UNIVERSITY OF TWENTE.

STUDY OF THE REGENERATION OF $K_2CO_3 \cdot 1.5H_2O$ FROM $KHCO_3$ VIA A TEMPERATURE AND WATER VAPOUR PRESSURE SWING.

BACHELOR OF SCIENCE THESIS

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ABSTRACT

This work analyses the impact of varying water vapour pressure and temperature on the yield of regeneration of $K_2CO_3 \cdot 1.5H_2O$ (potassium carbonate sesquihydrate) from $KHCO_3$ via the chemical reaction $2KHCO_3 + 0.5H_2O_{(g)} \leftrightarrow K_2CO_3 \cdot 1.5H_2O_{(s)} + CO_{2(g)}$. Two different approaches were used in experimental series. One was a test series where the water vapour pressure in the inflowing gas stream was kept stable and the reactor temperature was varied. In a second series, the reactor temperature was kept stable and the water vapour pressure in the inflowing gas stream was varied. The apparent activation energy E_a was determined to be in the range of -50kJ/mole. This is in line with the observation that an increase in temperature lowers the speed of reaction and the total amount of CO_2 desorbed in a given time frame. The value of E_a is subject to uncertainty due to equipment inaccuracies. An increase in water vapour pressure caused the reaction rate to increase. The proportionality is higher than the stoichiometric coefficient 0.5. It was furthermore shown that $k_{des}(T)$, the apparent desorption kinetic constant, depends linearly on the amount of $KHCO_3$ available. The reaction rate could be described by $r_{des}(T) = A * e^{-\frac{E_a}{RT}} * n_{KHCO_3} * [H_2O]^n$, where n>0.5. The description is based on the oversimplified assumption that the reaction is elementary and requires correction factors to properly depict reality.

1 INTRODUCTION

CO_2 is a leading driver of global warming and at the same time new wells for hydrocarbons are ever more difficult to develop and exploit. Considering the high energy density of hydrocarbons based fuels (e.g. fossil fuels), the beneficial properties of carbon based materials like plastics, and the extent of their current usage it seems unlikely for the demand for hydrocarbons to lower in the future. One approach to overcome both problems simultaneously is to use CO_2 as a feedstock for the creation of new hydrocarbons. In order for this process to be energetically feasible it should be powered by renewable energies and/or (low grade) waste heat. Burning traditional fuels would defeat the purpose of synthetically producing new fuels. This was the incentive to analyse the behaviour of potassium carbonate as a potential adsorbent to capture CO_2 from air. It was predicted by Duan et al. (2012) that this salt could adsorb CO_2 at room temperature even at concentrations as low as the 400 ppm which are present in air. The release of CO_2 can in principle occur at temperatures around 50°C. This is a temperature low enough to easily obtain it with low grade waste heat if a suffice amount of water vapour is present. If the for instance peak energy production during midday from renewable sources is consumed in combination with waste heat, it seems plausible to use potassium carbonate adsorbents for the capture of CO_2. The approach could therefore be used in an economic and ecologic manner. The reaction equation for this adsorption (to the right) and desorption (to the left) processes reads:

$$K_2CO_3 \cdot 1.5H_2O + CO_{2(g)} \leftrightarrow 2KHCO_3 + 0.5H_2O_{(g)} \qquad (1\text{-}1)$$

This work was written as a final assignment of the Bachelor Programme Advanced Technology at the University of Twente, the Netherlands. It was conducted at the Laboratory of Thermal Energy under the supervision of Prof. Gerrit Brem in the context of the PhD-thesis of Rafael Rodríguez Mosqueda. The PhD assignment stems from Antecy B.V. In the course of this study it is analysed what the influence of temperature and water vapour pressure are on the completeness or yield of desorption in order to find the mildest desorption conditions that still take most of the CO_2 out of the adsorbent. The research on potassium carbonate at these low temperatures is still relatively sparse so time had to be allocated for the determination of the right conditions to run experimental series. This study can be understood as work in progress since a number of experiments as well as further analysis are required in order to gain true understanding of the processes involved. It is therefore strongly encouraged to continue on some of the points given in this paper in further research.

2 METHODOLOGY

For this study mainly two methods were used. These are gathering of experimental data by means of a number of experiments and analysis of the data using primarily Matlab. The analysis was supported by a small literature study where the main focus lays on an article by Duan et al. (2012) who provided the basic idea for this research. The rest of the analysis was based on general principles and well known basic theory. All methods were applied simultaneously as more knowledge from analysis and literature study revealed points of improvement for the conduction of the experiments which in turn allowed for a deeper analysis. This iterative process was ended as soon as a satisfactory level of understanding had been reached in order to proceed with the next phase of structured experiment series. Two series were conducted. One series was aimed at understanding the effect of different water vapour pressures by varying the temperature in the humidifier and consequently the relative humidity. In the other one the water vapour pressure was kept constant and the temperature was varied in order to gain insight on the temperature dependency of the desorption.

2.1 Research question

The following research question was used for this study.

What are the mildest conditions of CO_2 *desorption via the regeneration of* $KHCO_3$ *towards* $K_2CO_3 \cdot 1.5H_2O$*?*

In order to make this question more tangible, a number of sub-research questions were formulated. The focus here lies on the clarification of “mildest conditions” for both parameters.

Q1: What is the influence of temperature on the rate of desorption and the total amount of CO_2 *desorbed?*

Q2: What is the influence of the water vapour pressure on the rate of desorption and the total amount of CO_2 *desorbed?*

3 LITERATURE STUDY

Duan et al. (2012) predicted a relation for the chemical potential for the system comprised of K_2CO_3, $K_2CO_3 \cdot 1.5H_2O$, and $KHCO_3$ at different temperatures and CO_2 and water vapour partial pressures. By setting the chemical potential equal to zero they calculated the P_{CO2} at equilibrium at different given P_{H2O} and temperatures. The resulting phase diagram is reproduced in Figure 3-1. The authors claim that there are different transition temperatures that determine the region of existence of the two different potassium carbonates and thus the possible adsorption-desorption equilibria. The expression found is reproduced in equation (3-1) where $\Delta\mu$ is the chemical potential in terms of pressure and temperature and $\Delta\mu^0$ is the only temperature-dependent chemical potential. The value of n_0 depends on the chemical reaction taking place, that is the CO_2 adsorption or desorption via the K_2CO_3 or the $K_2CO_3 \cdot 1.5H_2O$. For the CO_2 adsorption by $K_2CO_3 \cdot 1.5H_2O$, n_0 is -0.5.

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT * \ln\left(\frac{P_{CO_2}}{P_0}\left(\frac{P_{H_2O}}{P_0}\right)^{n_0}\right) \tag{3-1}$$

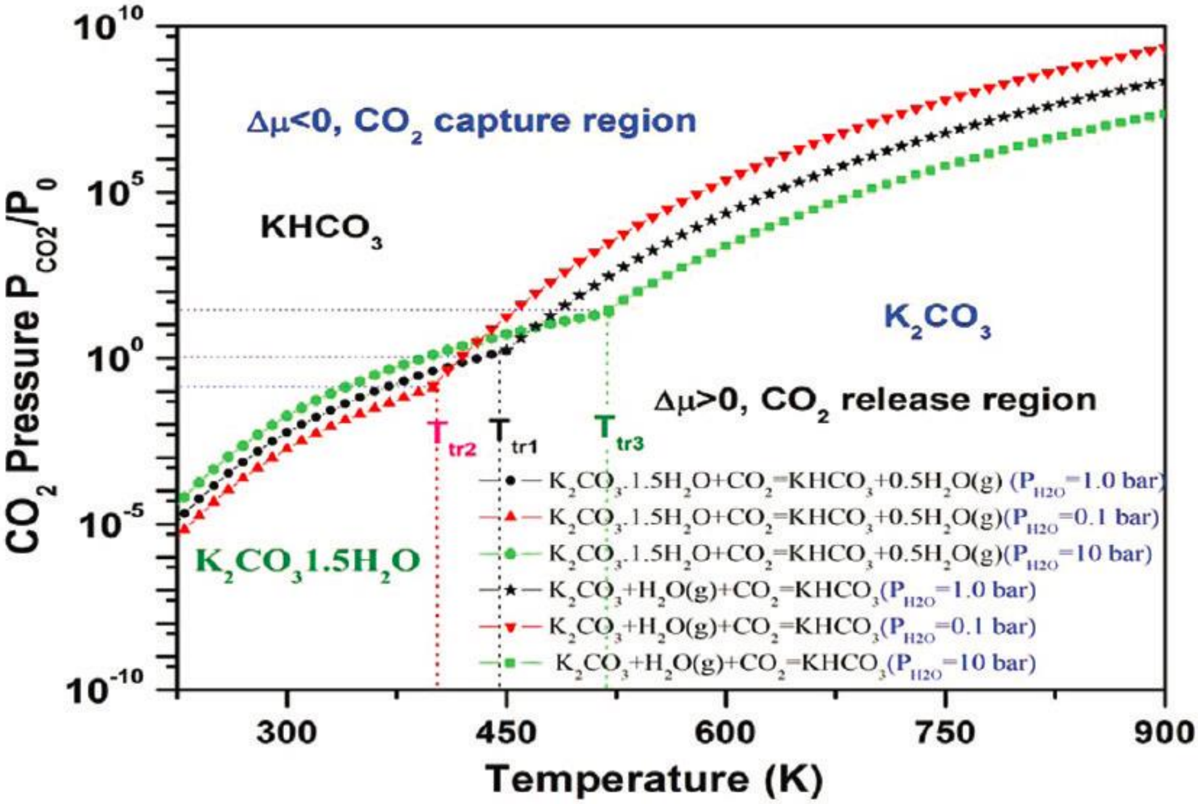

FIGURE 3-1: PHASE DIAGRAM AT THREE DIFFERENT P_{H2O} FOR THE SYSTEM K_2CO_3-$K_2CO_3 \cdot 1.5H_2O$-$KHCO_3$ IN TERMS OF P_{CO2} AND T. SOURCE: DUAN ET AL. (2012, P. 14467)

Given the lack of theoretical data to reproduce the plots reported by Duan et al. graphical extrapolation was used to come up with the theoretical equilibrium lines at the experimental conditions followed in the current study. Duan et al.'s results are approximated with the formula in equation (3-2). This was obtained by taking points in Figure 3-1 and solving equation (3-1) for $\Delta\mu^0$.

$$\Delta\mu^0(T) = -4.371 * 10^4 + 101.4 * T \tag{3-2}$$

Furthermore the equilibrium constant can be found using equation (3-1) as a function of temperature. For this the activity of the gases is approximated to its partial pressure divided by the reference pressure of 1 bar. The activity of the solids is taken as 1. It is also assumed that the reference pressure P_0 does not deviate from the pressure used in the experiment much and thus can be taken as equal. A last assumption is that both gasses behave like ideal gasses such that:

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \tag{3-3}$$

Combining equation (3-1), (3-2), and the made assumptions, the equilibrium constant $K_{p,des}$ in terms of the partial pressures can be found as shown in equation (3-4) for the desorption of CO_2 by the potassium carbonate sesquihydrate.

$$K_{p,des} = \frac{\left(\frac{n_{H_2O}}{n_{tot}}\right)^{0.5}}{\frac{n_{CO_2}}{n_{tot}}} \approx \frac{\left(\frac{P_{H_2O}}{P_0}\right)^{0.5}}{\frac{P_{CO_2}}{P_0}} = e^{\frac{\Delta\mu^0(T)}{RT}} \tag{3-4}$$

Lee et al. (2011) studied the adsorption by K_2CO_3 which differs in nature from the process analysed in this thesis, but still offers some insights. They state that a high water vapour pressure is required to transform the potassium carbonate into the sesquihydrate which then allows the adsorption of CO_2. This is in line with Duan et al.'s result which shows that a higher water vapour pressure increases the equilibrium pressure of CO_2 in the air stream when $K_2CO_3{\cdot}1.5H_2O$ is used. Lee et al. have worked with a temperature range of 50°C to 70°C, so it seems reasonable to use temperatures close to that range considering that they fit Duan et al.'s predictions.

4 EXPERIMENT SETUP

The flowsheet of the setup used for the experiments is shown in Figure 4-1 where the general direction of flow is from bottom to top. The system could perform 4 possible operations – adsorption of CO_2 by the adsorbent, desorption of CO_2 from the adsorbent, cleaning of the adsorbent, and cleaning of the molecular sieve column. For adsorption and desorption, dry air was used as a feed gas and for the cleaning operations, N_2 was used.

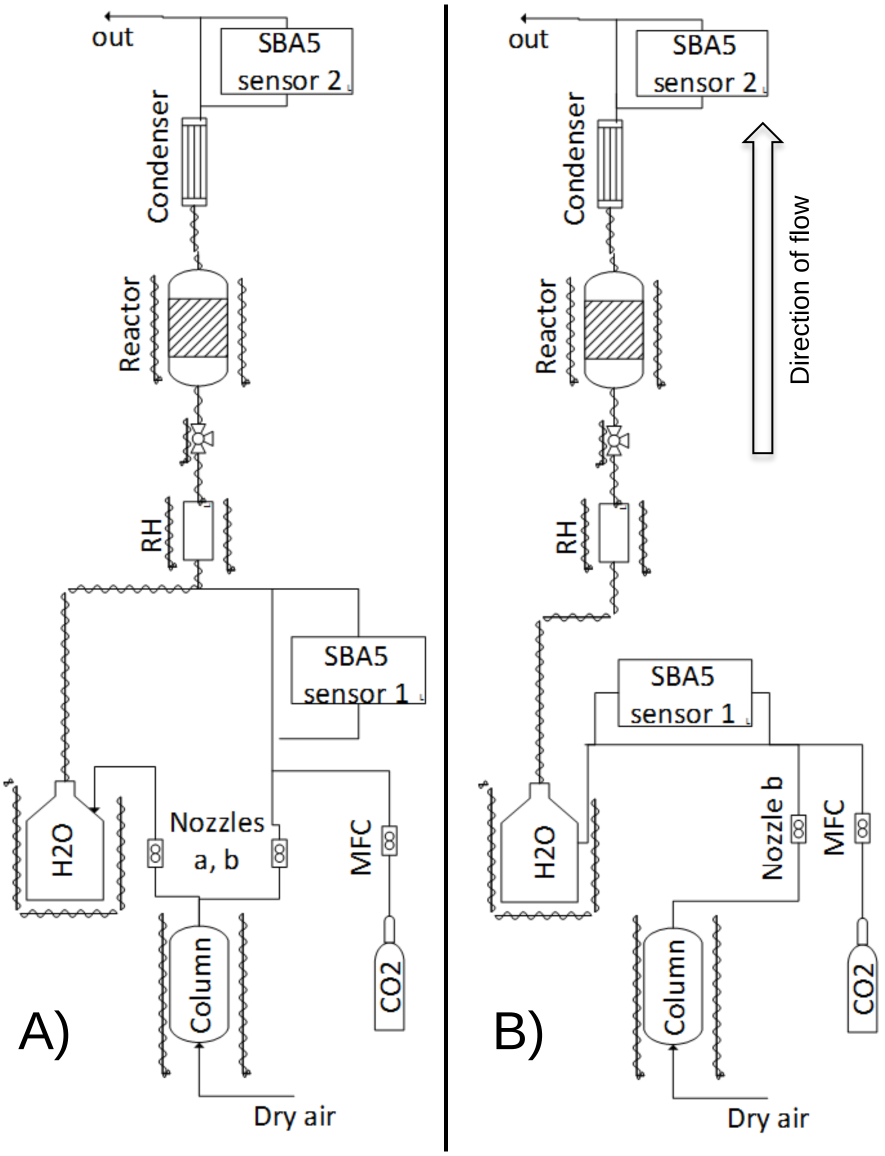

FIGURE 4-1: SETUP FOR THE EXPERIMENTS. FLOWS GO FROM BOTTOM TO TOP. A) IS THE SETUP USED FOR ADSORPTION AND B) IS THE SETUP USED FOR DESORPTION.

The main components which can be seen in Figure 4-1 are listed below together with their labelling in the drawing:

- Column: A reactor column filled with a 13X molecular sieve from Sigma-Aldrich, USA containing beads in a 4 - 8 mesh used to remove all CO_2 from the dry air.
- Nozzle a, b: For each two manual pressure regulators and a nozzle in series for volumetric flow control. The calibration of the nozzles shows a linear dependency on the pressure set before them and can be seen in Figure 4-2 and Figure 4-3.
- CO2: A CO_2 gas cylinder from Linde, Germany with a purity of 99.7%
- MFC: A mass flow controller with a capacity of up to 10 mL/min by Brooks Instrument, USA
- H2O: A flask filled with water through which the air stream was bubbled with a heating mantle around it. The water vapour content of the stream leaving the humidifier is saturated at the temperature of the water in the flask.
- SBA5 sensor 1, 2: SBA-5 CO_2 Gas Analyzer with a range of up to 30000 ppm from PP Systems, USA. Both sensors were either calibrated with CO_2-free air obtained with sodalime from Sigma-Aldrich, USA, or with nitrogen from the university grid. The sensors have a rated accuracy of 300 ppm. When testing both sensors in series with the same gas, it showed that sensor 2 had a lower reading than sensor 1 (≈10 to 20 ppm).
- RH: A relative humidity sensor provided by Omega Engineering, US
- Reactor: A stainless steel reactor with the inner dimensions 5.2cm*5.2cm*15cm. The adsorbent in the form of cylinders were placed in a metal cage above a metal mesh that functioned as gas distributor.
- Condenser: A condenser removing most of the moisture in the stream prior to enter the CO_2 analyser.

