

Solid/vapour sorption heat transformer

Design and performance

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Abstract

A high temperature high lift solid sorption based heat transformer has been successfully designed and tested. The sorption reactor concept is based on a tube-fin heat exchanger where the heat exchanging fluids can flow through the hollow fins. The plates were brazed together with porous metal foam that was impregnated with either of the sorbents, LiCl and MgCl₂. The adsorbate is ammonia. The batch system was tested as to the power delivered at high temperatures, 150–200 °C. Peak power at 200 °C was about 0.8 kW, the average power about 0.4 kW. The thermal efficiency, COP, was calculated from the experimental results to be 0.11. This is only 40% of the expected theoretical value and can largely be attributed to the thermal mass of the reactor.

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1. Introduction

The present concern about global warming and diminishing amount of readily available fossil fuels urges scientists and engineers all over the world to develop cleaner and more energy efficient processes. Especially challenging are concepts for reusing the enormous amounts of waste heat that are currently emitted to the environment by the chemical and refinery industries. The amount of industrial waste heat from actively cooled process streams is about 110 PJ/y for the Netherlands [1,2] (250 PJ/y including flue gasses). Assuming that the Netherlands' industry amounts to about 16% of Western Europe's and 3% of the World's industrial activities the total emitted industrial waste heat amounts up to 688 PJ/y (1562 PJ/y) and 3667 PJ/y (8333 PJ/y), respectively. The temperature window of this waste heat is 50–200 °C for process streams and up to about 600 °C for flue gasses. Reuse of this heat clearly leads to enormous energy savings and CO₂ emission reduction. The first area of application is upgrading waste heat to util-

ity level, e.g. 200–250 °C, for the middle pressure steam net, or to cooling level, e.g. below –40 °C, used for condensing highly volatile hydrocarbons. These temperature ranges offer the biggest energy saving potential [1,3] and the most viable market introduction.

Over two decades, many researchers have embarked on the development of solid sorption based heat pumps for either application. Research ranges from thermodynamic characterisation of working pairs [4–6] to improving on existing concepts by cascading basic heat pump cycles [7]. Solid sorption is endowed with serious intrinsic problems as to heat and mass transfer that have been tackled by many authors in different ways, leading to different designs of the sorption reactors.

Some researchers have tried to enhance heat conductivity by adding impregnated carbon fibers [8], others have used impregnated expanded graphite [9–11]. In cooling applications, graphite has been used as a sorbent [12]. Wang et al. [13] have presented a comprehensive review on current activities and status of heat transfer enhancing options, a majority of which concerns consolidated beds. In conclusion they state that many of these activities indeed resulted in enhanced thermal behaviour, however, they always led to worsened mass transport.

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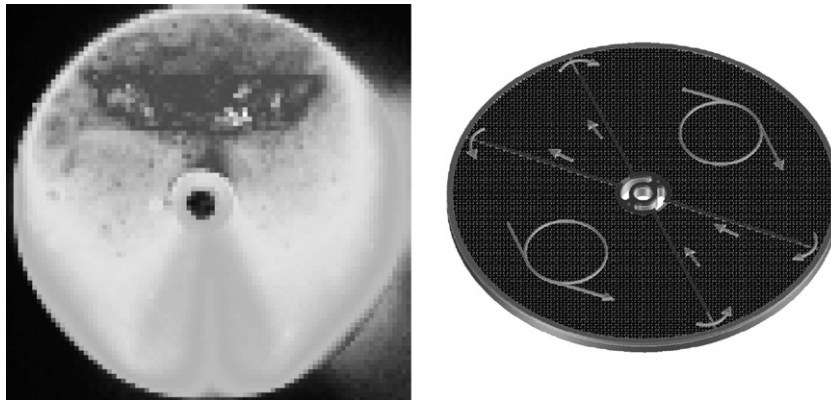


Fig. 1. Right: simplified flow pattern within the plate-mesh-plate hollow fin. Left: infrared image of a hollow fin initially at room temperature after just being switched to thermal oil of 60 °C, inlet upper half, outlet lower half.

The present paper deals with the design and experimental determination of the performance of a high temperature high lift solid sorption heat transformer based on a novel design of the heat exchanger in the sorption reactor. Innovative aspects comprise firstly the scale, about 1 kW heating power output at 200 °C, secondly driven by low temperature industrial waste heat, and thirdly the use of metal foam as a support and containment for the sorbent. This foam is expected to enhance thermal behaviour without limiting mass transfer.

