Structured Zeolite Adsorbents for CO2 Separation

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Structured zeolite adsorbents for CO$_2$ separation

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4$^{th}$ June 2012
Gas separation processes have many industrial applications. One way to separate a gas from a mixture is by selectively adsorbing it. Zeolites are microporous crystalline aluminosilicates with unique properties used for many processes including gas adsorption. Currently, traditional adsorbents in the form of beads and pellets are used in adsorption processes. But when high throughputs are required, high pressure drop and mass transfer resistance in pellet beds lead to decreased productivity and recovery and increased energy demand. For these reasons, structured adsorbents characterized by low pressure drop and better mass transfer are becoming increasingly important.

In this work, structured adsorbents in the form of steel monoliths coated by a thin zeolite NaX film were prepared and used for CO₂ adsorption from a CO₂/N₂ mixture. A new method for the synthesis of zeolite NaX films on steel monoliths was developed. The obtained films were homogeneous, ca 3 µm thick and were almost free from sediments and secondary products.

With the CO₂ breakthrough experiments it was demonstrated that the steel monoliths coated with zeolite had much lower adsorption capacity per unit volume of bed as compared to the zeolite pellets. However, the mass transfer zone (MTZ) of the breakthrough curves obtained using the monoliths was much narrower than the MTZ for the zeolite pellets indicating that the mass transfer resistance in the monoliths was
very low due to the low thickness of the zeolite film. Narrow MTZ together with the low pressure drop commonly observed for the monoliths could give a possibility to reduce cycle time in cyclic adsorption processes, increasing productivity and reducing energy demand. Compared to the zeolite coated ceramic cordierite monoliths investigated earlier, the coated steel monoliths had a higher adsorption capacity and almost as narrow MTZ, with a higher mass transfer coefficient, as obtained from the numerical modeling. This makes zeolite coated steel monolith a better alternative for the adsorption processes.

After further optimizations, zeolite coated steel monoliths could be employed to improve the performance of the gas separation processes.
To my family
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Introduction

Recovery and purification of the industrial products are the major unit operations in the chemical, petrochemical, environmental and electronic gas industries [1]. In a chemical process, although most of the value in chemical conversion is added via reaction, it is the separation that largely determines the capital cost of production. Nearly every chemical manufacturing operation requires the use of separation processes to recover and purify the products. The efficiency of the separation process has a significant impact on both the quality and the cost of the product.

Today, gas separation is a field of chemical engineering that is undergoing a great development. Many chemical industries are working on the recovery of hydrogen from product streams of ammonia plants, enrichment of air by oxygen for medical or metallurgical purposes, removal of water vapor, H$_2$S, and CO$_2$ from natural gas [2]. Moreover, one should not forget the big problem of increasing concentrations of carbon dioxide in the atmosphere, which in turn causes the greenhouse effect. The capture and storage of carbon dioxide has been identified as a potential solution to the problem of global warming. Efficient separation technologies are required for the removal of carbon dioxide from flue gas streams to allow this solution to be widely implemented [3, 4].

Adsorption is one of the most important methods to separate compounds from the industrial gas mixtures [2]. The separation is achieved when a certain component (called adsorbate) in a mixture attaches to the surface of a solid (called adsorbent) whereas the others remain in the gas stream.

Commonly used types of adsorbents are:

- oxygen-containing compounds such as zeolites and silica gel, which are polar and hydrophilic;
- carbon-based compounds such as activated carbon, which are non-polar and hydrophobic;
• polymer-based compounds, which can contain either polar or non-polar functional groups.

Zeolites represent one of the most innovative adsorbents for a wide range of applications including air separation, air drying, CO removal from reforming gas, and CO$_2$ removal from natural gas [1]. Zeolites are crystalline microporous aluminosilicates, mineral or synthetic, characterized by a pore network of molecular dimensions. Porous structure of zeolites provides them with a high surface area resulting in a high adsorption capacity.

The structure of adsorbents has to ensure a fast transport of the gaseous compounds. To meet these requirements, different geometries of adsorbents are used. Spherical pellets and rods are the most important forms of adsorbents [5]. Apart from that, many types of novel structured adsorbents have been studied and commercialized in the last decade including monoliths, laminates, foams and fabric structures.

**Objective**

The scope of the present work was to prepare an adsorbent in the form of a steel monolith coated with a thin film of zeolite NaX, to investigate its ability to adsorb CO$_2$, and to compare its performance with that of the zeolite beads and ceramic cordierite monolith coated with zeolite NaX.
2.1 Adsorption

2.1.1 Fundamentals of adsorption

Adsorption is the adhesion of molecules, atoms or ions to a solid surface due to the excess of the surface free energy caused by the bond deficiency [6]. It is possible to classify adsorption as physisorption, characterized by weak van der Waals forces, chemisorption, characterized by covalent bonds, and adsorption due to electrostatic forces [7]. An adsorption process can be described by an adsorption isotherm, which represents the amount of an adsorbate attached to an adsorbent as a function of the pressure of a gas or the concentration of a solute in solution, at constant temperature. Freundlich and Kuster (1894) were the first to introduce a purely empirical formula (Eq.1) to describe the isothermal adsorption of a gas on a solid surface [8]:

\[
\frac{x}{m} = KP^{1/n} \tag{1}
\]

where \(x\) is the amount of adsorbate adsorbed, \(P\) is the pressure of adsorbate, \(m\) is the mass of adsorbent, and \(K\) and \(n\) are empirical constants, which depend on the adsorbate-adsorbent system at a certain temperature.

In 1916, Irving Langmuir introduced a new model for the adsorption of gases on solids described by Eq.2 [9]:

\[
\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P} \tag{2}
\]
2.1 LITERATURE SURVEY - Adsorption

where $\theta$ is the fraction of the molecules adsorbed on the solid surface, $P$ is the gas pressure or concentration, $\alpha$ is the Langmuir adsorption constant, which increases with an increase in the binding energy of adsorption and with a decrease in temperature [9].

The model is based on the following assumptions:

1. The adsorption sites are the same over the entire surface of the adsorbent.
2. There are no interactions between adsorbed molecules.
3. The process evolves over time without changes.
4. Molecules of adsorbate can be adsorbed only on the empty sites of the adsorbent.

But all these hypotheses are not always true, because it is possible to find imperfections on the surface, adsorbed molecules sometimes can interact with each other, the mechanism of adsorption is not the same for all the molecules during the process, and the adsorbate molecules often bind to the adsorbate species on the surface.

When adsorbed molecules form multilayers on the adsorbent, because new molecules of adsorbate attach to the molecules already adsorbed, the Langmuir model is not valid to describe the process [10]. For this reason, in 1938, Brunauer, Emmett and Teller developed a new adsorption model described by Eq.3, called BET theory [10], from the initials of their family names.

$$\frac{1}{v[\left(\frac{p_0}{p}\right) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

where $p$ is the equilibrium pressure, $p_0$ represents the saturation pressure of adsorbate at the adsorption temperature, $v$ is the total adsorbed gas volume, $v_m$ is the adsorbed gas volume for a monolayer, and $c$ is the BET constant, which depends on the adsorption temperature.

BET theory represents an extension of the Langmuir model and it is based on the following hypotheses:

1. An adsorbent can adsorb gas molecules infinitely;
2. The layers that form do not interact with each other;
3. For each layer it is possible to apply Langmuir theory.

BET adsorption isotherm is commonly used to calculate the surface area of solids from the gas adsorption data [10].

Desorption is a process opposite to the adsorption and occurs in a system being in the state of sorption equilibrium between the bulk phase (fluid phase) and the adsorbing solid surface. When the concentration (or pressure) of the adsorbate in the bulk phase is lowered, some of the adsorbate is released from the surface of the adsorbent to the bulk phase. Temperature change can also cause desorption. As the temperature rises, desorption occurs, because the increase in temperature provides the energy required to break the bonds between the adsorbent and the adsorbate. Decrease of total pressure in case of gas adsorption also leads to desorption.

### 2.1.2 Breakthrough curve

Another way to characterize adsorption is by a breakthrough curve. The breakthrough curve represents the evolution of the adsorbate concentration in the flow from the adsorbent bed, commonly as a function of time. *Figure 1* shows a typical breakthrough curve with the relative concentration (concentration of the outgoing gas divided by the initial concentration of the incoming gas) on the y-axis, and time on the x-axis.

*Figure 1*. A typical breakthrough curve [11].
At the beginning of the adsorption process, all the adsorbate is adsorbed in the column, for this reason, the relative concentration of the adsorbate is zero. At the time \( t_B \) the adsorbent begins to be saturated with the adsorbate, so the relative concentration starts to increase \( (C_{out}/C_F = 0.05) \). At the time \( t_E \) the output concentration from the column is close to the initial one \( (C_{out}/C_F = 0.95) \), because the adsorbent is almost completely saturated, so the adsorbate passes through the column without being adsorbed to any larger extent. The area between \( t_B \) and \( t_E \) is called the mass transfer zone (MTZ). Eventually, the output concentration reaches the initial concentration and no adsorption occurs.

For a good separation, a sharp breakthrough curve (narrow mass transfer zone) with a long breakthrough time \( (t_B) \) is desirable. The shape of a breakthrough curve for the adsorption of a gas in a column packed with an adsorbent is affected by different parameters including bed height, gas flow-rate, and bed void fraction.

If the bed height is increased, there is an increase in the breakthrough time due to the increased adsorbent loading, see *Figure 2*. This plot also shows that for increasing bed height, the MTZ becomes broader due to a longer diffusion path length.

*Figure 2.* Breakthrough curves for different adsorbent bed heights [12].