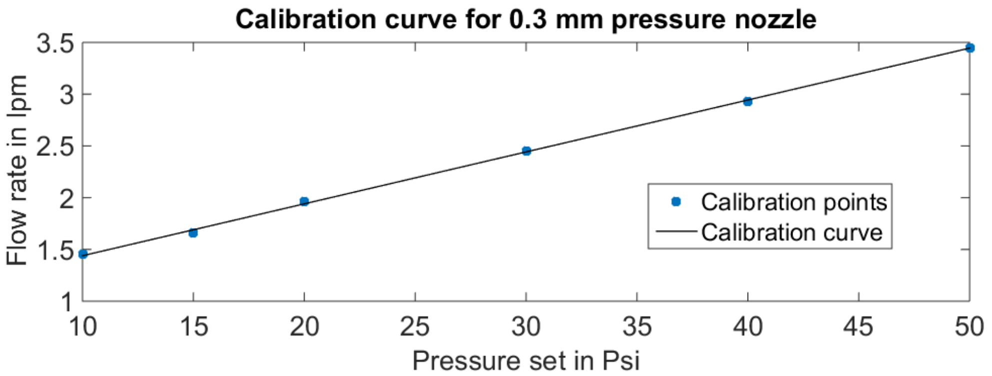

FIGURE 4-2: LINEAR CALIBRATION CURVE OF PRESSURE NOZZLE A WITH A HOLE DIAMETER OF 0.3 MM

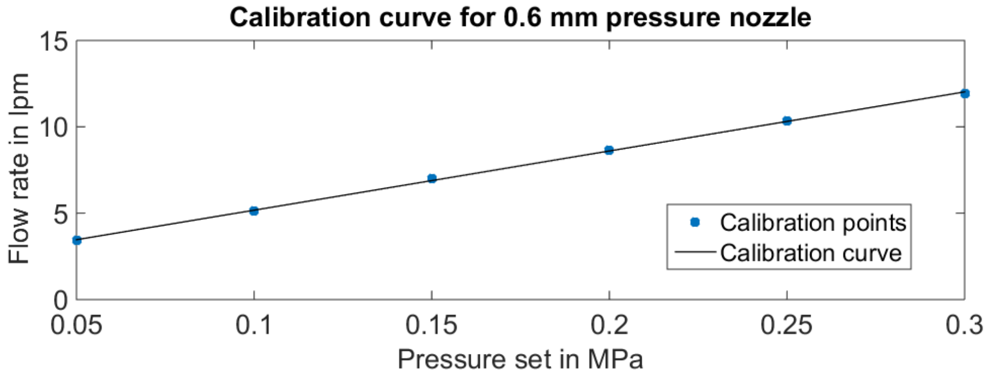

FIGURE 4-3: LINEAR CALIBRATION CURVE OF PRESSURE NOZZLE B WITH A HOLE DIAMETER OF 0.6 MM

4.1 CO_2 adsorbent

The CO_2 adsorbent used was comprised of a porous matrix in the form of activated carbon cylinders loaded with K_2CO_3 via the wet impregnation method. The relevant properties can be found in Table 4-1.

Type of carrier	Activated carbon cylinders
Supplier	Dalian Importers
Weight carrier in g	20.06
Weight K_2CO_3 in g	3.23
Amount K_2CO_3 in mmole	23.37
Loading in %wt g K_2CO_2 per g total	13.87
Surface area of unloaded carrier in m^2/g	376.7062
Surface area of loaded carrier in m^2/g	273.1901

TABLE 4-1: PROPERTIES OF CARRIERS AND THEIR LOADING WHICH WERE USED FOR THE EXPERIMENTS

The potassium carbonate was produced by Sigma-Aldrich with a purity of ≥99% where most of the impurity is insoluble matter (≤0.1%) and some phosphorus (≤0.0005%). The loading was done by first dissolving the potassium carbonate in demi-water and then bringing the carrier and solution in contact for a short time of around 2 seconds. The solution was composed of 93.19 g of potassium carbonate and 265.56 g of demi water resulting in a concentration of 35.1 w% g K_2CO_3 per g total. A fresh solution was however not used for the preparation of the adsorbent, the initial and final mass of the cylinders determined the amount of salt loaded on them accurately though. The weight of K_2CO_3 indicated in Table 4-1 is subject to some uncertainty since it hydrates relatively quickly and therefore had to be dried using a N_2 stream. This resulted in some moving of the cylinders which caused loss material due to the creation of dust.

The surface area indicated in Table 4-1 was measured using a BET analysis performed by the Catalytic Processes and Materials group on a clean activated carbon cylinder and an activated carbon cylinder which had already been loaded. It can be seen that the available surface area reduces to approximately 72.5% of the original value thus indicating that the loading process has smoothened the surface. This means that not all potassium carbonate sits on the surface and are consequently unavailable for adsorption and desorption. If an even distribution of the adsorbent over the original surface is assumed, then this results in a maximum working capacity of approximately 16 mmole.

In order to further understand the surface properties and to verify the successful loading, a microscopy of the surface of the cylinder was conducted. The resulting pictures are given in Figure 4-4 and clearly show the formation of crystals on the loaded carrier which presumably is K_2CO_3, $K_2CO_3 \cdot 1.5H_2O$, or $KHCO_3$.

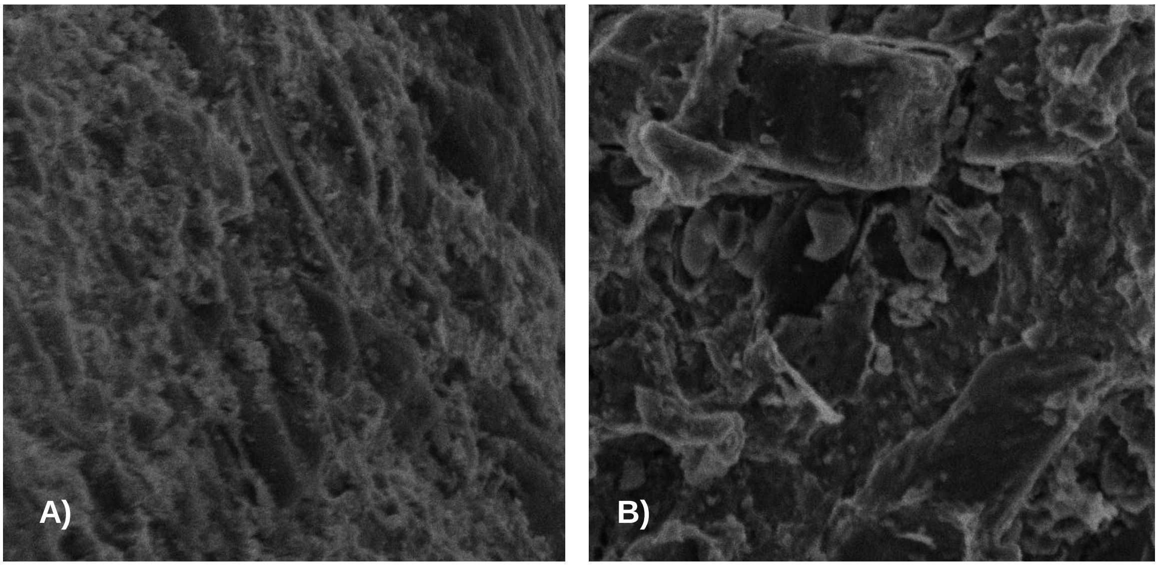

FIGURE 4-4: MICROSCOPY OF A) AN UNLOADED ACTIVATED CARBON CYLINDER AND B) OF AN ACTIVATED CARBON CYLINDER LOADED WITH K_2CO_3. THE IMAGES WERE OBTAINED WITH A MAGNIFICATION FACTOR OF 700, BUT ARE DUE TO AN INACCURACY IN THE LENGTH MEASUREMENT NOT FOR SCALE.

Furthermore an XRD scan was performed in order to ensure that the found crystals were really potassium carbonate. The result of this can be found in Figure 4-5 where the refraction pattern of a loaded and a non-loaded carrier can be seen. The clearest differences between the two probes can be seen at an angle of 32.6° and at 36.26°.

These angles were then compared to reference patterns in order to identify the present substances. The 36.26° correspond to a $KHCO_3$ phase which seems logical considering that time passed between loading the adsorbent and performing the XRD. This provided the opportunity for adsorption to already take place before the measurement.

The peak in the measurement at 32.6° is present in both XRD patterns, therefore it is expected to be intrinsic of the carrier. The difference in intensity between the two patterns might be explained due to different crystal orientation.

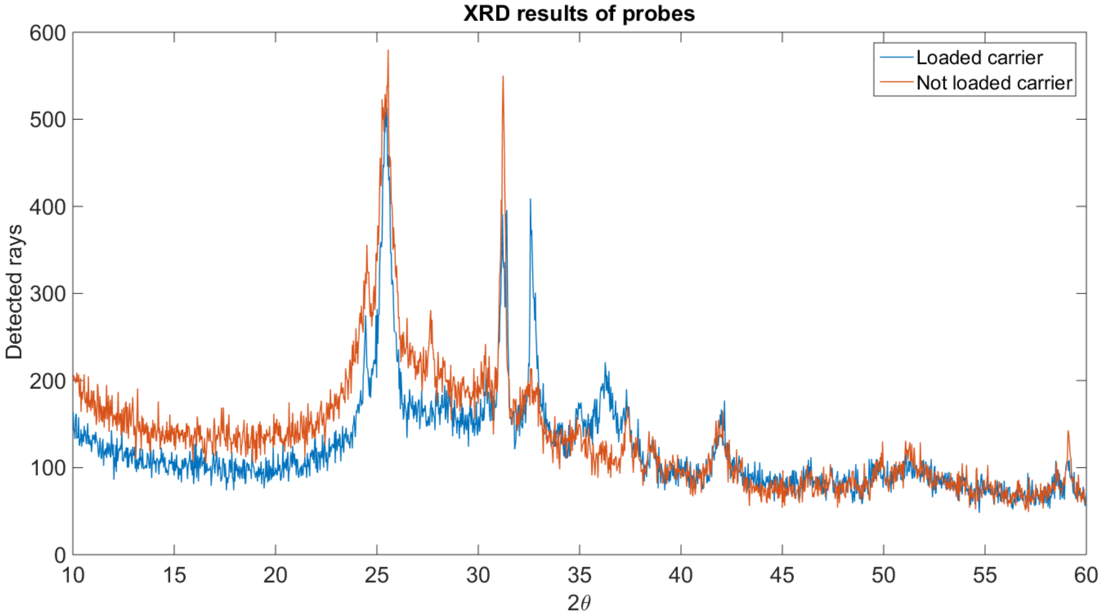

FIGURE 4-5: XRD SCAN OF AN UNLOADED AND A LOADED ACTIVATED CARBON CARRIER.

Considering both tests, it can be said with certainty that the K_2CO_3 has been loaded onto the activated carbon cylinders. Some of the adsorbent is most likely not at the surface reducing the available adsorption capacity.

4.2 Experimental procedure

Since the four basic functions – adsorption of CO_2 by the adsorbent, desorption of CO_2 from the adsorbent, cleaning of the adsorbent, and cleaning of the molecular sieve column – all had slightly different requirements, the way the setup was used also varied per usage. At first the desorption experiment is described since the focus of this work lies on desorption. Afterwards the differences to the other usages is described.

The setup used for desorption can be seen in Figure 4-1 B). Two experimental series were conducted, one for the analysis of the influence of temperature on the reaction and one for the analysis of the influence of water vapour pressure on the reaction. In addition a number of experiments were conducted before in order to determine the parameters for the experimental series. The desorption experiments were conducted as follows.

The feed of dry air from the university grid was fed through the molecular sieve column at a pressure of 5 bar(g) in order to remove the CO_2 contained in the stream. Next the flow was guided through nozzle B at a pressure of 0.15 MPa producing the desired flow rate of 7 lpm. Next the required amount of CO_2 is added by the MFC to produce a 400ppm stream. The CO_2 concentration is measured by the first CO_2 sensor. After the stream had passed the sensor, it was bubbled through the humidifier. For the experiments where the water vapour pressure should be constant, the water was preheated until it had reached a value reasonably close the desired temperature. For preheating, the three-way valve before the reactor was opened to let the flow escape to the environment. The lines between humidifier and reactor and also after the reactor were heated in order to prevent condensation. If it was desirable that the reactor was preheated before the experiment started, it was usually done for about 10 to 15 minutes. This increased the temperature of the reactor enough while still not heating up for too long time. The reason for this time limitation is that previous experiments had shown a mismatch in the CO_2 mass balance if the reactor was preheated too long. After the stream had passed the reactor, it was cooled down, the water vapour mostly condensed, the CO_2 concentration and the remaining water vapour pressure were measured, and the flow rate determined. The precise settings for the different desorption experiments can be found in Table 4-2.

Series	Water vapour pressure series	Temperature series
Humidifier preheated before experiment	No	Yes
Temperature set in humidifier	38 - 50 °C	50 °C
Reactor preheated	No	Yes
Temperature set in reactor	70 °C	60 - 90 °C

TABLE 4-2: SETTINGS FOR THE DIFFERENT DESORPTION EXPERIMENTS

For adsorption the setup can be seen in Figure 4-1 A). The flow rate was 10 lpm of which 7 lpm were guided through nozzle b combining with the CO_2 feed (4 mlpm) and 3 lpm went through nozzle a towards the humidifier. Both streams were combined again prior to entering the reactor to form the full flow. Due to the fact that not the entire flow passed the first CO2 sensor, the reading was around 571 ppm resulting in a combined stream concentration of approximately 400 ppm. The temperature of the water and the reactor was kept at 20 °C. The feed lines to the reactor were kept at 22 °C right after the humidifier and 20 °C after the flows had met. The rest of the experiment was conducted the same way as desorption.

For the cleaning of the adsorbent with N_2 the flow rate differed from 7 lpm up to 12 lpm depending on the experiment. The N_2-inflow was connected before the nozzles, skipping the molecular sieve columns, and then guided via nozzle b directly to the reactor. The feed line to the reactor was set to 90 °C and the reactor itself to temperatures ranging from 130 °C to 175 °C.

The cleaning of the molecular sieve columns was conducted by guiding a N_2-flow from nozzle a or b to the input of the column and then by heating the column up to elevated temperatures of 200 °C up to 250 °C. The outflowing air stream was either cooled down with a spiral and flushed through a CO_2 sensor or simply allowed to escape into the exhaust system of the laboratory.

Neither adsorption nor cleaning procedures are mentioned in the rest of this work, but it should be kept in mind how it was done since there is an impact on the conduction of the desorption experiments and the overall time consumption for the experimental work.

5 RESULTS AND ANALYSIS

The analysis of the experiments tries to address the two sub-research questions in order to find an answer to the main research question. First some theoretical derivations are given which are applied on the results of the experiments later. Secondly some observations are presented which were made before the two series. Only observations are added which add value to the scientific content of this work. Afterwards the two experimental series are analysed in more detail. At first the influence of reactor temperature is analysed followed by a section about the influence of water vapour pressure. The data from the used experiments can be found in Appendix A and in Appendix B.

5.1 Theoretical derivations

In this section, some derivations are given which are still independent of the data at hand and therefore purely theoretical in nature. The models explained here are used in the analysis of the concrete experimental series later.

5.1.1 Trapezoidal numerical integration

Since the data of the experiments is measured in discrete time steps, the data has to be numerically integrated. For the analysis the trapezoidal integration scheme was chosen since it assumingly provides the most accurate method. The idea behind the scheme is to connect consecutive data points by straight lines and then to integrate using this piecewise linear function. In mathematical terms this can be expressed using equation (5-1). The scheme overestimates the absolute integrated value of a curve bending away from the horizontal axis and underestimates one bending towards the horizontal axis due to the fact that it skips the curving between individual data points (MathWorks, 2015). For this experiment however the sampling frequency was high enough that this effect should be negligible. An implementation was not necessary since Matlab provides the function trapz to perform this integration.

$$\int_a^b f(x)dx \approx \frac{1}{2}\sum_{n=1}^{N}(x_{n+1} - x_n) * \left(f(x_n) + f(x_{n+1})\right) \tag{5-1}$$

5.1.2 Double exponential model

The double exponential model is an empirical model to describe a reaction involving two consecutive processes of different velocity which is frequently found in literature (Chiron, Guilet, & Deydier, 2003; Shan et al., 2012). The basic equation reads:

$$y(t) = A * e^{-k_1 * t} + B * e^{-k_2 * t} + C \tag{5-2}$$

Where:

- y(t) is the measured value
- A and B are pre-exponential factors
- k_1 and k_2 are decay constants of a fast and a slow process and are taken as kinetic constants.
- C is the equilibrium value

In order to apply this model, the first phase of the experiment cannot be regarded since the effect of the temperature and water vapour pressure not being stable still plays a role. The model should thus only be applied once these parameters have stabilized. Further the output should also be normalized to reach comparable results. Normalizing the amplitude, the measured value y(t) can be taken as:

$$y(t) = \frac{n_{CO_2,\,out} - n_{CO_2,\,in}}{n_{air,out}}(t) * \frac{\dot{n}_{air,\,out}}{n_{CO_2,\,init}} \tag{5-3}$$

Where:

- $\frac{n_{CO_2,\,out} - n_{CO_2,\,in}}{n_{air,out}}(t)$ is the difference in CO_2 concentration of the outflowing and the inflowing stream
- $\dot{n}_{air,\,out}$ is the molar flow rate of the entire stream
- $n_{CO_2,\,init}$ is the initial loading of the adsorbent with CO_2 in moles.

This normalization also allows for the dropping of the factor C from equation (5-2) since the difference between moles of CO_2 flowing in and out will approach 0 as time tends to infinity.

A second effect which has to be considered is that a higher flow velocity will lower the CO_2 concentration in the gas stream and thus increase the rate of desorption. This in turn influences the decay constants. To minimize this problem the flow rate was kept at an approximately constant level.

The benefit of this empirical description is that it provides an effective noise filter if the double exponential approximation is used instead of the real data making the analysis process easier to handle. For the final calculations presented in this work however the original data was used in order to increase reliability.