2. Design

The design of the sorption reactor is based on the notion that thin sorbent layers suffer least from heat and mass transfer limitations. When a thin layer option is chosen, obtaining a high heat exchanger area density is prerequisite. Care should however be taken as to the sorbent to metal ratio, which in this case may well lead to a reduced coefficient of performance (COP). A well-known concept in industry is the tube-fin heat exchanger. It suffers from the draw back that the diameter of the plates is the limiting factor for heat and mass transfer to and from the perimeter, i.e. perpendicular to the tube. We therefore designed a novel concept [14] in which the heat transfer fluid flows through hollow fins, thus allowing for much larger diameters. The hollow heat exchanger fin consists of two parallel stainless steel plates vacuum brazed together. The space in between is filled with a metal wire mesh that serves two purposes. First, since it is also vacuum brazed to both plates, it increases strength of the whole body. Second, it breaks up laminar flow within the fins for better heat transfer. In Fig. 1, the flow pattern is indicated together with an infrared picture of the heat exchanger just after switching from ambient to about 60 °C. On the outside of both plates a metal foam (Recemat NC-4753-05) is connected using the same technique. The porosity of the foam was 92%, the average pore diameter 0.51 ± 0.05 mm, and filament thickness 0.10 ± 0.02 mm. The foam-heat exchanger assemblies were stacked such that a space of about 3 mm is left for

vapour transport. Like this, the shortest pathway for both heat and mass transfer to the sorbent is perpendicular to the ‘fin’ and not perpendicular to the tube. The diameter of the fins is 350 mm, the thickness of the plate-wire mesh-plate ‘hollow fin’ assembly is 2 mm (plate: 0.5, wire-mesh thickness 1 mm, pitch 5 mm) and the foam thickness is 5 mm. The total thickness of the hollow fin plus foam is 12 mm. The foam was impregnated with the sorbent material. Impregnation was achieved by dipping the foam-heat exchanger assemblies in hot alcoholic solutions saturated with MgCl_2 or LiCl in an inert atmosphere. Traces of water were removed by adding the drying agent triethyl-orthoformate (3–5% by volume). In this way, about 20 mol of MgCl_2 and 40 mol of LiCl were deposited in the metal foam structure reducing the porosity of the whole body to $77 \pm 2\%$.

At ambient temperature the stoichiometric amount of ammonia was fed to the reactors (in total 160 mol = 3600 l STP) such that $\text{LiCl} \cdot \text{NH}_3$ and $\text{MgCl}_2 \cdot 6\text{NH}_3$ were formed. The valves between the two reactors were closed and each reactor was submitted to a temperature cycle allowing for decomposition and formation of $\text{LiCl} \cdot \text{NH}_3$ (to/from LiCl) and $\text{MgCl}_2 \cdot 6\text{NH}_3$ (to/from $\text{MgCl}_2 \cdot 2\text{NH}_3$) so as to equilibrate and homogenise the sorbent-vapour system.

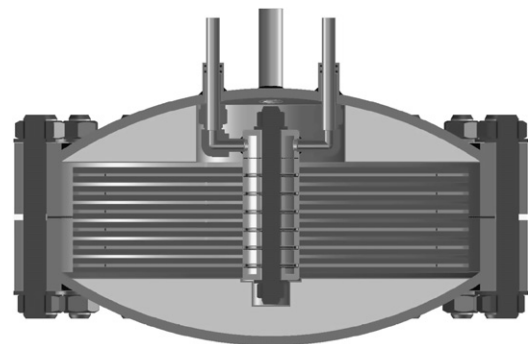


Fig. 2. Schematic drawing of the heat exchanger stack design. On the central axis the seals between subsequent plate-foam assemblies are visible.

In Fig. 2, the design is presented that shows how the subsequent ‘sandwiches’ are stacked using seals along the central tube. In Fig. 3 an impregnated stack is shown during mounting in the reactor. Due to safety regulations, for working with pressurized ammonia at high temperatures ($p = 20$ bar, $T = 250$ °C) along with the wish that the system can be opened non-destructively, the (thermal) mass of the reactor is really large (total about 100 kg). One heat exchanger assembly weighs about 12 kg and is loaded with 1,8 kg of sorbent (LiCl or MgCl_2).