When the flow-rate through the adsorption column is increased keeping the bed height constant, the breakthrough time decreases, see *Figure 3*. 
Bed void fraction is the ratio of empty volume in a packed column and the total volume of the column. This ratio can vary significantly depending on the geometry of an adsorbent. For the same weight of the adsorbent, the larger is the void fraction, the broader is the MTZ, again, due to the increased diffusion path length.
2.2 Zeolites

2.2.1 Zeolite structure

Zeolites are microporous aluminosilicate materials that have a structure composed of silica and alumina tetrahedra, in which the atoms of oxygen are connected by either silicon or aluminum. When aluminum enters the structure of silica, the framework becomes negatively charged, so the presence of counterions (cations) is necessary in the structure to keep the framework neutral. Chemical composition of zeolite can be described by the following formula [13]:

\[ M^{n+}_{x/n} \cdot xAlO_2^- \cdot ySiO_2 \cdot zH_2O, \]

where M is the counterion, n is the counterion valence, y/x the silicon/aluminum ratio and z the content of hydrate water [13].

The amount of Al within the framework can vary over a wide range, with Si/Al ≥ 1. Table 1 illustrates the differences in the zeolite properties depending on the Si/Al ratio.

**Table 1. Zeolite properties depending on the Si/Al ratio.**

<table>
<thead>
<tr>
<th>Si/Al ratio</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Decomposition T (°C)</strong></td>
<td>700</td>
<td>1300</td>
</tr>
<tr>
<td><strong>Unstable at pH</strong></td>
<td>Acidic</td>
<td>Basic</td>
</tr>
<tr>
<td><strong>Wettability</strong></td>
<td>Hydrophilic</td>
<td>Hydrophobic (Si/Al&gt;10)</td>
</tr>
</tbody>
</table>
2.2 LITERATURE SURVEY - Zeolites

There are more than 190 different zeolite framework structures, with pore size in the range of 4-14 Å [14]. Porous structure of the zeolite framework makes them act as molecular sieves.

About 40 zeolites can be found in nature, the first one was discovered in 1756 by the Swedish mineralogist A. F. Cronstedt [15]. According to the Structure Commission of the International Zeolite Association, each zeolite framework is identified by a three letters code [14].

![Diagram of zeolite frameworks](image)

*Figure 5. Molecular structures of the main types of zeolites [16].*

*Figure 5* shows the main zeolite frameworks. Zeolites with the FAU (faujasite) framework are probably the most industrially important. They have a three-dimensional structure with pores running perpendicular to each other. The pore diameter is about 8 Å. Faujasite zeolites are highly porous, and are thus scarce in nature because they convert to more condensed forms. Zeolites X and Y belong to the
2.2 LITERATURE SURVEY - Zeolites

FAU framework type and they differ just by the Si/Al ratio in the structure. It varies between 1 and 1.5 for the zeolite X, and between 1.5 and 5.6 for the zeolite Y. Due to that, they are used in different ways: zeolite X is mainly used for enriching air with oxygen or for air dehumidification by adsorption, whereas the field of use of zeolite Y is catalytic cracking in the FCC (Fluid Catalytic Cracking) process.

The most important property of zeolites is the high accessibility of the internal surface that makes more than 98% of the total surface area, which is typically around 300-700 m$^2$/g [1]. Large surface area provides zeolites with a high adsorption capacity per gram of material.

2.2.2 Zeolites for the separation of CO$_2$ from gas mixtures

Separation of gas mixtures by zeolites can be achieved due to two main mechanisms:

a) Preferential sorption;

b) Molecular sieving [17].

In sorption, the component that can adsorb on the zeolite surface is retained in the adsorbent bed, whereas the non-sorbing component passes through it.

Molecular sieving is a size-based separation, in which only the molecules that are smaller than zeolite pores can penetrate inside it and remain in the zeolite, whereas the other components remain in the gas stream [18].

Although there are plenty of natural and synthetic zeolites available, gas separations and purifications are limited to a few types of zeolites like A, X, and mordenite, mainly because they are very hydrophilic and polar [19-22]. Examples of applications of zeolites for the gas separation based on sorption are NO$_2$ separation by MFI (mordenite framework inverted) zeolite, CO$_2$ separation by FAU zeolite, air separation process producing 90 – 95 % O$_2$ by selective adsorption of N$_2$ on a cationic zeolite such as CaA (zeolite 5A) or, in more recent processes, low silica LiX (Al/Si = 1 with 100% Li$^+$), which has a higher selectivity and capacity for N$_2$ [23].
For the molecular sieving, common applications are the use of zeolite A adsorbent for gas drying and the separation of branched, cyclic and linear hydrocarbons [24]. In a real process, these two mechanisms may occur simultaneously and the separation process can be additionally affected by the difference in diffusivity of different components in a mixture [18].

There are a lot of factors that affect the selectivity of adsorption of a gas in a zeolite. The most important parameters for the separation of gas mixtures by zeolites are the size and the steric hindrance of the compounds as well as the thermodynamic and kinetic selectivity of the compounds towards the zeolite surface [5]. Zeolites have a high potential for \( \text{CO}_2 \) capture, reaching the adsorption capacity of 5.5 mmol of \( \text{CO}_2 \)/g of zeolite [5]. \( \text{CO}_2 \) adsorption is governed by the structure of the zeolites and the presence of exchangeable cations within the cavities of zeolites, which affect zeolite basicity and the electric field present in zeolite. The polarity of molecules is a factor that can change their interaction with the electric field. Compared to all the other types of molecules, \( \text{CO}_2 \) has one of the largest existing quadrupole moments, resulting in a strong interaction between the electric field in zeolites and \( \text{CO}_2 \), favoring its adsorption [25]. Both zeolite basicity and the intensity of the electric field vary inversely with the Si/Al ratio. A low Si/Al ratio causes the increase in the number of charged sites and basicity of the surface due to the substitution of \( \text{Si}^{4+} \) ions by the \( \text{Al}^{3+} \) ions. This in turn increases zeolite adsorption capacity and selectivity for \( \text{CO}_2 \). The size of the pores in zeolites and the formation of carbonates during the chemisorptions of \( \text{CO}_2 \) on zeolite also affect \( \text{CO}_2 \) adsorption. The most important process parameters influencing the adsorption of \( \text{CO}_2 \) are pressure, temperature and the presence of water vapor. \( \text{CO}_2 \) adsorption, as adsorption in general, increases with the increase of pressure and decreases with the rise of temperature in the process. The presence of water in the gas stream has to be avoided, because it decreases significantly the adsorption capacity of cationic zeolites by decreasing strength and heterogeneity of the electric field and by favoring the formation of bicarbonates on the zeolites, which require higher temperature for desorption [25].
2.3 Adsorbent configurations

2.3.1 Conventional and novel adsorbents

In the industrial gas separation and purification processes, columns packed with adsorbents are mainly utilized. Adsorption is followed by desorption of the strongly adsorbed component in order to regenerate the adsorbent. Therefore, separation becomes a cyclic process. Desorption can be achieved by either heating up the adsorbent (temperature swing adsorption, TSA) or by lowering the partial pressure of the adsorbed component in the gas phase (pressure swing adsorption, PSA).

The most common forms of zeolite adsorbents are the beads and the granules, consisting of small crystals (1 – 10 µm) agglomerated into a desired shape and size using a binder material [23]. Such design allows a particular distribution of pores with large inter-crystalline pores between zeolite crystals and small pores in the zeolite framework. Diffusion in the beads controls the mass transfer in these adsorbents, which is affected by the radius of the beads and the size of the zeolite crystals. Small pellets with small zeolite crystals display better mass/heat transfer kinetics. But with small pellets the pressure drop of the packet bed increases, and with increasing gas velocity, bed fluidization might occur [26]. Therefore, mass transfer and the pressure drop in the packed beds impose limitations for the PSA/TSA adsorption processes, in terms of cycle time, energy consumption and overall system efficiency.

It is possible to avoid these limitations by using non-particulate, novel adsorbent structures. For the separation processes, when high performance and low energy demand is required, the use of traditional adsorbent materials is not advisable. The alternative adsorbent structures should have good mass transfer kinetics with high mass transfer coefficients, together with a good volume working capacity, low pressure drop, and a low voidage for minimizing the size of the column.

There are many types of novel structured adsorbents that have been studied and commercialized in the last 10 years including monoliths, laminates, foams and fabric
structures. These structures can also be coated with a film of an adsorbing material thus acting as a support.

2.3.2 Monolithic adsorbents

Monoliths are structured materials composed of parallel channels. Examples of monoliths are shown in Figure 6.

![Examples of ceramic monolithic structures](image)

*Figure 6. Examples of ceramic monolithic structures [27].*

There are a lot of applications, in which these types of structures can be used, from catalytic combustion, biochemical and electrochemical reactors, to automotive catalytic convertors [28].

In Table 2, the main characteristics of monolithic adsorbent structures and traditional adsorbent materials are compared.
Table 2. Main differences between monolithic adsorbents and traditional adsorbents [5].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>MONOLITHIC ADSORBENTS</th>
<th>TRADITIONAL ADSORBENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>External specific surface area</td>
<td>Depends on the cell density and wall thickness</td>
<td>Depends on the pellet diameter</td>
</tr>
<tr>
<td>Void fraction</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Mass transfer resistance</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Adsorbent loading</td>
<td>Lower</td>
<td>Higher</td>
</tr>
</tbody>
</table>

External surface area per unit volume of adsorbent governs the performance of the non-porous adsorbents. For monolith structures, the wall thickness has to be low in order to increase the surface area and consequently adsorption capacity of the monolith. Increasing the cell density, which represents the number of cells per square inch of cross-sectional area (cpsi), it is possible to increase the external surface area as well [5].

Void fraction in monoliths is higher than in traditional adsorbents due to the presence of channels. Higher void fraction in its turn results in a lower pressure drop throughout the structure. At constant gas viscosity, monolith length and cross-sectional area, the pressure drop in monoliths increases with increasing cell density. At the constant cell density, the pressure drop decreases with decreasing wall thickness.

