Investigation of Silica Gels as Adsorbents in SO$_2$ Enriched Gases

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Flue gas cleaning in power plants is required to remove harmful components such as sulphur dioxide SO$_2$, mercury Hg, nitrogen oxides NO$_x$, volatile organic compounds VOC, hydrochloric acid HCl, hydrogen fluoride HF, heavy metals, dioxins, furans and fly ash. In this study, the adsorption performance of silica gels, the breakthrough behaviour regarding SO$_2$ rich gases and the regeneration of silica gels were investigated. Firstly, the influence of different grain sizes on the adsorption of SO$_2$ and secondly the ability of regeneration regarding different grain sizes and relative humidity of storing the silica gels were examined. The best silica gel achieved 25 % of dynamic adsorption capacity and 72 % of the breakthrough time compared to active coke. Suitable conditions for complete thermal regeneration of silica gels were found. Dependent on the grain size and relative humidity of storing the silica gels, a coarse grain and medium relative humidity of 45 % was favourable for a complete regeneration.

1 Introduction

Flue gas cleaning has received much attention due to the aspired environmental protection. The most frequently occurring pollutants are nitrogen oxides (NO$_x$), sulphur dioxides (SO$_x$), organic substances, halogen compounds and heavy metals (Hg) [1, 2]. Besides filters and selective catalytic reduction techniques, different materials are used to clean flue gases such as carbonaceous adsorbents (activated carbon, active coke), mineral adsorbents (zeolites), trass and combined materials [3].

Liberti et al. [4] investigated urban particulate matter from the atmosphere as well as fly ash from oil and coal electric power furnaces, from a cement factory or from iron and steel plants. They found that SO$_2$ is adsorbed on the surface of several particles, which is strongly influenced by humidity. Also DeBarr et al. [5], Daley et al. [6], Rodriguez-Mirasol et al. [7] and Kisamori et al. [8] investigated carbonaceous adsorbents such as activated carbons and activated carbon fibers (ACFs). DeBarr et al. [5] found out that both materials are beneficial as sorbents with a large capacity for SO$_2$. Daley et al. [6] and Kisamori et al. [8] confirmed the possibility of ACFs and Rodriguez-Mirasol et al. [7] of activated carbons to adsorb SO$_2$. Krzack [9], Heschel et al. [10] and Krzack et al. [11] investigated active cokes for flue gas cleaning.

Cole et al. [12] investigated ion exchange resins in the chloride form and molecular sieves to recover sulphur dioxide from waste gas. They found that ion exchange resins show adsorption capacities similar to activated charcoal. Sirkecioglu et al. [13] investigated clinoptilolite, a silica rich natural zeolite, to remove H$_2$S and SO$_2$ from natural gas, air and hydrocarbon gas streams. They spotted the adsorption capacity for SO$_2$ to be higher than for H$_2$S due to its higher permanent dipole moment. Also Tantet et al. [14] confirmed that hydrophobic zeolites could adsorb SO$_2$. They found that in the presence of water the adsorption of SO$_2$ is declined. Belyakova et al. [15] investigated the adsorption of SO$_2$ and CO$_2$ on silica gels with amines as functional groups. They figured out that the amount of adsorbed SO$_2$ is dependent on the surface concentration of amino groups. In addition, Thornsberry [16] confirmed that silica gels could be used as gas chromatographic separation materials for SO$_2$. Furthermore, Ahmed et al. [17] investigated aerogels containing components such as CaO and MgO in their structure to adsorb SO$_2$.