5.1.3 Desorption effects while the stream passes the adsorbents

In order to gain insight on what happens while the air is in contact with the adsorbent, the following analysis is performed. This reveals information about the forward and backward reaction rate which is crucial for the further processing of the data. The basis of the analysis is the definition of the reaction rate as can be seen in (5-4). Given the vast complexity of the system two major assumptions are taken in order to come up with a theoretical analysis.

- The CO_2 regeneration via the formation of the $K_2CO_3 \cdot 1.5H_2O$ is an elementary process so that the order of reaction with respect to each species is equal to its stoichiometric coefficient.
- The desorption rate only depends on the P_{H2O} and the adsorption rate only depends on P_{CO2}.

The made assumptions oversimplify the system at hand and should thus only be considered a first step before more complete models are developed which do not rely on these assumptions. They are necessary however in order to allow for any analysis to be performed at all. The water vapour bound in the potassium carbonate is not considered a gas.

$$
\begin{aligned}
r_{ad} &= k_{ad}(T) * [CO_2] = -\left.\frac{d[CO_2]}{dt}\right|_{\mathrm{ad}} \\
r_{des} &= k_{des}(T) * [H_2O]^{0.5} = \left.\frac{d[CO_2]}{dt}\right|_{des}
\end{aligned}
\tag{5-4}
$$

where the subscript *ad* indicates the variables belonging to adsorption and the subscript *des* indicates the variables belonging to desorption.

The dependency on the solid concentrations is implicitly assumed and will be accounted for later. This is necessary since there is not enough information available to apply more sophisticated models such as the Langmuir mechanism or the Eley-Rideal mechanism. Both require knowledge about the surface concentration of potassium carbonate which is unknown. If this information is available, it is advised to repeat the following derivation and to explicitly take the concentrations of the solids into account. This would allow for a verification of the assumed partial reaction order for the gasses as well as giving a less empirical description of the events.

The reaction equation is repeated for convenience.

$$
2KHCO_3 + 0.5H_2O_{(g)} \leftrightarrow K_2CO_3 \cdot 1.5H_2O + CO_{2(g)} \tag{5-5}
$$

Combining the two definitions of the reaction rate equation (5-6) is obtained. This is possible since the combined effect of adsorption and desorption determines the overall change in CO_2 concentration in the gas stream.

$$
\frac{d[CO_2]}{dt} = k_{des}(T) * [H_2O]^{0.5} - k_{ad}(T) * [CO_2] \tag{5-6}
$$

As a next step the assumption that the air in the air stream is in contact with the adsorbent for a certain amount of time is made. This time frame deduced from the flow rate and geometric parameters. This calculation is performed in equation (5-7).

$$
\begin{aligned}
v_{vol} &= v_{linear} * A = \frac{h_{cyl}}{t_c} * A \\
\Rightarrow t_c &= \frac{h_{cyl} * A}{v_{vol}} \approx \frac{0.021m * (0.052m)^2}{v_{vol}} \approx \frac{5.678 * 10^{-5} m^3}{v_{vol}}
\end{aligned}
\tag{5-7}
$$

where t_c is the contact time, h_{cyl} is the height of the probes in the reactor, A is the cross-sectional area of the reactor, and v_{vol} and v_{linear} are the volumetric and linear flow rate.

Using this result, integration (5-8) can be performed over the time span t_c. The integration can be understood as looking at a small volume of gas which flows along the adsorbent upon which it changes its CO_2 concentration. The result of this integration is known, since the inflowing and outflowing CO_2 concentrations of this volume of gas are both measured. For the integration it is assumed that apart from the gas concentrations everything else is constant over time and space. This is most importantly the loading of the adsorbent, the temperature, and the reaction mechanism. The assumption is valid due to the short contact time of gas stream and adsorbent compared to the running time of the experiment.

This assumption still allows for a the named factors like loading of the adsorbent, temperature and reaction mechanism to vary over the course of the experiment.

$$\int_0^{t_c} k_{des}(T) * [H_2O]^{0.5} - k_{ad}(T) * [CO_2]dt = [CO_2]_{out} - [CO_2]_{in} \tag{5-8}$$

As a next step, the water vapour concentration has to be defined in terms of the CO_2 concentration which can be done using the reaction equation as given in equation (5-9). Since both water vapour and CO_2 are both present in quite little amounts relative to the oxygen and nitrogen in the air, it is assumed that the total amount of moles does not change. Otherwise one would have to take into account the change of the total amount of moles due to the fact that upon desorption half a mole of water gets replaced by one mole of CO_2.

$$\begin{aligned}[H_2O] &= [H_2O]_{in} - \frac{1}{2}([CO_2] - [CO_2]_{in}) \\ &= [H_2O]_{in} + \frac{1}{2}[CO_2]_{in} - \frac{1}{2}[CO_2]\end{aligned} \tag{5-9}$$

The change of CO_2 concentration over time has to be described next. Here an assumption about the shape of this function has to be made. For this it is assumed that a first order system, i.e. an exponential function, can describe the behaviour accurate enough to serve as an approximation. The effect described earlier that two different processes happen simultaneously is on a far longer time scale than the time the air is in contact with the adsorbent. Therefore it can be assumed that the reaction rate does not vary for the integrated time span allowing the usage of a first order system. There are three points in time about which we have knowledge. Combining the known points and the assumed exponential function, the following description of the CO_2 concentration can be made. The known points are the inflowing concentration at t=0, the outflowing concentration at $t=t_c$ and equilibrium concentration at t=∞. The point at t=∞ assumes no change in the loading of the cylinders which can be interpreted as the gas flowing along an infinite bed of adsorbents all in the same loading state.

Care has to be taken since this is a different way of looking at the reaction from of what happens in the real experiments where each volume of gas passes only a short and finite bed of adsorbents. Flowing past that finite bed takes a time of t_c. So in the experiment there are continuously new volumes of gas and each volume of gas changes its CO_2 following equation (5-10). This causes the adsorbent to regenerate after a certain number of gas volumes making the inflowing and outflowing concentrations equal eventually.

$$\begin{gathered}[CO_2](t) = A * e^{-\tau * t} + B \\ [CO_2](0) = [CO_2]_{in}; [CO_2](t_c) = [CO_2]_{out}; [CO_2](\infty) = [CO_2]_{eq} \\ \Rightarrow B = [CO_2]_{eq}; A = [CO_2]_{in} - [CO_2]_{eq}; \tau = -\frac{1}{t_c}\ln\left(\frac{[CO_2]_{out} - [CO_2]_{eq}}{[CO_2]_{in} - [CO_2]_{eq}}\right)\end{gathered} \tag{5-10}$$

When checking the derivation of the exponential function support can be found that this approach is not wrong. If for instance the situation is chosen where the outflowing and inflowing concentrations are equal (i.e. the regeneration complete), then τ is equal to 0 resulting in a constant solution.

In order to find the equilibrium CO_2 concentration $[CO_2]_{eq}$ equation (3-4) can be used. Using this constant, the equilibrium equation can be set up and solved. At this point it has to be kept in mind that this equilibrium constant is based on theoretical thermodynamic considerations and that other effects might play a role as well in reality which limits the validity of this step.

$$K_{eq} = \frac{\left([H_2O]_{eq}\right)^{0.5}}{[CO_2]_{eq}} = \frac{([H_2O]_{in} - x)^{0.5}}{[CO_2]_{in} + 2x} \tag{5-11}$$

$$x = \frac{1}{2}\left(\frac{K_{eq}^2}{4} * \left(1 \pm \sqrt{8[CO_2]_{in}K_{eq}^2 + 16[H_2O]_{in}K_{eq}^2 + 1}\right) - [CO_2]_{in}\right) \tag{5-12}$$

Seeing that for a desorption we expect x to be positive, the solution is taken where the ± is in fact a +. The equilibrium concentration can now be defined in terms of known constants. The equilibrium constant is still temperature dependent.

$$[CO_2]_{eq} = [CO_2]_{in} - 2x \tag{5-13}$$

Knowing the equilibrium constant, there is a second derivation which can be made since the equilibrium constant is among others defined as the ratio of the forward and backward reaction rate which in this case are adsorption and desorption. This allows to define the adsorption rate in terms of the desorption rate as done in equation (5-14).

$$\begin{gathered} K_{eq} = \frac{k_{ad}(T)}{k_{des}(T)} \\ k_{ad}(T) = K_{eq} * k_{des}(T) \end{gathered} \tag{5-14}$$

Since at this point all parts of the integral are known, the integration can be performed. Due to the complexity of the integral the solution is rather lengthy and only reproduced here for reasons of completeness. At this point there is only one unknown variable left, namely the desorption rate k_{des} which can now be solved for.

$$\begin{multlined} k_{des}(T)t_c\left(K_{eq}\left(\frac{X_1 D_2}{t_c}\left(e^{t_c\left(\frac{D_1}{D_2}\right)^{\ln\left(\frac{1}{t_c}\right)}} - 1\right) - [CO_2]_{eq}\right)\right. \\ \left. - \frac{1}{X_3}\left(X_2\left(\tan^{-1}\left(\frac{X_4}{X2}\right) - \tan^{-1}\left(\frac{X_4}{X_2}\right)\right) - X_4 + X_5\right)\right) = -D_3 \end{multlined} \tag{5-15}$$

where:

$$\begin{aligned} D_1 &= [CO_2]_{eq} - [CO_2]_{out} \\ D_2 &= [CO_2]_{eq} - [CO_2]_{in} \\ D_3 &= [CO_2]_{in} - [CO_2]_{out} \\ X_1 &= \left(\frac{D_1}{D_2}\right)^{-\ln\left(\frac{1}{t_c}\right)} \\ X_2 &= \sqrt{2D_2 - 4[H_2O]_{in}} \\ X_3 &= \ln\left(\frac{D_1}{D_2}\right) \\ X_4 &= \sqrt{4[H_2O]_{in} + 2D_3} \\ X_5 &= 2\sqrt{[H_2O]_{in}} \end{aligned}$$

As a last step the dependency of the desorption rate on the amount of $KHCO_3$ has to be solved for. For this the amount of $KHCO_3$ has to be known. This can be done using a mass balance continuously over the whole experiment and then adding the amount of $KHCO_3$ present initially.

From the experiments it was found that the loading of the adsorbent is related linearly to the desorption coefficient k_{des} as described in equation (5-16). The factor a(T) is an empirical coefficient relating the loading of the adsorbent to the desorption rate. It is temperature dependent since this was not taken into account in the analysis so far. n_{KHCO3} is the loading of the adsorbent. Since both loading and the desorption rate can be found with the same data on the same time scale, the two datasets can be correlated.

$$k_{des}(T) = a(T) * n_{KHCO_3} \tag{5-16}$$

5.1.4 Arrhenius equation

The Arrhenius equation provides a widely used description for the dependence of the rate constant on the temperature. The equation reads:

$$k_{des}(T) = Ae^{-\frac{E_a}{RT}} \tag{5-17}$$

where A is a prefactor, R is the universal gas constant, and E_a is the activation energy. In order to determine the two unknowns, one can linearize the equation by taking the natural logarithm on both sides which results in equation (5-18). If also T is inversed, then a simple linear relation is the result where the unknowns are directly related to the y-intercept and the slope.

$$\ln\left(k_{des}(T)\right) = \ln(A) - \frac{E_a}{R} * \frac{1}{T} \tag{5-18}$$

5.2 General observations

Before the main series of the experiments were started, some tests were conducted in order to ensure a smooth execution of the two main series. These tests served to determine the right parameters and experimental approach while providing some qualitative insight as well which are reproduced here.

The first and most important general observation is that a lengthy preheating of the reactor leads to a mismatch in the CO_2 mass balance. The results of such a balance indicate that the amount of CO_2 which can be adsorbed rises with every experiment. This means that the process of preheating causes the loss of CO_2 from the adsorbent which could not be recorded. The assumption is that during preheating some significant desorption already takes place. This CO_2 rich volume of air is then flushed at high flow rates through the setup so that the sensors cannot record this fast enough.

A second observation can be seen from the figures in Appendix B where both temperature and relative humidity rise simultaneously in each experiment. It is quite apparent that the impact of the changing temperature is more significant than the impact of the changing water vapour pressure. This behaviour showed quite consistently in each experiment leading to the conclusion that it is more important to ensure a good temperature control than the water vapour pressure control for a fast process.

5.3 Temperature

In order to better understand the influence of temperature on the process the experimental series based on temperature variation is analysed. All data has been normalized by the amount of CO_2 in the adsorbent in the beginning of the desorption. This was done by numerically integrating the amounts of CO_2 adsorbed and desorbed in each experiment and summing up these contributions. The integration was performed using the trapezoidal integration scheme. The resulting cumulative loading can be seen in Figure 5-1. Not all of the experiments could be used for the further analysis of the influence of temperature due to problems during the execution such as wrong heating ramps or water vapour pressures. These problems did not affect the mass balance, but the assumption that temperature and water vapour pressure are constant is not true for the discarded experiments.

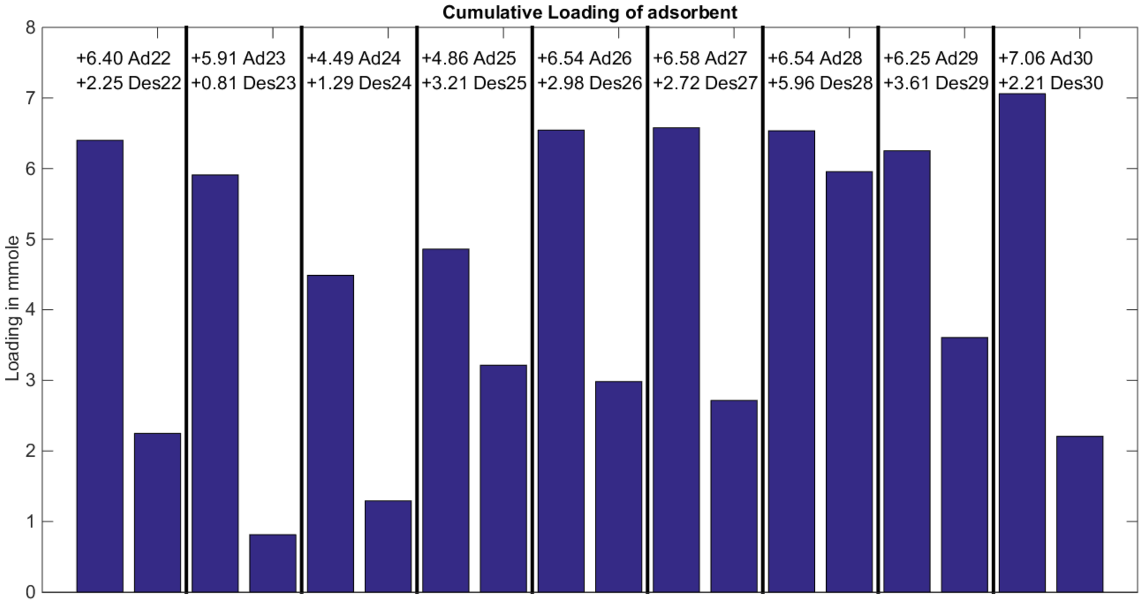

FIGURE 5-1: CUMULATIVE LOADING OF THE ADSORBENT AFTER EACH ADSORPTION AND DESORPTION. THE UPPER VALUE IS THE CUMULATIVE LOADING IN MMOL AFTER THE ADSORPTION AND THE LOWER VALUE AFTER THE DESORPTION.

As a next step, the amount of CO_2 desorbed per experiment is observed over time and the different desorption curves are plotted in a single graph. In order to make these experiments comparable with each other, the curves are normalized by dividing them by the initial loading. The result of this can be seen in Figure 5-2.

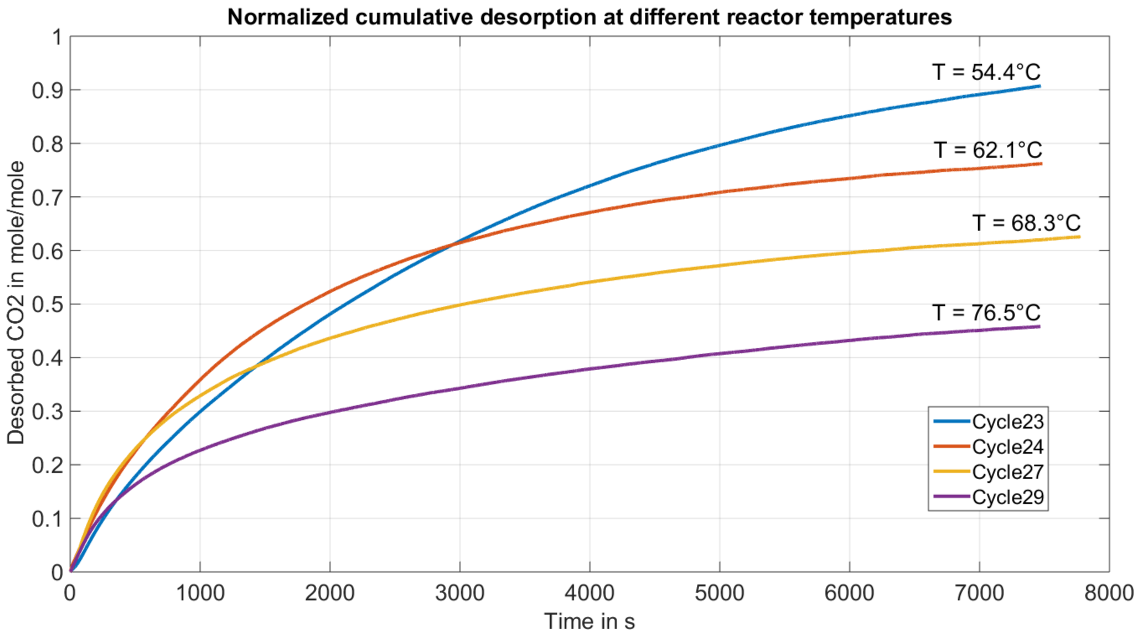

FIGURE 5-2: NORMALIZED CUMULATIVE DESORPTION AT DIFFERENT REACTOR TEMPERATTURES. THE TEMPERATURE INDICATION WITH EACH GRAPH REPRESENTS THE MEAN TEMPERATURE IN THE REACTOR CENTRE AFTER THE TEMPERATURE HAS STABILIZED. THE TEMPERATURE AT OTHER POINTS IS PROBABLY HIGHER SINCE THE HEATING WAS POSITIONED AT THE WALL OF THE REACTOR.

