Investigation of CO₂ Adsorption Performance and Fluidization Behavior of Mesoporous Silica Supported Polyethylenimine

Dang Viet Quang^a, Mustapha Soukri^b, Jak Tantana^b, Pradeep Kumar Sharma^b Thomas O. Nelson^b, Marty Lail^b, Luke J.I. Coleman^b, and M.R.M. Abu Zahra^{a,*}

^a*The Institute Center for Energy (iEnergy), Masdar Institute of Science and Technology, P.O.Box 54224, Masdar city, Abu Dhabi, UAE*

^b*Energy Technology Division, RTI International, Research Triangle Park, NC 27709-2194, USA*

**Tel.: +97128109181*

**Email:mabuzahra@masdar.ac.ae*

Abstract

A thorough and comprehensive study of different parameters affecting the sorbents prepared by impregnating polyethyleneimine (PEI) on silica for CO₂ capture has been conducted. The CO₂ capture performances of resulting sorbents were evaluated on both packed-bed and fluidized-bed reactors. Obtained results indicated that CO₂ adsorption-desorption performances of sorbents are greatly affected by the operation temperature in both simulated flue gas from coal fired power plant (SCF) and natural gas combined cycle power plant (NGCC). The optimal adsorption temperatures are from 50 to 80°C for NGCC flue gas and from 70 to 90 °C for SCF flue gas, while the optimal regeneration temperatures are from 110 to 130°C for both flue gas. Adsorbent containing 30 to 35 wt% PEI fluidized well with both simulated flue gas and steam. Results from this study revealed that PEI impregnated silica is a promising sorbents for CO₂ capture process, using a fluidized-bed reactor, from both coal-fired power and natural gas combined cycle power plants.

Key words: CO₂ capture; Adsorption; polyethyleneimine; CO₂ loading; Packed-bed reactor; Fluidization.

1. Introduction

CO₂ capture technologies have undergone significant development in the last several years, and today large-scale Carbon Capture & Sequestration (CCS) demonstrations are underway. Several concepts for capturing CO₂ in industrial processes and power plants are being developed. Among these, amine scrubbing based on CO₂ absorption using ethanolamine (MEA) solutions [1, 2] is considered as a current state-of-the-art industry process. However, the liquid phase amine scrubbing technology suffers from high regeneration cost, high degradation, and equipment corrosion [3-5]. As a result, there has been a strong interest to develop alternative more stable and less energy-intensive CO₂ removal technologies. Adsorption using solid sorbents [6-9], particularly amine-functionalized sorbents, is appealing due to their potentially lower energy requirements for sorbent regeneration [1, 2, 10-22]. By immobilizing amine functionalities on high-surface porous solid supports, the amino solid sorbents offer higher amine efficiency and thus superior sorbent performance [18, 19, 23, 24]. Among various solid sorbent supports including zeolites [25] activated carbons [26-29], activated alumina [30-32], and membranes [33], polyethyleneimine (PEI) impregnation on mesoporous silicas have been attracting great attention [6-9, 34-42], because of its simple preparation procedure which can be easily translated to commercial scale as well as the potential to reduce the overall costs related to CO₂ capture by reducing the energy required to release the CO₂ during regeneration [10].

Previous studies indicated that the heat of CO₂ adsorption reduced considerably by immobilizing amine on solid substrate. For example, the heat of CO₂ adsorption of sorbent prepared by immobilizing PEI on CARiACT G10 silica is around 50.0 kJ/mole [43]. 3-Aminopropyltriethoxysilane functionalized mesoporous silica generates the heat of CO₂ adsorption about 60.0 kJ/mole [44]. Meanwhile, the heat of CO₂ absorption of a conventional

aqueous MEA solution is much higher; it is about 85 kJ/mole [10]. Generally, the heat of CO₂ adsorption is reduced due to the impregnation of amine solvents on a solid support. Because of low heat capacity, solid sorbent also requires less the sensible heat to raise temperature of adsorption bed to the regeneration temperature, however, the most significance of solid sorbent is the avoidance of solvent vaporization which could account for 30–50% of total regeneration energy [10, 22, 42].

Nevertheless, several factors may influence the amine-containing sorbents performance, in particular, adsorption capacity, kinetics, and the stability of the sorbents under different operating conditions such as adsorption and desorption temperature, pressure and number of cycles as well as their interactions with different species that may occur in industrial gases. Typical species include not only impurities such as water vapor, SO₂, H₂S, NO_x and O₂ [45-52], but also CO₂ itself, which deactivates amine-containing materials under dry conditions [34, 51, 53].

The aim of the current study is to investigate the CO₂ adsorption performance and fluidization behavior of mesoporous silica-supported PEI under different operating conditions. Different types of silicas with various physical properties has been studied to evaluate their effect on the CO₂ capacity of the sorbent. In addition, different solvents and impregnating conditions were also thoroughly evaluated. The CO₂ adsorption performances of the resulting sorbents have been investigated in a packed-bed reactor (PBR) and their fluidization has been visually studied in fluidized-bed reactor (FBR). Finally, the influence of impurities on CO₂ adsorption performance during the long-term operation has been performed including humidity, oxygen and SO₂.

2. Experimental

2.1. Chemical reagents

Silicagels with different structural properties including 8 samples of irregular shape particles having different particles sizes and porosity, namely Silica from I to VIII and 1 spherical bead sample, namely Silica-IX were purchased from Sigma Aldrich. The irregular shape silica samples have surface area ranging from 155 to 353 m²/g, pore volume ranging from 1.1 to 1.2 cm³/g, and pore size ranging from 113 to 320 Å. All the silica substrates, used as support in this study, were dried at 130°C for 2 hours prior to impregnation with PEI. Branched polyethyleneimine (PEI, 99 % and average Mw $\approx$ 600) was obtained from Alfa Easer (Massachusetts, USA). Methanol (MeOH, 99.9%), ethanol (EtOH, 99.9%), and isopropanol (iPrOH, 99.9%) were provided by Fisher Scientific (Massachusetts, USA). Deionized (DI) water was collected from a centralized water deionizing and filtering system at RTI International.