A combined material was investigated by Zhao et al. [18] as they supported ether-functionalized imidazolium-based ionic liquids (EFILLS) onto porous silica gel particles by an impregnation method. By this material, a high SO$_2$ adsorption rate can be achieved. To date, various materials were investigated regarding the adsorption of SO$_2$ in flue gases. However, little attention has been paid to desorption of SO$_2$ for regeneration of the adsorbent materials, especially pure silica gels. It is known that carbon adsorbents can be regenerated [19, 20], but the regeneration process is associated with exorbitant effort since a specific residual load-
ing occurs [20]. Furthermore, the carbon surface reacts during an oxidative thermal treatment with the oxygen and leads to the formation of CO and CO₂ [19]. Due to the expensive treatment, only high performance activated carbons are regenerated, whereas most carbon based sorbents are designed as one-way products. In contrast, it is known that silica gels adsorbed with sulphurous components, such as H₂S, can be regenerated [21, 22]. In this study, the regeneration of silica gels regarding SO₂ rich gases and the regeneration of silica gels were investigated. Firstly, the influence of different grain sizes on the adsorption of SO₂ and secondly the ability of regeneration regarding different grain size and relative humidity of storing the silica gels was examined.

2 Experimental

This research work investigated the adsorption and desorption of sulphur dioxide (SO₂) on silica gels as new adsorbent in comparison with a commercial active coke. The material was characterized by the porosity P, average pore radius r, microscopic measurements and differential scanning calorimetry. The adsorption/desorption was distinguished by breakthrough curves and the silica gels dynamic adsorption capacity and the breakthrough time.

2.1 Materials

In recent studies from Klenert et al. [23, 24] silica gels as transparent heat insulation applications were investigated. Based on the results, an assortment of silica gels was chosen to investigate the SO₂ adsorption behaviour. To exclude property fluctuations of silica gels, an industrial silica gel with related properties named silica gel C, produced by Chemiewerk Bad Köstritz GmbH (Bad Köstritz/DE) was used for the studies. Samples of the initial material were dried at 50 °C, 100 °C and 150 °C for 30 min to remove physically adsorbed water before adsorption experiments. Simultaneously, commercial active coke HOK medium (RWE AG) was used as reference.

2.2 Analytical methods

Isotherms of low thermal adsorption (77 K) of nitrogen on the granular materials were measured (ASAP 2010, Micromeritics/DE) to analyze especially the micropores region (<2 nm). From the data obtained, the specific surface areas as well as the pore size distributions and the cumulative pore volume of the granular materials were determined. The Horwath Kawazoe method DIN 66135-4:2004-09 for analysis in micropores region was used. In mesopore region, the Barrett-Joyner-Halenda method (BJH) according to DIN 66134 for analyses in case of silica gels, and the BET method DIN ISO 9277 for HOK was used. The pore size distribution, the average pore radius and the cumulative pore volume in the meso- and macropores region of the materials was determined with a mercury porosimeter (PASCAL 140/440, Porotec GmbH/DE). Cumulative volume distributions were derived according to the standard DIN 66133/ISO 15901-1. To calculate the porosity of the materials, the true density p and the cumulative pore volume Vcum according to equation 1:

\[
P = \frac{V_{\text{cum}}}{\rho} \text{V}_{\text{ori}} \tag{1}
\]

The microstructure of the silica gels was investigated by scanning electron microscopy (SEM). For the SEM investigations (XL30ESEM-FEG, FEI/DE), the silica gels were dried at 150 °C, a number of grains were arranged on an object plate and then carbon sputtered. Furthermore, differential scanning calorimetry and thermogravimetric measurements (STA 409 PC/PG, Netzsch/DE) were used to characterize the behaviour of the material at elevated temperatures and to determine the maximum application temperature. The heating-up rate was 10 K/min and the DSC/ TG measurements were performed in synthetic air atmosphere with mostly 80 % N₂ and 20 % O₂. Different heat flows between the sample and reference were measured and, due to exothermal or endothermal reactions, various physical transformations were characterized [25]. Additionally, the change of the silica gels mass due to reactions while heating were determined.