From this graph, two observations can be made about the speed of desorption and about the total amount of CO_2 desorbed depending on the temperature. These observations already give a qualitative answer to the research sub question Q1. The effect on the first phase however cannot be confirmed with 100% certainty due to many other effects playing a role in the first phase. It is therefore given as a hypothesis rather than a conclusion.

A higher reactor temperature causes the CO_2 *to desorb faster during the first phase of the experiment*

A higher reactor temperature slows down the CO_2 *desorption on a longer time scale and lowers the total amount of* CO_2 *which can be desorbed in a long time frame.*

Both statements are limited to the temperature range where the desorption creates potassium carbonate sesquihydrate rather than only potassium carbonate only.

Based on this observation, it is reasonable to assume that two processes are involved, one which is enhanced by high temperature and one which is slowed down by high temperature. This does not mean that no other processes can happen, but the other processes are either very small, very fast, or very slow such that they are not visible in the data and will therefore not be regarded in this analysis. The process which is slowed down by high temperatures becomes the limiting process after some time. At this point it can only be guessed what these processes might be. The following effects might have an influence:

- There is a formation of an outer layer of regenerated sesquihydrate, such layer inhibits the continuation of CO_2 desorption via the decomposition of $KHCO_3$ due to mass diffusion limitations through the regenerated shell.
- There is a formation of a boundary layer of air with a high CO_2 content around the carrier slowing down the desorption process. This explanation requires that the air moves slowly

close to the carriers. In other words the air has to be slowed down or trapped near the carrier in some way which seems improbable considering the really high flow rates.

- The potassium carbonate needs to form the sesquihydrate which has a certain speed of reaction which can be regarded as the second step in the reaction. In this two-step reaction one of the processes is probably slower than the other and consequently becomes the limiting factor. Lee et al. (2011) also talk about the hydration as one of two processes involved.
- Water vapour needs to be pre-adsorbed by the porous carrier in order to subsequently react with a neighbouring $KHCO_3$ to regenerate it. An inhibition of this pre-adsorption will reduce the kinetics and the yield of CO_2 desorption.

Out of the four given ideas, the last two seem to be the most probable, but no experimental proof for this can be given at this point and the question is left for further research. Using this idea of multiple processes however, one can apply the double exponential model in order to make the next step in the analysis. The result from the double exponential model can be found in Table 5-1.

Experiment	**Flow rate in lpm**	**A**	**k_1**	**B**	**k_2**
23	6.7	4.143	4.314e-3	6.261	0.2979e-3
24	6.5	5.352	0.981e-3	2.237	0.2842e-3
25	6.8	6.535	2.376e-3	2.906	0.3966e-3
27	6.8	11.631	3.590e-3	4.133	0.4083e-3
29	6.8	4.479	2.447e-3	1.620	0.2202e-3

TABLE 5-1: COEFFICIENTS OF THE DOUBLE EXPONENTIAL FIT

By inspection it is obvious that the two processes could not be separated well by the double exponential fit. If a good separation was obtained then for each experiment the factors A and B should also have a similar ratio. For experiment 23, the fraction of A over B is approximately ⅔ while in 24 it is close to 2.5. This would mean that one of the processes is around 4 times more important in experiment 23 compared to experiment 24 which seems highly unlikely considering the generally comparable conditions. Similar reasoning can be applied to the other experiments as well as the factors k_1 and k_2 showing that the double exponential fit could not separate the processes. Upon inspection of the data it became clear that this is primarily due to noise in the data. Therefore the two processes cannot be analysed separately with the given data.

In a next step the theory from section 5.1.3 is applied from which a number of conclusions can be drawn. First of all it is possible to use equation (5-16) to describe the dependency of k_{des} on the current loading. The 95% confidence intervals for a(T) deviated not more than 1.40% if the double exponential function was used as outflow concentration and no more than 2.75% if the noisy raw data was used. Further all results lie in approximately the same range as Figure 5-3 indicates.

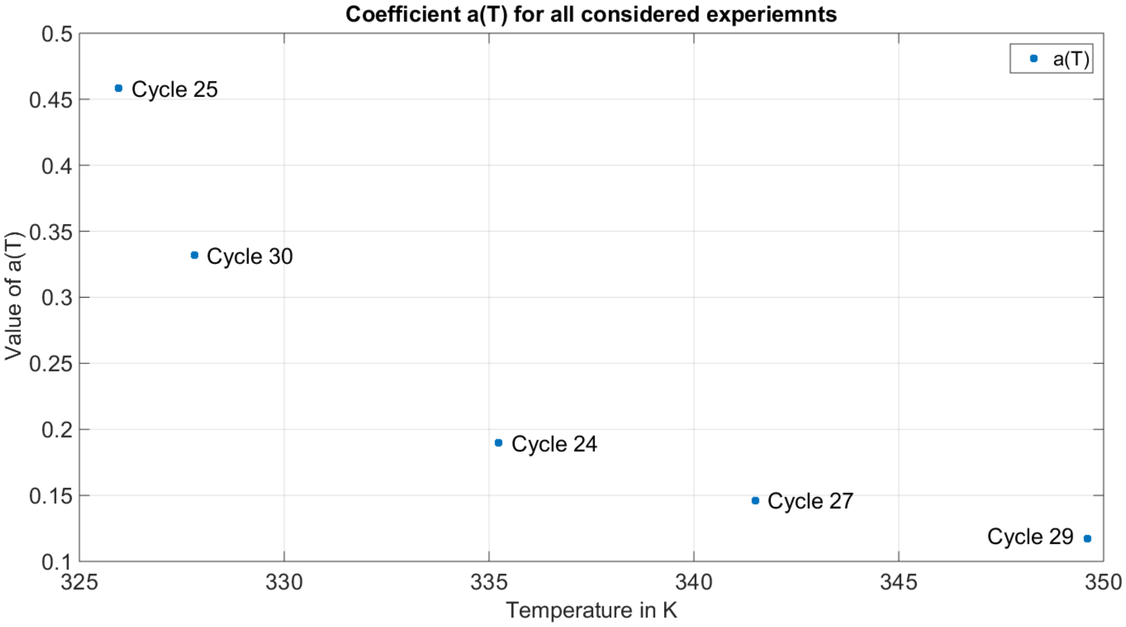

FIGURE 5-3: PARAMETER A(T) OVER THE MEAN STABLE TEMPERATURE OF THE CENTRE OF THE REACTOR USING THE RAW DATA AS BASIS FOR CALCULATION.

The values in Figure 5-3 quite obviously follow an exponential function which allows the application of the Arrhenius equation. This is allowed since the Arrhenius equation deals with the temperature dependence of a reaction and not with the concentrations. a(T) here is the factor relating the desorption coefficient k_{des} and temperature and is therefore the part of k_{des} which should follow some temperature dependent trend of the Arrhenius equation. The application of the Arrhenius equation is done in Figure 5-4 where a reasonable fit can be seen.

In this case the prefactor of the Arrhenius equation also contains a proportionality factor for the loading of the adsorbent (*b*) and a correction for a wrong assumption about the water vapour pressure ($c(P_{H2O})$) as will be explained in section 5.4. Therefore the factor A’ is defined as in equation (5-19) as the prefactor of the Arrhenius equation.

$$A' = A * b * c(P_{H_2O}) \tag{5-19}$$

where b is an empirical proportionality factor relating the current loading of the adsorbent and k(T) with the units $(\text{mole}_{KHCO3})^{-1}$, A is the prefactor from the Arrhenius equation with units $(s)^{-1}$, and $c(P_{H2O})$ is a unitless correction for the fact that the influence of the water vapour pressure was not correctly captured with the assumption in equation (5-4). Since the water vapour pressure only varies marginally, it is assumed to be constant for this part of the analysis making $b(P_{H2O})$ a constant as well. The definition of A’ is necessary in order to compensate for the simplifying assumptions made in section 5.1.3, explicitly since the activity of the water vapour was taken the same as in an elementary reaction.

The found values for the unknowns A’ and E_a are reproduced in (5-20). The apparent activation energy is negative which was to be expected seeing that a higher temperature slows down the desorption process. This does not mean that the activation energy of the actual reaction is in fact negative, but rather means that the term called activation energy in the Arrhenius equation is negative. It is known that negative values are indication of an inhibition of a process with increasing temperature. One explanation for this could be that higher temperatures cause the relative humidity to drop since the equilibrium pressure rises with temperature. This would make the water molecules more volatile and thus decrease the chance of them encountering a $KHCO_3$ molecule being next to the $KHCO_3$ on the surface of the adsorbent. The increased temperature would hinder a preadsorbtion of the water vapour by the activated carbon support which would otherwise bring the two molecules in contact.

$$A' = 1.219 \frac{1}{s * mol_{KHCO_3}} \qquad E_a = -53.1 \frac{kJ}{mol} \tag{5-20}$$

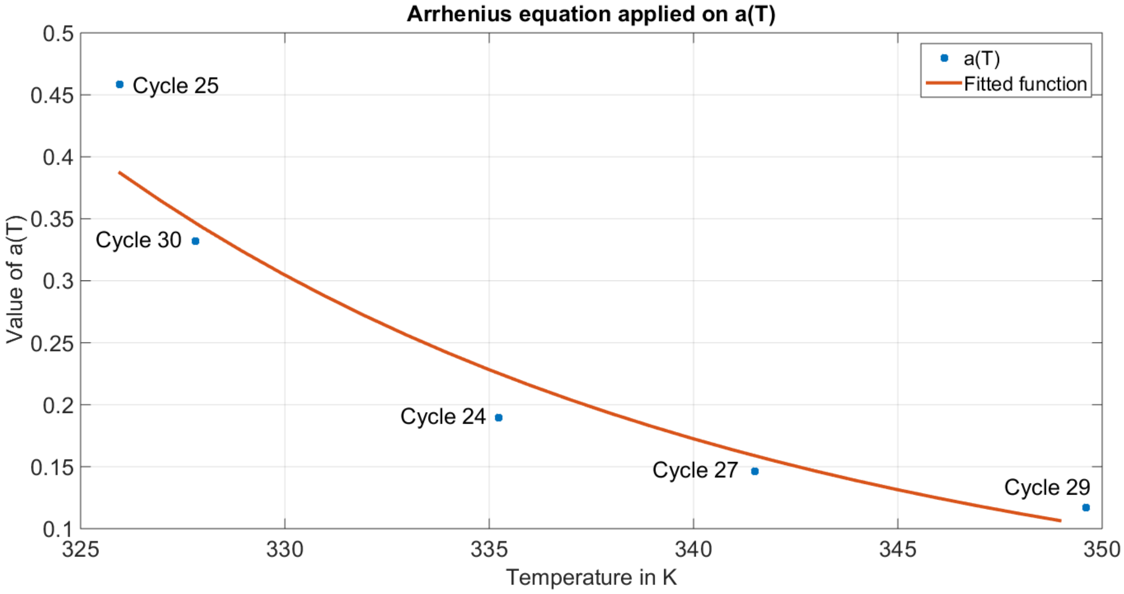

FIGURE 5-4: ARRHENIUS EQUATION APPLIED ON A(T)

Combining the previously found results, the following can be stated about the desorption coefficient k(T) which gives a quantitative answer to research question Q1:

The desorption coefficient $k_{des}(T)$ *follows the Arrhenius equation with an apparent activation energy of* $E_a \approx -50$ *kJ/mole.*

In order to gain complete understanding of the process, the factors b and $c(P_{H2O})$ in A' should be determined in the course of continued research. Using proper experiments and analysis this should be possible. Further the assumption that the loading of the adsorbent with CO_2 is linearly related to the desorption coefficient k_{des} which was made in equation (5-16) is supported by the fact that meaningful results are obtained with a very narrow 95% confidence interval of 2.75% at most. The following statement is therefore proposed without further proof:

The desorption rate r_{des} *is linearly proportional to the loading of the adsorbent with* CO_2*.*

5.4 Water vapour pressure

In order to understand the influence of the water vapour pressure on the process, again the cumulative loading for each experiment has to be known. The procedure for this is the same as for the temperature dependent experimental series and is thus not described again. The result can be seen in Figure 5-5.

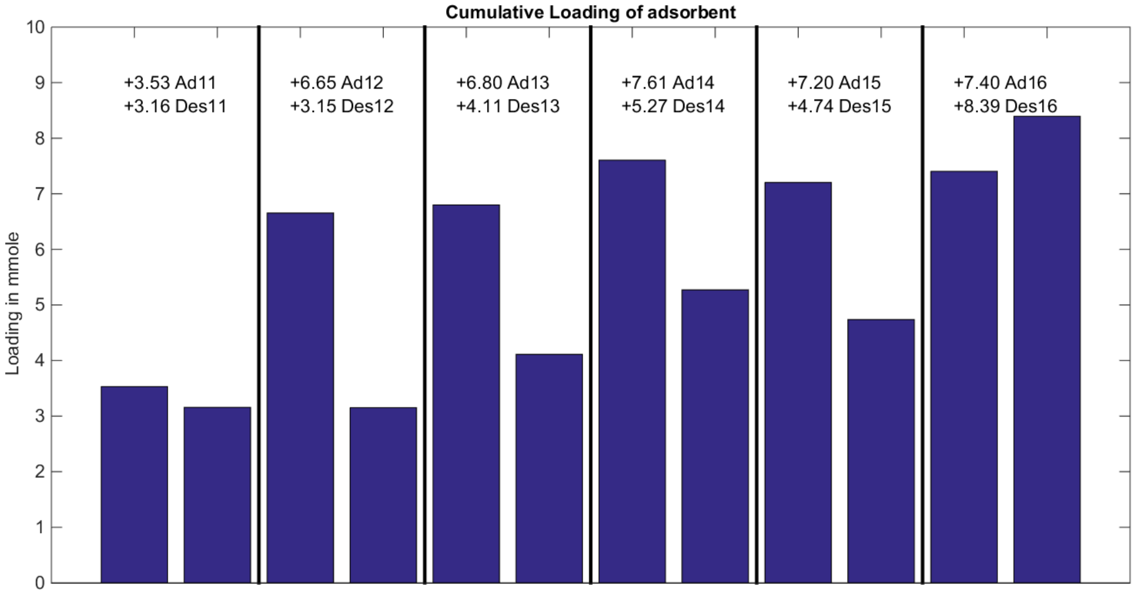

FIGURE 5-5: CUMULATIVE LOADING OF THE ADSORBENT AFTER EACH ADSORPTION AND DESORPTION. THE UPPER VALUE IS THE CUMULATIVE LOADING IN MMOLE AFTER THE ADSORPTION AND THE LOWER VALUE AFTER THE DESORPTION.

When working with the results displayed in Figure 5-5 care has to be taken since significant uncertainty exists about the loading and an offset has to be assumed. The reason for this is that desorption 11 was run with a long preheating time which caused an unrecorded loss of CO_2 as described in the general observations in section 5.2. It was only afterwards understood that this occurred. In order to compensate for this the amount of CO_2 desorbed in the cleaning with a N_2 flush after desorption 16 was taken as a reference value. Unfortunately technical problems occurred during that cleaning which again causes uncertainty about the absolute value of CO_2 contained in the adsorbent.

With the mass balance, the data from the desorption experiments can be normalized and compared by dividing the amount desorbed by the initial loading and displaying the different curves over time in the same graph. The result of this can be found in Figure 5-6. When viewing the figure it has to be kept in mind that the absolute loading is based on an estimate and therefore only the relation between the curves should be regarded, not the absolute desorption.

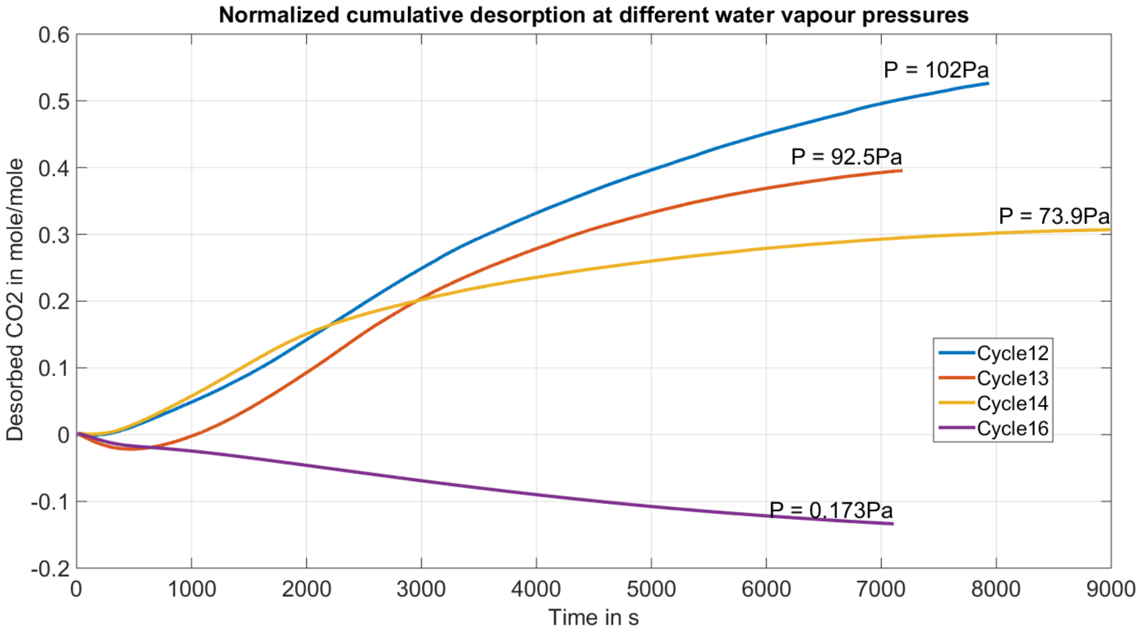

FIGURE 5-6: NORMALIZED CUMULATIVE DESORPTION AT DIFFERENT WATER VAPOUR PRESSURES. THE VALUES GIVEN IN TEXT FORM ARE THE WATER VAPOUR PRESSURES AFTER THEY HAVE STABILIZED.