2.2. Sorbent preparation

Typical adsorbent preparation procedure involved a wet modification method [35, 54]. First, a desired amount of PEI was dissolved in a solvent, which is MeOH, EtOH, iPrOH, or water, in a 1-L flask before adding a desired amount of silica under vigorous mixing in order to produce homogeneous slurry. The solvent was evaporated using a rotary evaporator (IKA RV 10 Rotovapor, USA). The resulting PEI-impregnated silica was dried in vacuum oven at 80°C over night before used for testing.

2.3. Sorbent characterization

Characterization of the prepared adsorbents involved the methods of surface area measurement, pore volume measurement, pore size measurement, nitrogen content analysis, and Thermal Gravimetric Analysis (TGA). The surface area, pore volume, and pore sizes were

measured by a nitrogen adsorption-desorption method using a Micromeritics Surface and Porosity Analyzer (ASAP 2020). First, sample was transferred into an analyzing tube with small bulb, whose mass was previously determined using analytical balance and degassed at 110°C for 10 h. The mass of analyzing tube containing sample was determined again after degassing and the tube was mounted on Micromeritics Surface and Porosity Analyzer for analyzing. The mass of sample was determined by the mass difference between the tube with sample after degassing and empty tube. The pore volume and pore size were calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption data. Nitrogen content within the sorbents was analyzed on a Thermo Scientific CNS elemental analyzer (Flash 2000). TGA was conducted on a thermogravimetric analyzer (SDT Q600), which involved heating sorbent samples from room temperature to 600°C in nitrogen gas at a rate of 10°C/min.

2.4. CO₂ adsorption-desorption on packed-bed reactor

The CO₂ adsorption – desorption performance of the adsorbent was investigated using packed-bed reactor system (PBR) designed and constructed by RTI International (RTI, North Carolina, USA) as shown in **Figure 1**. The composition of the feed gas was adjusted by changing the flow rate of individual gases controlled by mass flow controllers. Water vapor was introduced to the gas stream by flowing the mixture of air and N₂ to the temperature controlled humidifier (A). The temperature of the humidifier can be adjusted to vary the moisture content in the simulated flue gas stream.

The CO₂ stream combined with the N₂/Air/H₂O mixed gas at the outlet of the humidifier to avoid the CO₂ from dissolving in the water in humidifier, which would result in the increase acidity of the water and inaccurate CO₂ content in the simulated flue gas stream. The effluent of the PBR (B) entered a condenser (C) and water collector (D) to remove water vapor prior to

entering the CO₂ analyzer. The CO₂ concentration in the PBR effluent was analyzed using a Horiba CO₂ analyzer (VA-3000). PBR operated autonomously by National Instruments Lookout program coupled with customized PLC control developed by RTI's engineers. The software allows the PBR to be controlled according to preset test conditions (defined by operator) and to collect data points every second. The data including operating temperatures, the flow rate of input gases and CO₂ concentration in the output gas are recorded. The PBR is capable of performing multiple adsorptions-regeneration test cycles with varying test conditions without the need for operator attendance. In a typical experiment, approximately 2 g of adsorbent was mixed with silicon carbide beads, a filler and heat transfer material, then loaded into the PBR, which was made of stainless steel column with 1.27 cm inner diameter and 20 cm length.

A typical test undergoes 5 stages including 1) feed test, 2) purge, 3) adsorption, 4) regeneration, and 5) cooling. The feed test stage allows system to adjust the temperature of the process lines, humidifier, and reactor to defined values for the adsorption stage and to analyze and adjust the feed gas composition at the same flow rate being used in the adsorption stage. The feed gas can be tailored to various simulated flue gas conditions, in these tests in particular, flue gas from coal fired power plant (SCF) or natural gas combined cycle power plant (NGCC). The SCF flue gas has following composition: CO₂ = 15 vol%, O₂ = 4.5 vol%, and water vapor = 5.65 vol% in balance with N₂. The NGCC flue gas has following composition: CO₂ = 3 vol%, O₂ = 14 vol%, and water vapor = 5.65 vol% in balance with N₂. When the CO₂ concentration in the feed gas is stable, the system will enter the purge stage by flowing N₂ through the system until no CO₂ is detected in the outlet gas of the reactor. The adsorption stage is initiated by switching a valve to allow CO₂-laden feed gas to enter the reactor with a flow rate of 150 mL/min. The end of the adsorption process was determined by the breakthrough point for CO₂ which occurs when

CO₂ concentration in outlet gas reached 99.95% of that in the feed gas. The end of the adsorption stage may also be determined by the minimum and maximum adsorption times, which was defined as 30 and 45 min, respectively, for the SCF flue gas and 60 and 90 min for NGCC flue gas. The regeneration stage follows the adsorption and is carried out by flowing humidified N₂ through the reactor at the flow rate of 150 mL/min at a desired temperature. The regeneration end point was defined by the regeneration off-gas (outlet gas) having concentration of CO₂ of less than 0.1%. Otherwise, it was determined by the minimum or maximum desorption times of 30 and 45 min, respectively. The cooling of the system is performed by flowing N₂ at the flow rate of 350 mL/min to reduce reactor temperature to either the temperature of the adsorption stage or to room temperature (if the tests are complete). The CO₂ loading (wt%) was calculated from regeneration data by dividing the total amount of CO₂ desorbed by the mass of the adsorbent and multiplying with 100. The CO₂ loading is defined as the amount of CO₂, which desorbs at a specific regeneration condition and does not include CO₂ lean loading. Each test consisted of at least 3 adsorption-regeneration cycles and the CO₂ loading that is reported was taken as the average between all cycles.

