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Intrinsic Kinetics in Local Modelling of Thermochemical Heat Storage Systems

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\textbf{Abstract}

Thermochemical heat storage is expected to play an important role in the ongoing transformation of the European energy system. The efficiency of thermochemical heat storage systems largely depends on that of the reactor, since it limits the amount of the heat stored per unit volume as well as the rate of the heat recovery. Thus, the optimization of the reactor design is of great importance and can be achieved via local numerical modelling, where intrinsic parameters of the materials are utilized.

In the present study, we developed a procedure for the determination of the intrinsic kinetic parameters of ammonia sorption on metal halides and applied it to strontium chloride SrCl\textsubscript{2} – ammonia NH\textsubscript{3} working pair. A distinctive feature of the procedure is that the kinetic measurements were performed on a Sieverts type apparatus at constant temperature, which allowed resolving the common problem of heat-up time. Besides, the kinetic measurements were carried out using the optimal mass of SrCl\textsubscript{2} – expanded natural graphite composite material (70 mg of SrCl\textsubscript{2}), ensuring that the chemical reaction rate is not constrained by the heat and mass transfer limitations. As a result, the intrinsic kinetic equations of NH\textsubscript{3} sorption on SrCl\textsubscript{2} ammines were derived for the first time and were demonstrated to predict the experimental data, from which they had been computed, over a wide pressure-temperature range. In addition, the obtained intrinsic kinetics, as well as the ones found in literature, were implemented in a three-dimensional numerical model computing the
local temperature, pressure, and reaction advancement through the coupled equations of the heat transfer, fluid dynamics, and chemical reaction rate. The numerical results were compared with experimental data obtained on 466 mg of SrCl$_2$ powder at various pressure-temperature conditions. In contrast to the literature kinetics, the simulation results with the intrinsic kinetic equations were found to be in a good agreement with the experimental data, demonstrating the importance of using intrinsic parameters in the local modelling of sorption reactions.

**Key words:** thermochemical heat storage, SrCl$_2$-NH$_3$ working pair, intrinsic kinetic parameters, kinetic tetrads, modelling
1. Introduction

Over the past decade, energy storage has been identified by the European Commission as a topic of utmost importance for the ongoing transformation of the European energy system. Specifically, thermal energy storage is expected to play an important role in increasing the overall efficiency of energy systems [1,2]. This is particularly true for systems producing waste heat at temperatures below 100°C, so-called low-grade heat, which according to recent studies accounts for more than 45% of the global primary energy consumption [3]. Large quantities of low-grade heat can be stored reversibly in solid strontium chloride (SrCl_2) ammines upon exo-/endothalamic ab-/desorption of gaseous ammonia (NH_3) according to Eq. 1:

$$Sr(NH_3)Cl_2(s) + 7NH_3(g) \leftrightarrow Sr(NH_3)_8Cl_2(s) + 7\Delta H$$

where $\Delta H$ is the reaction enthalpy equal to 41.432 kJ/mole of NH_3 [4]. With such a reaction enthalpy, SrCl_2 offers a high heat storage capacity of 0.51 kWh/kg or 1579 kWh/m^3 at material level. Furthermore, it is environmentally benign, abundant and of relatively low cost, $2000-2500 /ton giving a final price of $3.9-4.9 /kWh. Given the abovementioned advantages, the working pair SrCl_2 – NH_3 has been widely studied for solid-state ammonia storage [5], [6] and deNO_x removal technology [7], for refrigeration applications [8]–[13] and thermochemical heat storage [14]–[19].

The operation of a thermochemical heat storage (TCHS) system utilizing the reversible sorption processes between NH_3 and SrCl_2 is shown in Figure 1.

![Figure 1. Sketch of a TCHS system operating in three working modes: NH_3 absorption (left), heat storage (middle), and NH_3 desorption (right). The modes correspond to discharging (left), heat storage (middle), and charging (right).](image)
As shown in Figure 1, the TCHS system consists of two main vessels - a reactor with a reactive bed of solid SrCl$_2$ and a container with liquid NH$_3$. In the storage mode, the connection between the two vessels is closed and the heat can be stored for any period without losses (middle). If the two vessels are connected, after being evaporated, gaseous NH$_3$ flows from the container into the reactor, where it gets absorbed by the salt and the heat of absorption is released (left). During charging, NH$_3$ is detached from the salt by the supplied heat and is condensed in the liquid NH$_3$ container (right). The system is considered to go through a full cycle upon the completion of two half-cycles, namely absorption and desorption.

The efficiency of the system largely depends on that of the reactor because the reactor determines how much heat can be stored in unit volume and how fast this heat can be recovered. Therefore, to achieve highest system efficiency, it is of primary importance to optimize the design of the reactor. This can be performed via spatially resolved (local) numerical modelling. In contrast to lumped-parameter (global) models, where the effect of different phenomena is lumped into a limited set of equations for a homogeneous control volume, local models compute the spatio-temporal evolution of state variables, such as local temperature, pressure, and reaction advancement [20].

The solid-gas reaction with the thermal effect (see Eq. 1) combines three processes, i.e. the heat transfer, mass transfer, and chemical reaction kinetics, and these three phenomena have to be modelled separately in a local model. Recently, much effort has been made for the precise characterization of the heat and mass transfer parameters of the working pair SrCl$_2$-NH$_3$ [21], [22]; however, the description of the chemical reaction kinetics, free from heat and mass transfer, is still missing. In literature, there are two studies, where the kinetic parameters of SrCl$_2$-NH$_3$ were determined on lab-scale reactors with around 210 g [13] and 2100 g [23] of the sorbent. Given the sorbent masses, it is obvious that the kinetic parameters reported in literature contain the effect of heat and mass transfer and hence can be used for global rather than local modelling.

In order to obtain intrinsic, i.e. free from heat and mass transfer, kinetic parameters of NH$_3$ sorption on SrCl$_2$ salt experimentally, one has to ensure that the temperature used in the kinetic analysis is that of the sample [24]. In addition, local NH$_3$ pressure within the sample must be uniform and equal to the one set for the kinetic experiment. To satisfy the abovementioned requirements, one must pay special attention to the following points:
1. Bulk sorbents have poor heat and mass transfer performance. For significant intensification of the heat and mass transfer within the sorbent bed, metal halides and in particular SrCl₂ can be confined within the porous heat conductive matrix of expanded natural graphite (ENG) [21], [25]–[28]. The importance of using composite material SrCl₂ - ENG for reliable characterization of the solid-gas reaction parameters was pointed out by Yuan et al. [13] and Wu et al. [29]. Even though the enhancement of the heat and mass transfer in the sorbent bed is necessary, it is not sufficient condition for obtaining intrinsic kinetic parameters without meeting the second one, stated below.