From this graph it can be concluded that a higher water vapour pressure leads to an overall better desorption thus giving a qualitative answer to the second research sub question Q2. Further cycle 16 which was run at the same temperatures as the other runs resulted in an adsorption which shows that there is a minimum water vapour pressure to be reached in order for the adsorbent to release CO_2 at all.

A higher water vapour pressure increases the amount of CO_2 *desorbed in a given time frame as well as increasing the speed at which* CO_2 *is desorbed. Below a certain minimum vapour pressure, adsorption occurs if some* $K_2CO_3 \cdot 1.5H_2O$ *is available.*

The found results are in line with the research conducted by Lee et al. (2011) who state that a low water vapour pressure limits the total CO_2 capture capacity.

Since in all experiments were conducted at the same temperature it is possible at this point to check the theory suggested in 5.1.3. Figure 5-7 shows the result of applying the theory on the data. If the theory was correct, the value for a(T) should approximately be a constant which it is not. If however the water vapour concentration is regarded simultaneously, there is a clear correlation visible. According to Figure 5-8 a(T) seems to have a dependency on the water concentration in the inflowing stream as well. This indicates that the assumption made in equation (5-4) is not correct and means that the partial reaction order of the water vapour is greater than the assumed 0.5. Due to the limited amount of data however, it is not possible to find the correct value. The explanation for this is that the reaction is not elementary as was assumed.

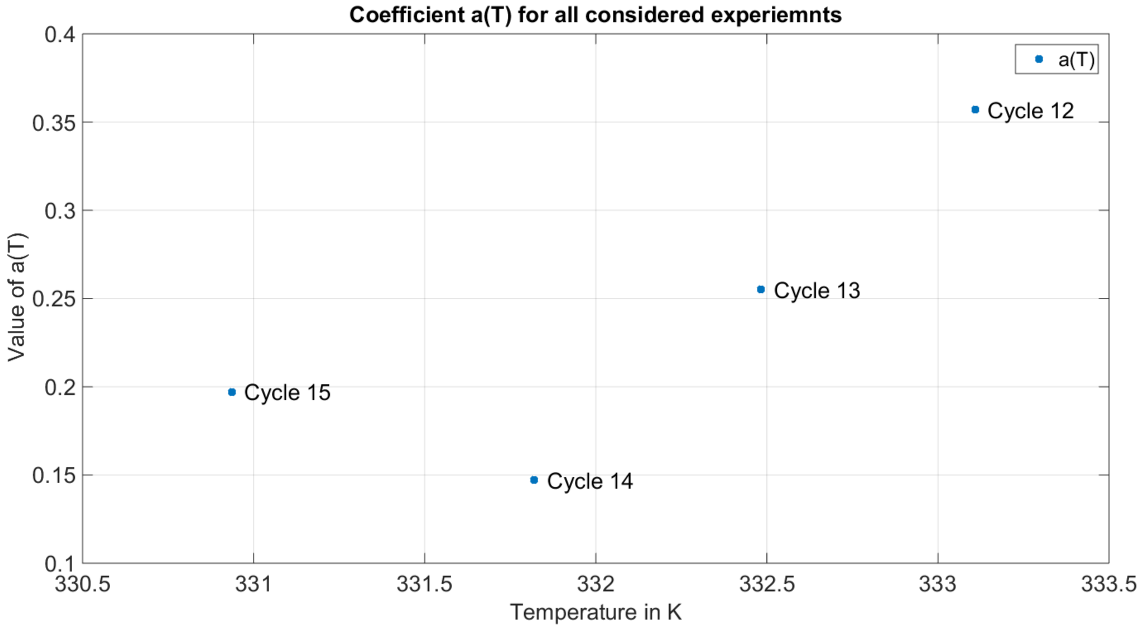

FIGURE 5-7: COEFFICIENT A(T) FOR ALL CONSIDERED EXPERIMENTS AS A FUNCTION OF TEMPERATURE.

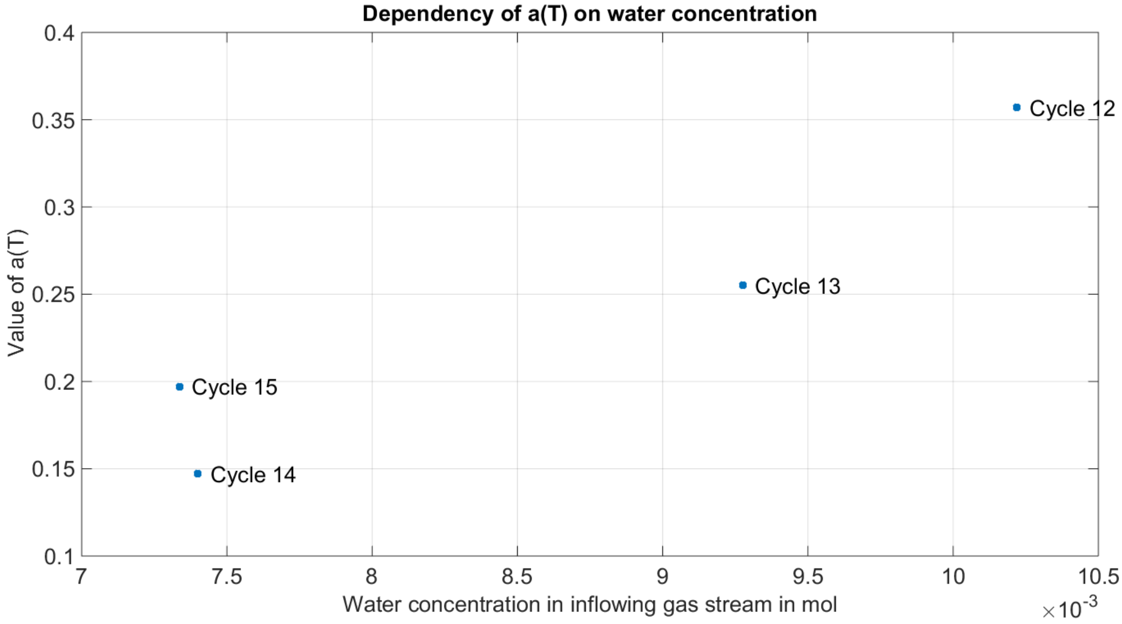

FIGURE 5-8: DEPENDENCY OF A(T) ON THE WATER CONCENTRATION.

The results from this section give therefore another qualitative answer to the research sub-question Q2:

The reaction rate r_{des} *is proportional to the water vapour concentration to a power higher than 0.5 which the stoichiometric coefficient. The approximation of describing the system as an elementary reaction is therefore not completely valid.*

Further analysis of the data does not seem to be feasible considering the limitations described in chapter 6 as well as the fact that the absolute loading of the adsorbent is uncertain.

6 LIMITATIONS

Throughout the conduction of the experiments many inaccuracies of equipment and in the procedure were discovered reducing the validity of the obtained results. The limitations connected to equipment are:

- The temperature indication in all graphs is based on the temperature in the centre of the reactor from a thermocouple which touched the carriers. This however does not give a good mean temperature of all the carriers. The outer carriers were hotter due to the fact that the heating was placed on the outside of the reactor. This means that the overall mean temperature is higher than the one used.
- The flow rate was set using manual valves. The scale was printed on the valves with steps of 0.2 MPa or 5 Psi depending on the unit used. This makes it impossible to set the same flow rate per experiment.
- The flow rate was measured using a gas meter at the outflow of the experimental setup. While the measurement can be considered relatively accurate there is uncertainty about leakage in the system. This is due to the fact that for changing the setup from adsorption to desorption mode, some equipment has to be connected and disconnected by hand and even with great care, errors happen sometimes. An example for this are cycle 25, 27, and 29 where the Peltier cooler experienced a leakage. The leak was only found after experiment 29 and the previously measured flow rates had to be corrected using an estimation.
- The relative humidity sensor RH had a wrong reading of the relative humidity. Using a calibration kit an error of 2% was found. This was only after most of the experiments had been run so that no new calibration was performed in order to not change the reading in comparison to the other experiments.
- The CO_2 sensors have a significant possible error which according to the producer is <1% of the calibrated range. Even with the lowest calibrated range of up to 30000ppm this means a possible error of 300ppm. In practice the two sensors read different values even when used in series with the same gas flowing through them as already stated in the section 4. This causes the CO_2 reading to be not reliable. It further means that the mass balances of CO_2 are influenced by this effect which creates quite significant uncertainty about the cumulative loading, especially if many experiments are performed after each other.

Taking all these effects together, the quantitative results of this study can merely be regarded as a proof of concept or an indication, but no quantitative values can be derived. For the qualitative results there is also uncertainty, but the trends in the data are so clear that they can be taken as correct even considering all these limitations.

7 CONCLUSIONS

The results obtained in this study are in line with what has been found in the brief literature study. Desorption occurred in the temperature and water vapour pressure ranges which were predicted by Duan et al. (2012) and were similar to the parameters used by Lee et al. (2011).

The most important finding of the experiments conducted is that a higher temperature slows down the desorption process. This is contradictory to desorption processes which in general are endothermic. For the water vapour pressure it was found that a higher water vapour pressure increases the overall amount of desorption as well as the speed of reaction. A high water vapour pressure however also means that the gas has to be at high temperatures in order to prevent condensation. Both trends showed consistently at each experiment and can therefore be concluded to be true. This gives an accurate answer to the main research question of what the influence of water vapour pressure and temperature on the rate of reaction is.

If these results are applied in practice this means that an optimum point has to be found where the temperature is low enough to not slow down the desorption process, but still high enough to ensure no condensation occurring at high water vapour pressures. Finding this optimum seems to be the main challenge in trying to answer the question of how the process can be run with the highest reaction rate. This conclusion is valuable for further research since it provides clear and practical guidelines for the next steps.

Next to these qualitative observations a number of quantitative results were obtained. Combining the results that the desorption rate depends linearly on the loading of the adsorbent, that the process follows the Arrhenius equation, and that the water vapour pressure has a greater influence than the stoichiometric coefficient 0.5, the reaction rate for desorption can be described as follows. n_{KHCO3} is the absolute loading with CO_2 in mole.

$$r_{des}(T) = A * e^{-\frac{E_a}{RT}} * n_{KHCO_3} * [H_2O]^m \ where\ m > 0.5 \tag{7-1}$$

It was further found that the apparent activation energy E_a is negative. The value found was -53.1 kJ/mole, but is subject to significant uncertainty due to equipment uncertainty and the low total number of experiments. The conclusion that E_a appears as negative in the order of -50kJ/mole indicates that the overall process is inhibited with increasing temperature. Equation (7-1) and the value for E_a provide a first step for the quantitative answer of the main research question. The fact that E_a was found to be negative shows that there is a process connected to the desorption process which is slowed down by elevated temperatures. The hypothesis is given that a higher temperature lowers the probability of a water molecule being adsorbed onto the activated carbon carrier. This in turn lowers the chance of encountering a $KHCO_3$ molecule on the surface of the activated carbon carrier which is necessary for the desorption to occur.

In addition, it can be concluded that two processes are involved in the desorption. This is based on the fact that the double exponential model can be applied. Further proof for this is that n in equation (7-1) is greater than 0.5. If it was an elementary reaction then it would have to equal 0.5

8 RECOMMENDATIONS FOR FURTHER RESEARCH

With the experiences from this study, a number of suggestions can be made for further research with the aim to give more quantitative answers to the research question of this work.

The first suggestion is to try to determine what the two processes involved are. Since the adsorption of water vapour is assumed to be the second process next to the reaction itself, it could be tried to feed moist air into the reactor containing a CO_2 concentration near equilibrium. This way there would be no desorption or adsorption happening which means that only adsorption of water vapour takes place. The adsorption would not occur by a chemical bonding , but might moisture the activated carbon carrier providing a better and quicker supply of water than if the potassium carbonate has to take it from air. In a second step the real desorption could be started. If the outflowing CO_2 concentrations follow an exponential curve, then this is a strong indication that water vapour adsorption is in fact the second process involved.

This procedure further enables a more accurate description of the events by an empirical exponential function. Having only one exponential it should be much easier to apply any desorption model or the theory suggested in 5.1.3. In turn this allows to determine the real desorption coefficient and consequently also the adsorption coefficient.

The second suggestion is to improve the accuracy of the equipment involved. After each calibration of the CO_2 sensors with CO_2 free air, they should also be calibrated relative to each other. The experience from the experiments showed that sensor 1 was more accurate than sensor 2 and that the difference between the sensors changed every time they were turned off and on again. A solution is that the read from sensor 1 could be taken as true value. Sensor 2 could then be calibrated relative to sensor 1 whenever the sensors were turned off and on again. This was also done for some experiments and it was found that a linear relation between the two values exists.

A further step to improve the accuracy is to use three way valves instead of actually disconnecting the tubes leading to and from equipment. This could lower the chance of leakages occurring. By putting valves before the pressure regulators, the regulators could potentially be left at the same setting removing that inaccuracy.

The last point of improving accuracy is to use more temperature sensors in the reactor which actually touch the carriers so that a better estimation of the temperature can be made. In order to create a good model for the temperature distribution, a steady state simulation of the heat flux could be performed. This way it would be much easier to determine a good value for the temperature.

A last suggestion for further research is to check the real working capacity of the adsorbent in order to have a good estimate of what the ratio of loaded to unloaded adsorbent is at each moment in time. This could replace the rather empirical approach used in this study by a more sophisticated theory.

9 ACKNOWLEDGEMENTS

I would like to thank Pr. Dr. Ir. Gerrit Brem for the provision of the assignment as well as guidance during the project. Further I would like to thank Rafael Rodriguez Mosqueda, Msc, for his support, advice, and help during the time of this work, and for the provision of material and equipment to conduct this research. A special thanks goes to Henk-Jan Moed who built the experimental setup used and provided practical help whenever needed. Further I would like to thank Antecy B.V. for initiating this project and providing financial support.

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Lee, S., Chae, H., Choi, B., Jung, S., Ryu, C., Park, J., . . . Kim, J. (2011). The effect of relative humidity on CO2 capture capacity of potassium-based sorbents. *Korean Journal of Chemical Engineering, 28*(2), 480-486. doi: 10.1007/s11814-010-0398-x

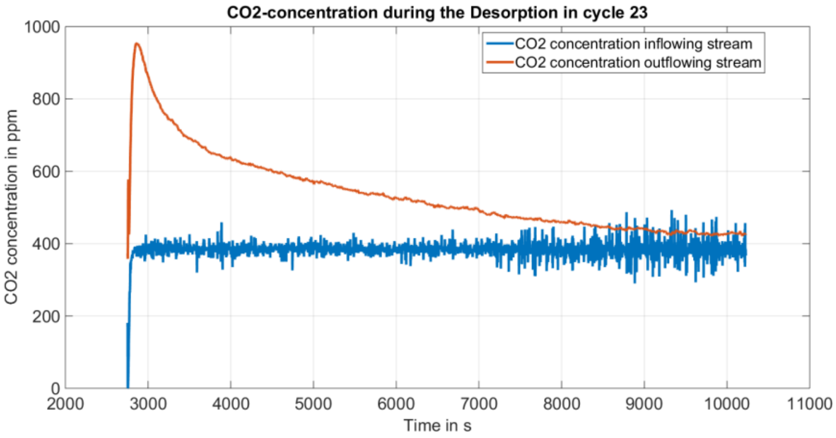
MathWorks. (2015). trapz Retrieved 18.07.2015, 2015, from http://nl.mathworks.com/help/matlab/ref/trapz.html

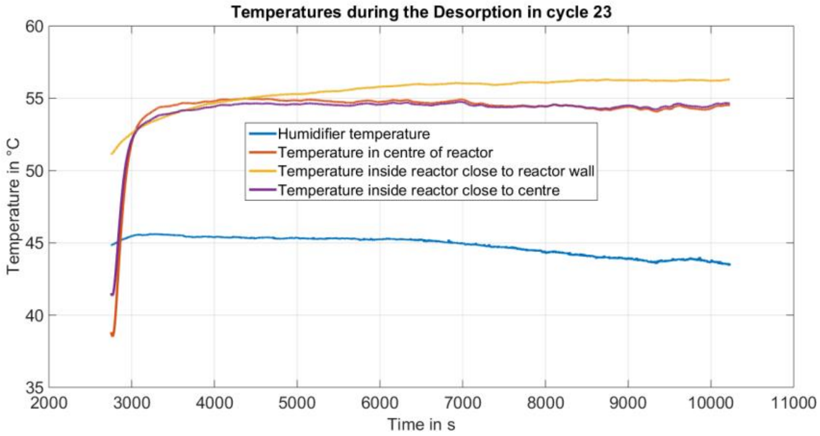
Shan, S., Jia, Q., Jiang, L., Li, Q., Wang, Y., & Peng, J. (2012). Preparation and kinetic analysis of Li4SiO4 sorbents with different silicon sources for high temperature CO2 capture. *Chinese Science Bulletin, 57*(19), 2475-2479. doi: 10.1007/s11434-012-5188-x