The difference in pressure drop can also be explained by the differences in tortuosity. In porous materials, tortuosity is the ratio of the diffusivity in the free space and the diffusivity in the porous medium [29]. Its value for monolithic adsorbents is 1, and for traditional adsorbents is 2-3. Lower tortuosity results in a lower pressure drop [5]. Monolith adsorbents have lower resistance to mass transfer as compared to the traditional adsorbents, meaning shorter diffusion path and low pressure drop. If the walls of a monolith are porous, the monolith will be characterized by the resistance to
mass transfer related to the pore diffusion within the walls of the monolith. The problem related to the diffusion within the walls can be overcome by reducing the wall thickness of the monolith or by using monoliths with non-porous walls. The structure of monolith solves many problems related to conventional adsorbents, for instance, fluidization and high pressure drop, but sometimes it can display low adsorbent loading, which represents the amount of adsorbent per bed volume. Adsorbent loading in a monolith is lower because it is composed of many channels resulting in a large void fraction. Monoliths with high cell density and low wall thickness could provide high adsorbent loading and short diffusion path length. The best way to exploit low pressure drop of the monoliths is by using long beds to give sufficient residence time and adsorbent loading.

Another possibility to increase adsorbent loading is to use monoliths coated with a thin film of an active adsorbent material having a porous structure to achieve high specific surface area. When a film is formed on the wall of the monolith, the void volume decreases, whereas the pressure drop increases. However, in case of parallel channel adsorbents it is easier to control void volume to obtain satisfactory performance considering both the pressure drop and the adsorption capacity [5].

2.3.3 Zeolite coated monoliths for CO₂ adsorption

For the purpose of CO₂ adsorption, zeolite coated monoliths could be used. Cordierite monoliths coated with zeolite NaX have previously been investigated as adsorbents for CO₂ [23]. Mineral cordierite ((Fe, Mg)₂Al₄Si₅O₁₈) has a tailored macrostructure, high porosity and low thermal expansion, which makes it also useful as a support in automative catalytic converters and as diesel particulate filter [30, 31]. However, the literature shows that high porosity of cordierite monoliths results in increased mass transfer resistance so the use of monoliths with lower or zero wall porosity would lead to better performance [5]. Steel monoliths with non-porous walls could be a better option than cordierite monoliths.
The monolith supports can be coated with zeolite using two different types of deposition techniques [13]:

- **Wash coating or slurry coating**, when the support is immersed into a solution that already contains zeolite crystals and precursors of binders based on alumina and silica. Calcination is necessary after immersion, to bind the crystallites to the support surface. The presence of the binder material makes the crystal layers not continuous, which is the disadvantage of this method.

- **Coating techniques using hydrothermal synthesis**.

Hydrothermal synthesis is a method of synthesis of crystals that depends on the solubility of minerals in hot water under atmospheric or higher than atmospheric pressure. A monolith is immersed into a synthesis solution in a batch or in a continuous reactor, which allows the formation and the growth of the crystals on the support, at high temperature. The advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases that are not stable at the melting point [32-34].

The main coating techniques using hydrothermal synthesis are:

- **a) dry gel conversion**, in which the monoliths are immersed into a solution containing aluminosilicate precursor, water and template. By drying and subsequent crystallization of the dry aluminosilicate gel, using steam at atmospheric pressure, compact zeolite coatings form [35].

- **b) in situ coating**, when the crystals nucleate directly on the support that is immersed into a solution or into a synthesis gel. In this way, under the right conditions, the crystals preferentially grow on the support and not in the solution. This method is good to obtain dense and homogeneous coatings.

- **c) synthesis by seeding**, see Figure 7:
Synthesis by seeding implies adsorbing a layer of zeolite crystals (seeds) onto the monolith surface followed by immersion of the monolith into a synthesis solution to facilitate the growth of the zeolite film on the monolith. The nucleation (formation of the first nucleus of the crystal) and the growth of crystals in the liquid phase can also occur, which is undesired because it results in the formation of sediments and the loss of nutrients. The main advantage of using seeding with crystals is that the crystals can easily intergrow on the support creating a homogeneous film with a very good coverage of the walls of the monolith. It is difficult to obtain homogeneous films thinner than about 10 µm with the in situ method, but that it is possible to do it using the seeding method [13]. This technique is flexible and allows the control of the film thickness and the orientation of the crystals in the film [36-38].
CHAPTER 3

Experimental

3.1 Coating of the monoliths

The supports used in this work were cylindrical steel monoliths with a cell density of 1200 cpsi (see Figure 8).

![Steel monoliths used in this work.](image)

**Figure 8.** Steel monoliths used in this work.

*Table 3.* Dimensions of the steel monolith used in this work.

<table>
<thead>
<tr>
<th></th>
<th>Monolith</th>
<th>Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Internal Diameter (mm)</strong></td>
<td>28</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Length (mm)</strong></td>
<td>152</td>
<td>150</td>
</tr>
<tr>
<td><strong>Wall thickness (mm)</strong></td>
<td>1</td>
<td>0.025</td>
</tr>
</tbody>
</table>

The zeolite used for coating was the sodium form of zeolite X (NaX, \(Na_2O*Al_2O_3*2.5SiO_2*6H_2O\)).

In this work, the *seeding method* was used for the growth of the film. It consisted of three main steps: 1) Pre-treatment of the support; 2) Adsorption of seed crystals; 3) Growth of seed crystals.
3.1 EXPERIMENTAL - Coating of the monoliths

3.1.1 Pre-treatment of the support

The support (steel monolith) can have contaminants, so in order not to affect zeolite crystallization it was cleaned by five rinses in a 0.1 M aqueous ammonia (NH₃) solution.

A 0.4 wt% solution of a cationic polymer (Redifloc 4150, EKA Chemicals, Sweden) in distilled water was used to render the monolith surface positively charged, ready to attach the negatively charged seeds. The pH was adjusted to 8 by addition of a 0.1 M aqueous ammonia solution. The cleaned support was treated with the solution for 1 h, rinsing it (emptying the monolith using gas and putting it back in the same solution) every 15 minutes. After charge reversal, the support was rinsed five times with a 0.1 M aqueous ammonia solution to remove the excess of the polymer.

3.1.2 Adsorption of seed crystals

A 1 wt% dispersion of zeolite X seeds with the size of 80 nm was used for seeding. The monolith was treated with the seed sol for 1 h to adsorb a monolayer of the seeds, with the steps of dipping and drying using compressed air every 15 min. Afterwards, the excess of the seeds was removed using five rinses with a 0.1 M aqueous ammonia solution. Between seeding and the film growth, the sample was kept in ammonia solution to avoid the formation of ammonia carbonate ((NH₄)₂CO₃) crystals.

3.1.3 Growth of the film

After seeding, zeolite X films were grown on monoliths by hydrothermal treatment in a clear synthesis solution in a continuous (see Figure 9), semi-batch and batch reactors.

The entire synthesis setup for the case of the continuous system was composed of a flask containing the synthesis solution, a peristaltic pump (ALITEA®-XV) that allowed the transport of the solution in the system, a pre-heater to heat the solution
over its boiling point, and a reactor containing the support. Both the reactor and the pre-heater were equipped with heating jackets with propylene glycol as a heating liquid.

In the reactor, the outer surface of the monolith was put in direct contact with the heating liquid to achieve better heat transfer. Two o-rings at the top and bottom of the monolith prevented the heating liquid from entering the channels of the monolith. At the same time, the synthesis solution was able to pass just inside the channels of the monolith and not in the space between the monolith and the reactor, occupied by the heating liquid.

![Continuous film growth system](image)

Figure 9. Continuous film growth system.
3.1 EXPERIMENTAL - Coating of the monoliths

The system also contained water cooled condensers above the pre-heater and the reactor to condense the vapors forming in the system at high temperatures. The synthesis solution was prepared by mixing aqueous solutions of aluminum sulphate octadecahydrate (solution a) and sodium metasilicate nonahydrate together with sodium hydroxide (solution b). 

Table 4 shows the composition of the used synthesis solution.

Table 4. Composition of the synthesis solution (total 2000 g).

<table>
<thead>
<tr>
<th>Solution a</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td></td>
</tr>
<tr>
<td>( \text{Al}_2\text{(SO}_4\text{)}_3 \cdot 18\text{H}_2\text{O} )</td>
<td>15.07</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>548.17</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution b</td>
<td>Amount (g)</td>
</tr>
<tr>
<td>Compound</td>
<td></td>
</tr>
<tr>
<td>( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} )</td>
<td>52.62</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>1267.37</td>
</tr>
</tbody>
</table>

The solution a had to be stirred for at least 1 h at ambient conditions, and solution b for at least 1.5 h, and after that they were mixed together and vigorously stirred for a few minutes forming the desired solution. The synthesis solution was first pumped to the pre-heater filled with silicone rubber pieces. The temperature in the pre-heater was set at 112 °C, which is close to the boiling point of the synthesis solution. This was done in order to degas the solution because high temperature decreases gas solubility in water. Silicone rubber pieces inside the pre-heater facilitated degassing due to nucleation of air bubbles on the hydrophobic surface of the material. After pre-heating, the reactor was filled with the solution from bottom to top. The pipe after the pre-heater was made of hydrophilic materials to prevent bubble formation in the reactor. Bubbles should be avoided in the system because they can clog the channels of the monolith preventing the formation of the film. When the reactor was filled with the solution and the temperature of the heating liquid around the monolith was raised to 92 °C (which corresponded to ca 86 °C inside the reactor), some bubbles formed on the bottom and on the top of the
monolith, due to the temperature rise and probably also due to the pressure drop over the monolith, caused by the flow of the synthesis solution through the narrow channels in the monolith. To remove the bubbles, the reactor was connected to an aspirator.

At the beginning of the reaction, the system was closed using valves A and B shown in Figure 9, and vacuum was applied to the system under 5 min, which allowed to completely remove the bubbles.