2. The heat and mass transfer are mass-dependent phenomena, meaning that their effect is more pronounced in larger samples. Thus, kinetic measurements must be performed on a sample of an optimal mass, which is small to eliminate the effect of the transfer processes, but large enough to give readout numbers well above the instrumental noise. The use of the optimal mass for obtaining reliable kinetic parameters was strongly advised by the International Confederation for Thermal Analysis and Calorimetry Kinetics Committee [24], and several kinetic studies have shown that this mass should be less than 1 g [30]–[32].

Therefore, combining the two aforementioned points, we will develop a facile procedure to obtain the intrinsic kinetics of chemisorption and will apply it to SrCl₂-NH₃ working pair. Then we will demonstrate the importance of using intrinsic kinetic parameters in local modelling of chemisorption processes. It will be done by comparing between the results from a spatially resolved model, with the obtained and literature kinetics implemented, and the experimental data. The originality of the developed herein procedure lies in using both conditions for the identification of kinetic parameters (heat and mass transfer intensification and optimal mass) as well as in performing kinetic measurements at constant temperature on a Sievert’s type apparatus, which allows resolving the common problem of heat-up time. Furthermore, we report for the first time the intrinsic kinetic parameters of NH₃ sorption on SrCl₂, as the ones found in literature contain the effect of the heat and mass transfer.
2. Experimental

2.1. Composite material preparation and its characteristics

ENG boards (apparent density 75 kg/m$^3$) were supplied by SGL carbon, and SrCl$_2$ (purity $\geq$ 98%) was delivered by Amminex, an industrial partner of the project. First, ENG cylindrical pellets (see Figure A 1(a) in Appendix A) of 10 cm$^3$ in volume dehydrated at 120°C for 8 h were immersed into ethanol for two hours to decrease the surface tension between the non-polar ENG and polar water-based SrCl$_2$ solution. Then, the samples were placed in SrCl$_2$ solution (33.3 % wt.) for two hours, after which they were dried in a ventilated oven at 90°C for 12 hours for the removal of the water. After that, the samples were further dried in a vacuum furnace at 300°C for 12 hours to eliminate the water absorbed by the crystals of the salt. It is worth mentioning that after the impregnation and drying the volume of the samples decreased by 52%. The composite material pellet is illustrated in Figure A 1(b) in Appendix A. The synthesized material has the following characteristics: the mass content of SrCl$_2$ is 55 %wt., and the apparent density is around 350 kg/m$^3$.

The information on how these characteristics were calculated can be found in Appendix B. The dimensions and mass of the pellet, before and after impregnation, were measured with a micrometer and a weighing balance, respectively. The resolution of the micrometer is 0.01 mm and the uncertainty is less than 0.001%. For the weighing balance, the resolution and uncertainty are 0.1 mg and less than 0.16%, respectively.

The optimal mass of the sample was determined through a series of kinetic measurements. These measurements were performed at same pressure-temperature conditions using gradually decreasing sample mass until the kinetic curves of two neighbouring masses coincide. Kinetic curve describes the dependence of the reaction advancement on time, and reaction advancement shows the degree of the sample saturation with NH$_3$. The procedure of mass in-dependency experiments is described in [24], and it was applied in several studies [30]–[32].

2.2. Experimental apparatus

For determining kinetic parameters of a sorption reaction, one has to obtain a series of reaction profiles, or, in other words, kinetic curves. In the present study, the kinetic parameters were determined using an in-house Sieverts type apparatus (see description below). In the apparatus, the temperature of the sample is measured by a thermocouple mounted at the bottom of the outer wall of the reactor, its tip being separated from the sample by 1 mm stainless steel wall. Such an
instrument configuration, where the temperature of the sample is measured indirectly, may lead to the systematic deviation between the thermocouple reading and the actual temperature of the sample, when carrying out constant heating rate experiments. As a result, this systematic error may have a profound effect on the values of the obtained kinetic parameters. Therefore, in order to avoid this error, isothermal heating programs were selected, and sufficient time was given for the sample temperature to equilibrate with that of a heating source before the start of any measurement.

The operating principle of the Sieverts type apparatus is based on measuring the change in gas pressure in a calibrated volume during sorption processes. The principle diagram of the Sieverts apparatus used for performing the kinetics measurements is shown in Figure 2.

![Figure 2. Schematic of the experimental setup used for the determination of the kinetic equations.](image)

The setup mainly consists of a reactor embedded in a tubular furnace, an NH₃ cartridge, and an NH₃ tank. The three elements, connected to each other via gas lines, form a gas system of 4.86 l total volume. The reactor, where the sample is placed, is a stainless steel tubular container of 10 mm in diameter and 30 mm in length with a wall thickness of 1 mm. The NH₃ cartridge filled with 132 g of ammoniated SrCl₂ serves as an NH₃ source to pressurize the system. The pressure is measured by a pressure sensor with a measuring range of [0 – 10 bar] and a noise level of less than 0.5 mbar. During the sorption experiments, the pressure drop was around 16 mbar. The temperature of the sample is measured with a K-type thermocouple mounted at the bottom of the
reactor. The resolution of the thermocouple is 0.1 K. For the purpose of evacuation, the system is connected to a vacuum pump.

One of the main advantages of using the Sieverts apparatus is that the reactor and the NH\textsubscript{3} tank can be separated by a valve, which allows the two reservoirs to maintain different pressures. This resolves the problem of heat-up time for isothermal measurements preventing unwanted absorption or desorption during the heating of the sample up to the temperature chosen for the kinetic measurements. The problem of heat-up time was discussed in detail by Vyazovkin et al. [24].