SO₂ adsorption was performed in a heated fixed bed reactor coupled with a downstream online SO₂ analyser (Ultramat Z23, Siemens/DE). The sorption tube consists of glass with a maximum bed diameter of 31 mm and a maximum bed height of 58 mm. Prior to adsorption, the silica gels were heated up to 150 °C for 30 min in a drying oven and were then filled in the glass tube with an average bed height of 20 mm. The reactor was heated up to 120 °C bed temperature for 1 h. After 40 min, the gas mixture of 32 l/h synthetic air (79 vol.-% N₂ and 21 vol.-% O₂) and 3 l/h of SO₂ (0.4 vol.-%, N₂ as residual gas) was lead into the aperture, streaming around the reactor in bypass until a constant gas flow and concentration of SO₂ was achieved after 20 min. Starting the adsorption investigation, the gas flow with 350–370 ppm SO₂ was introduced into the reactor for 30 min, passing through the bed from the top. Afterwards the heating was

![Experimental set up of SO₂ breakthrough curve measurements](image-url)
switched off and the inlet concentrations \(c_0\) were measured again to avoid drift bias. The logged values for time-dependent SO\(_2\) concentrations were used to visualize the breakthrough curves and calculate specific values such as breakthrough time (achieving \(c/c_0 > 0.1\)), breakthrough capacity and dynamic adsorption capacity (\(c/c_0 = 0.6\)). The mass change due to adsorption of SO\(_2\) on the sorbent was calculated by:

\[
\Delta m_{\text{SO}_2} = \frac{\eta_{\text{SO}_2}}{100} \cdot c_{\text{SO}_2} \cdot V \cdot 10^{-3} \cdot \frac{t}{60 \cdot \gamma_{\text{S}}} \quad [2]
\]

and the dynamic load capacity of the sorbent \(x_1\) by:

\[
x_1 = \frac{\Delta m_{\text{SO}_2}}{V} \quad [3]
\]

The regeneration of the sorbent was performed in a separate drying oven. The sorbent was heated up to 250 °C for 5 h in oxidizing atmosphere. Afterwards, the regenerated sorbents were tested again for their adsorption behaviour regarding breakthrough curve and dynamic adsorption capacity of the sorbent. The level of regeneration was calculated by:

\[
x_i = \frac{X_{\text{dyn}, i}}{X_{\text{dyn}, 1}} \quad [4]
\]

where \(X_{\text{dyn}, 1}\) is dynamic adsorption capacity of first adsorption and \(X_{\text{dyn}, 2}\) is dynamic adsorption capacity of second adsorption (after regeneration).

3. Results and discussion

3.1 Production of different grain size distributions of silica gels

In preliminary investigations, silica gel V1 as a promising material for SO\(_2\) adsorption was ascertained. Based on the results, systematic investigations of silica gels regarding the adsorption of SO\(_2\) were conducted. V1 was a statistic mixing, which was tested as it was produced. For adsorption measurements, three silica gels (V2/V2\(_{\text{reg.}}\), V3/V3\(_{\text{reg.}}\) and V4/V4\(_{\text{reg.}}\)) with different grain sizes were produced and compared with HOK medium as a standard material, as seen in Fig. 2.

Silica gels V2, V3 and V4 were first loaded with SO\(_2\) and then regenerated. The regenerated silica gels V2\(_{\text{reg.}}\), V3\(_{\text{reg.}}\) and V4\(_{\text{reg.}}\) correspond to V2, V3 and V4 and are identical with the material and porosity structure.

HOK medium exhibited a narrow grain size distribution with grains smaller than 2 mm, especially with mostly 0.4 mm in diameter. All silica gels are characterized by a broader grain size distribution compared to HOK medium and larger grains. Silica gel V2/V2\(_{\text{reg.}}\) is mostly characterized by grains larger than 2 mm in diameter and presents a coarse grain. Contrary, silica gel V3/V3\(_{\text{reg.}}\) exhibited fine grains mostly with smaller grains of 1 mm. V4/V4\(_{\text{reg.}}\) represented a bimodal grain size distribution with grains mostly between 0.4–1 mm and 2–3 mm. These different silica gels are investigated regarding the adsorption and desorption behaviour.