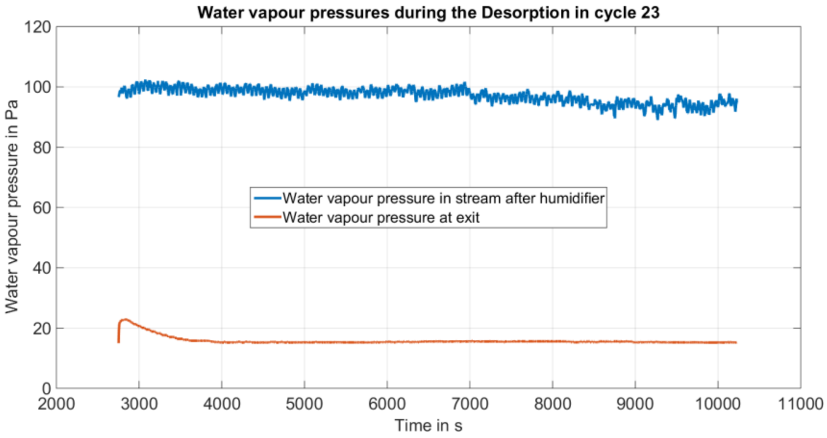
APPENDIX A DATA OF TEMPERATURE SERIES

In the following, all the data is given in form of graphs for the experiments which were used for the analysis in the temperature series. The other plots as well as numerical data can be provided upon request to c.olk@student.utwente.nl

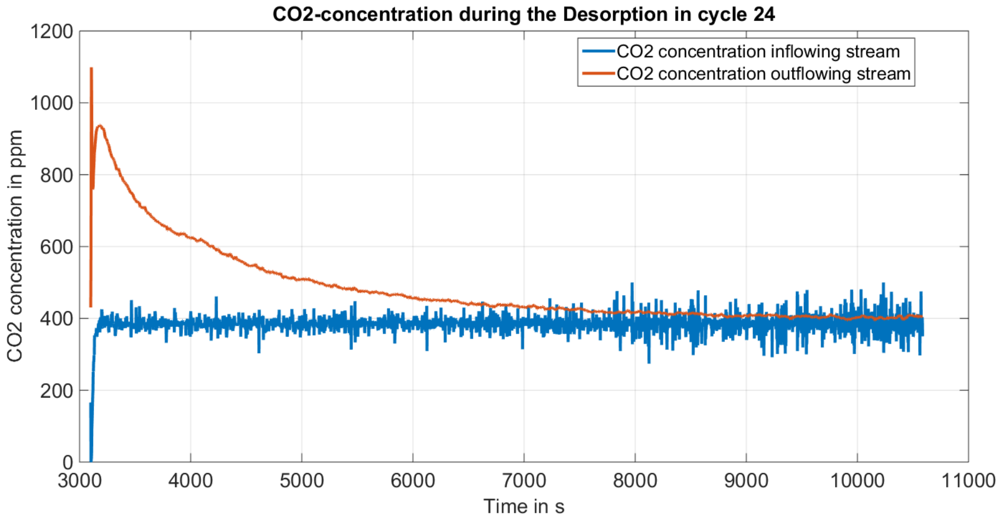
A.1 Cycle 23

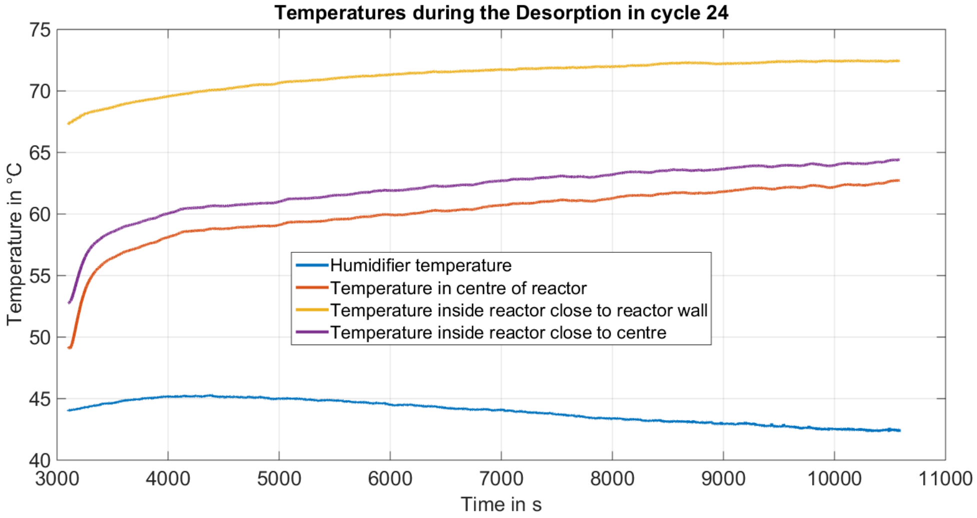


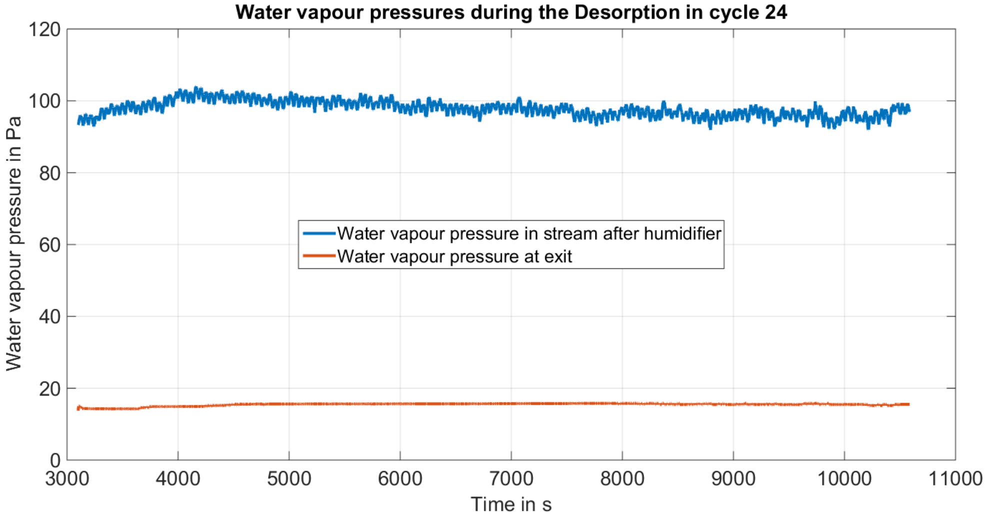




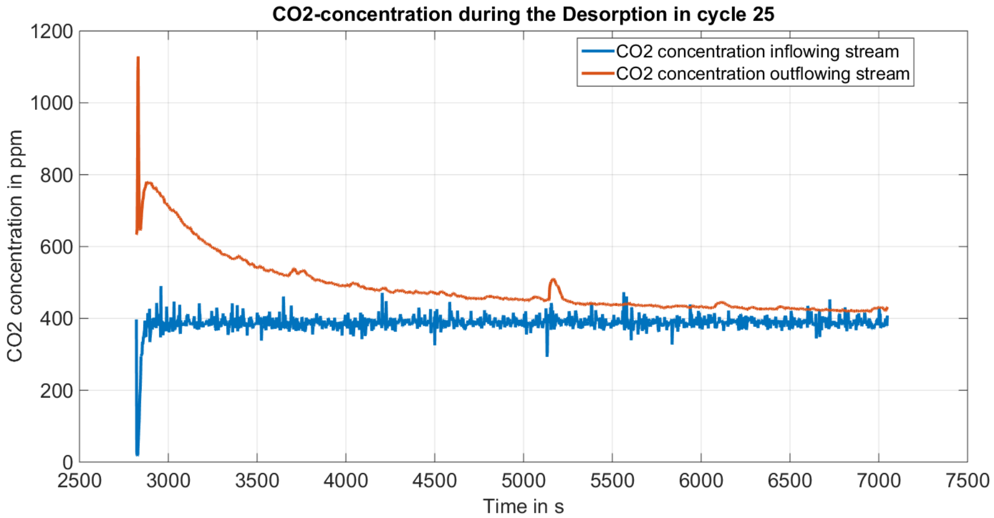
A.2 Cycle 24

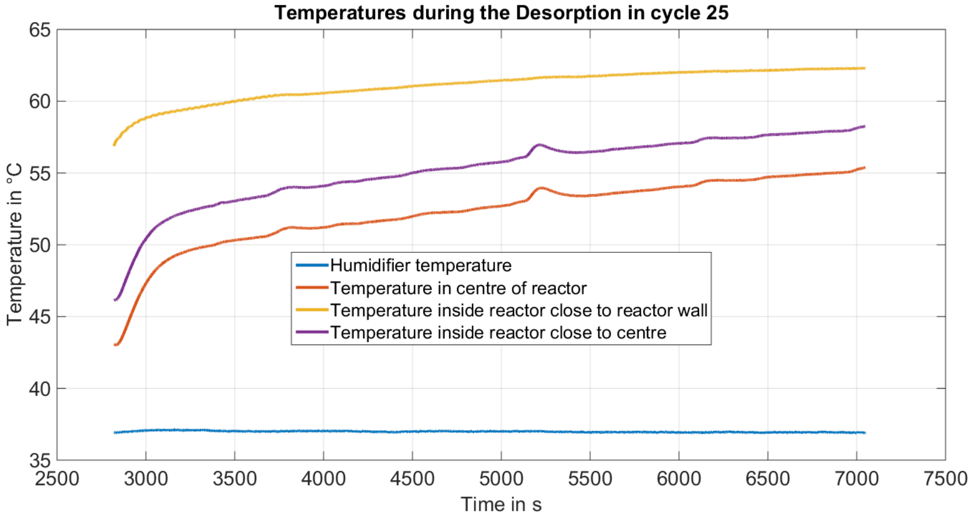

CO2-concentration during the Desorption in cycle 24

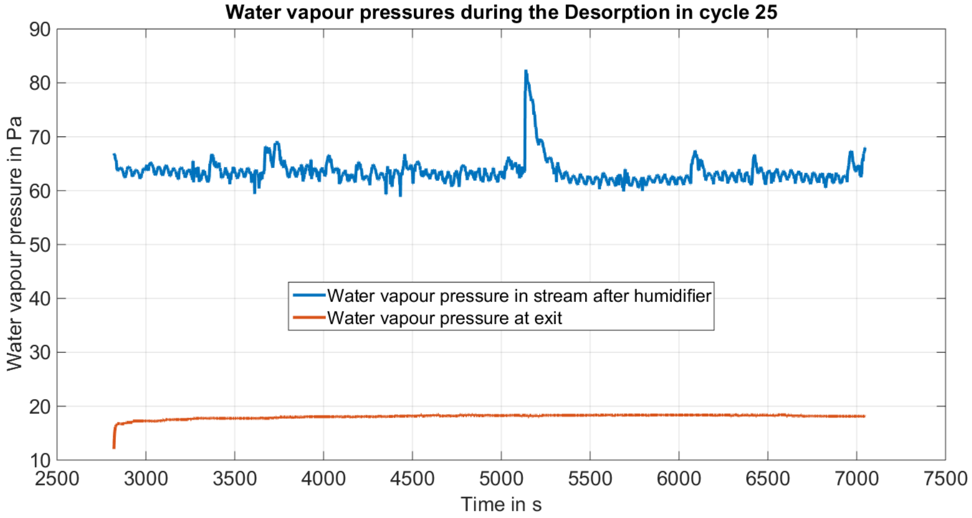

Temperatures during the Desorption in cycle 24


Water vapour pressures during the Desorption in cycle 24

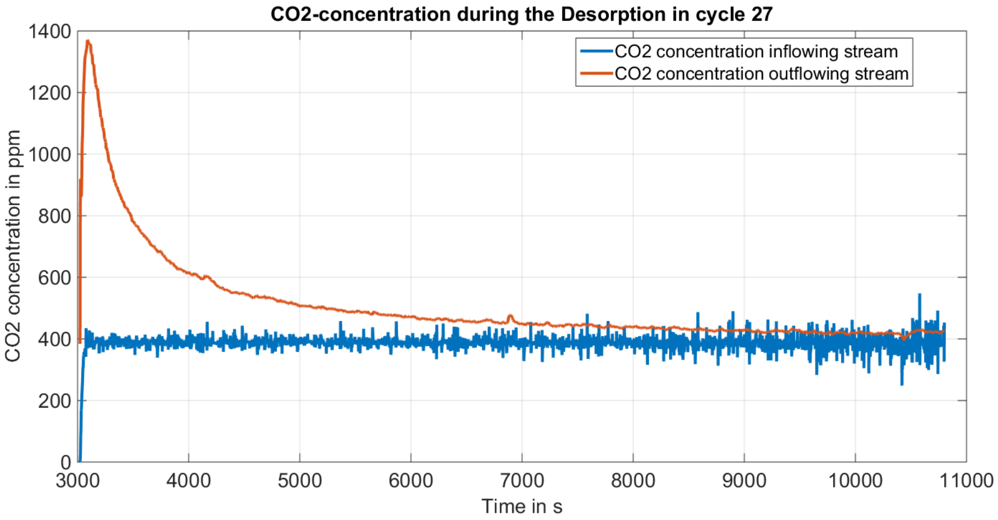
A.3 Cycle 25

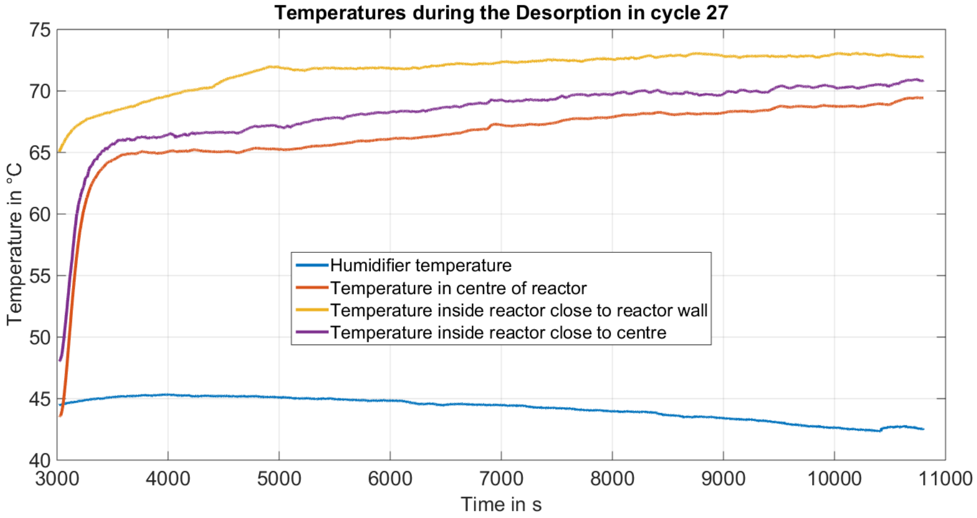

CO2-concentration during the Desorption in cycle 25

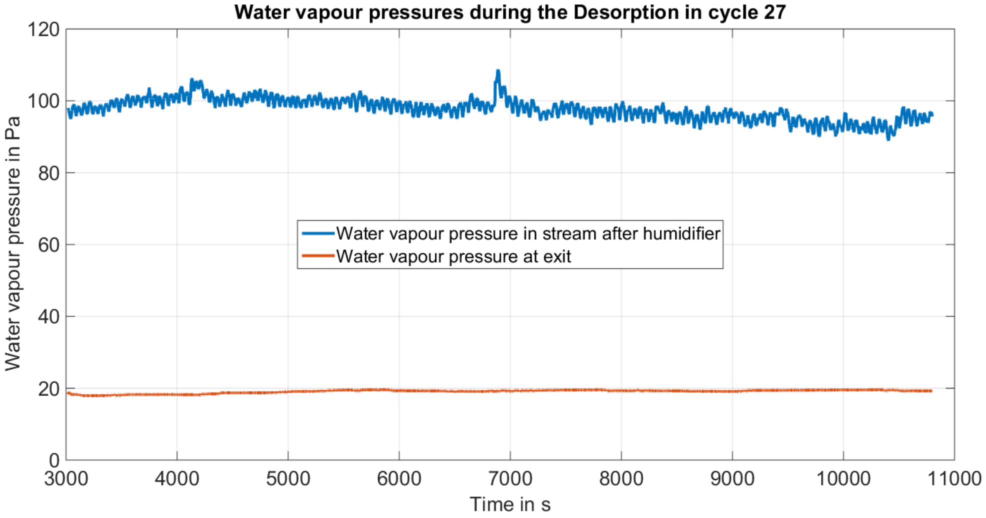

Temperatures during the Desorption in cycle 25


Water vapour pressures during the Desorption in cycle 25

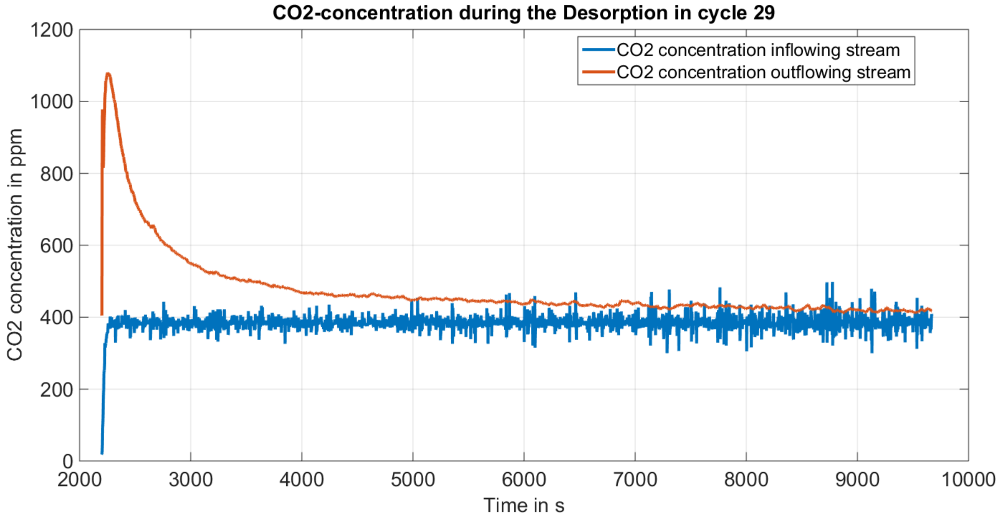
A.4 Cycle 27

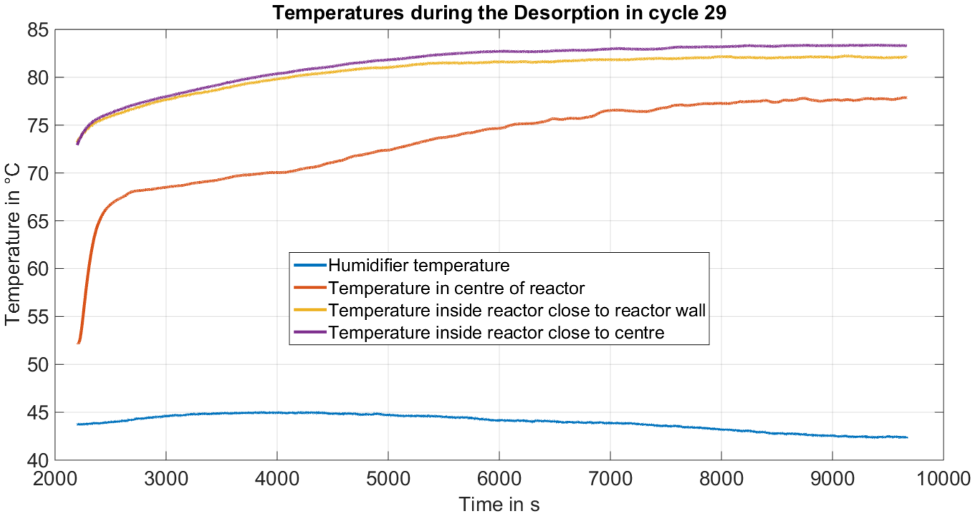

CO2-concentration during the Desorption in cycle 27
CO2 concentration in ppm
Time in s
CO2 concentration inflowing stream
CO2 concentration outflowing stream
0
200
400
600
800
1000
1200
1400
3000
4000
5000
6000
7000
8000
9000
10000
11000