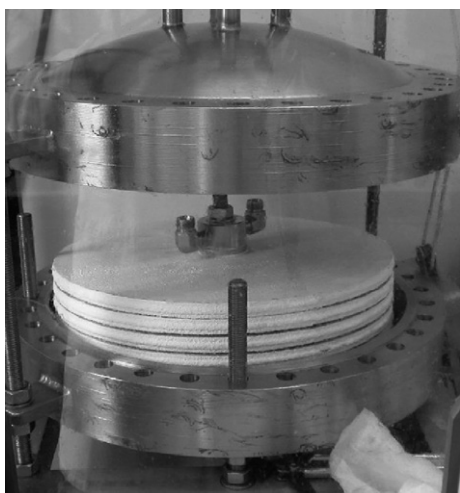


Fig. 3. Sorbent impregnated heat exchanger-foam stack mounted inside the reactor shell.

3. Testing conditions and results

In Fig. 4, a schematic of the low and high temperature reactors with the heating/cooling system, respectively are shown. The high temperature sorbent, HTS, is $\text{MgCl}_2 \cdot (2 \leftrightarrow 6)\text{NH}_3$, the low temperature sorbent, LTS, is $\text{LiCl} \cdot (1 \leftrightarrow 3)\text{NH}_3$, cycling between 2 and 6 and 1 and 3 NH_3 respectively. The temperatures (Pt100) and flows of in and out going thermal oil (Calflo LT) flows per reactor are measured (turbine flow meter Emo) as well as the ammonia vapour flow (Rotameter Siemens/Heinrichs) from one reactor to the other. The salt temperature was monitored using a thermocouple (type K) fixed between two subsequent foam-sorbent composites.

In Fig. 5, the heat transformer cycle is depicted. Two sets of reactors are needed to operate in a continuous manner.

In order to mimic normal operation conditions the LTS should cycle between T_{ambient} and $T_{\text{waste heat}}$, while the HTS cycles between $T_{\text{waste heat}}$ and T_{high} . The amount of heat necessary for heating the entire thermal mass completely obscures the heat output of the exothermic reaction. Therefore it was decided not to cycle the HTS thermally but to fix it at the appropriate T_{high} as depicted in Fig. 6. The chosen testing conditions are summarized in Table 1.

In Fig. 7 the cycling behaviour of the low temperature reactor is depicted and in Fig. 8 the power delivered or absorbed in the high temperature reactor along with the temperature fluctuations around the set point. Cycling behaviour was stable for at least 50 cycles for both reactors. Cycle times were taken quite long, 4 h, to be on the

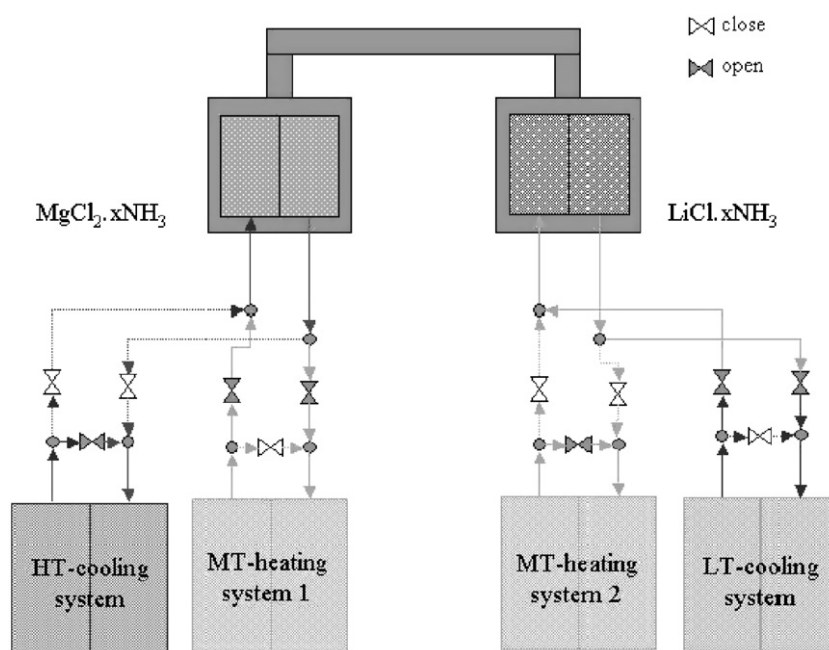


Fig. 4. Process flow diagram of the testing system (high T heat production (discharge) mode; in the charge mode open valves are closed and vice versa).