3.2 Adsorption behaviour of SO\(_2\) on silica gels and carbonaceous adsorbents

Different silica gels V1, V2 and V3 as well as HOK medium were investigated regarding the breakthrough curve of SO\(_2\) and the course of pressure during the adsorption. Fig. 3 shows the trends of the relative concentration \(c/c_0\) for all five materials. Silica gel V2 showed the earliest breakthrough with 0.8 mg SO\(_2\) loaded until breakthrough, whereas the silica gels V1 (1.9 mg), V3 (4.9 mg) and V3 (3.4 mg) exhibited larger values. After 90 min adsorption, nearly the initial SO\(_2\) concentration was achieved for every silica gel. Contrary, HOK medium showed a very low rise of the breakthrough curve with a large breakthrough time with 13.2 mg SO\(_2\) loaded. The discontinuity of the silica gel breakthrough curves can be traced back to the properties of the filling. At silica gel V1, the discontinuity appeared at 20–23 mg SO\(_2\) loaded, for V2 at 12–15 mg SO\(_2\) loaded, for V3 at 20–25 mg SO\(_2\) loaded. This discontinuity was for V4 at 5–7 mg SO\(_2\) loaded (Fig. 3). Contrary, HOK medium showed a very constant SO\(_2\) concentration of silica gels V1–V4 and HOK over time.
adsorption behaviour without almost any discontinuity. Although the absolute pressure at 5.5 mbar in maximum is small, the course of pressure seemed to have an influence on the adsorption behaviour. With a constant pressure behaviour on the filling, a constant curve progression could be achieved (Fig. 4). Every silica gel showed a discontinuity of the curve progression about that time the pressure drop took place. This pressure drop seemed to appear especially for the silica gel V3 with the highest fine grain content. This discontinuity suggests to not optimal grain size distributions leading to irregular streaming in different grain heights. This can be verified by Sonnenburg [26] and Klöker et al. [27] as they concluded that in fillings local velocity maxima do exist and the streaming is not uniform.

The more efficient adsorption behaviour of HOK medium deduced from many aspects, especially the narrow grain size distribution with mostly fine particles at 0.4 mm (Fig. 2) and the optimal streaming behaviour of HOK medium (Fig. 4).

The influence of particle size on adsorption behaviour was investigated by Karau et al. [28] and Yean et al. as they confirmed that fine particles could increase the breakthrough time. This mechanism can be explained by the shortened diffusion path length without a high mass transfer resistance within the adsorbent particles [29]. Rasmuson [30] found a delay of the breakthrough point and faster reached adsorption equilibrium by using smaller particles. The pore size distribution of a typical silica gel and HOK medium in the micropores region is represented in Fig. 5, whereas Fig. 6 shows the meso- and macropores region of the materials. It is assumed that the pore size distribution of the silica gels V1, V2 and V3 and V4 is similar since only the grain size distribution was changed.

The pore size distribution of HOK medium was bimodal with pores in the micropores region, especially 0.4 nm and pores in the macropores region about 100 nm. HOK medium mostly consisted of 49 % micropores (<2 nm) and 42 % macropores (>50 nm) with a BET surface of 267 m²g⁻¹ and 55 % porosity. Contrary, the silica gel showed a bimodal pore size distribution, with a larger micropores ratio at 0.3 nm and meso pores at 5–10 nm. Almost no macropores were existent. The silica gel mostly possessed of 50 % meso pores (2 nm < pore size < 50 nm) with a BJH surface area of 446 m²g⁻¹ and 54 % porosity. Especially in micropores adsorption mechanisms take place, whereas meso and macropores serve as gas transport pathways [31]. Therefore, HOK medium is advantageous to pass gases fast from the outside to the inner surfaces.
From Fig. 7, the surface structure of HOK medium (A) and silica gel (B) could be determined. HOK medium exhibited a much coarser structure with bigger particles. Contrary, the silica gel showed a more even structure. As Iler [32] investigated, silica gels consist of an aggregation and polymerization of particles in a three-dimensional Si–O–Si microstructure. In atmospheres with water vapour, HOK medium acts as a catalyst and converts SO2 with O2 to SO3 and reacts with H2O to H2SO4, which is described by Tseng et al. [33] and Kast [34] with

