Investigation into NH$_3$-MnCl$_2$ and NH$_3$-CaCl$_2$ Reaction Rates for the Development of a Thermal Transformer

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ABSTRACT

The use of chemical adsorption to store and upgrade waste heat has attracted increasing attention over the past decade. Thermochemical transformers require little additional energy input to operate, and have flexible operating temperatures owing to the wide choice of working pairs available. An investigation was carried out to determine the effect of driving temperature on reaction rate for two chloride salts - MnCl$_2$ and CaCl$_2$ - with ammonia. Salt-ENG composite discs were manufactured and exposed to a step temperature change with a Large Temperature Jump system. The synthesis and decomposition rate of CaCl$_2$·(8-2)NH$_3$ was found to be similar, however the rate of MnCl$_2$·(6-2)NH$_3$ decomposition was found to be nearly three times faster than synthesis. Both the LTJ results and additional Rubotherm data pointed to regions where synthesis and decomposition reactions happen at different temperatures and pressures to those routinely cited. When both salts were combined within a resorption Thermal Transformer, a lift of 18.5°C was achieved when operating at a maximum pressure of 8.19 bar and with T$_{LOW}$ = 25.0°C, T$_{MID}$ = 105.7°C, and T$_{HIGH}$ = 124.2°C. Allowing the pressure within the CaCl$_2$ reactor to first rise to 16.89 bar led to a lift of 38.8°C, where T$_{LOW}$= 25.0°C, T$_{MID}$ = 107.6°C, and T$_{HIGH}$ = 146.4°C.

Keywords: Thermal transformation; chemical adsorption; waste heat

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1 INTRODUCTION

An estimated 21% of all primary industrial energy input is released in the form of low-grade waste heat at temperatures of less than 100°C [1]. Despite the abundance of low-grade waste heat rejected by industry, there are few industrial processes that require heat input at similar low temperatures. There has traditionally been little consideration of heat reutilisation methods within industry, although over the past decade, one such method, thermal transformation, has attracted increasing attention [2].

One such method for upgrading heat to more useful temperatures is chemical adsorption, a reversible ligand-complex reaction commonly involving a solid and a gas. Common chemical adsorbents include metal hydrides, metal oxides and metal chlorides and common adsorbates include ammonia, water and methanol [3]. Despite the technology currently having limited commercial potential, chemical adsorption transformers remain of interest as they can be driven by low grade waste heat and have flexible operating temperatures owing to the wide range of metal chloride working pairs [4]. This paper identifies the reaction kinetics of ammonia and two metal chloride salts, Calcium Chloride (CaCl₂) and Manganese Chloride (MnCl₂), and demonstrates their use in a chemical adsorption thermal transformer.

2 MATERIALS

Thermal transformation using metal chloride salts is achieved in two stages. During the first stage, the charging stage, the low temperature salt (LTS) is cooled (\(Q_{\text{out}}\)) by a low temperature heat source, usually the ambient environment, to temperature \(T_{\text{LOW}}\). The high temperature salt (HTS) is simultaneously heated by a waste heat stream at an intermediate temperature (\(T_{\text{MID}}\)) and the working fluid is adsorbed onto the LTS and desorbed away from the HTS (4-1 Fig. 1).

During the second discharging phase, the LTS is now heated by the intermediate temperature. This causes the working fluid to desorb from the LTS and adsorb to the HTS at a higher pressure (2-3 Fig. 1). This action causes exothermic reaction heat to be released (\(Q_{\text{out}}\)) at a higher temperature (\(T_{\text{HIGH}}\)), and it is this heat release which is the goal of the transformation process. Fig. 1 shows one full thermal transformation cycle on a pressure-temperature plot, otherwise known as a Clapeyron diagram.

![Fig. 1 Clapeyron Diagram for Heat Transformation](image-url)
The choice of salt pair is affected by the following criteria: system operating temperatures, system operating pressures, desired temperature lifts, safety and cost. A working temperature range of 20°C to 160°C was established, representing the difference between ambient temperature and the safe operating temperature limits of the apparatus. The maximum pressure of the system was also restricted to 20 bar owing to design limitations, giving a range of candidate salts in Fig. 2. Further exclusions were made because of the low molar quantities of ammonia released by certain salts, with the working salt pair of CaCl$_2$ and MnCl$_2$ selected after further safety and cost screenings. The values of enthalpy and entropy for the chosen salts are given in Table 1.