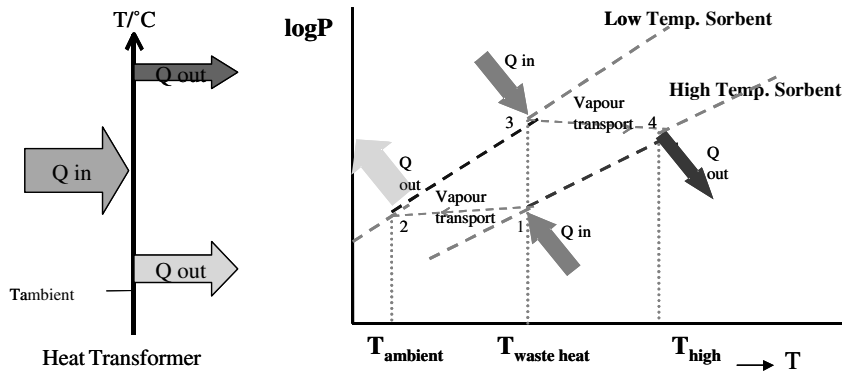


Fig. 5. Schematic of the heat transformer cycle.

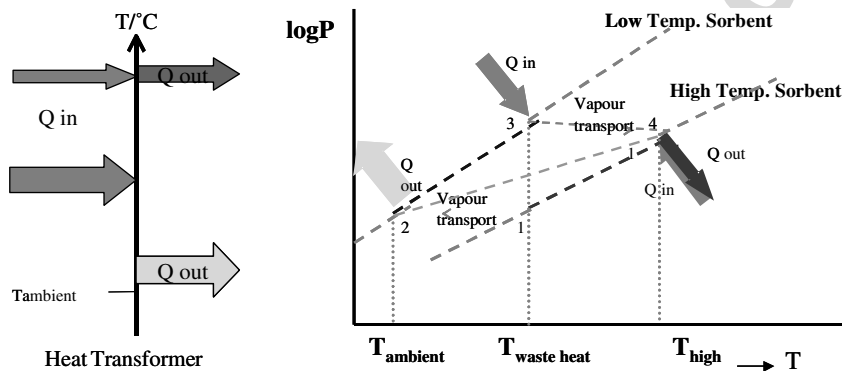


Fig. 6. Schematic of the heat transformer cycle testing conditions.

Table 1
Temperatures applied to the LTS and HTS reactors

$T_{Cooling}$ LTS (°C)	T_{Middle} LTS (°C)	T_{Middle} HTS (°C)	T_{Output} HTS (°C)
20	150	165	165
20	150	175	175
20	150	190	190
20	155	200	200

safe side. Although the performance of the reactor *a-priori* allows for much shorter cycle times, the behaviour of the sorbents with respect to mass transport was uncertain. When only the period during which high temperature heating power was produced is taken into account, about 40 min, the COP was calculated to be 0.11. This is only 40% of the theoretically obtainable value under these conditions.

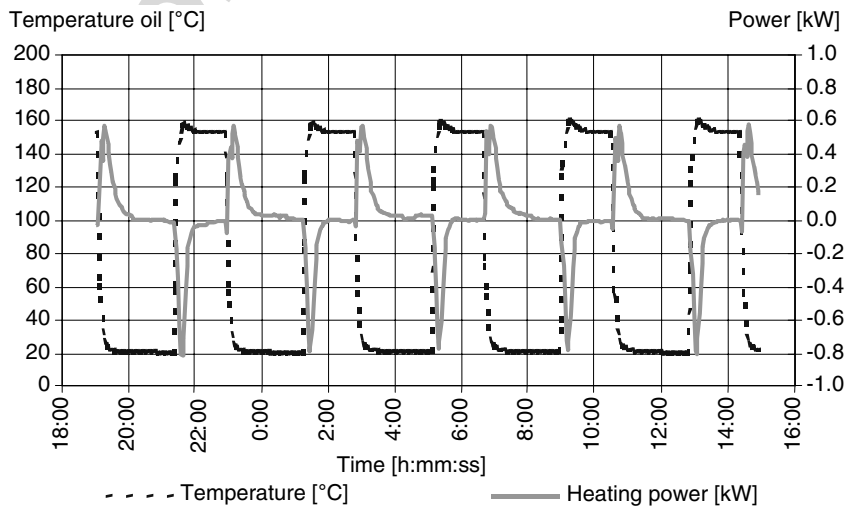


Fig. 7. Cyclic behaviour of the low temperature reactor.