The solution was pumped through the reactor at a flow rate of 6 mL/min for 6h and 40min.

All the modification to the experimental conditions introduced in the course of the work will be described in the Results and discussion chapter.
3.2 Characterization

3.2.1 Scanning electron microscopy (SEM)

SEM images were used to obtain information about the thickness and the morphology of the films grown on the steel monoliths. The images were taken by a Zeiss Merlin field emission scanning electron microscope. To be able to investigate the zeolite film on the walls of the channels, it was necessary to cut the steel monoliths into smaller parts, see Figure 10.

![Figure 10. Schematic illustration of the sample preparation for the SEM investigations.](image)

Three rectangular pieces (3.0 cm x 0.5 cm x 2.6 cm) of a monolith were cut out to verify that the same morphology and thickness of the film were obtained along the whole monolith. Moreover, each of these pieces was nicked with a saw to the middle and then cooled down in liquid nitrogen to further break it in two pieces along the notch. In this way, open and undamaged channels were obtained, easy to be analyzed, and impossible to obtain by cutting the pieces.

For each sample, several channels at the edge and in the middle of the sample were analyzed. From the obtained images, it was possible to estimate film thickness and observe the morphology of the film.
3.2.2 X-ray diffraction (XRD)

To confirm that the synthesized material was zeolite NaX, a monolith sample and a sample of the zeolite NaX pellets were examined by XRD. The obtained XRD patterns were compared with the reference patterns.

The equipment used in this work was a PANalytical Empyrean X-ray Diffractometer equipped with a PIXcel3D detector. The X-ray tube used was an Empyrean Cu LFF HR.

The scans were performed with the step size of 0.026° and in the 2-theta range of 5°-60°.
3.3 CO₂ adsorption

3.3.1 Setup for the adsorption experiments

The experimental setup consisted of three main sections (Figure 11):

1) Gas feed section;
2) Adsorption column;
3) Gas analysis section.

Gas feed section was composed of a bottle of nitrogen (99.99 %, Linde Gas) and a bottle of a CO₂/N₂ mixture (10% CO₂).

The two bottles were connected to a flow line of the system that split into the adsorption line directed to the adsorption column and a by-pass line connected directly to the volumetric flow meter.
3.3 EXPERIMENTAL - CO$_2$ adsorption

The second part was mainly composed of the adsorption column, which was 30.9 cm long and had the internal diameter of 3.2 cm.

In addition, there were a pressure meter to measure the pressure drop over the column, and two thermocouples located on the top and on the bottom of the column. The column was surrounded by a heating coil connected to a temperature regulator in order to maintain the temperature of the column at the desired value. The column was covered by an insulating material to minimize heat loss.

The Gas Analysis Section was composed of a CO$_2$ analyzer (IR 1507 last response CO$_2$ infrared transducer) and a volumetric flow-meter.

All the experimental data were collected and stored in a computer.

3.3.2 CO$_2$ adsorption experiments

CO$_2$ adsorption experiment were conducted in the form of temperature swing adsorption and consisted of two steps:

1) Adsorption;
2) Regeneration;

The *adsorption step* was conducted at room temperature (20-25 °C) and atmospheric pressure, with the CO$_2$/N$_2$ flow of 1 L/min along the column, filled with the adsorbent, for a time higher than the time needed to saturate the adsorbent.

In order to set the gas flow to the required value, the by-pass line was used. In this line, the flow was set to 1.11 L/min, in order to reach 1 L/min in the adsorption line.

The *regeneration step* was necessary to desorb CO$_2$ from the adsorbent. Regeneration was done at high temperatures, with the N$_2$ flow of 0.2 L/min.

Two different regeneration conditions were used, see Table 5.
### 3.3 EXPERIMENTAL - CO₂ adsorption

**Table 5. Conditions for the regeneration step.**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Temperature (°C)</th>
<th>Time at target temperature (h)</th>
<th>Heating/cooling rate (°C/min) (from room temperature to room temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>300</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>120</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Condition A was used prior to the first adsorption experiment to ensure that the zeolite is dry and contains no adsorbed species. Condition B was used between subsequent adsorption cycles to imitate the industrial conditions where regeneration at 300 °C is not feasible.

These regeneration temperatures were chosen for the following reasons.

According to the study by Agualar-Armenta [39], CO₂ can be completely desorbed already at 120 °C, so this temperature should be sufficient to regenerate zeolite between the adsorption cycles. For water removal, much higher temperature is required (up to 400 °C) so activation of zeolite at 300 °C was performed prior to the first adsorption step.

To compare mass transfer resistance due to external diffusion for different adsorbent geometries, the breakthrough experiments were performed using glass beads, uncoated steel monolith and uncoated cordierite monolith. The breakthrough adsorption experiments were run on zeolite NaX beads and zeolite-coated steel monoliths and the results were compared to the results obtained previously for zeolite-coated cordierite monoliths [23]. Physical properties of the materials used in the breakthrough experiments are shown in Table 6.
Table 6. Physical properties of structures used in this work.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Diameter/Cel l size (mm)</th>
<th>Adsorbent mass (g)</th>
<th>Adsorbent width (mm)</th>
<th>$\epsilon$ [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass beads</td>
<td>5.0</td>
<td>-----</td>
<td>-----</td>
<td>0.4</td>
</tr>
<tr>
<td>Zeolite pellets</td>
<td>2.0</td>
<td>177.44</td>
<td>1.0</td>
<td>0.38</td>
</tr>
<tr>
<td>Cordierite monolith 400 cpsi [20]</td>
<td>1.1</td>
<td>-----</td>
<td>-----</td>
<td>0.84</td>
</tr>
<tr>
<td>Cordierite monolith coated 1200 cpsi [20]</td>
<td>0.7</td>
<td>N.A.</td>
<td>0.0025</td>
<td>0.86</td>
</tr>
<tr>
<td>Steel monolith 1200 cpsi</td>
<td>0.5</td>
<td>-----</td>
<td>-----</td>
<td>0.9</td>
</tr>
<tr>
<td>Steel monolith coated 1200 cpsi</td>
<td>0.5</td>
<td>5 g per monolith</td>
<td>0.003</td>
<td>0.9</td>
</tr>
</tbody>
</table>

In Table 6, $\epsilon$ is the bed voidage.

For the steel and cordierite monoliths, $\epsilon$ was calculated using the following equation [5]:

$$
\epsilon_{\text{monolith}} = \left( \frac{2R_1}{R_1 + R_2} \right)^2
$$

(4)

where $R_1$ is the internal channel radius, $R_2$ is the external channel radius (including the channel wall thickness).

In order to test CO$_2$ adsorption in zeolite-coated steel monoliths, the monoliths were mounted in the column as shown in Figure 12.
Graphite tape (AESSEAL, Sweden) resistant at 300 °C was used to connect the two monoliths, and to fill the gap between the walls of the column and the monoliths, so that the gas passed only through the channels of the monolith but not between the monolith and the column wall. The void space at the top of the column above the monolith was filled with glass beads as shown in Figure 12.
CHAPTER 4

Numerical simulation

A mathematical model was necessary to describe the dynamic behavior of the adsorption system. The simplest model, which could be applied to the system used in this work, was an isothermal system with one adsorbing component (CO₂) in an inert carrier (N₂), with a single mass transfer zone (MTZ). The model was fitted to the experimental data obtained from the breakthrough experiments using Matlab 7.12.0 in order to calculate adsorption and mass transfer parameters useful to compare the capacity of the different adsorbents used in this work.

4.1 Mathematical model for the adsorption system

For an isothermal system with a single MTZ, differential mass balances for an element of the column and for an adsorbent particle were used. The considered element of the bed, through which a fluid stream with the adsorbable component flows, is shown in Figure 13.
In Figure 13, \(c(t,z)\) is the concentration of the adsorbate component in the fluid phase, \(z\) is the distance along the column, \(v\) is the interstitial velocity of the fluid and \(\bar{q}\) is the loading of the adsorbate in an adsorbent pellet averaged over the pellet [40]. The average loading has the units \([\text{mass of adsorbate/mass of adsorbent}]\) and is calculated using Eq. 5 [40]:

\[
\bar{q} = \left(\frac{3}{R_p^3}\right) \int_0^{R_p} R^2 q dR
\]

(5)

where \(R_p\) is the adsorbent pellet radius.

Considering the system as a general axially dispersed plug flow, the differential fluid phase mass balance for the column element is [40]:

\[
-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left(\frac{1 - \epsilon}{\epsilon}\right) \frac{\partial \bar{q}}{\partial t} = 0
\]

(6)

where \(D_L\) is the axial dispersion coefficient, \(t\) is time, and \(\epsilon\) is the voidage of the adsorbent bed.

The *interstitial velocity* \(v\) is the velocity through a packed bed given by [41]:

\[
v = \frac{u}{\epsilon}
\]

(7)

where \(u\) is the *superficial velocity* defined as [41]:

\[
u = \frac{Q}{S}
\]

(8)

In Eq.8, \(Q\) is the volumetric flow rate of the fluid and \(S\) is the cross-section area of the column.

The first term in Eq.6 represents the axial dispersion within the bed; the second is the convective flow of the adsorbate within the bed; the third is the accumulation of the adsorbate in the fluid phase, and the fourth represents the rate of adsorption.
The dispersed plug flow is a flow model, which considers axial dispersion along the column. When the term $-D_L \partial^2 c / \partial z^2$ is negligible, the plug flow model is valid and the equation becomes a first order hyperbolic equation. Plug flow is a simple model where the velocity of the fluid is assumed to be constant across any cross-section perpendicular to the axis of the system without any boundary layer on the inner wall of the system [42].

The mass balance for an adsorbent particle is described by the following function [40]:

$$\frac{\partial \bar{q}}{\partial t} = f(q, c)$$

(9)

Eq.9 states that the rate of adsorption is a function of both the fluid phase concentration and the loading in the adsorbent.