<table>
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<th>Line</th>
<th>Salt</th>
<th>$\Delta H$ [J/mol]</th>
<th>$\Delta S$ [J/mol K]</th>
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<td>8</td>
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</tr>
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</tr>
<tr>
<td>14</td>
<td>Mn 6-2</td>
<td>47416</td>
<td>228.07</td>
</tr>
</tbody>
</table>

Tab. 1 Chosen Salts with Enthalpy and Entropy values

3 SALT-ENG COMPOSITE

The metal chloride salts were combined with Expanded Natural Graphite (ENG) to form composite adsorbents, as pure metal chlorides suffer from swelling and agglomeration when exposed to ammonia, affecting their heat and mass transfer characteristics [5]. The use of ENG offers further benefits, namely increased thermal conductivity, porosity and surface area. 10mm thick annular ENG discs were cut, with an external diameter of 25.4mm and internal bore diameter of 6mm (Fig. 4). The internal bore improved mass transfer, ease of loading and allowed for thermocouple placement. A novel impregnation method was used, in which the ENG discs were submerged in a concentrated salt-water solution, exposed to a vacuum, drained and finally heated to 250°C to remove all traces of water. Solubility testing was conducted to determine the maximum quantity of salt in the ENG discs. Maximum salt quantities of 1.12g per disc and 0.81g per disc for CaCl$_2$ and MnCl$_2$ respectively were achieved with concentrations of 62.5g/100ml and 60g/100ml.

4 LTJ TESTING

4.1 LTJ Method

The Large Temperature Jump (LTJ) method involves applying a step temperature change to ammoniated metal chloride salts in near-isobaric conditions, and was used to
assess the dynamic properties of the salts. Every applied temperature corresponded to a certain driving temperature (±ΔT) - the difference in temperature from the lines of constant concentration (isosteres). The reaction rate was measured by recording the resulting pressure changes within the system, with synthesis and decomposition corresponding to a decrease and an increase in pressure, respectively.

Fig. 3 Schematic of LTJ Test Rig

A schematic of the LTJ rig is presented in Fig. 3. The reactor consisted of a 1 inch stainless steel inner pipe containing the metal chloride-ENG discs, surrounded by a 1 1/2 outer pipe circulating silicone oil. Two baths at different temperatures, and a pneumatic valve switching system, were used to provide the step change in temperature. A storage vessel, containing two water cooled six litre tanks, was used to add volume to the system and regulate the gas temperature. The LTJ rig was assembled inside an isothermal chamber, maintained at 20°C.

Driving temperatures were calculated using data from Neveu [4], as shown in Table 1, and these were used to set the bath temperatures. On completion of each half-cycle, the baths were switched to allow the other half-cycle to run. For the investigation of synthesis reaction rates, T_HIGH was fixed at 97.8°C for CaCl_2 and 171.3°C for MnCl_2; for the investigation of decomposition reaction rates, T_LOW was fixed at 53.1°C for CaCl_2 and 90.4°C for MnCl_2. Table 2 shows the range of driving temperature differences and T_eq used to test both salts. In both tests, twelve salt-ENG discs were loaded into the reactor containing 4.60g and 3.15g of CaCl_2 and MnCl_2 respectively.

<table>
<thead>
<tr>
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<th>CaCl_2</th>
<th>MnCl_2</th>
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<tbody>
<tr>
<td>T_eq</td>
<td>81.8</td>
<td>69.1</td>
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<tr>
<td>Δ T</td>
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<tr>
<td></td>
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</table>

Tab. 2 Table of Driving Temperatures
An automated system, using a custom LabVIEW program, was created to control the LTJ rig. The program automated the bath switching based on a pressure stability criterion: once the system pressure remained within 2mbar over a 15 minute period, the next half-cycle was initiated.

