling valve (0.02 to 0.1 MPa) that is operating with a scroll type pump. Depending on the cycle of the measurement, only one of the three pressure-controllers is active. The set pressure can be varied between 0.02 and 2 MPa and is measured with an accuracy of 0.5% full scale. The Coriolis mass flow meters are from Bronkhorst type Mini coriolis. The maximum mass flow is 278 mg NH3 per second and is measured with an accuracy of 0.5% of full scale.

In comparison with previous descriptions [8] the mass flow meters have been upgraded and placement of the temperature sensors is improved.

Lithium Chloride observation experiment: The ROSATI test installation allows to observe the phases of the sorbents by using the endoscope. Earlier studies on the phase boundaries of lithium chloride suggested a liquid phase for temperatures above 90^{o}C and an ammonia pressure of 0.5 Mpa or higher [3]. Therefore an experiment was conducted with the goal to observe this liquid phase and to determine its response to the desorption of ammonia. Therefore lithium chloride was heated to 60^{o}C and exposed to an ammonia pressure of 0.05 MPa. The pressure was increased to 0.5 MPa to form lithium-trisammine. Subsequently the salt temperature was increased to 120^{o}C.

Magnesium chloride kinetics experiment: A series of adsorption and desorption measurements have been conducted using reactor temperatures set between 120 and 200^{o}C and ammonia pressures set between 0.05 MPa to 1 MPa and a cycle time of at least 1 hour. The goal of this experiment is to determine the relation between the reaction time and the driving force expressed as the relative pressure (dp/p).

Calcium chloride durability experiment: The uptake of ammonia by calcium chloride has been measured in the first adsorption cycle and again after more than 300 adsorption and desorption cycles. Goal of this experiment is to determine the durability of the calcium chloride (and the ROSATI setup).

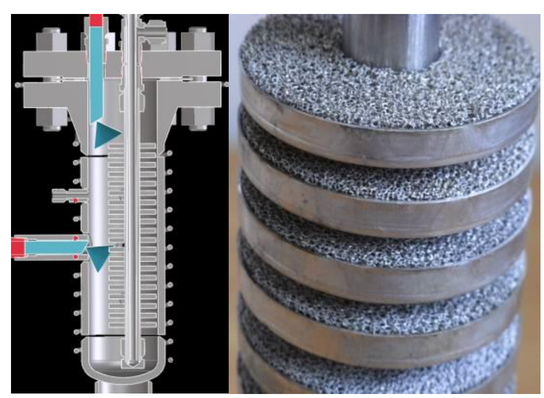

Figure 2. Left: Schematic cross-section of the reactor vessel (blue arrows show endoscope positions). Right: A

picture of the ”empty” finned foam tube heat exchanger outside of the reactor.

3. RESULTS

Test installation measurements

The ROSATI test-installation has been constructed and operated within its specifications. The isothermal desorption and adsorption of ammonia sorbate on various salts has been realized, albeit at lower pressure than originally anticipated. Cold spots in the piping and the endoscope were identified as origins for condensation of ammonia. The isobaric testing while switching between the two temperatures for adsorption and desorption of the ammonia was also possible. Swift temperature change is provided by the two different temperature loops. Correction for thermal losses is possible through calculation of the reactor design and also through blank measurements. Also a combined test program of temperature and pressure change as in a chemical heat pump cycle can be imposed on the salt reactor.

The durability of the test-installation was proven by repeated cycling of the reactor while desorbing and adsorbing ammonia in a stand-alone operation. The duration of the experiment is then limited by the ammonia content of the gas cylinder. Other points of attention for operation are the filling reservoirs of the oil baths, the supply of thermostated coolant to the endoscope and the formation of sorbent dust that might hamper the correct function of valves and mass flow meters.

The use of a protective environment when the reactor is assembled has shown its benefits for reactor handling while assembling the reactor loaded with (hygroscopic) salts in the test-installation. However, disassembling and cleaning of the test installation is more cumbersome.

***Lithium chloride reactor** (formation of a liquid phase)*

Figure 3 shows the pressure-temperature track (orange line) that was imposed on the lithium chloride filled reactor. Melting of the solid trisammine phase was observed at 0.5 MPa ammonia pressure and a reactor temperature over 90 °C. The presence of a solid liquid phase transition was anticipated and the design of the finned tube reactor proved to be suitable. When the reactor was heated further to 120 °C, the decomposition of the molten phase showed violent foaming of the molten salt due to the escaping ammonia gas (Figure 4) This fluid behavior resulted in material loss from the reactor.