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \]  

[5]

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]  

[6]

However, in the adsorption experiments the SO2/N2 gas stream was not enriched with H2O vapour and thus especially SO3 was generated at HOK medium. Although in the test gas a dry gas atmosphere was existent, silica gels can build SO3 and H2SO4 as in the reactions [5] and [6] (presented in Fig. 8–9). The unloaded silica gel showed a distinctive endothermic peak at approx. 90 °C due to the evaporation of adsorbed water on the pore surfaces. With increasing temperatures (100–700 °C), a broad exothermic hump was existent and can be traced back to the condensation and densification process of silanol groups to siloxane groups, in which water molecules are produced [35, 36]. The curve progression of the loaded silica gel was completely different with no endothermic peak but a plateau at the temperature range 35–60 °C and a broad but more intensive exothermic hump from 100–700 °C. The maximum of exothermic hump was existent at the same temperature at 450 °C for both silica gels but the rise of the loaded silica gel was steeper than for the unloaded silica gel. Based on these results, it can be concluded that firstly, in the adsorption process at 120 °C water molecules are built by condensation of silanol groups to siloxanes, which can react with SO3 to H2SO4. Secondly, at higher temperatures in the DSC/TG measurements, again water molecules are generated by condensation processes of silanols to siloxanes, which can form H2SO4. Therefore, the higher exothermic enthalpy is characteristic for the reactions [5] and [6] and the SO3 is physically bonded on SiOH groups in a first step and is then converted with O2 to SO3 and reacts with H2O to H2SO4. The thermogravimetric measurements showed, that the unloaded silica gel (11 mass-%) exhibited a stronger distinctive mass loss than the loaded silica gel (9 mass-%) but a parallel curve progression. The mass difference can be traced...
The breakthrough time as well as the adsorption capacity can be increased with decreasing grain size. Therefore, V2 with a coarse grain of 2 mm exhibited the smallest breakthrough time (9.8 s/g), dynamic breakthrough capacity (0.1 mg/g) and adsorption capacity (0.3 mg/g) compared to V3 with 1 mm fine grains (25 s/g, 0.3 mg/g and 0.6 mg/g) and V1 with statistically mixed grains (48 s/g, 0.5 mg/g and 1.1 mg/g). V4 exhibited a similar dynamic breakthrough capacity of 0.2 mg/g due to its coarse grains of 3 mm. Karau et al. [28], Yean et al. [29] and Rasmuson [30] found out that decreasing particle sizes lead to shortened diffusion path lengths without a high mass transfer resistance within the adsorbent particles. Tsai et al. [37] confirmed as well that smaller particles enhance the adsorption rate and contribute to a larger length of the used bed than coarse particles. Furthermore, fine grains contribute to larger pressures over the adsorbent than coarse grains (Fig. 4). The statistic grains led to the best results, which can be explained by the optimal adsorption and streaming conditions with a high quantity of small particles. This can be verified by a high pressure over the filling compared to V2 and V3 (Fig. 4) and therefore a high mass transfer by shortened diffusion path length was reached. In fact, V4 exhibited the highest pressure but the bimodal grain size distribution led to disadvantageous streaming behaviour. Therefore, the best silica gel V1 achieved 25% of dynamic adsorption capacity and 72% of the breakthrough time compared to HOK medium.