2.5. Fluidization and adsorption-desorption studies using the prepared sorbents and a fluidized bed reactor

The fluidization and adsorption-desorption performance of the prepared adsorbents were studied in a fluidized-bed reactor system (FBR) designed by RTI. A schematic illustration of the FBR is shown in **Figure 2**.

The FBR allows for adsorption-desorption cycling tests to be conducted at ambient pressure and at temperatures ranging from room temperature to 140°C. The composition of the feed gas was controlled by adjusting the flow rate of two mass flow controllers, MFC5 for N₂ flow and

MFC6 for CO₂ flow, and the feed rate of a water pump. A micro pump was used to supply a precise amount of water into steam generator (A), where the temperature was held at approximately 300°C to ensure that all supplied water was converted to steam. The steam was combined with a mixture of N₂/CO₂ gases from MFC to form the simulated flue gases used in the adsorption tests. The simulated flue gases then entered a glass fluidization column (B), 80 cm in height and 2.54 cm in diameter. Noted that the steam was used solely as the CO₂-stripping agent in fluidization column. The temperature of the column (B) is controlled by heating oil from circulation bath. The gas exiting column (B) flowed through a cyclone (C), condenser (D), and water collector (E) to remove fine particles and water vapor before entering a CO₂ analyzer and then being vent. In a typical experiment, a predefined amount of sorbent was loaded into the column (B) in order to obtain a bed height of about 15 cm. The sorbent bed was first fluidized with N₂ until fluidization stabilized and the desired setting temperature was reached. For each adsorbent sample, the fluidization performance was tested by using 3 different gas compositions: N₂, simulated flue gas, and steam. The pressure drop across the column at various gas velocities was recorded to analyze the fluidization characteristics of the adsorbent.

3. Results and discussion

3.1. Adsorbent characterization

The properties of the silica substrate ([Silica-I](#)) and its sorbents containing various PEI concentrations are listed in **Table 1**. [In this study, PEI impregnation was conducted in MeOH. Adsorption was conducted at 65°C in the SCF flue gas and regeneration was conducted at 110°C in humidified N₂ containing 6.65 vol% of water vapor.](#) The porous properties of the silica support decreased upon impregnation with PEI from zero to 45 wt% PEI loading. In fact, both the surface area and pore volume of the sorbent decreased almost linearly as a function of increased

PEI concentration (**Figure 3**). However, the pore size decreases from 150 Å to about 110 Å irrespective of the PEI concentration (**Figure S1**). In contrast to the porous properties, the bulk density of the adsorbent increases along with the increase in the PEI concentration (**Figure 4**), since the empty volume inside silica structure is being filled by the PEI molecules.

The elemental analyses (**Table 1**) revealed that mesoporous silica impregnated with 30–45 wt% PEI contains 8.77–13.16 wt% of organic bound nitrogen, respectively. These results confirm that the PEI was successfully impregnated onto the silica substrate by the wet impregnation method.

The thermal stability of the solid sorbent under a range of operating temperatures (between 50 to 130°C for adsorption and regeneration, respectively) are of critical importance. Thus, TGA analyses were performed on representative samples and the results are shown in **Figure 5**.

The TGA analyses confirmed that silica substrate is strongly resistant to thermal treatment as it lost only 1.18 % of its weight up to about 100°C (caused by moisture evaporation) and then remained stable when temperature increased to 600°C. However, the TGA profile of these two different adsorbents differs significantly from the silica substrate. The initial weight loss at 100°C is attributed to the evaporation of absorbed water, and significant weight reduction was observed around 250–425°C with an overall weight loss of 29.1 and 36 wt% for 30 and 37.5 wt% PEI impregnation, respectively, which is likely due to the decomposition of the PEI. These results clearly indicate that these sorbents are suitable for the desired CO₂ capture process, in which the operating temperatures are lower than 150°C.

3.2. Effect of PEI concentration on CO₂ loading performance

The CO₂ adsorption on silica supported PEI is mainly based on the reaction of CO₂ with amino groups. Since the branched PEI contains primary, secondary, and tertiary amino groups, there are several mechanisms that account for the CO₂ adsorption on the adsorbent [55]. First, a chemical adsorption occurs through reactions between CO₂ molecules and primary and secondary amino groups to form carbamate species (**Eq. 1**) or possible carbonate species in the presence of water (**Eq. 2**). Second, chemical adsorption takes place via a reaction between CO₂ molecules and tertiary amino groups in the presence of water to form bicarbonate products (**Eq. 3**) [56]. These are reversible reactions; the carbamate and carbonate species can be decomposed at high temperature to regenerate amine and free the CO₂ gas. In general, the chemical adsorption usually occurs with a relatively high rate at the initial stage, about 15-30 min and then slows down due to less availability of active and exposed amino groups as well as slow dispersion rate of CO₂ into the adsorbent structure. Therefore, in the later adsorption stage, in addition to the chemical adsorption, the physical adsorption of CO₂ onto the adsorbent should be considered as well [35, 57]. PEI-based adsorbent contains numerous polar sites on the surface and pore wall. Those polar sites can attract CO₂ molecules by forming a weak Van der Waal interaction to induce a physical adsorption. The physical adsorption is particularly enforced at low temperature and high pressure. In this study, the SCF and NGCC flue gas have relatively low CO₂ concentration at ambient pressure; the CO₂ physical adsorption could be negligible. Thus, the CO₂ adsorption capacity of the sorbent is mostly contributed by the chemical adsorption.