The dynamic response of the system is given by the solution $[c(z,t), \bar{q}(z,t)]$, which implies solving concurrently Eq.6 and Eq.9 at a certain equilibrium and with the initial and boundary conditions imposed on the column [40].
4.2 Analytical solution of the model for the numerical simulation

Analytical solutions to the general mass balance (Eq. 6) are available but in order to be able to use them, a number of simplifying assumptions and approximations must be valid.

As anticipated, one of them is the equilibrium relationship describing the system. The general form of the equilibrium isotherm is described by the following equation [40]:

\[ q^* = f(c) \]  \hspace{1cm} (10)

where \( q^* \) is the equilibrium value of the adsorbate concentration in the adsorbent and \( c \) is the concentration of the adsorbate in the fluid phase.

Adsorption equilibrium can be described by a linear or a non-linear (e.g. Langmuir) isotherm. For a linear isotherm, \( q^* \) is proportional to the adsorbate concentration in the fluid phase, according to the Henry’s law [40]:

\[ q^* = K \cdot c \]  \hspace{1cm} (11)

where \( K \) is the Henry constant, which depends on the adsorbent, the fluid phase and the temperature of the system. In this case it is dimensionless because both \( q^* \) and \( c \) are concentrations.

The linear equilibrium isotherm is applicable at low concentrations of the adsorbate when adsorbate loading is low.

Having defined the equilibrium in the system, with the assumption that is a trace system (low concentration of the adsorbate), it is possible to study its dynamics. Considering the transfer of a single component at low concentration and constant interstitial velocity along the length of the column, and assuming plug flow as flow model, the differential phase mass balance (Eq.6) becomes [40]:

\[ \nu \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left( \frac{1 - \epsilon}{\epsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \]  \hspace{1cm} (12)
4.2 NUMERICAL SIMULATION – Analytical solution of the model for the numerical simulation

Eq.12 must be solved with an appropriate rate expression, which must be consistent with the adsorption equilibrium isotherm.

Under the assumption that the mass transfer resistances may be lumped into a single parameter, the rate of adsorption may conveniently be expressed as [40]:

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - q)$$

(13)

where $k$ (s$^{-1}$) is the mass transfer coefficient of the adsorbate in the system.

For an adsorbent bed, which is initially free from the adsorbate (perfectly regenerated adsorbent), and for step change in adsorbate concentration at the bed entrance at time zero, the initial and boundary conditions are [40]:

$$t < 0, \quad q(R, 0, z) = c(0, z)$$

(14)

$$t \geq 0, \quad c(t, 0) = c_0$$

(15)

Solving simultaneously Eq.11-15, a solution for the breakthrough curve can be obtained.

In order to express Eq.12 and Eq.13 in dimensionless form to simplify the calculations, the following dimensionless variables can be introduced [40]:

Dimensionless concentration of the adsorbate in the fluid phase:

$$\Phi = \frac{c}{c_0}$$

(16)

dimensionless loading of the adsorbate on the adsorbent:

$$\varphi = \frac{\bar{q}}{q_0}$$

(17)

where $q_0$ is the loading in equilibrium with the feed concentration, $c_0$ [40].

Dimensionless bed length:

$$\xi = \frac{kKz}{v} \left( \frac{1 - \varepsilon}{\varepsilon} \right)$$

(18)
**Dimensionless bed time:**

\[ \tau = k \left( t - \frac{z}{v} \right) \]  
(19)

The resulting equations for fluid mass balance and adsorption rate in dimensionless form are [40]:

\[ \text{Fluid mass balance} \quad \frac{\partial \Phi}{\partial \xi} + \frac{\partial \varphi}{\partial \tau} = 0 \]  
(20)

\[ \text{Rate equation} \quad \frac{\partial \varphi}{\partial \tau} = \Phi - \varphi \]  
(21)

For these equations, different analytical solutions can be found.

The analytical solution chosen to describe the breakthrough curves obtained in this work was the \textit{Klinkenberg equation} [43]:

\[ \frac{c}{c_0} = \frac{1}{2} \cdot \text{erfc} \left( \sqrt{\frac{\xi}{\tau}} - \sqrt{\frac{\xi}{8}} - \sqrt{\frac{\tau}{8}} \right) \]  
(22)

In this equation, \text{erfc}(x) is the complementary error function defined by [44]:

\[ \text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \]  
(23)

where \text{erf}(x) is the Gauss error function, which is defined according to the following equation [44]:

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \]  
(24)

Using MATLAB, the Klinkeberg model was fitted to the experimental data obtained from the breakthrough experiments and the mass transfer coefficient (k) was calculated.

The mass transfer coefficient was used to calculate the effective diffusivity, which for the beads is estimated by [45]:
\[ D_{e,\text{beads}} = \frac{kr^2}{15} \] (25)

where \( R \) is the radius (m) of a bead.

For the beads the mass transfer resistance is dominated by the size of the adsorbent particle. Their geometry is approximated to a sphere.

For the case of a monolith coated with a film of adsorbent (zeolite), the mass transfer resistance is dominated by the film thickness and the geometry can be approximated by a slab [45]:

\[ D_{e,\text{film}} = \frac{kl^2}{3} \] (26)

where \( l \) (m) is the film thickness.
Results and discussion

5.1 Synthesis and analysis of the NaX films on steel monoliths

5.1.1 Synthesis using continuous reactor

*Figure 9* in the Experimental part shows the final and the best arrangement of a continuous reactor system that was designed in this work. Several modifications had to be made to the existing system (not shown) to improve its performance, see *Table 7*.

*Table 7. Changes introduced to the synthesis system in the course of this work.*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial system (not shown)</th>
<th>Final system (<em>Figure 9</em>)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of monoliths in the reactor</td>
<td>Two stacked on top of each other and connected by a silicon rubber</td>
<td>One</td>
</tr>
<tr>
<td>Direction of flow</td>
<td>Top to bottom</td>
<td>Bottom to top</td>
</tr>
<tr>
<td>Pre-heating temperature (°C)</td>
<td>100 or no pre-heating</td>
<td>112</td>
</tr>
<tr>
<td>Degassing</td>
<td>Air pressure (every 15 minutes during the synthesis)</td>
<td>Aspirator (5 min before the synthesis) and silicon pieces inside the pre-heater</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>Flow rate (mL/min)</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 8 shows the thickness of the NaX films on the walls of the channels of the monoliths obtained using the non-modified synthesis system with and without pre-heating. For each monolith, the differences in film thickness along the height of the monolith and its cross-sectional area were noticed.

**Table 8.** Thickness (µm) of the NaX film obtained with the preliminary synthesis system. Letters A and B represent the thickness on two opposite edges of the cross-sectional area of the monolith, whereas C is the thickness in the center of the monolith.

<table>
<thead>
<tr>
<th></th>
<th>Pre-heating at 100°C</th>
<th>Without pre-heating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>2nd Monolith</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOP</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>BOTTOM</td>
<td>1</td>
<td>1.8</td>
</tr>
<tr>
<td>1st Monolith</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOP</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>BOTTOM</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The film obtained with pre-heating was overall thicker compared to the one grown without pre-heating, because the solution entering the reactor was already heated, allowing a longer synthesis time. The film grown with pre-heating had also a smaller gradient for the thickness along the height of the column and the cross-sectional area of the monolith.

In Figure 14, two SEM images of NaX films obtained with and without pre-heating are show.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

Figure 14. SEM images of the NaX zeolite film obtained with (left) and without (right) pre-heater.

A secondary product with a ball-of-yarn shape was observed in these films (see Figure 15). According to the previous studies [20], these balls were identified as hydroxy sodalite (HS) crystals. They usually form when the reaction is conducted at too high temperatures or when the reaction time is too long, allowing the initiation of a secondary reaction, transforming NaX to HS.

Figure 15. SEM image of the NaX zeolite film containing hydroxysodalite.

The presence of hydroxysodalite is not desired because it has a bad performance as an adsorbent. In fact, its structure does not allow adsorption of CO$_2$ inside the material because its pores are too small.
The distribution of the secondary product on the NaX film was not homogenous, but varied along the height of the two monoliths and the cross-sectional area. The presence of HS was higher near the edges of the monolith and lower in the center, probably because at the edge the temperature of the solution was higher. Moreover, an uneven distribution of hydroxysodalite was observed along the height of the reactor. This was due to the composition of the synthesis solution that changed from top to bottom of the reactor due to depletion and nucleation taking place in it.

Using the air pressure system, the problem of the air bubbles formation in the synthesis solution was not completely solved. Some bubbles were observed during the reaction, and due to the degassing step every 15 min, the reaction took too long time.

To prevent air bubble formation in the synthesis solution, the modifications described in Table 7 were introduced. By changing the flow direction, the formation of bubbles due to the pressure drop was decreased. The aspirator decreased the pressure in the reactor so the gases (air) present in the solution could be easily removed. In fact, just one evacuation prior to the reaction was necessary to avoid air bubbles for all the reaction time.

Only one monolith was coated with zeolite at a time to avoid any influences caused by the connection of the monolith and to reduce the film thickness gradient along the height of the system.

The pre-heater was also filled with pieces of silicon rubber, which is a hydrophobic material, useful to nucleate air bubbles in the synthesis solution in the pre-heater. The temperature in the pre-heater was increased above the boiling point of the solution to decrease the formation of the bubbles in the reactor. All these modifications allowed avoiding air bubbles in the monolith channels.

At the same time, the higher temperature in the pre-heater resulted in the formation of hydroxysodalite. Its distribution was not homogeneous but increasing from bottom to top for the same reason as explained before.