2.2.1. Absorption mode

For the absorption measurements, the sample was placed and sealed in the reactor. These operations were performed in an argon glove box, where the level of water does not exceed 0.1 ppm, to avoid any water absorption by hydrophilic SrCl\textsubscript{2}. Then, the reactor was connected to the rest of the Sieverts apparatus, and all volumes, except the NH\textsubscript{3} cartridge, were evacuated for one hour using the vacuum pump. The value of the residual pressure in the system after 1 h under active vacuum was around 4.5 mbar. Then, the NH\textsubscript{3} tank was filled with gaseous NH\textsubscript{3} by heating the NH\textsubscript{3} cartridge until the desired pressure was reached. During the filling of the system with NH\textsubscript{3}, the valve between the reactor and the rest of the system was kept closed to avoid NH\textsubscript{3} absorption by the sample. The heat required for keeping the sample at constant temperature was supplied by the furnace. To ensure that the temperature of the sample had a set value during the absorption, the reaction was initiated one hour after the temperature measured by the thermocouple had reached the programmed value. The kinetic measurement was started by opening the valve connecting the reactor to the rest of the system and stopped with the stabilization of the pressure in the system. Since we have observed the change in the absorption rate after the first sorption cycle, each sample was subjected to at least one NH\textsubscript{3} absorption and desorption prior to the kinetic measurement.

2.2.2. Desorption mode

In principle, the desorption measurements follow the absorption ones; therefore, the sample was already placed in the Sieverts apparatus as described above. Before the start of the desorption test, the temperature of the sample should reach the desired value; however, the increase in temperature may cause anticipatory decomposition of the ammoniated salt. Therefore, to avoid NH\textsubscript{3} desorption,
the pressure in the reactor was maintained above equilibrium pressure. Equilibrium pressure was
determined using the Van’t Hoff equation:

\[ p_{eq} = p_0 e^{-\frac{\Delta H}{RT} + \frac{\Delta S}{R}} \]  

Eq. 2

where \( p_0 \) is a reference pressure; \( \Delta H \) and \( \Delta S \) are the reaction enthalpy and entropy equal to 41.432
kJ/mole of NH\(_3\) and 228.6 J/(K \cdot \text{mole of NH}_3), respectively [4]; \( R \) is the gas constant; and \( T \) is
the temperature of the sample.

Once the sample temperature has stabilized (dwell of 1 h), the desorption was started by opening
the valve between the reactor and the rest of the system. Desorption was finished when the pressure
in the system got stable.

3. Theory

The equation of the solid-gas reaction kinetics is generally expressed as follows:

\[ \frac{dx}{dt} = k \cdot f(x) \]  

Eq. 3

where \( x \) is the reaction advancement at time \( t \); \( k \) is the rate constant; \( f(x) \) is the function
determining the reaction model.

The rate constant is a function of the salt temperature \( T \) and NH\(_3\) pressure \( p \) over the sample and
can be expressed as follows:

\[ k = k_0 \cdot h(p) \cdot e^{-\frac{E_a}{RT}} \]  

Eq. 4

where \( k_0 \) is the pre-exponential factor; \( E_a \) is the activation energy of the reaction; \( h(p) \) is the
pressure impact function expressing the degree of the discrepancy between the actual gas pressure
in the system \( p \) and the equilibrium gas pressure over the salt \( p_{eq} \) (see Eq. 2).

Combining Eq. 3 and Eq. 4 results in the expanded form of the kinetics equation:

\[ \frac{dx}{dt} = k_0 \cdot f(x) \cdot h(p) \cdot e^{-\frac{E_a}{RT}} \]  

Eq. 5

Thus, the kinetics of the solid-gas reaction can be described by a kinetic tetrad, consisting of \( k_0, f(x), h(p) \), and \( E_a \).
In order to determine the kinetic tetrad, the following procedure was applied:

1. First, Pressure-Time curves were obtained from two series of kinetic experiments carried out at constant pressure and temperature. While one of the series was to be performed at the same temperature but different pressures, the other set was taken at different temperatures but fixed pressure.

2. The obtained Pressure-Time curves in (1) were converted into Reaction advancement-Time curves using the following formula:

   - For absorption
   
   \[ x = \frac{p_{\text{beg}} - p}{p_{\text{beg}} - p_{\text{end}}} \]  
   \[ \text{Eq. 6} \]

   where \( p_{\text{beg}} \) is the pressure at the beginning of the experiment; \( p \) is the pressure at time \( t \); \( p_{\text{end}} \) is the pressure at the end of the experiment, when it reaches a plateau.

   - For desorption

   \[ x = \frac{p - p_{\text{beg}}}{p_{\text{end}} - p_{\text{beg}}} \]  
   \[ \text{Eq. 7} \]

3. Reaction advancement derived in Eq. 6 and Eq. 7 was inserted in the reaction models presented in the work of Vyazovkin et al. [24]. The function \( g(x) \) is the integral form of \( f(x) \):

   \[ g(x) = \int \frac{dx}{f(x)} = kt \]  
   \[ \text{Eq. 8} \]

   According to Eq. 8, the dependence of \( g(x) \) on time should result in a straight line. Therefore, among the models listed in [24], the one with the highest coefficient of determination (R²) to a linear trend line was selected. The slope of the line revealed the rate of the reaction \( k \).

4. For the series of the kinetics experiments taken at constant temperature, a graph illustrating the dependence between the pressure impact function \( h(p) \) and the rate constant \( k \) was plotted. Eq. 9 shows a mathematical formula of this graph derived from Eq. 4:

   \[ h(p) = \frac{e^{\frac{E_a}{RT}}}{k_0} \cdot k \]  
   \[ \text{Eq. 9} \]
Since the measurements were taken at the same temperature, the coefficient before the argument \( e^{\frac{E_a}{RT}} \) is constant, and hence the dependence \( h(p) \cdot k \) should be as linear as possible. This was the criterion for the selection of the power function, the general form of which is presented in Eq. 10.

\[
h(p) = \pm \left( \frac{p - p_{eq}}{p_{eq}} \right)^n \quad \text{Eq. 10}
\]

where “+” is for absorption and “-” for desorption; \( p_{eq} \) is the equilibrium NH\(_3\) pressure over the salt at the given temperature of the salt \( T \). The equilibrium pressure was calculated from the Van’t Hoff equation (Eq. 2).

5. In order to determine the values of the pre-exponential factor and the activation energy, \( \ln k \frac{h(p)}{h(P)} \) was plotted as a function of inverse temperature for the set of the experiments obtained at constant pressure. This dependence can be derived from Eq. 4 and be expressed as follows:

\[
\ln k - \ln (h(P)) = \ln k_0 - \frac{E_a}{RT} \quad \text{Eq. 11}
\]

Thus, the pre-exponential factor was calculated from the intercept between the linear trend line to the data and y-axis, and the activation energy was retrieved from the slope of the trend line.

6. The goodness of the obtained tetrads was evaluated by comparing the kinetic curves from the obtained model with the experimental kinetics curves, from which the tetrads had been computed.