### 3.3 Regeneration of silica gels

Besides the adsorption of silica gels, the regeneration of the granular materials was investigated. The granular materials were loaded in a first experiment with SO$_2$, dried at 250 °C for 5 h and stored at a relative humidity of 20–70% for 10–18 days. The influence of the grain size distribution and relative humidity during the storage on the adsorption performance (breakthrough time, dynamic breakthrough capacity and dynamic adsorption capacity) of different silica gels compared to HOK medium shown in Tab. 1. The dynamic breakthrough capacity is the amount of SO$_2$ adsorbed in the silica gels after breakthrough time, when the relative concentration exceeds c/c$\_0 = 0.1$. However, to get a better comparison of different measured silica gels with low breakthrough times, the dynamic adsorption capacity is determined to be the adsorbed SO$_2$ mass at a relative concentration of c/c = 0.6.
second adsorption of SO2 on silica gels was investigated. The grain size distributions are analysed in 3.1. Each initial silica gel V2, V3, V4 exhibited exactly the same grain size distribution like their correspondent V2\textsubscript{reg}, V3\textsubscript{reg}, V4\textsubscript{reg} since only the regeneration process differs from each other. In Fig. 10–12 the first adsorption as well as the second SO2 adsorption (after regeneration) on silica gels V2, V3 and V4 is shown. Silica gel V2\textsubscript{reg} is the only silica gel, which could be regenerated completely with nearly identical breakthrough time and adsorption capacity like its correspondent V2 (Fig. 10) with 1,1 mg SO2 loaded until breakthrough. Contrary, the silica gels V3\textsubscript{reg}, V4\textsubscript{reg} (4,9 mg /4,5 mg) and V4\textsubscript{reg} (3,4 mg/1,7 mg) could not be regenerated completely with different breakthrough and adsorption behaviours. Therefore, silica gels V3\textsubscript{reg}, and V4\textsubscript{reg} exhibited a steeper curve progression of adsorption with a rather saturation than their correspondent V3 and V4. Furthermore, silica gel V3\textsubscript{reg} with the highest fine grain content (Fig. 2) exhibited the highest pressure of 19 mbar as well as the largest pressure drop of 14 mbar over the filling (Fig. 13). Contrary, silica gel V2\textsubscript{reg} with the largest grain size exhibited the smallest pressure of approx 3,7 mbar as well as the smallest pressure drop of 0,7 mbar. Silica gel V4\textsubscript{reg} with both fine and coarse grain size showed a medium pressure of 4,4 mbar and a pressure drop of 0,4 mbar. Due to the smallest pressure drop at silica gel V4\textsubscript{reg}, the breakthrough curve was very uniform. The relation between grain size and pressure/pressure drop was found at the first loaded silica gels (chapter 3.2) and can be verified for regenerated silica gels as well. In Tab. 2, the breakthrough time, the dynamic breakthrough capacity and dynamic adsorption capacity of silica gels V2\textsubscript{reg}, V3\textsubscript{reg}, V4\textsubscript{reg} are shown. In comparison to the prior experiments, the breakthrough time of the regenerated silica gels declines except of V2\textsubscript{reg}. This is due to the circumstance that the residual loading after the regeneration treatment lowers the time until c/c0 = 0,1 is achieved (especially V4\textsubscript{reg}) and the not uniform streaming behaviour (especially V3\textsubscript{reg}). Regarding to the breakthrough time and the dynamic breakthrough capacity and dynamic adsorption capacity, silica gel V3\textsubscript{reg} exhibited the highest value of 2.1 s/g, 0,2 mg/g, 0,7 mg/g due to its small grain size of 1 mm (Fig. 2). Therefore, the small grain size generated, firstly, a larger pressure over the filling (Fig. 13) and secondly shortened diffusion path lengths than in cases for the silica gels V2\textsubscript{reg} and V4\textsubscript{reg} (28–30).