5 LTJ RESULTS AND DISCUSSION

Figures 5 and 6 show the CaCl$_2$ synthesis and decomposition curves for driving temperatures ranging from 0°C to 16°C. Complete synthesis was seen only for driving temperatures of 6°C and above, and complete decomposition at temperatures of 12°C and over. For MnCl$_2$, complete synthesis was seen at all driving temperatures, and complete decomposition at temperatures of 16°C and over. Only where $\Delta T$ was 16°C did the decomposition processes appear fully complete for both CaCl$_2$ and MnCl$_2$ – signified by the plateaued pressure lines at approximately 6.2 bar in Fig. 6 and Fig. 8. Cycle times ranged from 1800s for CaCl$_2$ decomposition where $\Delta T$ was 16°C, to 6000s for MnCl$_2$ synthesis at $\Delta T$ of -2°C.
The rate of the first stage of CaCl$_2$ decomposition, crossing CaCl$_2$·(8-4)NH$_3$, was largely unaffected by the driving temperature (which was calculated using the CaCl$_2$·(4-2)NH$_3$ isostere). The theoretical amount of ammonia adsorbed or desorbed during each LTJ cycle was calculated to be 3.830g and 1.705g for CaCl$_2$ and MnCl$_2$ respectively. CaCl$_2$ only achieved 63.6% of this, whereas MnCl$_2$ achieved between 90.4% and 91.0% for decomposition and synthesis. Figures 9 and 10 show how the rate of MnCl$_2$ decomposition and synthesis varied with driving temperature difference. The rate of MnCl$_2$ decomposition changes, at $0.0642 \times 10^{-3}$ g$_{NH_3}$ g$^{-1}_{SALT}$ s$^{-1}$ ΔT$^{-1}$, was nearly three times faster than synthesis, which was $0.0271 \times 10^{-3}$ g$_{NH_3}$ g$^{-1}_{SALT}$ s$^{-1}$ ΔT$^{-1}$. The rate is given as a ratio of ammonia mass to the total salt mass in the system. The salt had a CaCl$_2$:MnCl$_2$ mass ratio of 1:1.70, when designed to cycle between CaCl$_2$·(8-2)NH$_3$ and MnCl$_2$·(6-2)NH$_3$.

![Fig. 9 Rate of ammonia-MnCl$_2$ synthesis](image9)

![Fig. 10 Rate of ammonia-MnCl$_2$ Decomposition](image10)

![Fig. 11 Rate of ammonia-CaCl$_2$ synthesis](image11)

![Fig. 12 Rate of ammonia-CaCl$_2$ Decomposition](image12)
Figures 11 and 12 show how the sorption rate varied with driving temperature for CaCl$_2$. The rate of decomposition, at $2.36 \times 10^{-3}$ g$_{NH_3}$/g$_{SALT}$ s$^{-1}$T$^{-1}$, was marginally times faster than synthesis, which was $2.04 \times 10^{-3}$ g$_{NH_3}$/g$_{SALT}$ s$^{-1}$T$^{-1}$.

Figure 13 shows the decomposition and synthesis driving temperatures used for the CaCl$_2$ LTJ tests, in addition to the isosteres from Neveu [4]. A Rubotherm magnetic suspension balance was used to determine the position of synthesis and decomposition isosteres, and these are also shown on Figure 13. These additional isosteres contradict the existence of only one line of constant concentration for both synthesis and decomposition. They also partially support the areas of incomplete sorption found either side of the isosteres published by Neveu. For example, they support the incomplete CaCl$_2$ synthesis seen below driving temperatures of 6°C, however they do not explain the incomplete decomposition behaviour seen at driving temperatures of between 6°C and 10°C.

Figure 14 shows the MnCl$_2$ driving temperatures used in the LTJ, superimposed on data from Neveu and data obtained using the Rubotherm. The newly obtained data indicates that synthesis occurs at lower temperatures than published by Neveu, with decomposition occurring at similar temperatures and pressures. However, the behaviour of neither the MnCl$_2$ synthesis or decomposition reactions can be explained by the new data. The placement of the synthesis MnCl$_2$·(6-2)NH$_3$ isostere suggests that a driving temperature of 8°C is needed for a reaction to be successful, however driving temperatures of 2°C or greater fully completed, albeit with extensive cycle times. MnCl$_2$·(6-2)NH$_3$ decomposition did not occur until a driving temperature of 12°C was reached, despite all other isostere data indicating that any positive driving temperature would lead to a complete reaction.

Figure 15 displays the MnCl$_2$ synthesis
rate and CaCl\(_2\) decomposition rate – both of importance during a transformer upgrading cycle. The rates are equal, at \(1.38 \times 10^{-3} \text{ gNH}_3 \text{ g}^{-1} \text{ SALT s}^{-1}\), at an absolute temperature of 94.8°C. This indicates that a \(T_{\text{MID}}\) close to, or above, this point is preferable to avoid \(\text{NH}_3\) release from CaCl\(_2\) being the limiting step.