4. Numerical modelling

A numerical model of NH\(_3\) sorption on SrCl\(_2\) salt was developed. The model computes spatio-temporal evolution of reaction advancement, temperature, and pressure through solving the kinetic equation along with the heat and mass transfer equations. As an input for the kinetic equation, we used three sets of kinetic tetrads – the one determined herein and the ones published in literature [13], [23]. The modelling results were compared with the experimental data, which were obtained on a sample larger than the optimal mass.

4.1. Experimental data
A series of absorption and desorption experiments was performed on 466 ± 0.5 mg of SrCl$_2$ powder using the Sieverts type apparatus. To ensure good heat transfer between the sample and the heat source/sink, the salt was wrapped in a cube with a side length of 1 ± 0.05 cm made of aluminium foil. Thus, the apparent density of SrCl$_2$ $\rho_{\text{app}}$ was 466 kg/m$^3$. To let ammonia in, an opening of 1 ± 0.05 cm in length was made in the aluminium foil using a paper cutter. A series of absorption experiments was performed at same pressure (4.5 bar) and various temperature (25, 30, and 35°C). For desorption, one set of measurements was performed at same pressure and various temperature (50, 55, and 60°C), and another one was conducted at same temperature (55°C) and different pressure (0.5, 1, and 1.5 bar). As a result, curves showing the change in the pressure over time were obtained. The curves were then converted into kinetics curves using Eq. 6 and Eq. 7 for absorption and desorption, respectively.

### 4.2. Model

In the numerical model, a porous medium containing the salt and gaseous NH$_3$ was represented by a cube of 1 cm$^3$. An aluminium layer of 0.016 mm in thickness was placed around the cube to represent the aluminium foil used during the Sieverts experiments. NH$_3$ inlet/outlet was made by cutting off a block (1 cm in length, 0.016 mm in depth, and variable width $d$) from one of the sides of the cube. The geometry of the model is presented in Figure C1 in Appendix C. The temperature of the outer wall of the aluminium layer was set equal to the temperature used during the experiment.

The absorption model developed in this study couples the kinetics of the chemical reaction with the heat and mass transfer. In the case of the desorption model, it was computed with and without the mass transfer physics for 0.5 bar and 55°C. These conditions were chosen among the others because they provide the fastest desorption rate and thus contain the largest effect from the mass transfer. We observed a small deviation between the results of the two simulations (within 3 %) but a significant decrease in computation time for the model without the fluid dynamics. For these reasons, we have computed the desorption model for the other pressure-temperature conditions without including the fluid dynamics equations.

The governing equations for the heat and mass transfer are listed in Appendix D. Equations describing the kinetics of the sorption processes are presented in Table 1.
Table 1. Kinetics equations and their elements for NH₃ sorption on SrCl₂ obtained in this study and found in literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Parameter</th>
<th>Absorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Equation</td>
<td>( \frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT} \cdot f(x) \cdot \left( \frac{p - p_{eq}}{p_{eq}} \right)^n} )</td>
<td>( \frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT} \cdot f(x) \cdot \left( \frac{p_{eq} - p}{p_{eq}} \right)^n} )</td>
</tr>
<tr>
<td>Reported in Results and Discussions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huang et al. [23]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Equation</td>
<td>( \frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT} (1 - x)^M \frac{p - p_{eq}}{p_{eq}}} )</td>
<td>( \frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT} (1 - x)^M \frac{p_{eq} - p}{p_{eq}}} )</td>
</tr>
<tr>
<td></td>
<td>( k_0, s^{-1} )</td>
<td>0.0190</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>( E_a, \text{J/mole} )</td>
<td>6921</td>
<td>9000</td>
</tr>
<tr>
<td></td>
<td>( M )</td>
<td>2.96</td>
<td>3.02</td>
</tr>
<tr>
<td>Yuan et al. [13]</td>
<td>Equation</td>
<td>( \frac{dx}{dt} = Ar (1 - x)^M \left( \frac{1 - \frac{p}{p_{eq}}}{\frac{p_{eq}}{p}} \right) )</td>
<td>( \frac{dx}{dt} = (Ar + A \cdot T) \cdot x^M \cdot (1 - \frac{p_{eq}}{p}) )</td>
</tr>
<tr>
<td></td>
<td>( Ar )</td>
<td>0.001631</td>
<td>0.02413 (( x &gt; 0.8 ))</td>
</tr>
<tr>
<td></td>
<td>( A )</td>
<td>-</td>
<td>0.0004598 (( x &lt; 0.8 ))</td>
</tr>
<tr>
<td></td>
<td>( M )</td>
<td>2.071</td>
<td>1.1</td>
</tr>
</tbody>
</table>

5. Results and Discussion

5.1. Determination of the optimal mass

To determine the salt optimal mass for the kinetics measurements, four samples of the composite material made of ENG and SrCl₂ were tested. The mass of SrCl₂ in the composite material samples were 61.0, 70.0, 146.0, and 186.0 mg. The value of the standard deviation is less than 0.5 mg for all the masses. All the prepared samples were of cubic shape. The desorption tests were performed under 1 bar of NH₃ and 45°C, and during the absorption measurements the samples were subject to NH₃ pressure of 2.5 bar at 20°C. As a result, Pressure-Time curves were obtained and then converted into kinetics curves using Eq. 6 and Eq. 7. The observed pressure changes were below 0.05 bar for all experiments and were assumed to have negligible impact on the reaction kinetics. The kinetics curves are shown in Figure 3(a) and Figure 4(a), and their comparison to each other, absolute difference, is plotted as a function of time in Figure 3(b) and Figure 4(b), respectively.
Figure 3. Determination of the optimal mass for the desorption kinetic measurements: (a) kinetic curves obtained at one bar and 45°C for different masses of the composite material. In legend: the mass of SrCl₂ used; (b) Dependence of the absolute difference between the two curves, obtained for two different masses mentioned in legend, on time.