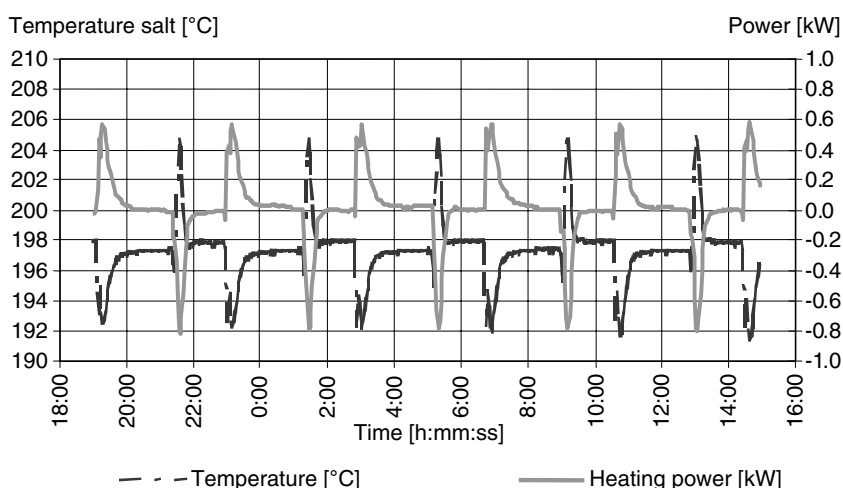


Fig. 8. Heating power produced or absorbed and the corresponding temperature fluctuation of the sorbent as the low temperature reactor is cycled and the high temperature reactor is set 'fixed' at 200 °C.

$$\text{COP} = \frac{Q_{\text{HT,sunload}}}{Q_{\text{LT,load}} + Q_{\text{HT,load}}}$$

Extrapolated to a system in which the high temperature reactor does cycle between middle and output temperature the COP would have been about 0.14 whereas the targeted value was 0.3. The low performance can be attributed partly to the high thermal mass of the system and partly to the accessibility of the sorbent as can be inferred from post-test inspection of the foam–sorbent composite.

Running the heat transformer for a prolonged time span resulted in clogging of the ammonia flow meters located in between the two reactors. After dismantling the system this appeared to be due to sorbent that had disintegrated to sub-micron dust particles, supposedly under the action of repeated swelling and shrinking during the test cycles. Furthermore, the slit space between the subsequent sorbent layers, intentionally left open for mass transfer, appeared to have filled with sorbent that under swelling during absorption was driven out of the foam structure. This effect is clearly detrimental for mass transfer of ammonia to the sorbent, thereby lowering the output power.

From these measurements it can be derived that under the present conditions (thermal oil flow of about 1.75 l/min per hollow fin) $U \cdot A$ is about 45 W/K. In the case without foam and sorbent this value is 1590 W/K [14]. This yields an effective thermal conductivity for the 5 mm thick foam–sorbent composite of about 1.5 W/m K. This is clearly an improvement with respect to a commonly found [15] fixed bed value of about 0.1–0.5 W/m K.

4. Discussion and conclusions

The pair of solid–vapour sorbents $\text{MgCl}_2 \cdot (2 \leftrightarrow 6)\text{NH}_3$ and $\text{LiCl} \cdot (1 \leftrightarrow 3)\text{NH}_3$ is fit for the practical purpose of upgrading industrial waste heat with a lift of at least 50 °C. Handling of these very hygroscopic materials is

not straightforward but is expected to be manageable on an industrial scale. The novel design of the 'tube-hollow-fin' heat exchanger seems adequate from the heat transfer point of view, the fixation, however, of the sorbent in the metal foam needs improvement. Thin films of sorbent, preferably applied in the highest ammoniated form, on planar surfaces are likely to provide a better starting point as to stability and mass transfer. Inherent porous structures, with low volume changes on cycling, that can easily be 'painted' on heat exchanger surfaces are viable candidates for mechanically stable systems. Especially new compounds like metal organic frameworks [16], calixarenes [17] and the like may after some retailoring live up to the expectations, provided the heats of sorption are high enough.

Although the design is not yet optimal and maybe not yet fit for scaling up to MW scale, the present experiments show to the best of our knowledge for the first time the feasibility of a high temperature high lift heat transformer on the scale of 1 kW, driven by low temperature heat. The large thermal mass of the reactor, imposed by the strict safety regulations for high-pressure ammonia at high temperature, did not allow for testing under practical conditions i.e. both reactors cycling. In conclusion it may be stated that solid sorption based heat transformers still hold the promise to play an important role in future energy saving options in industry.

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