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Resorption heat pump development

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Abstract

The development of a resorption heat pump for domestic use is described. The cycle uses the alternate adsorption and desorption of ammonia between two salts – sodium bromide and manganese chloride. The equilibrium and dynamic behaviour of both salts with ammonia has been measured using the Large Temperature Jump (LTJ) technique and a good match found between experimental and modelled data. This has been used to design a nominal 2.5 kW heat pump as a demonstrator to confirm the results. The bench scale machine can be driven by a high temperature source of pressurised water at up to 170 °C, the low temperature input is from water between 5 and 15 °C and the output is between 40 and 60 °C. It uses a simple cycle consisting of one low-pressure phase followed by a high-pressure phase, without any heat recovery, moving ammonia from the Low Temperature Salt (LTS) sodium bromide reactor to the High Temperature Salt (HTS) manganese chloride reactor and vice versa. A practical machine would have two such sets of reactors and recover heat between them, but this level of complexity is avoided in the demonstrator. Despite this, initial results are extremely encouraging having achieved repeatable ammonia cycling between the reactors.

Keywords: Ammonia; Heat pump; Resorption.

1. Introduction

The chemisorption of ammonia into halide salts has been studied over many years: it was first observed by Faraday [1] who recognised its potential for generating a heating or cooling effect; more recently it gained attention in the ‘80s and ‘90s, primarily by Spinner [2], and many others: Goetz et al., [3], Lebrun and Spinner, [4]; Mazet and Spinner [5].

Cycles using chemisorption can be applied to refrigeration, heat pumping, and thermal transformation and may either use a single salt in a reactor together with a system for evaporating and condensing the refrigerant, or a resorption cycle in which the refrigerant is adsorbed or desorbed between two salts. More complex three salt cycles with varying degrees of complexity and heat recovery are also possible. A simple heat-pumping cycle is illustrated in Figure 1.

A Low Temperature Salt (LTS) and a High Temperature Salt (HTS) are contained in separate reactors that are connected, the whole being in the presence of ammonia that is either present as a gas, or a chemically adsorbed phase with the salts. The equilibrium lines for the reaction with each salt are illustrated on the Clapeyron diagram, Figure 1. In reality, there can be hysteresis between adsorption and desorption, but this is omitted for clarity. Starting at low pressure, the LTS is heated from ambient, perhaps at 0°C, which desorbs ammonia. In the case of NaBr as illustrated 5.25 mols are desorbed. The ammonia is adsorbed in the HTS (4 mols for $MnCl_2$) generating useful output at 60°C. When the reactions are complete in the low-pressure phase, the HTS is heated by a high temperature heat source at around 150°C. Both salts’ state moves up the equilibrium line until they are at 60° and 150°. During the pressure rise there is little adsorption or desorption because no heat is removed from the LTS, but on reaching the high-pressure phase, heat can be removed from the LTS at 60 °C whilst more heat enters the HTS at 150 °C. The reactions proceed at a nominal constant temperature until complete and the LTS again contains its maximum quantity of ammonia. To return to the

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starting condition in the low-pressure phase, the LTS is cooled back to ambient whilst the HTS is adiabatic. A real machine would most likely feature two sets of reactors operating out of phase so that heat from the cooling LTS could be used to pre-heat the other HTS. Advantages of a resorption cycle are the absence of an evaporator, condenser, or any refrigerant control valves, plus a wide range of salts to choose from that may be matched to required temperatures.