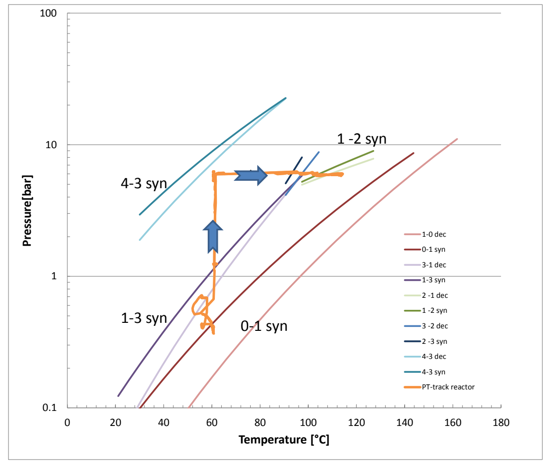

Figure 3. Overlay of the phase diagram and the temperature-pressure track (orange line, blue arrows show direction of path in time) as executed by the ROSATI test installation for lithium chloride salt. The lines show the various **syn**thesis and **dec**omposition reactions of LiCl ammines.

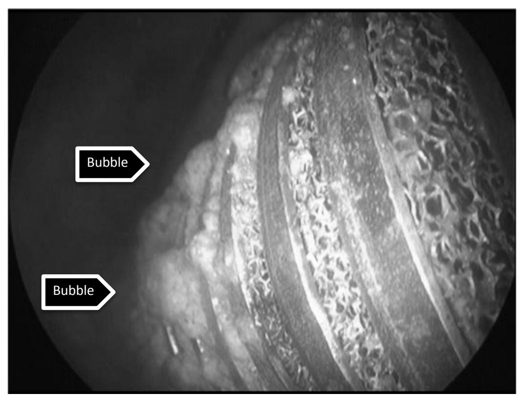

Figure 4. Picture from the endoscope showing foaming molten lithium chloride slat in the filled reactor

***Magnesium chloride reactor** (performance testing)*

For magnesium chloride confined in a finned tube aluminium foam reactor (Figure 6), the salt was subjected to various conditions in which the driving-force for the reaction was varied by the ammonia pressure. The imposed pressure was related to the equilibrium pressure for given reactor temperature [1] and shows that increased driving force yields increased reaction rate. This is shown in the figure (Figure 5). The reaction time of the adsorption or desorption of ammonia on the salt was determined based on 90% of the theoretical energy output. The reaction times vary between 10 and 40 minutes but are well within the set cycle time of 1 hour.

Based on these results, indicating the performance of this reactor design at various operating conditions, a thermal design could be extrapolated for a pilot-scale and a full-scale design for a chemical heat transformer.

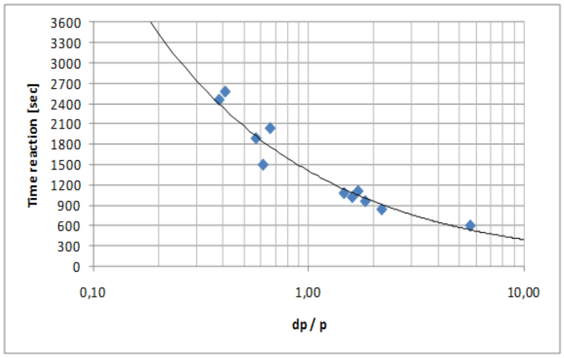

Figure 5. The reaction time as a function of the driving force, expressed as the ratio of the pressure difference from equilibrium and operating pressure. Blue dots show measured values, the line the best fit (spline).

Figure 6. Picture from the endoscope showing the texture in the solid magnesium chloride filled reactor while exposed to ammonia.

Calcium chloride *(endurance testing)*

The reactor, filled with calcium chloride, was tested with temperature swing and pressure swing operation modes (Figure 7). In total more than 300 sorption cycles were made. A degrading trend in mass sorption/desorption and related thermal effects was found. Post-test analyses showed that a large volume of salt was outside the finned alumina foam reactor part. Comparison of pre-test (Figure 9) and post-test images (Figure 10) suggest that roughly half of the salt has expanded outside the foam and is now located between the reactor fin and the foam.