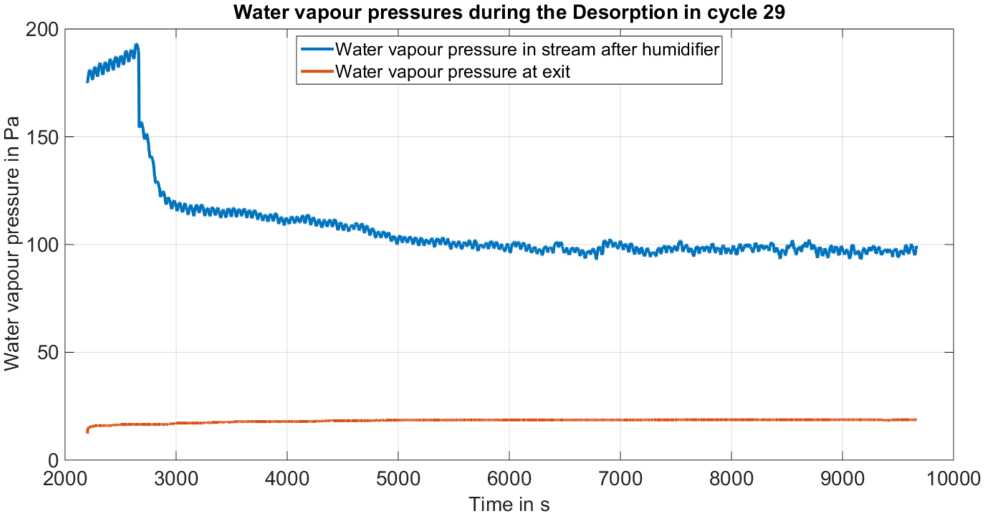

Temperatures during the Desorption in cycle 27
Temperature in °C
Time in s
Humidifier temperature
Temperature in centre of reactor
Temperature inside reactor close to reactor wall
Temperature inside reactor close to centre
40
45
50
55
60
65
70
75
3000
4000
5000
6000
7000
8000
9000
10000
11000


Water vapour pressures during the Desorption in cycle 27
Water vapour pressure in Pa
Time in s
Water vapour pressure in stream after humidifier
Water vapour pressure at exit
0
20
40
60
80
100
120
3000
4000
5000
6000
7000
8000
9000
10000
11000

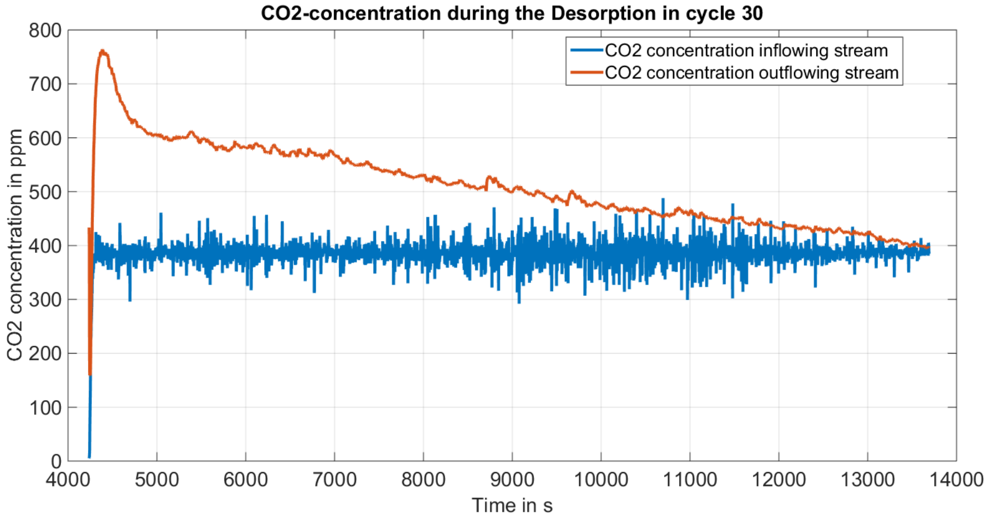
A.5 Cycle 29

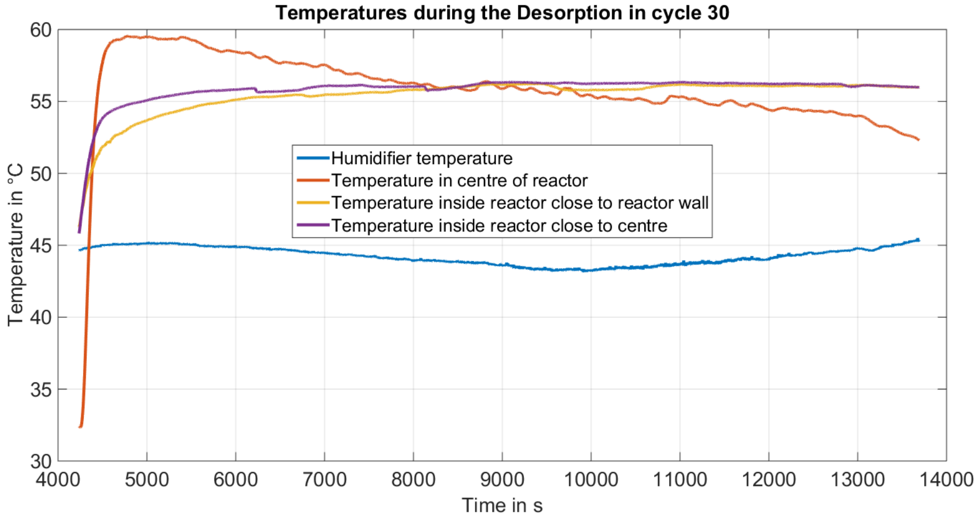

CO2-concentration during the Desorption in cycle 29

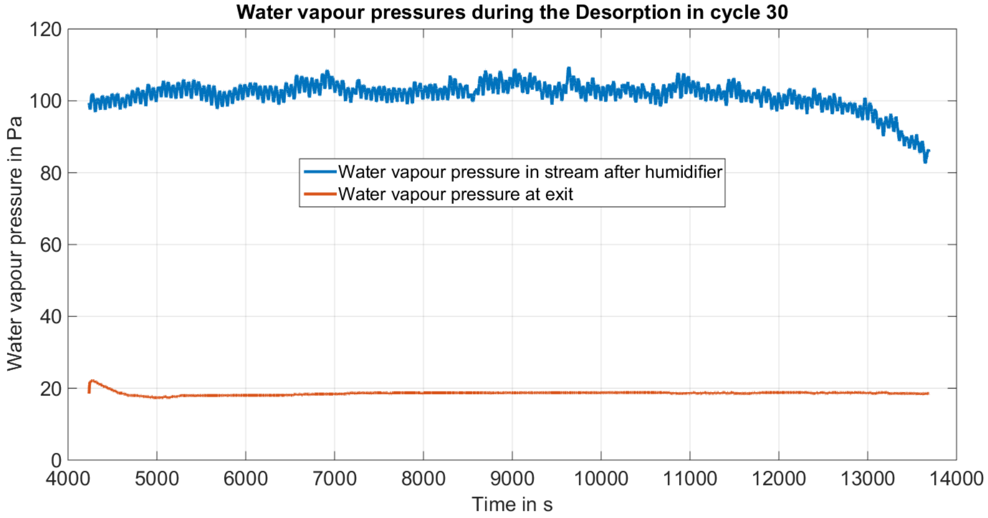

Temperatures during the Desorption in cycle 29


Water vapour pressures during the Desorption in cycle 29

A.6 Cycle 30


CO2-concentration during the Desorption in cycle 30
CO2 concentration inflowing stream
CO2 concentration outflowing stream
CO2 concentration in ppm
0
100
200
300
400
500
600
700
800
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Time in s

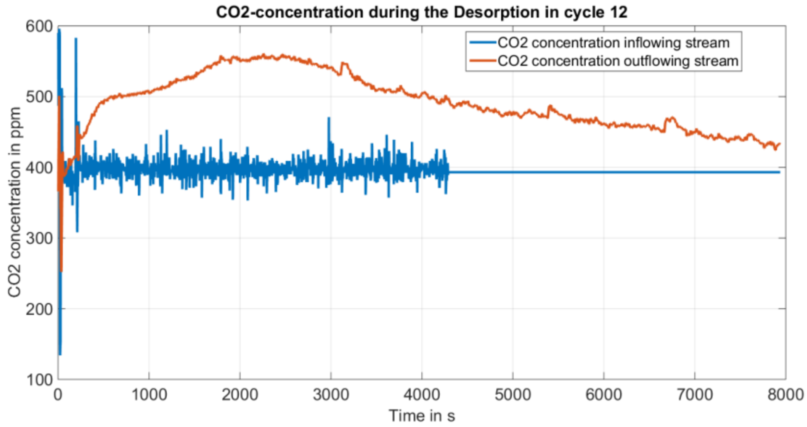

Temperatures during the Desorption in cycle 30
Humidifier temperature
Temperature in centre of reactor
Temperature inside reactor close to reactor wall
Temperature inside reactor close to centre
Temperature in °C
30
35
40
45
50
55
60
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Time in s

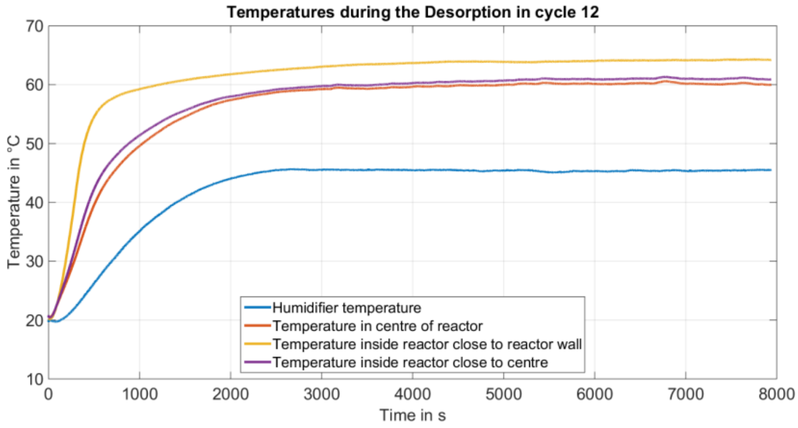

Water vapour pressures during the Desorption in cycle 30
Water vapour pressure in stream after humidifier
Water vapour pressure at exit
Water vapour pressure in Pa
0
20
40
60
80
100
120
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
Time in s

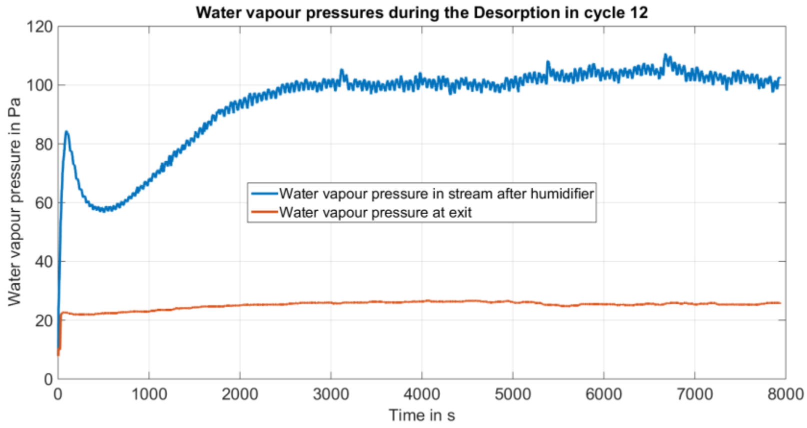
APPENDIX B DATA OF WATER VAPOUR PRESSURE SERIES

In the following, all the data is given in form of graphs for the experiments which were used for the analysis in the water vapour pressure series. The other plots as well as numerical data can be provided upon request to c.olk@student.utwente.nl