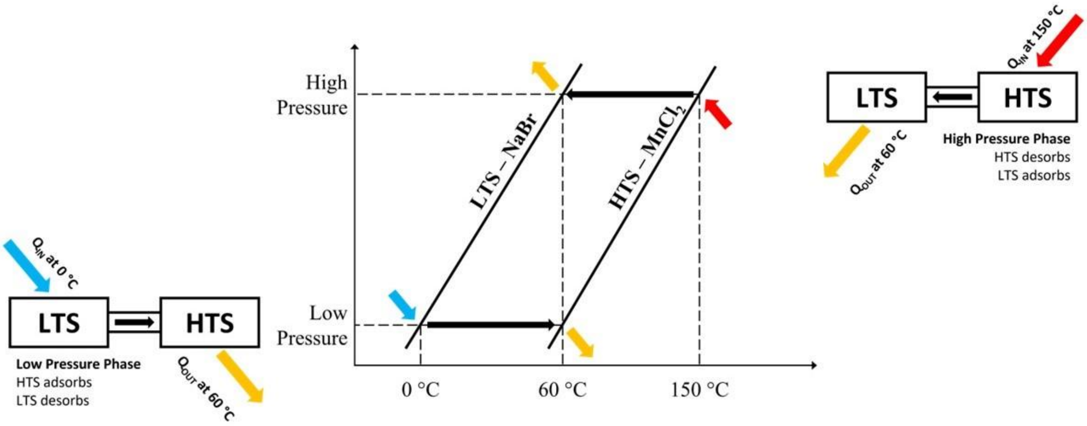


Fig. 1. Simple resorption heat pump cycle. Red, orange and blue arrows indicate heat flows, black arrows are used for ammonia flow.

However, practical difficulties have prevented successful exploitation of the cycle in the past. These are mainly due to slow reaction dynamics (hour-long cycles) and agglomeration of the salts (when used in bulk form) leading to a loss in reactivity. Both drawbacks can be overcome by dispersion of the salt within a porous matrix. Keeping the crystals small and separate prevents agglomeration. Additionally, if the matrix is highly conductive, such as Expanded Natural Graphite (ENG), the overall heat transfer is improved and reaction times reduced, as reported by van der Pal [6]. In this study the salts are impregnated into ENG sheet (SIGRATHERM® Graphite Lightweight Board, ECOPHIT® L10/1500). The measured sheet density is 196 kg m^{-3} and the thermal conductivity in the plane of the sheet is 26 $Wm^{-1}K^{-1}$ as obtained from the manufacturer's data sheets.

2. Material Thermodynamic and Rate Equations

The methodology used to determine properties and governing rate equations is described by Hinmers et al. [7]. The Large Temperature Jump (LTJ) technique is used on small (approx. 10 mm diameter impregnated ENG discs) samples that are rapidly heated or cooled. The reactor vessel is connected to an empty buffer vessel which maintains a nearly constant pressure, similar to that in a full system in desorption (or adsorption), whilst careful measurement of the small increase in pressure yields the time history of ammonia evolution (or devolution). Matching the experimental results with a simulation model reveals the controlling parameters that can be used to design a full system. The reaction is dominated by heat transfer, but chemical reaction rate parameters are also revealed, together with the proportion of the impregnated salt that is able to take part in the reaction. The reaction rate equation used is:

Desorption:

$$\frac{dX}{dt} = A_{DES}\left(1 - \frac{p_{EQ}}{p}\right)(1 - X)^{n_{DES}} \tag{1}$$

Adsorption:

$$\frac{dX}{dt} = A_{ADS}\left(1 - \frac{p_{EQ}}{p}\right)(X)^{n_{ADS}} \tag{2}$$

where: X = reaction advancement ($1 > X > 0$)
t = time (s)
p = pressure
p_{EQ} = equilibrium pressure
$A_{DES}, A_{ADS}, n_{DES}, n_{ADS}$ are constants