Theoretically, the CO₂ adsorption capacity should be linearly increased as a function of the amino group density (PEI concentration in the sorbent). According to the Reaction (1), (2), and (3), higher PEI concentration should result in an increase in the CO₂ adsorption capacity due to their right shift. However, the experimental results showed a different scenario as seen in **Figure 6**.

The CO₂ loading capacity is initially increased with higher PEI concentration (from 30 to 40 wt%), then appears to stabilize at a maximum CO₂ loading with even higher PEI concentration (up to 45 wt%). According to previous studies [35, 58], the CO₂ adsorption capacity of silica-supported sorbents increases with increasing PEI concentration, but only to a specific point and then a decrease in performance actually occurs with even higher PEI loading. In the light of this finding, we examined the porosity of sorbents and as already highlighted in **Table 1**, a significant reduction of the adsorbent pore volume and pore size suggest that the pores were filled with the PEI. At higher PEI concentrations, as the polymeric amine packs into the substrate pores, it is likely that numerous pores become full. Thus, the PEI molecules packed inside the pores likely become condense and display as solid particles, in which, the majority of the amino groups allocated inside particles [35, 58]. Hence, they become inaccessible and do not take part in the adsorption of CO₂. This assumption is asserted by experimentally molar ratio of CO₂/N shown in Table 1. The molar ratio of CO₂/N reduced as the N content increased by the higher PEI impregnated concentration.

3.3. Effect of solvent on CO₂ loading

According to a literature survey, PEI impregnation is usually conducted using methanol (MeOH) as a solvent to produce PEI/silica slurry. MeOH is frequently used because it is miscible with PEI, easy to evaporate due to low boiling point, and relatively inexpensive. However, it is a

toxic solvent with relatively high vapor pressure and may not make an ideal choice as a commercial solvent. Therefore, we investigated other solvents including ethanol (EtOH), isopropanol (*i*PrOH), and water (H₂O) as possible replacements for MeOH in the sorbent preparation. The effect that different solvent have on the CO₂ loading was examined and the results are presented in **Figure 7**.

The prepared adsorbent with the lowest CO₂ loading (9.1 wt%) was actually the one prepared using MeOH. When MeOH was replaced by other solvents, the CO₂ loading were consistently improved, with the EtOH-prepared sorbent having the highest CO₂ loading (10.9 wt%). By using EtOH as a replacement to MeOH, CO₂ loading was enhanced 19.3 % and EtOH does not have the same toxicity and environmental concern as MeOH. It is not clear for us the reason for this improvement, however, it is likely due to the different conformation of PEI inside silica structure causing by using different solvents. Because CO₂ loading of the sorbent was improved by replacing MeOH with EtOH, the EtOH solvent will be used to prepare sorbent for the following experiments.

3.4. Effect of adsorption and regeneration temperature on CO₂ loading performance

Several studies indicated that the CO₂ adsorption rate of amine supported mesoporous silica is regulated by chemical reaction between CO₂ and amino groups in the sorbent and undergoes two typical stages, before and after breakthrough time [18, 59, 60]. The first stage is controlled by reactions among CO₂ molecules and the ready-accessible active sites (amino groups). In the second stage, the adsorption rate is dominated by the diffusion rate of CO₂ to active sites, which are located inside the condense structure of PEI in the sorbent. The first stage occurs in few

minutes, while the second stage continues until it reaches the thermodynamic equilibrium, which may take several hours or days.

For this reason, the CO₂ adsorption capacity measured at the equilibrium is usually much higher than the CO₂ loading at the first 10-30 min. **Because the measurement of the CO₂ adsorption capacity consumes more time, the CO₂ loading reported in this study involves the first stage of the adsorption only.** In practical application, the CO₂ loading at the first stage is more significant due to its high adsorption rate. Therefore, the adsorption parameters at the breakthrough (90% CO₂ removal) such as the breakthrough time (BT) and CO₂ loading at breakthrough become very important to evaluate the performance and effectiveness of the sorbent. Longer breakthrough time and higher CO₂ loading at the breakthrough allow to lengthen sorbent retention in the reactor, which helps slow down the sorbent circulation rate. The slow sorbent circulation rate will help decrease the energy requirement for heating the sorbent bed and this results in the reduction in energy consumption.

The effect of adsorption temperature on the CO₂ loading of the sorbent is presented in **Figure 8. Tests conducted on sorbents (Silica-I) containing 37.5 wt% PEI impregnated using EtOH as solvent. The sorbent was regenerated at 110°C in humidified N₂.** As the adsorption temperature elevated from 30 to 50°C, the CO₂ loading increased and reached to a maximum at 50°C for both simulated flue gases. The maximum loadings recorded were 13.6 and 9.6 wt% for SCF and NGCC flue gases, respectively. Once we increased the adsorption temperature above 50°C, the CO₂ loading dropped for both cases (SCF flue gas and NGCC flue gas). Even though, the sorbent loses its adsorption capacity at higher temperature, CO₂ loading on the sorbent is effectively performed at large temperature range (from 30 to 100°C). However, to find the optimum temperature for the process to enhance CO₂ removal efficiency and energy saving, the

breakthrough time and CO₂ loading at the breakthrough were considered. The optimum temperature should maximize both breakthrough time and CO₂ loading at breakthrough. As seen in **Figure 8**, both breakthrough time and CO₂ loading at the breakthrough reached maximum values at certain temperature range and the result suggested that the optimum adsorption temperatures are 70–90 °C for SCF flue gas and 50–80 °C for NGCC flue gas, respectively.