Additionally, the image in Figure 16 shows the presence of aggregates with the radii ranging from ca. 5 to 20 µm on the top of the film.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

These aggregates were identified as sediments coming from the synthesis solution. For a long time at high temperature, nucleation of crystals could start, with further deposition of the crystals on the film. The sediments should be avoided because they can modify or block the adsorption of CO$_2$ on the zeolite film.

The results obtained after the modification of the synthesis system (see last column in Table 7) are shown in Table 9.

Table 9. Thickness (µm) of the NaX film obtained using the modified synthesis system.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOP</td>
<td>1.2</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>BOTTOM</td>
<td>2</td>
<td>2.3</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 16. SEM image illustrating the formation of sediments on the zeolite film.

Figure 17 shows the cross-section of the NaX film produced.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

Figure 17. Zeolite film obtained with the modified synthesis system.

The results in Table 9 show that there was a big gradient in the film thickness between the top and bottom of the monolith. Accordingly, to avoid this gradient and the formation of hydroxysodalite, the synthesis was run with an increased flow-rate of 10 mL/min.

Continuous system at higher flow-rate and lower pre-heating temperature

Increasing the flow-rate allowed more even distribution of the nutrients along the height of the reactor without being consumed at the beginning of the synthesis. The formation of hydroxysodalite was reduced but large amounts of sediments were still present.

Additionally, much more solution was required for the reaction time of 6 h and 40 min at this flow rate.

For these reasons, instead of modifying the flow-rate, the pre-heating temperature was decreased to 100 °C. The resulting films showed less sediments but more hydroxysodalite, with the increasing amount from the bottom to the top. A larger thickness gradient along the height of the monolith was also observed, see Table 10.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

Table 10. Zeolite film thickness (µm) obtained when changing the flow-rate and the pre-heating temperature.

<table>
<thead>
<tr>
<th></th>
<th>Flow-rate increased to 10 mL/min</th>
<th>Pre-heating temperature decreased to 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>TOP</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>BOTTOM</td>
<td>1.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

From all the results described above it was concluded that the continuous reactor provided a zeolite NaX film that was not homogeneous along the reactor height and the cross-sectional area of the monolith, with the presence of a secondary product identified by its structure as hydroxysodalite, and often with the presence of sediments on the top of the film.

The presence of hydroxysodalite and the sediments was due to the stagnation of the already reacted solution with a different concentration inside the system. When the solution flowed through the reactor, the mixing of the old solution and the fresh solution coming with the continuous flow took place. In this way, the same solution remained inside the system for a long time at the reaction temperature. This led to the nucleation of crystals inside the solution and a secondary reaction with the formation of HS, which afterwards was adsorbed by the zeolite film. Moreover, the accumulation of crystals nucleated (in the form of NaX or HS) in the solution led to the formation of aggregates, which then could be deposited on the surface of the film. This was confirmed by analyzing the solution at the output from the reactor; it was milky with small dispersed particles.

For these reasons, another type of system was used: the semi-batch reactor.
5.1.2 Synthesis using semi-batch reactor

A semi-batch reactor is a reactant system in which both continuous and batch inputs and outputs are present.

In practice, the system was the same as the continuous reactor shown in Figure 9, but this time the solution was pumped into the reactor very quickly with the heating system already at the reaction temperature. There was no pre-heater in the semi-batch system. After filling the reactor, the flow was stopped and the system full of synthesis solution was ready to react.

Five steps of 1 h and 20 min [20] were performed. Prior to each step, the system was refilled.

The film obtained with the semi-batch system still presented a certain amount of hydroxysodalite, spread homogeneously in the monolith, with some sediments present, too. The reason was probably that when the solution was replaced, the flow made it mix with the old solution creating stagnation inside the system, because the solution was not completely replaced as it could be with e.g. a batch reactor.

Table 11 shows the results obtained using the semi-batch system.

Table 11. Zeolite film thickness (µm) obtained using the semi-batch reactor.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOP</td>
<td>0.8</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>BOTTOM</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The film showed gradients in the film thickness along the height of the monolith and the cross-sectional area. In addition, the thickness was overall thinner as compared to that obtained with the continuous reactor.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

This experiment led to conclusion that the main reason for the thickness gradient along the cross-sectional area of the monolith was the velocity gradient inside the reactor.

When a fluid flows in a tube, the tube walls create a resistance due to that flow. This resistance ($\Sigma$) depends on the fluid viscosity, the tube radius and the length of the tube according to the following relationship [46]:

$$\Sigma = \frac{8\mu L}{\pi r^4}$$

(27)

where $L$ is the tube length, $\mu$ is the fluid viscosity, and $r$ is the tube radius.

Assuming a laminar flow, the resistance inside the flow is not the same along the radius of the tube but has a profile shown in Figure 18.

![Figure 18. Velocity profile for the laminar flow [46].](image)

The velocity is expressed by the following function [46]:

$$v(r) = v_m \left(1 - \frac{r^2}{R^2}\right)$$

(28)

where $v_m$ is the maximum velocity corresponding to the superficial velocity and $R$ is the maximum radius of the tube.

This kinetic effect affected the synthesis and the film thickness along the cross-sectional area of the monolith. At the maximum velocity in the center, more nutrients were fed into the central part of the monoliths leaving the edges with fewer nutrients. More nutrients allowed the formation of a thicker film. For this
reason, the conclusion was made that the flow of the solution should be avoided or should be lower. However, with a lower flow rate there would be stagnation of the solution with the formation of secondary products and sediments. So finally, the study led to the use of a new type of system: the batch reactor.

5.1.3 Synthesis using batch reactor

Batch reactor is characterized by the absence of flow in the system. The solution was replaced manually after each reaction step. The experiment was conducted in a new reactor, a simple plastic vessel connected on the top to a condenser to collect the vapors formed during the reaction at high temperature. The vessel containing the monolith with the solution was immersed in an oil bath to reach the temperature of the reaction. The oil bath temperature was set to 100 °C and the solution temperature was about 92°C. The synthesis was performed in five steps of 1 h and 20 min each [20]. The monolith after each step was rinsed four times in a 0.1 M ammonia solution. *Figure 19* shows the results for the NaX film thickness (µm) obtained with the batch reactor.
Figure 19. Variation of the zeolite film thickness (µm) along the diameter of the monolith obtained using the batch reactor.

From the results in Figure 19 it is possible to see that the gradient along the cross-sectional area significantly decreased at the bottom, confirming the theory of the velocity gradient for the continuous and semi-batch reactors. There was still a radial gradient at the top of the monolith and a gradient along the height of the monolith, as in the other experiments. A possible explanation could be as following. When the reaction took place, the system was at high temperature (92°C), which created a lot of vapor in the system. The vapor reached the reflux system and condensed due to the decreased temperature. The liquid from the condensation dripped down into the solution and acted as an agitator of the solution, mixing it above the monolith and in the channels. The mixing brought new nutrients to the top of the monolith leading to the growth of a thicker film. The dripping occurred in the center of the cross-sectional area of the monolith, so the channels in the center presented a thicker film on the top of the monolith.

Figure 19 shows that the film thickness was overall quite thin. The reason for that was the reaction temperature that was not 92°C for all 80 min of the reaction, but
there was a heating time corresponding to 25 minutes (zeolite X starts to form at about 80°C), as it is shown in Figure 20.

![Figure 20. Temperature change in the solution during 1 h and 20 min of the reaction.](image)

55 minutes corresponding to the real synthesis time were probably not enough to synthesize a thick NaX film.

On the top of the obtained film, some HS was observed. This means that the reaction time for each synthesis step should not be increased.

Accordingly, to overcome the last defects of the film, the following measures were taken:

- A plastic disk with the diameter of the reactor was placed on the top of the monolith in the reactor, to avoid the mixing of the solution on the top caused by the dripping of the condensate.
- To increase the overall film thickness avoiding the formation of the secondary products (HS), the new reaction time was calculated. For the real reaction time of 55 min, the overall reaction time for all 5 steps was 55*5 = 275 min. To increase the film thickness, two more steps were added (7
steps in total). The new real reaction time for each step was $275/7 \approx 40$ min, and adding the time necessary for the heating of the solution (25 min), the new time for each step was estimated at 65 min.

Conducting the reaction with 7 steps of 65 min each at the same condition as the other batch experiment, the results shown in Figure 21 were obtained.

![Graph showing variation of the zeolite film thickness along the diameter of the monolith](image)

*Figure 21. Variation of the zeolite film thickness (µm) along the diameter of the monolith obtained using the modified batch reactor.*

According to the results, the obtained film had nearly the same thickness along the length and the cross-section of the monolith.

*Figure 22* shows an SEM image of the film obtained with the modified batch reactor.
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

Figure 22. NaX film obtained using the modified batch reactor.

The NaX film was homogeneous, with a very good intergrowth of the crystals, and with a very few particles of HS and sediments. However, the film thickness was only about 0.9 µm. To get a thicker film, the synthesis containing 7 steps was performed three times (in three days) on the same monolith. Synthesis of new layers of the NaX film on the old film did not lead to any undesired products or modifications of the underlying layers.

After three days of synthesis it was possible to obtain the results shown in Figure 23.

Figure 23. Variation of the zeolite film thickness (µm) along the diameter of the monolith obtained after three reactions.
Figure 23 shows that the thickness of the film obtained after three reactions, each one of 7 steps of 65 minutes, had a slightly bigger gradient along the cross-section of the monolith, compared to that with one reaction shown in Figure 21. This was due to the fact that the thickness difference was multiplied by three. A small gradient was observed along the height of the monolith as Figure 23 illustrates. This could probably be explained by the natural convection that took place in the solution during the synthesis. Figure 24 shows two side-views of the NaX film produced after three reactions.

![Figure 24. SEM images of a section of the NaX film (3µm) after three reactions.](image)

Figure 25 shows the top-views of the NaX film produced after three reactions.