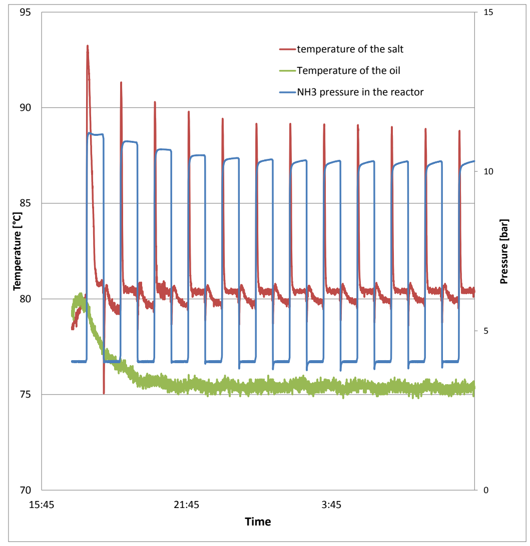

Figure 7 Cycling performance of a calcium chloride filled reactor at high pressure.

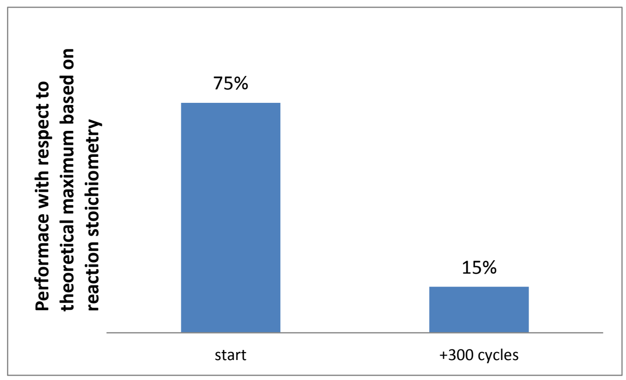

Figure 8. Comparison of ammonia uptake by $CaCl_2$ as fraction of the theoretical maximum (g/g), after the first cycle and after more than 300 cycles.

Figure 9. Picture of the pre-test condition of the finned foam tube reactor filled with dry calcium chloride

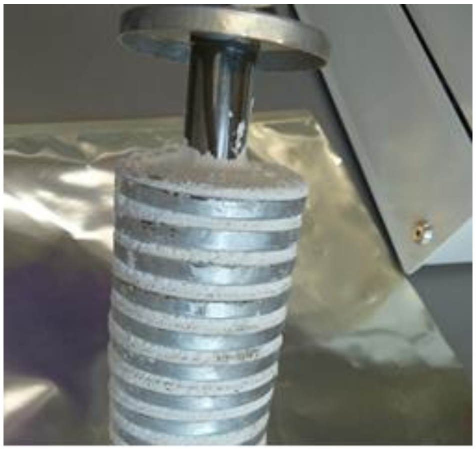

Figure 10. Picture of the post-test condition of the finned foam tube reactor showing the redistribution of the ammonia containing salt.

4. DISCUSSION

The ROSATI test set-up has proven to be a valuable asset in the testing of chemical heat pump materials. In that respect the additional visual information obtained through the endoscope has helped in the selection of working pairs. For performance testing the critical issues on the mass flow determination have been addressed and the revamped installation is more reliable.

The interpretation of the data and the related explanation of observed performance are still not straightforward. Automated data analyses and additional modeling of heat and mass transfer are additions to the ROSATI test installation that could improve the results obtained at lesser operating time and costs.

Three salts have been tested in the ROSATI setup under various conditions and for various reasons. Although the experiments are not comparable, two salts have proven to be inadequate for application in the used reactor type. The lithium chloride shows violent foaming when heated to 120^{o}C and causing salt to move around the setup.

The calcium chloride measurements show reduced performance over time. The reactor type of "finned foam tube reactor" might not be the right type for salts in which a large volume expansion is anticipated. Calcium chloride ammonia phases show a large volume expansion [9],[10]. The increase of volumes to 15 times its original volume have been reported [11], without deterioration of the reactivity. In the used finned foam reactor, the foam could have become detached from the heat conducting fins. This loss in thermal contact results in a loss of "active" material. Possible alternatives could be sought in a refined distribution of salt on a heat conducting surface, for example in the already proven concept of expanded natural graphite composites [12], [13].

5. CONCLUSIONS

Materials testing have shown that magnesium chloride is a viable material for the chemical heat transformer. A clear relation between reaction time and a relative pressure difference was found with less than 1500 seconds cycle times for dp/p of 1.

The lithium chloride melts under temperature and pressure conditions exceeding respectively 90^{o}C and 0.5 MPa and is not recommended for solid sorption heat pump applications if these conditions occur.

The finned foam tube reactor is unsuited for application of salts that show large volumetric changes during adsorption and desorption of ammonia.

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