The reduction in CO₂ loading, as the adsorption temperature increased, is expectable due to the nature of the reactions between amine and CO₂. These reversible and exothermic reactions (Reaction 1, 2, and 3), will shift to the left at a higher temperature, which is more favorable to desorption than the adsorption and as the results, CO₂ loading decreases with the increase in the adsorption temperature. This explanation, however, only satisfied the CO₂ adsorption mechanism at above 50°C. Below 50°C, the CO₂ loading increased with the increase in the adsorption temperature. Apparently, there is another element that dominates the adsorption at low temperature range. As discussed earlier, the way PEI is packed at low temperature (amino groups are partially confined in particles), causes less accessibility to CO₂ gas. As temperature increases, the particle-like PEI becomes more flexible and expendable, allowing more amino groups to expose to CO₂, which results in higher CO₂ adsorption capacity.

The effect of regeneration temperature on the [cyclic CO₂ loading](#) of the sorbent was also studied. To investigate this effect, the temperature in the adsorption stage was held constant at 65°C, while temperature in regeneration stage was varied from 90–150°C for both SCF and SNCC flue gases. The obtained results are shown in **Figure 9**. From this figure, it is clear that the CO₂ loading was significantly enhanced by the increase in the regeneration temperature in both cases. In fact, between 90–130°C, the CO₂ loading increases rapidly and almost linearly as a function of regeneration temperature. The rate of CO₂ loading increase while increasing the

regeneration temperature then slows down at higher temperature (above 130°C) for both flue gases (SCF and NGCC). These results are in good agreement with those from previous study where the CO₂ desorption from loaded PEI/silica sorbent increased monotonically with temperature [61].

Nevertheless, the lean CO₂ loading of the sorbent (The lean loading is the amount of absorbed CO₂ per gram of sorbent that is not desorbed at regeneration temperature) should be taken into account. When the regeneration temperature is high enough (~150°C, **Figure 9**), the sorbent will be fully desorbed and the lean loading will reach zero. Therefore, the increase in regeneration temperature will reduce the lean loading and results in higher cyclic CO₂ loading.

It is clear that the higher regeneration temperature helps enhance the CO₂ loading, however, the increase in temperature may cause many unexpected problems such as higher energy requirement, sorbent degradation (thermal and oxidative), and shortening the lifecycles of the sorbent. For example, by increasing regeneration temperature from 130 to 150 °C while keeping adsorption temperature at 80 °C, the CO₂ loading improves only 5.2 % but the energy required for heating sorbent bed from 130 to 150 °C increases 40% for both SCF and NGCC flue gases. The increments of CO₂ loading and sensible heat with raising temperature from 100 to 150 °C shown in **Figure 9** (inset) indicated that sensible heat increases linearly, while CO₂ loading increment slows down with an inflection point at 130 °C. An optimal regeneration temperature should help maintain a reasonable CO₂ loading, while saving energy and avoiding rapid degradation. The result suggested that the optimal temperature for adsorbent regeneration lies in the range of 110 to 130 °C.

3.5. Adsorption kinetics and CO₂ removal efficiency

3.5.1. SCF flue gas conditions

The kinetics of CO₂ adsorption onto the adsorbent (Silica-I) was studied for adsorption under SCF flue gas conditions. The results of these studies are shown in **Figure 10**. As exhibited in this figure, the CO₂ adsorption was rapid during the first few minutes of adsorption with more than 99% of CO₂ removal efficiency. After few minutes the adsorption rate was slowing down and CO₂ removal efficiency was reduced sharply, as indicated by the increase of CO₂ concentration in the effluent which quickly reached the CO₂ level in the feed gas. In general, the CO₂ breakthrough time was observed within the first 3 to 5 min, but was longer as the adsorption temperature was elevated.

The results presented in **Figure 10** indicate that the accumulative CO₂ loading, which is the percentage of CO₂ loading at specific time in comparison with the loading at the end of test, as well as the CO₂ concentration in the effluent, increased dramatically at the first few minutes and slightly changed after the breakthrough. The CO₂ concentration in the effluent mostly reached its feed gas level, while, the accumulative CO₂ loading continued to increase. As discussed earlier, although the breakthrough was observed, the CO₂ concentration in effluent was almost similar to that in influent, the adsorption is still occurring until equilibrium. This results in the continuous increase in accumulative CO₂ loading.

In **Figure 10**, the CO₂ loading percentage at the breakthrough is intercept between the accumulative CO₂ loading curve and a vertical dashed line which originates from the breakthrough point. If considering the breakthrough (90% CO₂ removal) as a criteria to evaluate the sorbent performance, it was found that the CO₂ loading percentage at the breakthrough was improved significantly with the rise in the adsorption temperature (**Table 2**).

The CO₂ loading at the breakthrough (**Table 2**) attained a maximum at an adsorption temperature of 70°C (6.85 wt%). The variation in the CO₂ loading at the breakthrough was

similar to the change in the breakthrough time. These results further confirmed that the adsorption rate of the sorbent was enhanced by increasing adsorption temperature. However, both the CO₂ adsorption capacity and breakthrough time tend to decrease as the adsorption temperature is above 90°C.

3.5.2. NGCC flue gas conditions

The results of kinetic studies of CO₂ adsorption from NGCC flue gas at 65°C is shown in **Figure 11**. The results are similar to the kinetic observation in the SCF flue gas. CO₂ adsorption is rapid at the beginning and the CO₂ removal efficiency reached > 98% within the first 10 min. The percentage of accumulative CO₂ loading at the breakthrough, CO₂ loading at the breakthrough, the breakthrough time, and total CO₂ loading are shown in **Table 3**.

The breakthrough time as well as the CO₂ loading at the breakthrough reached maximum value at 50°C. The change in the CO₂ loading at the breakthrough is analogous to that in the total CO₂ loading, which increases to a maximum at 50°C (7.35 wt%) and reduced at higher temperature. Though, the sorbent operating in the NGCC flue gas has a longer breakthrough time and higher CO₂ loading at the breakthrough compared to the SCF flue gas case; the maximum CO₂ loading at the breakthrough was 7.35 wt% in the NGCC flue gas compared to 6.85 wt% in the SCF flue gas, the overall CO₂ loading in the NGCC flue gas is lower than the loading in the SCF flue gas.