![Figure 25. SEM images of the top-view of the NaX film (3µm) after three reactions.](image)
5.1 RESULTS AND DISCUSSION – Synthesis and analysis of the NaX films on steel monoliths

In Figure 25 is possible to notice the presence of HS on the top of the film with some sediments distributed in the channels of the monolith. Their quantity increased with the number of the reactions, so probably the long time of the reaction (7 steps) affected the synthesis.

Nevertheless, NaX films obtained using the batch reactor were quite homogeneous, with the thickness of 3 µm, and could be used in the CO₂ adsorption studies.

5.1.4 X-ray diffraction analysis of the adsorbents

X-ray diffraction was used to confirm that zeolite NaX was formed on the monolith support in the synthesis by comparing its XRD pattern with that of the NaX pellets. Figure 26 shows the X-ray diffraction patterns of the NaX film on steel monolith and of the commercial NaX pellets.

Figure 26. XRD patterns for the NaX film on steel monolith (red) and NaX commercial pellets (blue).
The XRD pattern for zeolite pellets was identified as zeolite X, with the main peaks present between 5° and 35°. The same peaks were present in the XRD pattern of the coated monolith, confirming the presence of the NaX film on the walls of the channels of the steel monolith. In the latter case the peaks had a lower intensity because the amount of zeolite X on the support was very low compared to the amount of NaX in the pellets. In the XRD pattern of the NaX film on steel monolith it is possible to observe a very intensive peak at 45°. This peak corresponds to the material of the support (steel).
5.2 Adsorption performance of NaX zeolite

5.2.1 Breakthrough profiles

At first, the breakthrough profiles for different types of supports were compared to understand the influence of the support geometry on the breakthrough curve. Figure 27 shows the breakthrough profiles for different bed configurations including: empty column, glass beads, steel monolith with 1200 cpsi and ceramic cordierite monolith with 400 cpsi.

![Breakthrough curves for different support geometries.](image)

Empty column gave a broad breakthrough front due to a high dispersion of the flow in it.

The glass beads resulted in a shorter breakthrough time because of a lower void fraction (0.4) compared to that of the steel monolith with 1200 cpsi (0.9) and cordierite monolith with 400 cpsi (0.8). The ceramic cordierite monolith with 400 cpsi exhibited a slightly longer breakthrough time than the steel monolith with 1200 cpsi, either due to the filling of the pores present in cordierite walls with gas [6] or due to the adsorption of CO$_2$ on cordierite.
Cordierite monolith with 1200 cpsi was not tested in this work, but according to the previous studies [6], it would give a broader mass-transfer zone than that obtained for a 400 cspi cordierite, see Figure 28.

![Breakthrough fronts for cordierite monoliths with different cell densities](image)

**Figure 28.** Breakthrough fronts for cordierite monoliths with different cell densities [6].

A higher cell density corresponds to a higher number of walls separating the channels, and for the case of porous walls as in cordierite, a higher wall number results in a higher mass transfer resistance and broadening of the mass-transfer zone [6].

So at the same cell density, the steel monolith would exhibit a narrower MTZ as compared to the cordierite monolith, that is, a better mass transport.

So the steel monolith was found to be a better option than cordierite for gas separation using zeolite coated monoliths.

In the case of the steel monolith, the space between the monolith and the column had to be filled with a graphite tape to prevent the gas from passing on the side of the monolith as described in the Experimental part.

**Figure 29** shows the breakthrough front obtained using a steel monolith without tape between its external surface and the internal surface of the column.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

**Figure 29.** Breakthrough profile of a steel monolith with 1200 cpsi without the tape.

Without the tape, the flow exhibited a double MTZ. When the tape was used, a single mass-transfer zone was observed, see Figure 27.

CO₂ adsorption was investigated using:
- Commercial NaX pellets with the size of 2 mm;
- Zeolite NaX coated steel monolith with the film thickness of ca 3 µm.

**Figure 30** shows the breakthrough profile for CO₂ for the column filled with NaX pellets (ca 177 g) and the temperature variation at the exit from the column during the adsorption. The experiment was conducted after activation of the material at 300 °C.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

Figure 30. CO\textsubscript{2} breakthrough curve and temperature measured at the outlet of the column for NaX pellets.

The concentration front showed a breakthrough time of ca 50 minutes, with a single MTZ. After the breakthrough, the concentration did not reach quickly the initial value. This was due to the variation of the temperature in the column during adsorption, as the temperature trend shows. Adsorption is an exothermic process and the released heat increased the temperature in the adsorbent bed. Since the temperature was measured at the outlet from the column, the temperature did not increase sharply at the beginning of the experiment because the adsorption took place mainly at the beginning of the column and the gas flow had time to cool down before it reached the temperature detector. As the adsorption front moved along the column, the temperature increase became more significant. Increased temperature reduced the rate of adsorption resulting in a broadening of the MTZ. When the adsorbent started to saturate, the heat release decreased and the temperature started to decrease too.

CO\textsubscript{2} adsorption experiments were performed at different flow-rates of the CO\textsubscript{2}/N\textsubscript{2} mixture.
Figure 31 shows the breakthrough profile of the system with pellets at three different flow-rates.

![Graph of breakthrough profiles](image)

**Figure 31.** Breakthrough profiles for NaX pellets for different values of flow-rate.

The results were in agreement with Figure 3 discussed above and indicated that with increasing flow rate the breakthrough time decreased, because more adsorbate was entering the adsorbent per unit of time, so the adsorbent needed less time to become saturated.

As it is possible to notice in Figure 31, even small changes of the flow-rate resulted in a significant shift of the breakthrough curve.

To model a cyclic temperature swing adsorption process, after activation of the adsorbent at 300 °C, three adsorption steps were performed with the regeneration at 120°C in between.

*Figure 32 shows the breakthrough fronts for three adsorption cycles using NaX pellets.*
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

The graph shows that regenerating at 120 °C resulted in almost the same adsorption behavior as after activation at 300 °C. When regenerating at 120 °C, the breakthrough time became slightly lower for each cycle, probably because some CO$_2$ molecules remained on the adsorbent surface, reducing its adsorption capacity. The results in Figure 32 suggest that 120°C is a high enough temperature for the regeneration of the adsorbent.

Figure 33 shows the breakthrough profile and temperature variation for CO$_2$ adsorption on two NaX coated steel monoliths with the film thickness of ca 3 µm. As with the pellets, adsorption was conducted after a step of activation at 300 °C.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

Figure 33. CO$_2$ breakthrough curve and temperature trend at the outlet of the column for NaX coated steel monoliths (film thickness ca 3 µm).

The concentration front showed a breakthrough time of ca 4.5 minutes, with a single narrow MTZ. The temperature increase during the adsorption was much lower due to low adsorption capacity of the zeolite coated monolith.

As with the pellets, three adsorption cycles were performed using the monoliths, with regeneration at 120°C between the adsorption steps. Figure 34 shows the breakthrough fronts of NaX coated monoliths for three adsorption cycles.
Figure 34. \( \text{CO}_2 \) breakthrough curves of NaX coated steel monoliths (film thickness ca 3 \( \mu \text{m} \)) for three adsorption cycles.

The figure shows that regenerating at 120 °C resulted in almost the same adsorption behavior as after activation at 300 °C.

When regenerating at 120 °C, the breakthrough time became slightly lower for the second and third cycles as compared to the first one, probably because some \( \text{CO}_2 \) molecules remained on the adsorbent surface, reducing its adsorption capacity. The results, again, suggest that 120°C is a high enough temperature for the regeneration of the adsorbent.

*Figure 35* shows the breakthrough profiles for the NaX pellets and NaX coated steel monolith after activation at 300°C.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

The breakthrough profile for the zeolite coated monolith was very steep compared to that for the pellets. This is due to a higher mass transfer resistance in the zeolite beads with a diameter of 2 mm than in the zeolite film with the thickness of 3 µm. The breakthrough time was ca10 times shorter for the coated monolith than for the pellets due to the difference in the adsorbent loading (see Table 6).

The higher adsorption capacity is the main advantage of using zeolite pellets, but at the same adsorbent loading the NaX coated steel monoliths would probably give better performance, with a narrower MTZ and a shorter cycle time.

Finally, the performance of zeolite coated steel monoliths used in this work was compared to the performance of the zeolite coated cordierite monoliths used in the previous work by Fateme Rezaei [6].

*Figure 35.* CO$_2$ breakthrough profiles of NaX pellets and NaX coated steel monolith.

*Figure 36* shows the breakthrough profiles of NaX coated cordierite monoliths[6]. Comparing the results in *Figure 33* and the breakthrough curve of a NaX film with the thickness of 2.5 µm on a ceramic cordierite monolith with 1200 cpsi in *Figure 36*, it is evident that the breakthrough time for the steel monolith was at least 4 times higher than for the cordierite monolith due to a higher loading of zeolite in the steel monoliths.
Another important parameter to compare is the width of the MTZ of the two curves. The time between the breakthrough and the saturation of the adsorbent was about 1 min for the coated cordierite monoliths and about 2 min for the coated steel monoliths with the same cpsi, which was much lower than the time for the zeolite pellets (about 2 hours!). Keeping in mind that the adsorption capacity (expressed by the breakthrough time) of the zeolite coated steel monoliths was at least 4 times higher than that of the coated cordierite monoliths, the conclusion can be made that zeolite coated steel monoliths showed overall much better performance in CO$_2$ adsorption experiments.
5.2.2 Analysis of the breakthrough profiles using numerical modeling

The analytical solution of the mathematical model for the adsorption process (see Eq.22), was fitted to the experimental data (breakthrough curves) with the overall mass transfer coefficient $k$ as the fitted parameter. 

*Figure 37 and Figure 38* show the experimental and the fitted CO$_2$ breakthrough curves for the NaX pellets and NaX coated steel monoliths with 1200 cpsi, respectively.