Figure 4. Determination of the optimal mass for the absorption measurements: (a) kinetic curves taken at 2.5 bar and 20°C for different masses of the composite material. In legend: the mass of SrCl₂ used in the test is indicated; (b) Dependence of the absolute difference between the two curves, obtained for two different masses mentioned in legend, on time.
Comparing the desorption curves in Figure 3(a), one can observe that the largest increase in the desorption rate occurred when the sample mass decreased from 146 to 70 mg. The absolute difference between the two desorption curves exceeded 24% (Figure 3(b)). However, with further mass reduction, from 70 to 61 mg, the kinetics for the higher mass appeared to be faster. The reason for the faster kinetics of the higher mass sample may lay in higher contact area between the sample and the heat source. The contact area depends on the shape of the sample, as well as on the position of the sample relative to the heat source. In our experiment, it was easy to control the location of the sample, but making samples of exact same geometry, considering their small size (~0.4 cm³), was challenging. Therefore, the difference in the sample geometry could explain such a behavior of the desorption curves. Despite this, the deviation between the curves appeared to be lower than acceptable variation set to 5%.

Compared to the results from the desorption, the deviation between the absorption curves is not that large (Figure 4(a)). For example, the 70 mg kinetic curve reproduces the other curves within 6% error, while in case of desorption the value of discrepancy surpasses 24% (Figure 4(b)). This brings us to the conclusion that the mass of the sample has greater effect on the desorption rate compared to the absorption rate, at least for the used pressure-temperature conditions.

As a result, 70 mg of SrCl₂ was set to be the optimal mass, i.e. the maximum mass to be used to suppress any limitation from the mass and heat transfer while keeping a good accuracy of the kinetic measurements for the determination of the sorption tetrads.

5.2. Determination of intrinsic kinetics

5.2.1. Desorption

For the first step of determining the close-to-intrinsic kinetics of NH₃ desorption from Sr(NH₃)₈Cl₂, two series of desorption measurements were carried out on the composite sample containing 70 mg of SrCl₂. One of the desorption sets was performed at one bar and various temperature (45, 50, 55, and 60˚C), and the other one was carried out at 55˚C and various pressure (0.5, 1, 1.5, and 2 bar). The obtained Pressure-Time curves were converted into Reaction advancement-Time curves, using Eq. 7. Figure 5 shows the results of this step with the desorption curves at various temperature (Figure 5(a)) and various pressure (Figure 5(b)).
Figure 5. Desorption kinetic curves obtained on the composite material of the optimal mass (70 mg of SrCl\textsubscript{2}) at (a) one bar and various temperature (45, 50, 55, and 60°C) and (b) at 55°C and various pressure (0.5, 1, 1.5, and 4.5 bar). X axis is plotted in log scale.

To determine the rate-limiting step of the desorption, the curves in Figure 5 were linearized with the models presented in [24]. The best accuracy of linearization (R\textsuperscript{2} > 0.99) was reached using the contracting sphere reaction model described by the expression \( g(x) = 1 - (1 - x)^{\frac{1}{3}} \). This equation is the integral form of \( f(x) = 3 \cdot (1 - x)^{\frac{2}{3}} \). Figure 6 illustrates the linearized curves at various temperature (Figure 6(a)) and various pressure (Figure 6(b)).
Figure 6. Linearization of the desorption kinetic curves obtained on the composite material of the optimal mass (70 mg of SrCl₂) at (a) 1 bar and various temperature (45, 50, 55, and 60 °C) and (b) 55 °C and various pressure (0.5, 1, 1.5, and 2 bar). Chemical reaction mechanism used for the linearization is described with the function \( g(x) = 1 - (1 - x)^\frac{1}{3} \). Reaction advancement \( x \) used is in the range 0 - 0.9.

The contracting sphere reaction model was found to describe other solid-gas reactions, for example, between solid MgCl₂ and gaseous NH₃ [32] and solid K₂CO₃ and H₂O vapour [30].

Table 2 shows the values of the reaction rate \( k \) obtained as slope of the curves in Figure 6.

### Table 2. Desorption rate constants obtained for various temperature and pressure.

<table>
<thead>
<tr>
<th>( T, °C )</th>
<th>( p_{eq}/p )</th>
<th>( k, 1/s )</th>
<th>( R^2 )</th>
<th>( p, \text{bar} )</th>
<th>( p_{eq}/p )</th>
<th>( k, 1/s )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>2.272 ( \cdot 10^4 )</td>
<td>0.9983</td>
<td>0.5</td>
<td>2.823 ( \cdot 10^{-1} )</td>
<td>0.9897</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.4 ( \cdot 6.67 \cdot 10^{-4} )</td>
<td>0.9988</td>
<td>1</td>
<td>1.166 ( \cdot 10^{-1} )</td>
<td>0.9979</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>1.8 ( \cdot 1.181 \cdot 10^{-6} )</td>
<td>0.9979</td>
<td>1.5</td>
<td>5.3 ( \cdot 10^{-4} )</td>
<td>0.9991</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>2.2 ( \cdot 1.183 \cdot 10^{-3} )</td>
<td>0.9929</td>
<td>2</td>
<td>1.5 ( \cdot 1.14 \cdot 10^{-4} )</td>
<td>0.9967</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The rate constants at various pressure were plotted against pressure impact function expressed by Eq. 10. The value of exponent \( n \) was set to 1.9, giving best fit to a straight line and an activation energy higher than the reaction enthalpy as expected for endothermic reactions. The dependence of the pressure model \( h(p) \) on the rate constant at various pressure is illustrated in Figure 7 together with a linear trend line, which coefficient of determination (\( R^2 \)) is 0.9779.
Figure 7. Pressure dependence function \( h(P) = \left( \frac{p_{eq} - p}{p_{eq}} \right)^{1.9} \) versus reaction rate for close-to-intrinsic desorption kinetic study. \( p_{eq} \) is defined in Eq. 2.

Extracting the rate constants at various temperatures from Figure 6(a) allowed drawing Arrhenius plot, \( \ln \left( \frac{k}{h(P)} \right) \) as a function of inverse temperature, as shown in Figure 8. The coefficient of determination (R\(^2\)) of the fitted linear trend line is 0.9877.

Figure 8. Arrhenius plot of NH\(_3\) desorption from SrCl\(_2\).
From the Arrhenius plot, the intercept and the slope of the trend line were found to be 10.52 and -5275.1, respectively. These values correspond to $ln k_0$ and $-\frac{E_a}{R}$, respectively. Thus, the pre-exponential factor $k_0$ and the activation energy $E_a$ of the desorption were found to be 36754 s$^{-1}$ and 43.9 kJ/mole, respectively.

The kinetic equation obtained in this analysis was computed for the experimental pressure-temperature conditions. Figure 9 depicts desorption profiles under various temperature and pressure. The kinetic model predicts the experimental data over a wide range of pressure and temperature. However, the predictions by the kinetic model slightly underestimates the desorption rate when the pressure in the system tends to equilibrium pressure (Figure 9(b) – 2 bar).