Fig. 15 \(\text{NH}_3\) Synthesis and Decomposition Rates

6 THERMAL TRANSFORMER

6.1 Thermal Transformer Method

Fig. 16 displays the completed thermal transformer. The reactors used were of the same diameter as in the LTJ rig. The low temperature reactor (LTR) (1) was loaded with 84 discs, totalling 103.8g of CaCl\(_2\), and the high temperature reactor (2) was loaded with 200 discs, totalling 164.2g of MnCl\(_2\). Two automated valve switching systems, (3) and (4), were connected to the low temperature bath (6) and two high temperature baths (7) and used to generate the step change in temperature. A cold water bath (5) was used to cool the store vessel, used to depressurise the system if the operating pressures were exceeded. Initially, both the charging and discharging phases were conducted with both reactors connected as one system at a uniform pressure, so as decomposition occurred in one salt, synthesis occurred immediately in the other salt. A further cycle was tested, in which the charging and discharging phases were conducted with the reactors isolated at different pressures. At the end of the charging phase, when decomposition of the HTS and synthesis of the LTS had completed, the high temperature reactor was isolated. The LTS was then heated by \(T_{\text{MID}}\) and the pressure in the low temperature reactor increased. Once the pressure within the low temperature reactor had reached 20 bar, the valve isolating the HTS was opened and ammonia synthesised with the HTS – giving a higher temperature lift.

Fig. 16 Thermal Transformation Set-up

6.2 Thermal Transformer Results and Discussion

The temperature evolution curves within each reactor can be seen in Figure 17. During the first cycle, a lift of 18.5°C was achieved, where \(T_{\text{LOW}} = 25.0°C\), \(T_{\text{MID}} = 105.7°C\), and \(T_{\text{HIGH}} = 124.2°C\). This compared
to a maximum theoretical $T_{\text{HIGH}}$ of 139.5°C. During the second cycle, where the MnCl$_2$ reactor was isolated, allowing the pressure to rise to 16.89 bar, a lift of 38.8°C was achieved, where $T_{\text{LOW}} = 25.0°C$, $T_{\text{MID}} = 107.6°C$, and $T_{\text{HIGH}} = 146.4°C$, and $T_{\text{HIGH,MAX}}$ was 162.2°C.

Figure 18 shows the first cycle, where a lower lift was achieved, on a Claperyon diagram. The pressure evolution inside each reactor, for both transformation cycles, can be seen in Figure 19. During the lower lift, the pressure rose from 1.61 bar to 8.19 bar, whereas the higher lift led to an increase from 1.59 bar to 16.89 bar. The drop in temperature within the CaCl$_2$ reactor during second stage of the second cycle indicates that complete CaCl$_2$ decomposition did not complete whilst the MnCl$_2$ reactor was isolated earlier in the cycle. The peak pressure during this earlier stage was 16.89 bar, which corresponds to an equilibrium temperature of 108.5°C. As this was close to the driving temperature of 107.6°C, it indicates that there are physical limitations with using the isolation method to achieve a high temperature lift.

7 Conclusion

An investigation was carried out to determine the effect of driving temperature on reaction rate for two chloride salts – MnCl$_2$ and CaCl$_2$ – with ammonia. Salt-ENG composite discs were subjected to a step temperature change inside a Large Temperature Jump system. The synthesis and decomposition rate of CaCl$_2$·(8-2)NH$_3$ was found to be similar, however the rate of MnCl$_2$·(6-2)NH$_3$ decomposition was found to be nearly three times faster than synthesis. Furthermore, both
the LTJ results and Rubotherm results point to regions where synthesis and decomposition reactions happen at different temperatures and pressures to those routinely cited. When both salts were combined within a resorption Thermal Transformer, a lift of 18.5°C was achieved when operating at a maximum pressure of 8.19 bar and with $T_{\text{LOW}} = 25.0^\circ\text{C}$, $T_{\text{MID}} = 105.7^\circ\text{C}$, and $T_{\text{HIGH}} = 124.2^\circ\text{C}$. Allowing the pressure to rise to 16.89 bar led to a lift of 38.8°C, where $T_{\text{LOW}} = 25.0^\circ\text{C}$, $T_{\text{MID}} = 107.6^\circ\text{C}$, and $T_{\text{HIGH}} = 146.4^\circ\text{C}$.

8 Recommendations for further work

It is assumed that rate is only a function of driving temperature. Rate could also be influenced by system pressure and reaction progression (% completion). Repeating the LTJ experiments over a range of pressures, the effect of pressure on rate could be determined. By increasing the number of driving temperature investigated, more data would be available to determine how routinely cited isosteres differ from experimental data. Investigating different salt working pairs would provide operating data for a wider range of systems.

References