![NaX Pellet](image)

*Figure 37. Experimental and fitted CO$_2$ breakthrough curves of NaX pellets (2 mm in diameter).*

The figure shows that the Klinkeberg equation could describe the experimental data quite well. At the breakthrough time, the model fitted perfectly the experimental data but started to deviate around $C/C_0=0.5$. This was due to the variation of the temperature in the column during the adsorption process as demonstrated in *Figure 30*. One of the assumptions for the model was an isothermal system ($T=\text{const}$), so the model was not able to describe the process with significant temperature variations.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

Figure 38. Experimental and fitted CO$_2$ breakthrough curves of the NaX coated steel monoliths with 1200 cpsi (film thickness ca 3 µm).

Similar result was observed for the zeolite coated steel monolith. The model fitted the experimental data well during the first half of the process and then started to deviate after C/C$_0$=0.6. But for the monolith the deviation was less pronounced due to the lower variation of temperature during the adsorption process, as confirmed by Figure 33.

The best fit of the model for the two adsorbents was obtained with the mass transfer coefficients (k) shown in Table 12. In the same table, the corresponding effective diffusivities estimated using Eq.25 and Eq.26 are shown.
5.2 RESULTS AND DISCUSSION – Adsorption performance of NaX zeolite

**Table 12.** Fitted mass transfer coefficients (k) and calculated effective diffusivities (De) for the two different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Mass transfer coefficient k [1/s]</th>
<th>Effective Diffusivity De [m^2/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX pellets</td>
<td>0.214</td>
<td>1.43 \cdot 10^{-8}</td>
</tr>
<tr>
<td>NaX coated steel monolith</td>
<td>4.042</td>
<td>1.2 \cdot 10^{-11}</td>
</tr>
</tbody>
</table>

The larger mass transfer coefficient for the NaX film was due to its lower mass transfer resistance to the passage of the CO$_2$ because the film was more than 300 times thinner than the pellet radius. The mass transfer coefficient for the zeolite coated steel monoliths was also significantly higher than the one obtained for the zeolite coated cordierite monoliths with the same cpsi and film thickness of ca 2.5 µm. This result indicates that coated steel monoliths have much better mass transfer properties and are thus more suitable for CO$_2$ adsorption applications than zeolite coated cordierite monoliths.
Conclusions

A new method for the synthesis of NaX zeolite films on steel monoliths was developed for the purpose of using the monoliths in CO$_2$ adsorption. A continuous homogeneous zeolite film with the thickness of 3 µm and very small amount of secondary products and sediments was grown on steel monoliths using a batch reactor. It was demonstrated that the batch reactor was better alternative than a continuous reactor or a semi-batch reactor for the synthesis of NaX films.

The zeolite coated steel monoliths displayed very sharp breakthrough fronts, with a higher mass transfer coefficient and longer breakthrough time as compared to the zeolite coated cordierite monoliths with the same epsi. These results suggest that steel monoliths are more suitable than cordierite monoliths to be used as a support for the zeolite films.

The adsorption capacity of the zeolite coated steel monoliths was much lower than that of the zeolite pellets due to lower zeolite loading. On the other hand, the MTZ for the monoliths was much narrower than for the pellets whereas the mass transfer coefficient was much higher suggesting that zeolite coated steel monoliths could be a good alternative to pellets in cyclic adsorption processes aiming at reducing the cycle time.

At higher adsorbent loadings, the performance of zeolite coated steel monoliths could approach that of the traditional pellets. Due to the low pressure drop and excellent mass transfer characteristics, structured zeolite adsorbents in the form of coated monoliths could be used to optimize the performance, energy demand, and cost of gas separation processes.
7. FUTURE WORK

Future work

- Developing a thicker NaX film (ca 10 µm) to try to approach the adsorbing performances of the traditional beads.
- Determining experimentally the maximum zeolite film thickness, at which the diffusion resistance starts to reduce the adsorption performance of a steel monolith.
- Developing a new model taking into consideration thermal effects during adsorption to obtain better fitting of the model to the experimental data.
- Improving the synthesis method for the NaX film to optimize the time of reaction and also the operation costs.
- Deepening the knowledge about the secondary reactions (formation of HS) that can take place during the formation of the NaX film.
ACKNOWLEDGEMENTS

It is a pleasure to thank the many people who made this thesis work possible, hereby I mention only a few of them.

First of all I would like to acknowledge my Italian supervisor Professor Maria Cantarella and Professor Jonas Hedlund for giving me the opportunity to have this wonderful abroad experience and to work on this interesting project at Luleå University of Technology.

It is difficult to overstate my gratitude to my supervisor, Dr. Elisaveta Potapova, or rather Lisa, for the patient guidance, encouragement and advice she has provided throughout my time as her student. I have been extremely lucky to have a so kind supervisor who cared so much about my work, and who responded to my questions and queries so promptly. I will miss her constant wonderful smile tackling problems and her caring for assisting encouraging attending to provide support.

Special thanks to my lab supervisor Dr. Johanne Mouzon. With his enthusiasm, his inspiration, and his great efforts to explain things clearly and simply, he helped to make laboratory work fun for me. Throughout my thesis period, he provided encouragement, sound advice, good company, knowledge and lots of good ideas. He has been as an older brother for me. I would have been lost without him.

I would also like to thank Assoc. Prof. Mattias Grahn for his cooperation in different processing steps of my work.

Moreover, this thesis work could not be done without the help given me by the people at the Division of Sustainable Process Engineering at Luleå University of Technology. I would like to thank each of them and particularly Lic. Eng. Danil Korelskiy, Lic. Eng. Jonas Helmerius, Lic. Eng. Iftekhar Uddin Bhuiyan and M. Sc.
Acknowledgements

Gustavo Garcia for their useful help in the laboratory and Dr. Anuttam Patra for his psychological support during the most difficult period.

I would like to thank all the city of Luleå, a beautiful and amazing place. I will never forget it. I know I will miss it so much, so I am sure I will definitely return one day, because here I will leave one part of my heart.

I would like to thank particularly all my corridor mates in Luleå at Väderleden 11 Jongwan Choi, Vincent Combes, William Nomicith, Oscar Rodriguez Pasqual, and Edouard Guchia, for making me feel like a member of a family.

A particular thank to one of my best friends Giuseppe Timperio, for having been always close to me the last years, and for welcoming me as a brother in Lulea. With him it was an experience even more wonderful.

I wish to thank all my dear best friends, for helping me get through the difficult times, and for all the emotional support, comaraderie, entertainment, and caring they provided.

Lastly, I wish to thank my entire dear family for providing a loving environment for me: my father Giovanni Luciano, my mother Maria Antonietta Pasquale and my brother Domenico Luciano. To them I dedicate this thesis work.


[16] Eng.-Poh. Ng., Svetlana Mintova, “Nanoporous materials with enhanced hydrophilicity and high water sorption capacity”, Laboratoire de Matériaux à Porosité Contrôlée, UMR-7016 CNRS, ENSCMu, Université de Haute Alsace, 3 rue Alfred Werner, 68093 Mulhouse, France.


References


[34] I. Perdana, D. Creaser, O. Ohrman, J. Hedlund, “NO\textsubscript{x} adsorption over a wide temperature range on Na-ZSM-5 films”, J.Catal., vol. 234, pp. 219-229, 225.


MATLAB programs used for the modeling of the breakthrough data:

clear all;
clc;

xdata=[0.008333333  0.019444444 0.028055556 0.041666667 0.052777778 0.069444444];ydata=[0.001917102  0.001917102 0.001887726 0.001841016 0.001885547 0.001849943];

% Supposed values k and K;
x0=[630;500]

k=lsqcurvefit(@equation1,x0,xdata,ydata)

function q = equation1(x,xdata,ydata)

% Flow rate [m^3/h]
Q=0.06;
% Diameter of the base of the column [m]
d=0.032;
% Column section [m^2]
s=(d./2).^2.*3.14;
% Superficial velocity [m/h]
u=Q./s;
% Column lenght [m]
z=0.309;
% Void volume
e=0.38;
% Intertitial velocity [m/h]
v=u/e;
% Dimensionless bed lenght
csi=((x(1).*x(2).*z)./v).*((1-e)./e);
% Dimensionless bed time
tau=(x(1).*(xdata-z./v));

q=1/2.*erfc((csi).^((1/2)-(tau).^((1/2)-(1/8).*(csi).^((1/2)-(1/8).*(tau).^((1/2)))));

clear all
clc
% Flow rate [m^3/h]
Q=0.06;
% Diameter of the base of the column [m]
d=0.032;
% Column section [m^2]
s=(d./2).^2.*3.14;
Appendix

% Superficial velocity [m/h]
\[ u = \frac{Q}{s} \]
% Column length [m]
\[ z = 0.309 \]
% Void volume
\[ e = 0.38 \]
% Intertitial velocity
\[ v = \frac{u}{e} \]
% Henry constant
\[ H = 625 \]
% Mass coefficient
\[ k = 770 \]
% Time [h]
\[ x = 0.01:0.001:4 \]
% Dimensionless bed length
\[ \text{csi} = \left( \frac{k \cdot H \cdot z}{v} \right) \cdot \left( \frac{1-e}{e} \right) \]
% Dimensionless bed time
\[ \tau = \left( k \cdot \left( x - \frac{z}{v} \right) \right) \]
\[ q = \frac{1}{2} \cdot \text{erfc} \left( \text{csi}^{(1/2)} - \tau^{(1/2)} - \frac{1}{8} \cdot \text{csi}^{(1/2)} - \frac{1}{8} \cdot \tau^{(1/2)} \right) \]

\[
xdata = [0, 0.008333333, 0.019444444, 0.028055556, 0.041666667, 0.052777778];
\]
\[
ydata = [0.003965617, 0.001917102, 0.001917102, 0.001887726, 0.001841016, 0.001885547];
\]
plot(x, q, xdata, ydata);
axis([0.01 4 0 1.1])