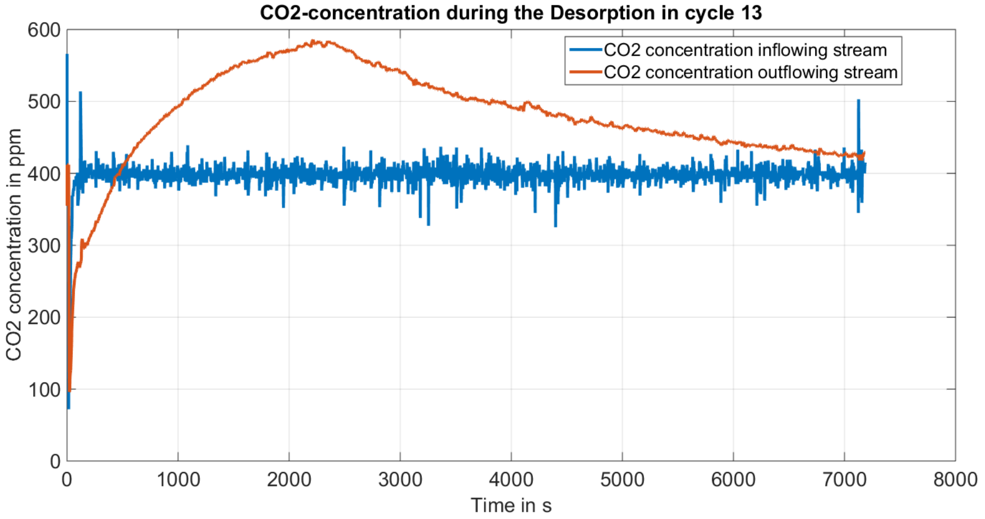
B.1 Cycle 12



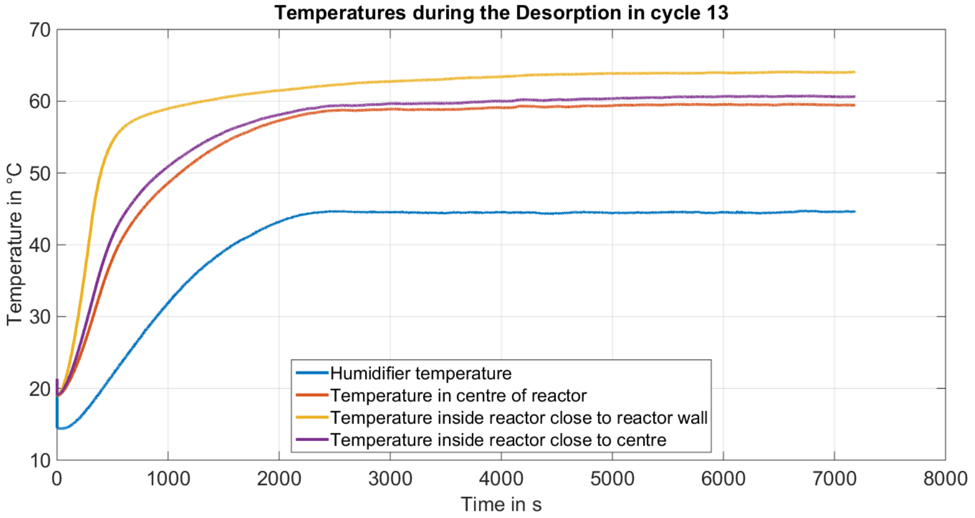




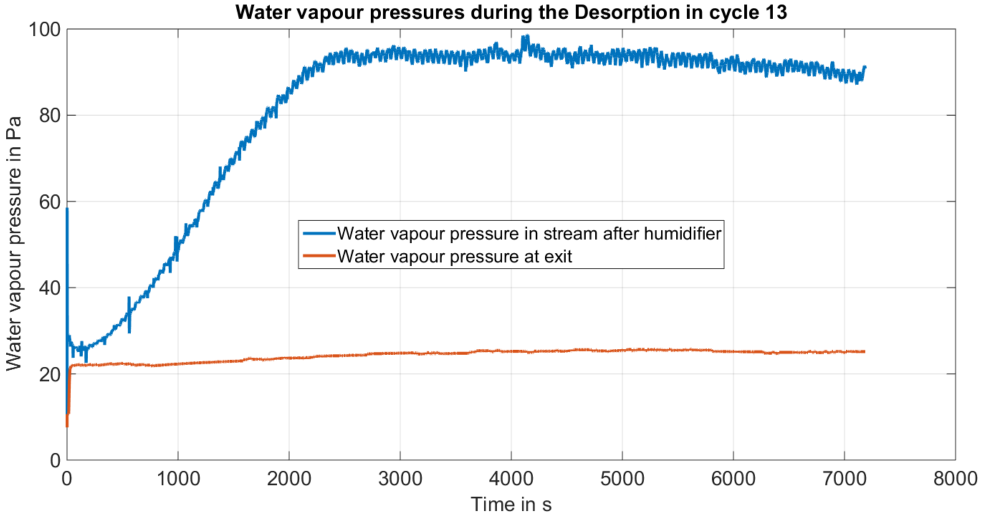
B.2 Cycle 13



CO2-concentration during the Desorption in cycle 13

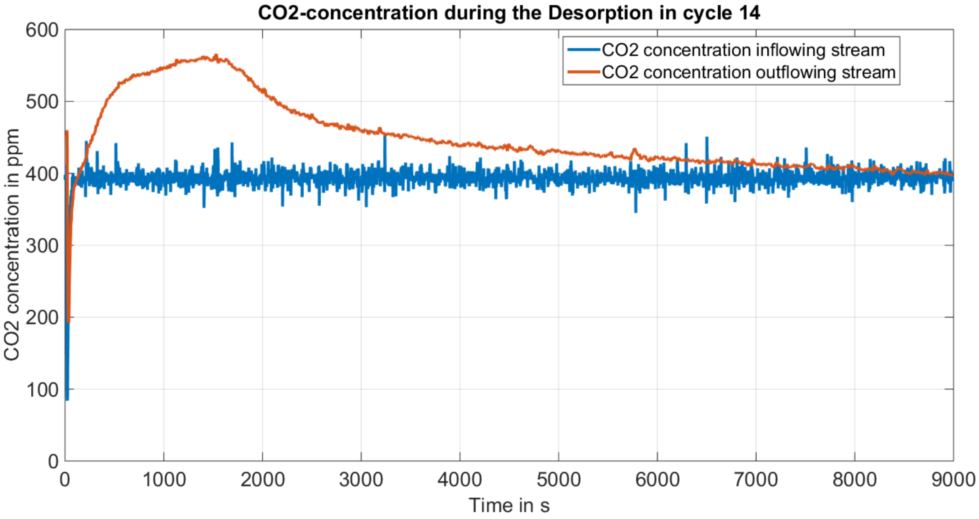


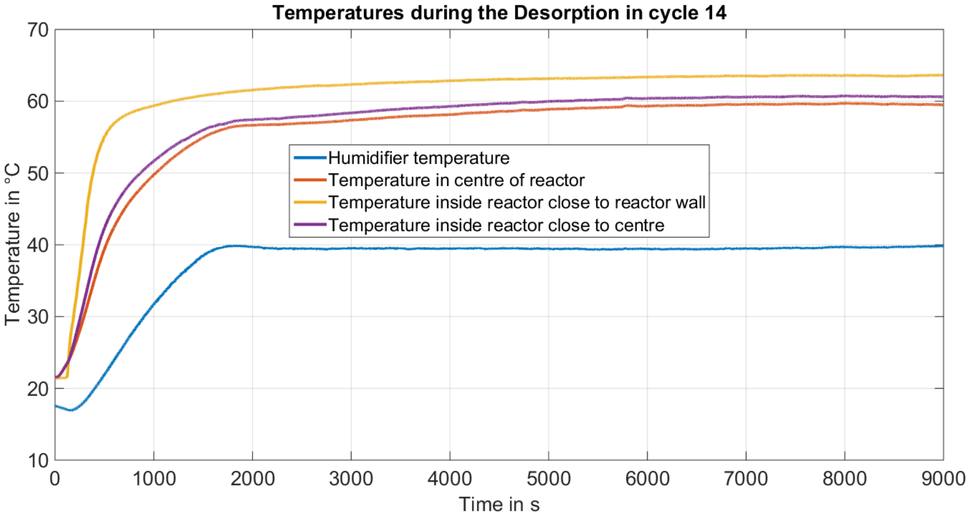
Temperatures during the Desorption in cycle 13

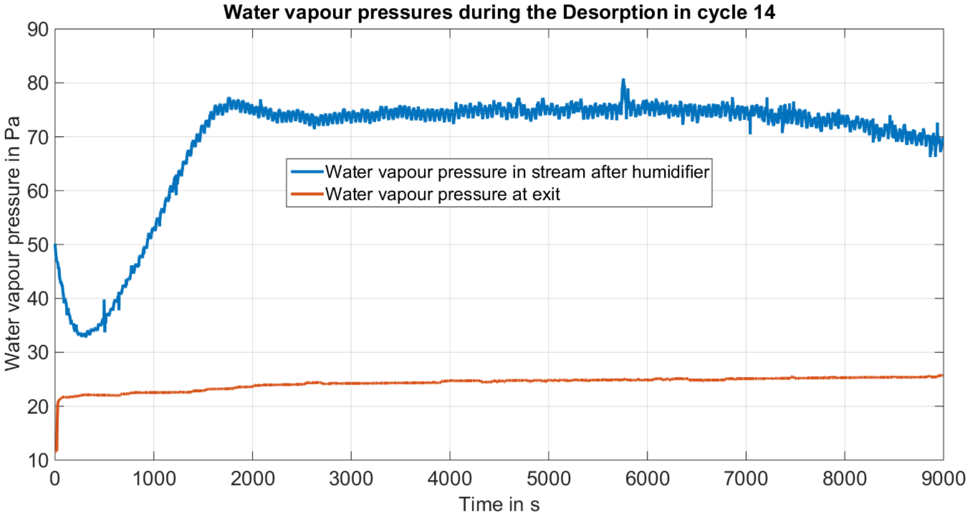


Water vapour pressures during the Desorption in cycle 13

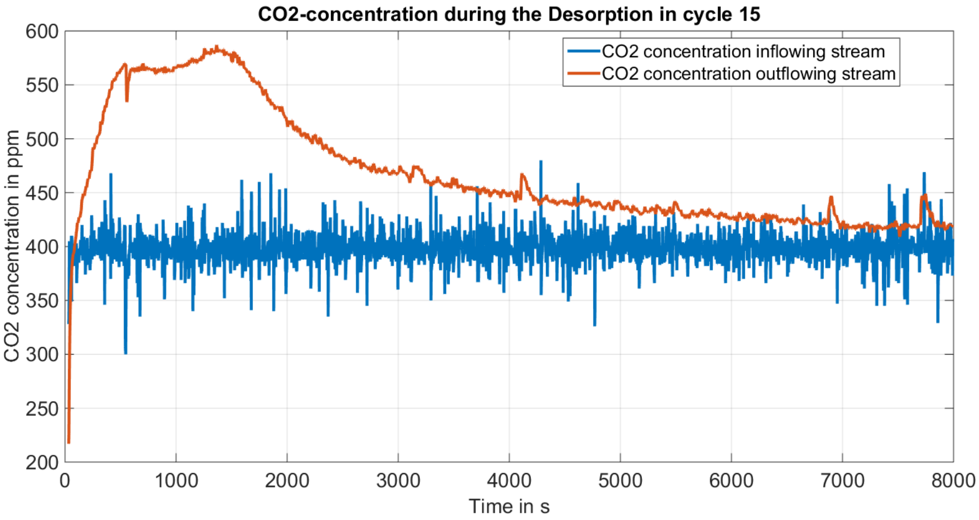
B.3 Cycle 14

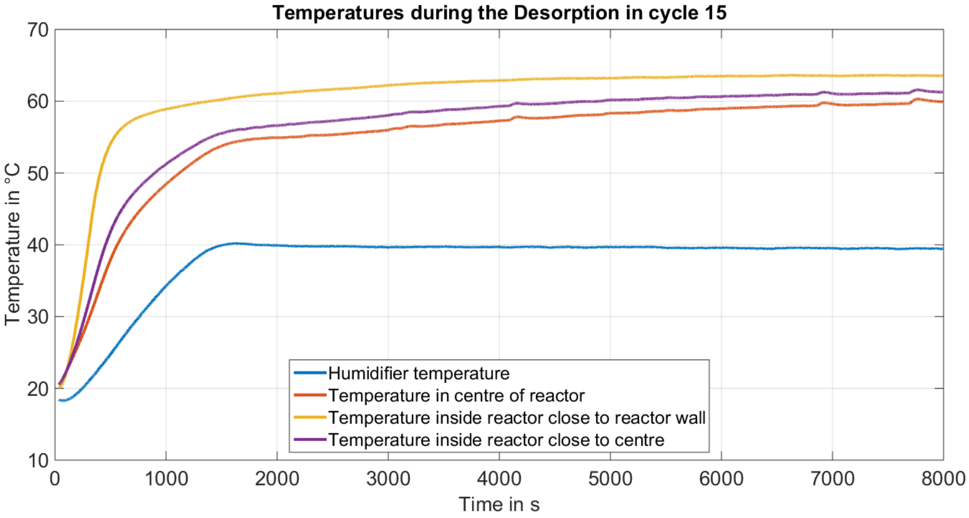

CO2-concentration during the Desorption in cycle 14

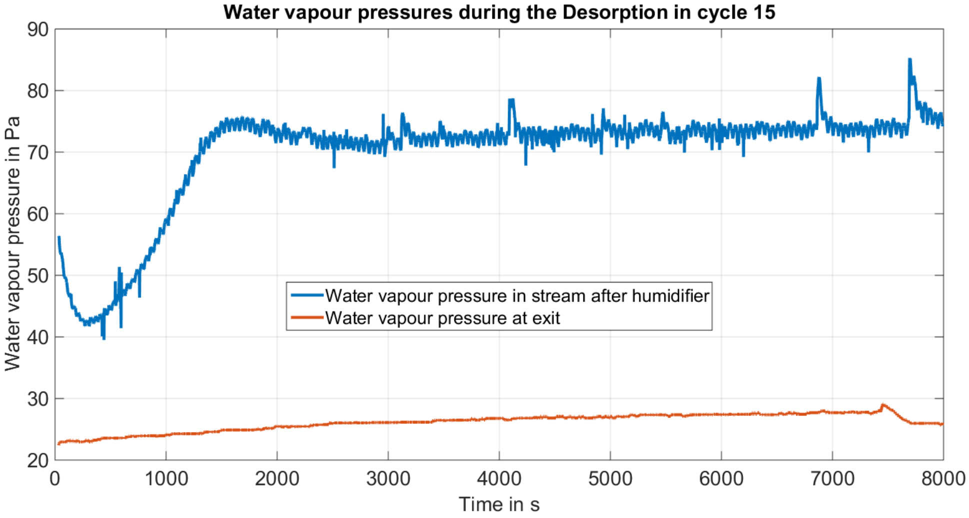

Temperatures during the Desorption in cycle 14


Water vapour pressures during the Desorption in cycle 14

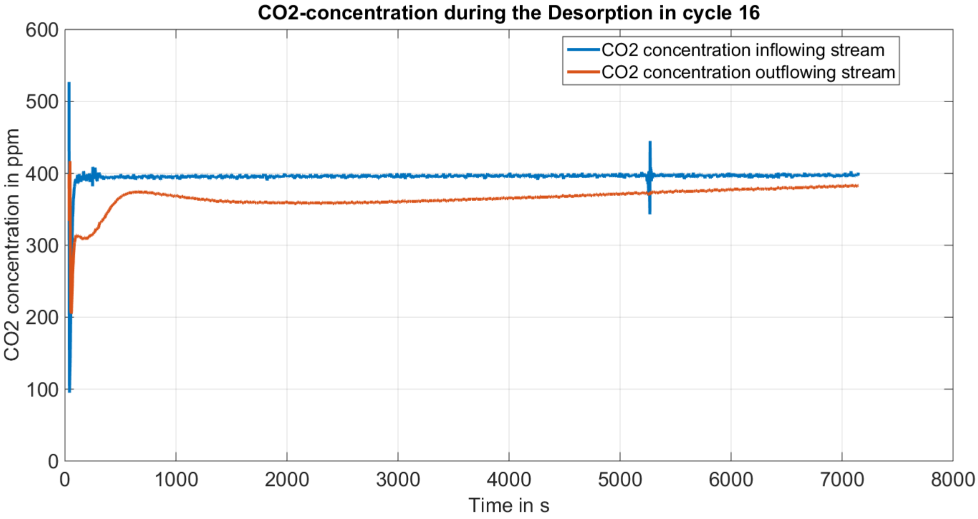
B.4 Cycle 15

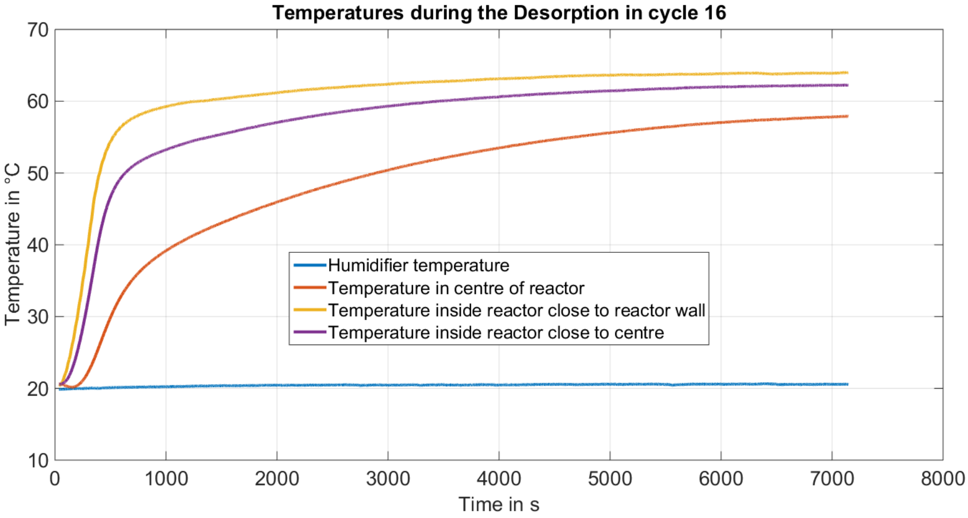

CO2-concentration during the Desorption in cycle 15
CO2 concentration in ppm
Time in s
600
550
500
450
400
350
300
250
200
0
1000
2000
3000
4000
5000
6000
7000
8000
CO2 concentration inflowing stream
CO2 concentration outflowing stream

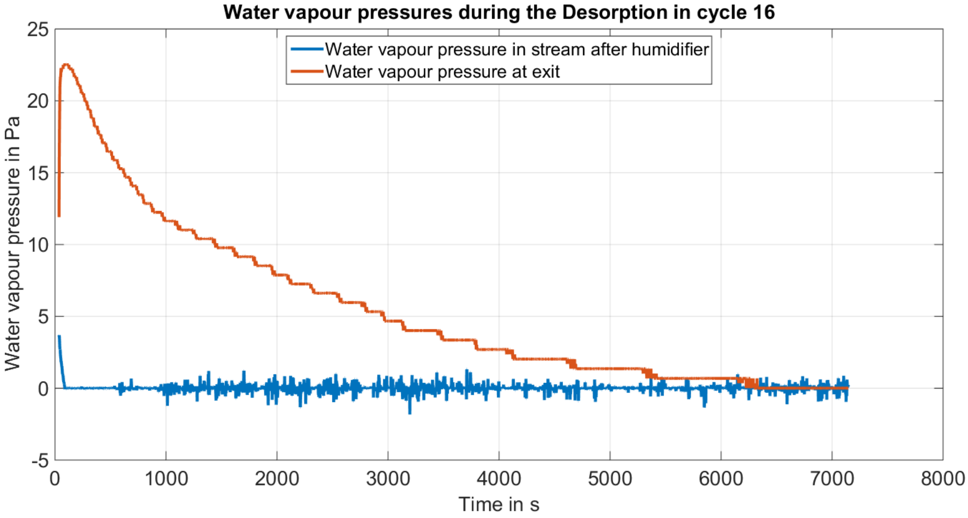

Temperatures during the Desorption in cycle 15
Temperature in °C
Time in s
70
60
50
40
30
20
10
0
1000
2000
3000
4000
5000
6000
7000
8000
Humidifier temperature
Temperature in centre of reactor
Temperature inside reactor close to reactor wall
Temperature inside reactor close to centre


Water vapour pressures during the Desorption in cycle 15
Water vapour pressure in Pa
Time in s
90
80
70
60
50
40
30
20
0
1000
2000
3000
4000
5000
6000
7000
8000
Water vapour pressure in stream after humidifier
Water vapour pressure at exit

B.5 Cycle 16


CO2-concentration during the Desorption in cycle 16
CO2 concentration in ppm
0
100
200
300
400
500
600
Time in s
0
1000
2000
3000
4000
5000
6000
7000
8000
CO2 concentration inflowing stream
CO2 concentration outflowing stream


Temperatures during the Desorption in cycle 16
Temperature in °C
10
20
30
40
50
60
70
Time in s
0
1000
2000
3000
4000
5000
6000
7000
8000
Humidifier temperature
Temperature in centre of reactor
Temperature inside reactor close to reactor wall
Temperature inside reactor close to centre


Water vapour pressures during the Desorption in cycle 16
Water vapour pressure in Pa
-5
0
5
10
15
20
25
Time in s
0
1000
2000
3000
4000
5000
6000
7000
8000
Water vapour pressure in stream after humidifier
Water vapour pressure at exit