As discussed above, the CO₂ loading and adsorption kinetic are temperature-dependent, therefore there is a need to determine an optimum operating temperature for the adsorption process. The optimum temperature should be beneficial in regard to both the CO₂ loading and breakthrough time performance. It is evident from the experimental results presented (**Figure 8**) that the prepared sorbent can operate at a wide temperature range. However, the optimum working temperature varies with the CO₂ concentration in the flue gas. The best operating temperature for

the NGCC flue gas ranges from 50 to 80 °C (**Figure 8**, dash line) which achieved a CO₂ loading at the breakthrough from 6.56 to about 7.35 wt% and the BT from 22.4 to 23.7 min. By comparison, the optimum temperature range is higher for the SCF flue gas at about 70 to 90°C (**Figure 8**, dotted line) with a CO₂ loading at the breakthrough from 6.74 to 6.85 wt% and the BT from 4.8 to 5.0 min, respectively. The broad and relatively high working temperature has a significant effect on the CO₂ capture process in term of energy saving. It can help reduce the cooling energy required during adsorption while also makes narrower the temperature gap between the adsorption and desorption process which will help decrease the sensible heat requirement. These results indicates that the prepared sorbent is capable of effective CO₂ removal from both SCF and NGCC flue gases.

3.6. Effect of silica substrate on CO₂ loading performance

3.6.1. Effect of silica bead type

In this study, silica was used as substrates to impregnate PEI. Silica is a porous material, which is produced by acidizing a solution of sodium silicate. This type of silica is formed by a variety of tiny silica particles (primary particles) that connects together through the condensation of Si-O-Si bonding. Pores in silica are irregularly shaped and formed by gaps and empty channels within the network of silica primary particles. Two types of silica (silica spherical bead and silica gel) are usually produced. The former can be used as desiccant without any further processing as the beads are produced with desired diameters. The latter is produced as a gel and must be broken into smaller size particles that are required by specific applications. These smaller particles have irregular shapes in associated with a larger number of opening pores compared to bead type. In this study, both types of silicagel were used, impregnated with 37.5 wt% PEI and test for CO₂ adsorption performance to determine any effect incurred by the silica

type used. Adsorption and regeneration were conducted at 65°C in SCF flue gas and 110°C in humidified N₂, respectively. Results from this study are presented in **Table 4** showing the properties of 1 PEI impregnated silica spherical bead (Silica-IX) and 8 PEI impregnated silicagel samples (Silica from I to VIII).

The sorbent prepared using the silica spherical bead results in a lower CO₂ loading (10 wt%) compared to a silicagel (Silica-VII, 11.5 wt%) having similar pore size and particle size. In another experiment, the CO₂ loading of Silica-IX containing 35 wt% PEI is 8.7 wt%, which is lower than that of Silica-I containing the same PEI concentration prepared in the same MeOH solvent (9.8 wt%). These results indicate that the irregular-shaped silicagel may be a superior substrate choice for CO₂ adsorption application. The lower CO₂ loading on the spherical silica sorbent may be due to the lower surface area and pore volume of that particular substrate. Moreover, the difference in CO₂ loading between two silica substrates is most likely due to the difference in their surface properties, particularly the density and status of silanol groups (Si-OH) which affect the dispersion of the PEI into the silica structure [62, 63]. In addition, the difference in the surface conformation of the silica spherical beads and those silicagel particles also influences the impregnation of the PEI. The silica spherical beads have a convex surface; the chemical potential of atoms on such a surface is higher than that on a flat and concave surface. The silicagel particles possess irregular shapes, which have mostly flat or rough surface with a lower chemical potential compared to convex surface of spherical beads. Thus, the impregnation of the PEI on the silicagel particles is more effective than that on the spherical beads.

3.6.2. Effect of the pore size and particle size

The porous properties of silica *i.e.* pore volume and pore size in particular, have significant influence on the PEI impregnation and the CO₂ adsorption performance of the

resulting sorbent. The above discussion indicated that the silicagel particles are more favorable to the PEI impregnation than the spherical ones; thus silicagel particles were used to investigate the effect of the pore size on the CO₂ adsorption capacity. Most silicagels selected for this study had similar pore volume ranging from 1.1–1.2 cm³/g, while BET surface area and pore size vary from 155–353 m²/g and 113–320 Å, respectively. The pore size distributions of silica impregnated with 37.5 wt% PEI using EtOH were presented in Figure S2 and 3. Table 4 presents the result obtained from this study and shows no clear relation between the BET surface area and the CO₂ loading of the sorbent. However, the pore size and particle size have a very pronounced effect on the CO₂ loading. Silica-VIII has the largest pore size among the samples investigated (320 Å) and the associated sorbent has the highest CO₂ loading. In general, the results show that the irregular-shaped silicagels with larger pore size result in sorbent with higher CO₂ loading capacity.

To investigate the effect of particle size on an adsorbent's CO₂ adsorption, the silicagel was categorized into three groups of closely related average pore sizes. The first group includes Silica-II and Silica-III with average pore sizes 113.2 and 122.9 Å, respectively. The second group consists of 4 samples with average pore sizes ranging from 150 to 155 Å (Silica-I, Silica-IV, Silica-V, and Silica-VI). The third group has two samples with an average pore size 284 and 320 Å (Silica-VII and Silica-VIII). In the group 1 and 2, test results indicate a similar trend in the influence of the particle size on the CO₂ loading capacity, *i.e.* the CO₂ loading was enhanced by reduction in the silica particle size. However, this effect was not observed in group 3. Thus, the variation in the silica particle size has a great effect on the CO₂ adsorption performance of the prepared sorbent. This effect is more apparent and pronounced in the silica with small pore diameters.