![Figure 9](image)

**Figure 9. Desorption kinetic curves obtained experimentally and numerically. Computed kinetic curves are represented by triangles, while experimental curves are plotted as solid lines. X axis is plotted in log scale.**

### 5.2.2. Absorption

To find the kinetic tetrad of NH$_3$ absorption into Sr(NH$_3$)$_2$Cl$_2$, the same steps as for the desorption analysis were taken.

The sample of the optimal mass (70 mg of SrCl$_2$) was subject to 2.5 bar of gaseous NH$_3$ at four different temperatures – 20, 25, 30, and 35°C. In addition, the same sample was exposed to various pressure (1.5, 2, and 4.5 bar) of NH$_3$, while the reactive bed temperature was kept at 30°C. The
results of the measurements at various temperature and various pressure are illustrated in Figure 10(a) and Figure 10(b), respectively.

Figure 10. Absorption kinetic curves obtained on the composite material of the optimal mass (70 mg of SrCl$_2$) at (a) 2.5 bar and various temperature (20, 25, 30, and 35°C) and (b) 30°C and various pressure (1.5, 2, 2.5, and 4.5 bar).

After linearizing the seven absorption curves, the chemical reaction mechanism described by $g(x) = 1 - (1 - x)^{1/3}$ was selected. The selection was based on the value of the average $R^2$ of the linear trend lines fitted to the linearized curves. For the selected mechanism, the average $R^2$ was equal to 0.98. Figure 11 shows the linearized curves.
Figure 11. Linearization of absorption kinetic curves obtained on the composite material of the optimal mass (70 mg of SrCl$_2$) at (a) 2.5 bar and various temperature (20, 25, 30, and 35°C) and (b) 30°C and various pressure (1.5, 2, and 4.5 bar). Chemical reaction mechanism used is described with the function $g(x) = 1 - (1 - x)^{\frac{1}{3}}$. Reaction advancement $x$ used is in the range 0 - 0.9.

Table 3 shows the values of the reaction rate obtained as slope of the curves in Figure 11.

**Table 3. Absorption rate constants obtained for various temperature and pressure.**

<table>
<thead>
<tr>
<th></th>
<th>2.5 bar</th>
<th></th>
<th></th>
<th>30 °C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, °C</td>
<td>$p/p_{eq}$, bar</td>
<td>$k$, 1/s</td>
<td>$R^2$</td>
<td>$p$, bar</td>
<td>$p/p_{eq}$, bar</td>
<td>$k$, 1/s</td>
</tr>
<tr>
<td>20</td>
<td>6.7</td>
<td>9.59 · 10$^{-4}$</td>
<td>0.9995</td>
<td>1.5</td>
<td>2.3</td>
<td>1.8 · 10$^{-4}$</td>
</tr>
<tr>
<td>25</td>
<td>5.0</td>
<td>7.4 · 10$^{-4}$</td>
<td>0.9994</td>
<td>2</td>
<td>3.0</td>
<td>2.8 · 10$^{-4}$</td>
</tr>
<tr>
<td>30</td>
<td>3.8</td>
<td>6.4 · 10$^{-4}$</td>
<td>0.994</td>
<td>2.5</td>
<td>3.8</td>
<td>6.4 · 10$^{-4}$</td>
</tr>
<tr>
<td>35</td>
<td>2.9</td>
<td>4.9 · 10$^{-4}$</td>
<td>0.9983</td>
<td>4.5</td>
<td>6.8</td>
<td>2.2 · 10$^{-3}$</td>
</tr>
</tbody>
</table>

The pressure dependence function, expressed in Eq. 10, was plotted against the rate constants at various temperature, as shown in Figure 12(a). The highest degree of linearization was achieved with $n$ equal to 1.8. The coefficient of determination ($R^2$) in this case was found to be 0.9975.
Figure 12. (a) Pressure dependence function over reaction rate for close-to-intrinsic absorption kinetics. (b) Arrhenius plot of NH$_3$ absorption into SrCl$_2$ – close-to-intrinsic kinetics.

Then, to find the kinetic parameters, such as pre-exponential factor and activation energy, the dependence of $\ln\frac{k}{h(P)}$ on inverse temperature were plotted together with a linear trend line ($R^2=0.9954$). Extracting the intercept and the slope of the trend line (17.003 and -7949.1 respectively) resulted in getting the following parameters: $k_0 = 2.423 \times 10^7$ s$^{-1}$ and $E_a = 66.1$ kJ/mole.

The determined absorption kinetic equation was computed for the pressure-temperature conditions used in the experiment. Figure 13 depicts absorption profiles under various temperature (a) and pressure (b). From Figure 13, one can conclude that the absorption model is in a good agreement with the experimental data when comparing the experimental reaction profiles (triangles) to the corresponding simulations (solid lines). However, as well as for the desorption, the numerical predictions slightly underestimate the absorption rate for small pressure difference, when actual pressure in the system tends to the equilibrium one (Figure 13(b) – 1.5 bar).

Figure 13. Absorption kinetic curves obtained experimentally and numerically. Computed kinetic curves are represented as triangles, while experimental ones are plotted as solid lines.

5.3. Numerical model vs. Experiment
Experimental and numerical results for NH₃ absorption at 4.5 bar and various temperature (25, 30, and 35°C) are presented and compared in Figure 14. As described above, the experimental data was collected on 466 mg SrCl₂ wrapped in aluminium foil with an opening. As it was challenging to measure precisely the width of the opening, we investigated its effect on the absorption kinetics by computing the intrinsic model and the literature models using various opening size.

![Kinetic curves of NH₃ absorption on 466 mg of SrCl₂ at 4.5 bar and (a) 25°C; (b) 30°C; and (c) 35°C. Experimental and numerical results are indicated as solid line and triangles, respectively. In the legend: the source from where the kinetic equation was taken / the width of the aluminium opening. Note that Yuan et al. / 0.48 mm and Huang et al. / 0.48 mm coincide with Yuan et al. / 9.60 mm and Huang et al. / 9.60 mm, respectively.]