However, V2 is the only silica gel which could be regenerated (compare Tab. 1 and Tab. 2). This fact can be reasoned by the different storage of silica gels after regeneration. Silica gel V4\textsubscript{reg} was stored in a very dry atmosphere in 10 % relative humidity, whereas V2\textsubscript{reg} was stored at 45 % and V3\textsubscript{reg} in a very wet atmosphere with 70 % relative humidity. It seemed to be an optimum of storage conditions in a medium relative humidity for adsorption. Overall, a specific concentration of H2O molecules in the atmosphere is needed to rehydrate the Si–O–Si surface of silica gels with SiOH bonds and to ensure the SO2 adsorption. In Fig. 14, the levels of regeneration of silica gels V2\textsubscript{reg}, V3\textsubscript{reg} and V4\textsubscript{reg} regarding dynamic breakthrough capacity (c/c0 = 0.1) and breakthrough time (c/c0 = 0,1) are shown. Silica gel V2\textsubscript{reg} exhibited the highest level of regeneration of 100 % dynamic adsorption capacity and 100 % breakthrough time. Silica gel V3\textsubscript{reg} achieved a level of regeneration that was 67 % regarding the dynamic breakthrough capacity and 84 % regarding the breakthrough time. Silica gel V4\textsubscript{reg} attained the smallest level of regeneration with 45 % regarding the dynamic breakthrough capacity and 47 % regarding the breakthrough time. A noteworthy destruction of the pore surface and geometry of the silica gels after thermal regeneration can be excluded since at least V2\textsubscript{reg} showed complete capability of regeneration. Furthermore, Iler [32] constituted that the loss

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**Table 2** Breakthrough time, dynamic breakthrough capacity and dynamic adsorption capacity of silica gels V2\textsubscript{reg}, V3\textsubscript{reg} and V4\textsubscript{reg}.

<table>
<thead>
<tr>
<th>Material</th>
<th>V2\textsubscript{reg}</th>
<th>V3\textsubscript{reg}</th>
<th>V4\textsubscript{reg}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakthrough Time [s/g]</td>
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<td>21</td>
<td>8</td>
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<tr>
<td>Dynamic Breakthrough Capacity [mg/g]</td>
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<td>0,2</td>
<td>0,09</td>
</tr>
<tr>
<td>Dynamic Adsorption Capacity (c/c0 = 0.6) [mg/g]</td>
<td>0,4</td>
<td>0,7</td>
<td>0,4</td>
</tr>
</tbody>
</table>

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**Fig. 13** Pressure over different regenerated fillings
of adsorption capacity can also be reasoned by dehydration even at temperatures where the loss of surface through sintering does not occur. From these results can be concluded that the relative humidity seemed to have a larger impact on adsorption of regenerated silica gels than the grain size, since $V_{2\text{reg.}}$ with 45% relative humidity and despite a coarse grain size of 2 mm led to the highest level of regeneration.

4 Conclusions

In this study, the adsorption performance and the breakthrough behaviour regarding SO_2-rich gases as well as the regeneration of silica gels were investigated. Firstly, the influence of different grain sizes on the adsorption of SO_2 and secondly the ability of regeneration regarding different grain size and relative humidity of storing the silica gel were examined.

It was found that the breakthrough time as well as the dynamic adsorption capacity can be increased with decreasing grain size. Therefore, silica gels with a coarse grain size of 2 mm exhibited the smallest breakthrough time and adsorption capacity compared to silica gels with 1 mm fine grains. Small grains lead to shortened diffusion path length without a high mass transfer resistance within the adsorbent particles [28–30] and contributed to larger pressures over the adsorbent than coarse grains. The best silica gel achieved 25% of dynamic load capacity and 72% of the breakthrough time compared to standard HOK medium.

Complete regeneration of silica gel was possible with the highest level of regeneration of 100% adsorption capacity and 100% breakthrough behaviour. Dependent on the grain size and relative humidity of storage of silica gels, a coarse grain and medium relative humidity of 45% was favourable for a complete regeneration.

A complete regeneration of adsorbents is economic (conversion, transport, waste removal) and safety-related interesting since conventional carbonaceous adsorbents such as HOK medium or active coke are not regenerated in the industry. For a favourable regeneration, an exorbitant effort is necessary such as regeneration temperatures up to 850 °C [20, 41]. Further disadvantages of thermal regeneration of carbonaceous materials are the loss of carbon and the treatment of exhaust gases [41, 42].

In further investigations, especially the grain size distribution for optimal adsorption and breakthrough times can be accepted if multiple regenerations are possible.

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References