Average pore size due to the PEI impregnation was reduced on all silica samples with average pore size below 155 Å and Silica-VIII with larger average pore size (320 Å) but large particle size (200-500 µm). The pore size reduction was, however, not observed on Silica-VII and IX, which have large pore size and small particle size (Table 4). It is not clear, but likely that the larger fraction of small pores in the small particles was filled with PEI in comparison with large particles, which results in the shift of pore size distribution toward larger pore sizes.

3.7. Long-term operation and the effect of impurities on CO₂ loading performance

In commercial application, sorbents should be durable and tolerate high temperature and chemical impurities in order to maintain desirable CO₂ adsorption capacities, selectivity, and adsorption kinetics over long term operation under relevant process conditions. In this study, the stability of prepared sorbents (Silica-I) was evaluated after long-term operation in the packed-bed reactor under SCF and NGCC flue gas conditions. Adsorption and regeneration temperatures were kept at 65 and 110°C, respectively for every cycle. Moreover, the effect of SO₂ impurity on the sorbent performance was evaluated by adding different SO₂ concentration into the SCF flue gas. As exhibited in **Figure 12**, the adsorption capacity of the sorbent operating in “clean” flue gas (i.e. without SO₂) slowly drops by 16.6 % after 335 cycles in SCF flue gas (**Figure 12A**) and by 7.6 % after 265 cycles in NGCC flue gas (**Figure 12B**).

The adsorption capacity is higher in the SCF flue gas, but the rate of CO₂ loading loss is faster; 13.4 % for the SCF flue gas compared to much lower 7.6 % loss rate for NGCC flue gas after 265 cycles. Since the CO₂ concentration in SCF flue gas (14.7 vol%) is higher than that in NGCC flue gas (3 vol%), while the O₂ content in SCF flue gas (4.5 vol %) is much lower (14 vol % in NGCC flue gas), the faster degradation rate in the SCF flue gas is most likely due to a

higher CO₂ concentration in the flue gas which may accelerate the formation of heat-stable urea [51].

In a commercial power plant, SCF flue gas will contain a certain amount of SO₂, the level of which is usually dependent on the type of coal used and the desulfurized technology (if any) deployed at the power plant. Similar to aqueous amine solvents, SO₂ can deactivate a solid sorbent by irreversibly reacting with amino sites to form a product which is not regenerable at desired process conditions and will lead to a reduction of the CO₂ loading. The effect that SO₂ has on CO₂ adsorption performance can be seen in **Figure 12C** and **12D**. CO₂ loading was dramatically reduced as the SO₂ impurity was introduced into the flue gas. SCF flue gas containing 50 ppm SO₂ caused 43.4% loss in the CO₂ loading after 108 adsorption-regeneration cycles (**Figure 12C**). The impact was more severe using a SO₂ concentration of 200 ppm in the SCF flue gas, resulting in 60.1% of the CO₂ loading lost after only 88 cycles (**Figure 12D**). Photos of the sorbent before and after long-term operation test, shown in **Figure 12** (inset), provide a visual observation of the sorbent degradation. These pictures show that the original white sorbent darkens after 335 cycles in “clean” SCF flue, but turned yellowish-brown with the addition of SO₂ into the flue gas. It is apparent from these results that the presence of SO₂ in the flue gas is a critical issue that will affect the solid adsorbent-based CO₂ capture process at commercial scale. The SO₂ concentration in flue gas varies and can reach above 200 ppm depending on the types of coal and selected technology of power plant [64]. Thus, a deep desulfurization system to eliminate SO₂ will likely be required for application in coal-fired power plants. However, the desulfurization can be omitted for a natural gas combined cycle power plant because the flue gas from such a power plant contains a negligible amount of SO₂.

3.8. Fluidization study

3.8.1. Fluidization with N_2 gas

Fluidization tests were conducted with N_2 to investigate the fluidization behavior of the CO_2 adsorbent. The sorbent used for these experiments is silica-VI impregnated with various PEI concentrations. Small, smooth bubbles were observed when the minimum fluidization velocity (μ_{mf}) for the sorbent bed was achieved suggesting that this adsorbent falls into the category of Geldart B particles [65, 66]. **Figure 13** exhibits the variation in pressure drop across the column as a function of increasing superficial gas velocity.

At the beginning of this experiment, the pressure drop increased dramatically with the superficial gas velocity until the μ_{mf} , it is around 0.5 (m/s), was achieved and the fluidization was occurred. Following this point, the pressure drop became constant irrespective of the increase in the superficial gas velocity at least until the superficial gas velocity reached 3 m/s then rose with increasing superficial gas velocity. These results indicated that the smooth fluidization only occurs between minimum fluidization velocity 0.5 and 3 m/s. At higher superficial gas velocities the process is dominated by bubbling-slugging fluidization. Therefore, the superficial gas velocity of 3 m/s is considered as minimum slugging velocity (μ_{ms}). The difference in these two fluidization regimes can visually observed in the pictures shown in **Figure 13** (inset **A** and **B**). The same fluidization behavior was observed on the adsorbent containing 35 and 37.5 wt% PEI. Moreover, the fluidization behavior of the sorbent with N_2 is not influenced by a change in the temperature. As shown in **Figure 14**, similar fluidization was obtained at 50, 75 and 110°C.