In case of the intrinsic model, the increase in the size of the aluminium opening (from 0.48 to 9.6 mm) was found to speed up the absorption kinetics after the degree of absorption reaches 0.5, especially at higher absorption temperatures. This observation is reasonable, as in general the contribution from the mass transfer should get more pronounced at higher absorption temperatures as well as at lower medium porosity and hence lower permeability. In addition, it was observed that further increase in the width does not lead to further acceleration of the reaction rate. Despite the fact that the intrinsic model becomes independent of the mass transfer at width of 9.6 mm, in practice the width was observed to be closer to the lower limit of the parametric range (0.48 mm). In contrast to the intrinsic model, the variation in the width size in the literature models did not result in any change of the reaction profile, indicating that such a contribution from the mass transfer is negligible for the literature kinetics.
The absorption profiles computed with the use of the intrinsic tetrad at width of 0.48 mm reproduce nicely the experimental kinetic curves, while the kinetic curves simulated with the use of the tetrads found in the literature are much slower than the experimental ones. Since for the determination of the kinetic tetrads both Huang et al. [23] and Yuan et al. [13] used large samples, where NH$_3$ has to diffuse over long distances, it is reasonable to assume that the literature kinetic parameters include a rate limiting effect of the mass transfer, which results in slower simulated absorptions. In addition to mass transfer, the literature kinetic equations include the contribution from the heat transfer, which also decelerates the overall kinetics.

The desorption kinetic curves obtained at 1 bar and various temperature (50, 55, and 60°C) and at 55°C and various pressure (0.5, 1.0, and 1.5 bar) are presented as markers for the numerical models and as solid lines for the experimental data in Figure 15.

![Figure 15. Kinetics curves of NH3 desorption from SrCl$_2$ at: (a) 1 bar and 50°C; (b) 1 bar and 55°C; (c) 1 bar and 60°C; (d) 55°C and 0.5 bar; (e) 55°C and 1 bar; (f) 55°C and 1.5 bar. Experimental and numerical results are indicated as solid line and markers, respectively.](image-url)
slower reaction advancement. The same explanation as for the absorption holds for the slower desorption curves: the parameters determined by Huang et al. [23] or Yuan et al. [13] include a rate limiting effect from heat and mass transfer leading to slower kinetic curves.

6. Conclusions

In the first part of this study, the kinetic tetrads (pre-exponential factor, activation energy, reaction model, and pressure impact function) of ammonia sorption on SrCl₂ ammines were firstly identified by a developed herein facile procedure for obtaining intrinsic kinetics of chemisorption reactions. According to this procedure, the kinetic measurements were performed on a porous composite SrCl₂-ENG sample of an optimal mass (70 mg of SrCl₂), ensuring that the rate of the chemical reaction was not limited by the heat and mass transfer. To resolve the common problem of heat-up time, the measurements were carried out on a Sievert’s type apparatus using isothermal programs. This constitutes the originality of the reported procedure. The obtained kinetics were demonstrated to be in a good agreement with the experimental data obtained on the composite sample of the optimal mass at wide pressure-temperature range.

In the second part of the paper, the obtained kinetics and the ones found in literature were implemented in our local numerical model, calculating independently the rate of the chemical reaction, the heat transfer and the fluid dynamics. The numerical results were compared with the experimental data obtained on 466 mg of SrCl₂ powder at different pressure-temperature conditions. In contrast to the literature parameters, the obtained herein kinetics were shown to align with the experiments, highlighting the importance of using intrinsic parameters for local modelling of chemisorption processes. This finding underlines the significance of the method developed in the first part of the paper.

The presented and applied in this work facile procedure can be used by other researchers for reliable identification of intrinsic kinetic parameters of ammonia sorption on other metal halides. Furthermore, the obtained kinetics can be applied in local modelling of SrCl₂-NH₃ systems, especially for the purpose of optimization, where the particularities of the heat and mass transfer are decisive.
Acknowledgements

This work was supported by NordForsk Nordic Neutron Science Programme through the project “Neutrons for Heat Storage” [grant number 82206].
Figure A 1. Illustration of (a) ENG pellet and (b) composite material pellet.
Appendix B

- The volume of the ENG pellet $V_{ENG}$ was calculated as follows:

$$V_{ENG} = \pi \cdot \left(\frac{D_{ENG}}{2}\right)^2 \cdot H_{ENG} \quad \text{Eq. B 1}$$

where $D_{ENG}$ and $H_{ENG}$ are the diameter and height of the ENG pellet measured by a micrometer. The standard deviation of the successive measurements for $D_{ENG}$ and $H_{ENG}$ is ± 0.40 mm and ± 0.16 mm.

- The volume of the composite material pellet $V_{comp}$ was calculated as follows:

$$V_{comp} = \pi \cdot \left(\frac{D_{comp}}{2}\right)^2 \cdot H_{comp} \quad \text{Eq. B 2}$$

where $D_{comp}$ and $H_{comp}$ are the diameter and height of the composite material pellet measured by a micrometer. The standard deviation of the successive measurements for $D_{comp}$ and $H_{comp}$ is ± 0.35 mm and ± 0.18 mm.

- The decrease of the pellet in volume $\phi$ was computed as follows:

$$\phi = \frac{V_{ENG} - V_{comp}}{V_{ENG}} \quad \text{Eq. B 3}$$

- The mass content of the salt (SrCl$_2$) in the composite material was calculated as follows:

$$w_{SrCl_2} = \frac{m_{comp} - m_{ENG}}{m_{comp}} \quad \text{Eq. B 4}$$

where $m_{comp}$ and $m_{ENG}$ are the masses of the composite material pellet and ENG pellet, respectively.

- The apparent density of the composite material was calculated as follows:

$$\rho_{app\_comp} = \frac{m_{comp}}{V_{comp}} \quad \text{Eq. B 5}$$
Appendix C

Figure C 1. Geometry of the 3D model developed in COMSOL. The width of the opening ($NH_3$ inlet) is 0.48 mm (a) and 9.6 mm (b).
Appendix D