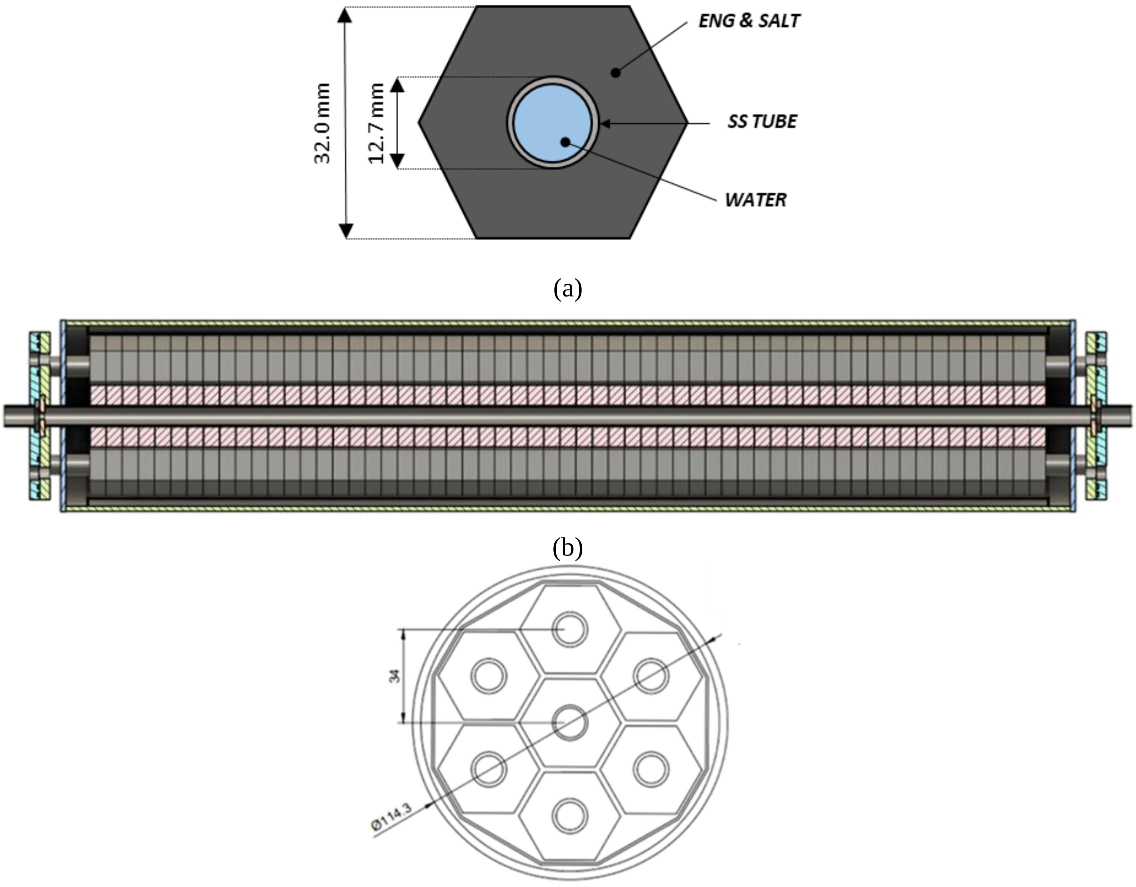
When there is hysteresis the lines on the Clapeyron diagram indicating adsorption and desorption are not equilibrium lines and so the slope does not correspond to the enthalpy of reaction which is determined as in [7], by heating the sample slowly and isosterically in a vessel with minimal void volume.

An interesting outcome of identifying the different parameters is that the overall power density and rate of ammonia sorption/desorption is found to be dominated by heat transfer rather than chemical kinetics. We suppose that in previous studies insufficient attention was paid to heat transfer. In particular, the overall cycle time (for a complete reaction) is highly sensitive to the thermal contact resistance between the ENG and the metal surface used to conduct heat in and out of it.

3. Design of 2.5 kW Demonstrator

The LTJ tests were carried out on 10 mm diameter ENG-salt composite discs contained within the tube of a heated, or cooled, stainless steel double-pipe heat exchanger. However, this would not be a suitable design for a demonstrator since the sensible heat load of the stainless steel would result in low COPs. Instead, the design was based on hexagonal ENG plates with a central hole, Figure 2 (a). Many such ‘nut-shaped’ discs may be mounted on a stainless-steel tube which heats or cools them from their centre. The model parameters and heat transfer properties were used in a simulation model to explore the design trade-off between COP and power density with different central hole diameters and across-flat dimensions. There is no precise optimum, but one criterion was to achieve a mean power density of at least 1 kW per litre of reactor volume.