The equation governing the heat transfer in the porous medium can be written as follows:

\[(\rho c_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_{\text{NH}_3} C_{p \text{NH}_3} \mathbf{u} \cdot \nabla T + \nabla(-k_{\text{eff}} \nabla T) = Q \]  \hspace{1cm} \text{Eq. D 1}

where \((\rho c_p)_{\text{eff}}\) is the effective volumetric heat capacity of the porous medium; \(T\) is the temperature; \(\rho_{\text{NH}_3}\) is the density of \(\text{NH}_3\) calculated using the ideal gas law; \(C_{p \text{NH}_3}\) is the specific heat capacity of \(\text{NH}_3\); \(\mathbf{u}\) is the velocity vector of \(\text{NH}_3\); \(k_{\text{eff}}\) is the effective thermal conductivity of the porous medium; \(Q\) is the heat released/absorbed during absorption/desorption. The heat \(Q\) can be calculated using the following formula:

\[Q = \pm \frac{dx}{dt} \cdot N_s \cdot \Delta H \]  \hspace{1cm} \text{Eq. D 2}

where “+” and “-” are used for absorption and desorption, respectively; \(\frac{dx}{dt}\) is the reaction rate; \(N_s\) is the molar density of \(\text{NH}_3\); \(\Delta H\) is the reaction enthalpy. The molar density of \(\text{NH}_3\) was calculated as follows:

\[N_s = \frac{\rho_{\text{SrCl}_2 \text{app}}}{M_{\text{SrCl}_2}} \cdot N_{\text{st}} \]  \hspace{1cm} \text{Eq. D 3}

Where \(\rho_{\text{SrCl}_2 \text{app}}\) is the apparent density of \(\text{SrCl}_2\), equal to 466 kg/m\(^3\); \(M_{\text{SrCl}_2}\) is the molar mass of \(\text{SrCl}_2\), and \(N_{\text{st}}\) is the number of \(\text{NH}_3\) moles reacting with one mole of \(\text{SrCl}_2\) in accordance with Eq. 1 in the main text of the paper.

The effective properties of the porous medium were calculated as follows:

\[(\rho c_p)_{\text{eff}} = \varepsilon \cdot \rho_{\text{NH}_3} \cdot C_{p \text{NH}_3} + (1 - \varepsilon) \cdot \rho_{\text{salt}} \cdot C_{p \text{salt}} \]  \hspace{1cm} \text{Eq. D 4}

\[k_{\text{eff}} = \varepsilon \cdot k_{\text{NH}_3} + (1 - \varepsilon) \cdot k_{\text{salt}} \]  \hspace{1cm} \text{Eq. D 5}

where \(\varepsilon\) is the salt porosity; \(C_{p \text{NH}_3}\) and \(k_{\text{NH}_3}\) are the specific heat capacity and the thermal conductivity of \(\text{NH}_3\) taken from the database of Engineering Equation Solver (EES 2016); \(\rho_{\text{salt}}, C_{p \text{salt}}, k_{\text{salt}}\) are the density, the specific heat capacity, and the thermal conductivity of the salt. All the properties of the salt depend on the reaction advancement and are assumed to change linearly between ammoniated \((\text{Sr(NH}_3)_8\text{Cl}_2)\) and non-ammoniated \((\text{Sr(NH}_3)\text{Cl}_2)\) states. The properties of the salt in ammoniated and non-ammoniated states are presented in Table D 1.
**Table D 1. Properties of Sr(NH$_3$)$_2$Cl$_2$ and Sr(NH$_3$)$_8$Cl$_2$ used in modelling.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Sr(NH$_3$)$_2$Cl$_2$</th>
<th>Sr(NH$_3$)$_8$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density</td>
<td>kg/m$^3$</td>
<td>2440</td>
<td>1380</td>
</tr>
<tr>
<td>Porosity</td>
<td>n.a.</td>
<td>0.79</td>
<td>0.37</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>J/kg/K</td>
<td>$649.8 + 3.524 \cdot T + 0.0021 \cdot \frac{T^2}{T^3} [33]$</td>
<td>$576.296 + 3.124 \cdot T + 0.07 \cdot \frac{T^2}{T^3} [33]$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/m/K</td>
<td>0.75 [22]</td>
<td>0.75 [22]</td>
</tr>
</tbody>
</table>

The true densities of monoamine $\rho_1$ and octaammine $\rho_8$ were computed as mass of a unit cell divided by its volume. Information on the unit cells of the monoamine and octaammine can be found in [34] and [35], respectively.

The porosity of the reactive bed $\varepsilon$ were computed using the following formula:

$$
\varepsilon = 1 - \frac{\rho_{SrCl_2\text{app}} \cdot (1 + \frac{\mu_{NH_3}}{\rho_{SrCl_2} \cdot [1 + N_{st} \cdot x]})}{\rho_1 - x \cdot (\rho_1 - \rho_8)}
$$

*Eq. D 6*

Please note that $x$ is equal to null in case of monoamine, and it is 1 for octaammine.

The heat flux transferred between the aluminium foil and the porous salt was calculated as follows:

$$
q = h_w (T_u - T_d)
$$

*Eq. D 7*

where $h_w$ is the heat transfer coefficient between the aluminium foil and the porous medium; $T_u$ and $T_d$ are the temperatures upside and downside, respectively. For the desorption model, the heat transfer coefficient was assumed to change linearly from 265 till 65 W/m$^2$/K. On average, it gives a value of 165 W/m$^2$/K, reported by Huang *et al.* [23]. The change in the heat transfer coefficient reflects the change in the volume of the salt and the decrease in the contact area between the salt and the aluminium foil [36]. For the absorption model, the heat transfer coefficient was assumed constant and equal to 165 W/m$^2$/K, as the absorption is not driven by temperature but pressure.

The diffusion of NH$_3$ in the porous medium was described with the following equations:
where \( Q_m \) is the mass of NH\(_3\) absorbed/released during absorption/desorption per time per reactive bed volume; \( M_{NH_3} \) is the molar mass of NH\(_3\); \( p \) is the local NH\(_3\) pressure; \( \mu \) is the dynamic viscosity of NH\(_3\); \( \kappa \) is the hydraulic permeability of the salt layer. The hydraulic permeability of the porous salt can be calculated through the Carman-Kozeny equation [37], approximating the salt particles as spherical:

\[
\kappa = \frac{\varepsilon^3}{180(1-\varepsilon)^3} d_p^2
\]

Eq. D 11

where \( d_p \) is the salt particle diameter. The particle diameter was assumed to be that of the crystallite size [38]. The crystallite size was determined from the X-ray powder diffraction (XRPD) pattern of the pristine SrCl\(_2\) powder using Williamson-Hall analysis. The crystallite size was found to be around 100 nm.
References


373, 2013.


193, 2019.


Highlights:
1. A method to measure intrinsic kinetic parameters of chemisorption was developed.
2. Intrinsic kinetic equations for SrCl$_2$-NH$_3$ were obtained for the first time.
3. The intrinsic kinetics was demonstrated to align with the experiment.
4. The intrinsic kinetics were compared with the ones found in literature.