The dimensions decided on were a central hole diameter of 12.7 mm and 32 mm across the flats, Figure 2 (a), with a predicted power density of 1.4 kW per litre [8]. Since several metres of tube would be needed the concept was to have seven tubes in a hexagonal bundle within a stainless-steel shell that contains the ammonia, as in Figure 2 (b) and (c).



(a)

(b)

(c)

Fig. 2. (a) ENG-salt composite dimensions, (b) longitudinal cross-section through the reactor design concept with a bundle of seven tubes and (c) frontal cross-section through the reactor design concept.

Fig. 3. Demonstrator and ThermExS rig during charging.

The complete demonstrator is connected to the laboratory ‘ThermExS’ test stand which can supply pressurised water from three different thermostatically controlled baths. Pneumatically controlled valves are used to switch hot water to the HTS reactor during the high-pressure phase, cold water to the LTS during the low-pressure phase and to remove heat (simulating the heat pump load) from both reactors as required, as in Figure 1. Inlet and outlet stream temperatures are measured using PRTs and the flow rate is measured by Coriolis meters. In addition, the mass flow of ammonia gas moving from one reactor to another is measured using a Coriolis meter. The demonstrator is controlled and monitored by an NI cDAQ linked to a PC and using LabView^{TM}. Figure 3 shows the nearly completed demonstrator being charged with ammonia, whilst monitoring the pressure and temperature.

4. Preliminary Results

At the time of writing a limited number of test conditions have been conducted and not fully analysed; however, initial results show that the resorption machine operates well.

In the following figures the test conditions were:

4 cycles at 165/40/15 °C with a cycle time of 2600 seconds (43 minutes 20 seconds).
5 cycles at 170/40/15 °C with a cycle time of 2500 seconds (41 minutes 40 seconds).

The cycle times were designed to allow full ammoniation and de-ammoniation of each salt reactor in both pressure phases, therefore allowing the resorption reaction to run to completion. Figure 4 shows the mass flow rate of ammonia being transferred from one salt reactor to the other, taken directly from the Coriolis meter. Positive values are during the low-pressure phase, peaking at around 1.6 to 1.7 g/s of ammonia, and negative values are during the high-pressure phase, peaking at -0.5 to -0.6 g/s.

Figure 5 shows the pressure variation over the cycles between the low- and high- pressure phases. Note there are three pressure transducers in the ammonia line (LTS-side, Mid and HTS-side), which match well across the pressure range. In the 165/40/15 °C tests, the demonstrator cycles between 0.35 bar and 9.00 bar. In the 170/40/15 °C tests, the pressure cycles between 0.35 bar and 9.45 bar.

Although the preliminary data is encouraging in showing the consistency of the resorption cycle, when analysing the initial data during the first cycles, the power output is less than the designed target of 2.5 kW. However, the cycle times used are much longer than optimal to ensure the resorption reaction completes. Future work will test the demonstrator at a variety of temperature and cycle time conditions to ascertain overall system performance; in particular, by optimising and reducing the cycle time the power should increase.

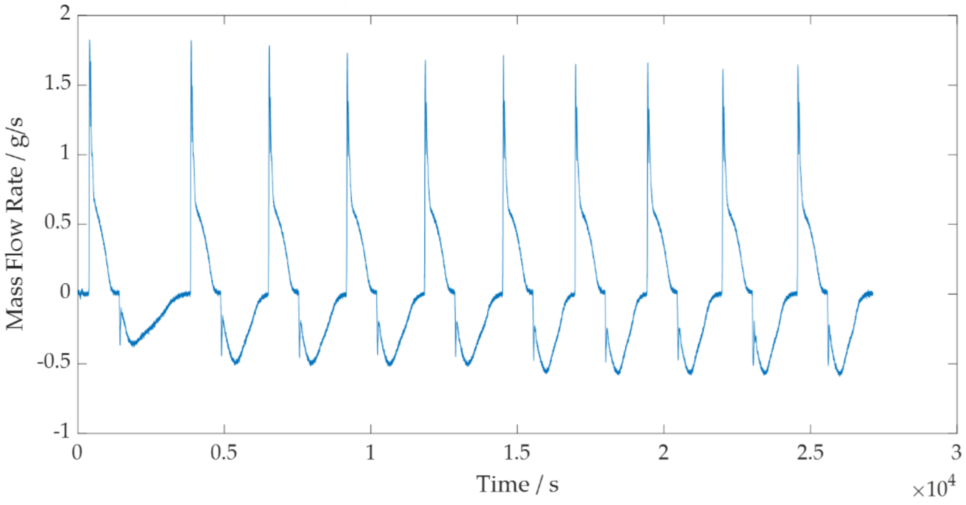


Fig. 4. Mass flow rate of ammonia in each salt during repeated resorption cycles.

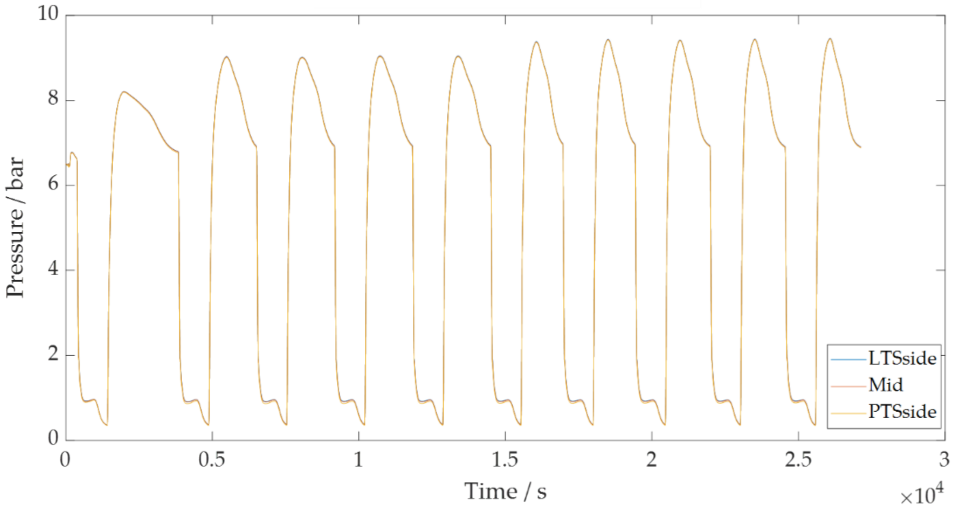


Fig. 5. Pressure variation between the low- and high- pressure phases during repeated resorption cycles.

5. Conclusions

A resorption heat pump cycle using ammonia as the refrigerant, sodium bromide as the low temperature salt and manganese chloride as the high temperature salt is proposed. The salts are dispersed in ENG to improve conductivity and remove any danger of salt agglomeration. LTJ testing on small samples was used to determine equilibrium properties, hysteresis effects, heat transfer and reaction rate limitations. This data was used to design a nominal 2.5 kW demonstrator. The reactors utilise seven parallel heating/cooling tubes in a shell and tube arrangement, with pressurised water on the tube side and the ENG-salt composite on the ammoniated shell side. Each tube fits tightly within many ENG hexagons impregnated with a salt.

Initial testing is very encouraging, showing repeatability and good transfer of ammonia between salts during resorption. Further testing will optimise the cycle time and enable a performance envelope to be calculated and checked against theory. A practical machine would use two pairs of reactors with a heat recovery phase between reactors to enhance the performance.

Acknowledgements

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