A recent study on the fluidization of PEI impregnated mesoporous silica published by Zhang et al [67] indicated that the sorbent smoothly fluidized between minimum air flow rate and up to 10 L/min (equal a superficial gas velocity of 4.73 m/s). This maximum superficial gas velocity for a smooth fluidization is higher than μ_{ms} in the current study (3 m/s). The fluidization

of the sorbent is mostly affected by particle size, density, interaction between particles and column wall. It is likely that the change in the fluidization behavior with increasing superficial gas velocity is resulted from the interaction among PEI impregnated silica particles and aggregates. The particles tend to stick together due to the cohesiveness of the PEI. At a gas velocity below μ_{ms} , the collision is not strong enough to stick a large amount of particles, thus the process fluidizes smoothly. At gas velocity greater than μ_{ms} , the particles and aggregates have high kinetic energy and the collision of such particles and aggregates results in the formation of larger aggregates. Those larger aggregates enhance the interaction between aggregates and the wall of fluidization column causing slugging in the fluidizing bed and the increase in pressure drop. Thus, above μ_{ms} the fluidization of the sorbent is similar to that of Geldart D particles [66].

3.8.2. *Fluidization with simulated flue gas*

Above discussion indicated that adsorbent exhibits fluidization at a superficial gas velocities below μ_{ms} and bubbling slugging fluidization at superficial gas velocities beyond μ_{ms} with dry N_2 gas. The characteristics of dry N_2 gas, however, are much different with that of the flue gas, which contains a certain amount of water vapor. The PEI impregnated silica can adsorb the water from flue gas and changes the properties, the density in particular [22]. Increasing in the sorbent humidity will enhance the interaction among particles as well as the interaction between particles and column wall, which will cause the change in sorbent's fluidization characteristics. Moreover, the fluidization in flue gas usually occurs at the same time with the adsorption of CO_2 on the sorbent, therefore, the fluidization of the sorbent in flue gas needs to be investigated.

In this experiment, fluidization tests were continued by using a simulated flue gas with a composition of CO₂ ~15 vol% and humidity ~8 vol% in balance with N₂ at different temperatures. It was postulated that the sorbent may become more cohesive with higher PEI concentration, particularly in the presence of water vapor; therefore, the fluidization of sorbent containing 30, 35, and 37.5 wt% PEI were examined. Initially, the experiments were carried out at 75°C to determine the variation in the pressure drop with increasing superficial gas velocity. The tests were started with a gas velocity of 2 m/s since a lower velocity could not be established due to a limitation of the minimum flow rate of the quantitative pump. Pressure drop change, with increasing gas velocity, were recorded at 75°C with sorbents of various PEI content as is depicted in **Figure 15**.

Results of these experiments revealed that the sorbent fluidization behavior varies with changing PEI content. Interestingly, the increase in the pressure drop for the 30 wt% PEI sorbent is more rapid than the ones containing 35 and 37.5 wt% PEI. This, however, does not prove that fluidization behavior is better for samples containing higher PEI loadings. Actually, visual observation during these experiments indicated that the 30 wt% PEI sorbent exhibited superior fluidization behavior with a smooth bubbling regime at a relatively low gas velocity, which was then associated with slugging at a higher velocity. In contrast, smooth fluidization was not visually observed in higher PEI loading sorbents, instead of fluidization, the bed expanded, and particles became adhesive and connected together to form an aggregate network. The kinetic energy provided by the gas flow is not strong enough to break down this aggregate network. In this situation, an extra energy is usually applied to separate the particles from bigger aggregates. Several researches have tried different methods to improve the fluidization of cohesive particles including vibration, mixing, and sound assistance [68-72]. In this work, the tests were conducted

at different temperatures from 75 to 110°C to investigate the possibility to minimize this effect and improve the fluidization. Visual observations indicate that the 30 wt% PEI sorbent fluidized well at this temperature range. However, the 35 wt% PEI sorbent fluidized at a temperature greater than 90°C, meanwhile 37.5 wt% sorbent did not fluidized at this temperature range. These results further confirm the effect of water vapor in the flue gas and the PEI content on the fluidization behavior of the sorbent. In fact, water vapor in the flue gas plays a significantly important role in a CO₂ capture process; it does not only help improve the CO₂ adsorption capacity, but also lessens the degradation of the sorbent [51]. To attain good fluidization, the PEI concentration of the sorbent should be taken in consideration and the optimal concentration, based on this studies, should be between 30-35 wt% PEI.

3.8.3. *Fluidization with steam*

As highlighted before, the fluidization of the sorbent is considerably influenced by the presence of water vapor in the flue gas. In commercial application of this solid sorbent technology, the regeneration process is envisioned to be carried out by flowing steam or water vapor-enriched gas through regenerator at a desired temperature. It is theorized that fluidization of PEI impregnated silica under such conditions may prove to be challenging. In this study, the fluidization behavior of different sorbents containing 30, 35, and 37.5 wt% PEI under steam was investigated at 110°C, a frequently-used temperature for the regeneration process. The fluidization results from these experiments are shown in **Figure 16**.

As seen in this figure, the samples containing 30 and 35 wt% PEI fluidized well, while the sample containing 37.5 wt% PEI slugged significantly at the range of gas velocities studied. Obviously, the sorbent containing 37.5 wt% PEI becomes more cohesive in the presence of water vapor, resulting in stronger interaction among particles and formation of larger aggregates. In

contrast to previous fluidization tests with simulated flue gas that form porous channels in the sorbent bed, fluidization with the steam causes significant slugging, causing the sorbent bed to be lifted up as the steam flow is applied. These results further confirmed that the prepared sorbents can be regenerated in a fluidized bed reactor using steam, but PEI impregnated concentration on the sorbent has an important effect on the fluidization behavior in the presence of water vapor.

3.8.4. Adsorption-regeneration cycle in the fluidized-bed reactor

In addition to performing fluidization experiments, the fluidized-bed reactor (FBR) was also used for CO₂ adsorption-regeneration testing. In a typical adsorption-regeneration cycle, the sorbent was first fluidized with N₂ at a desired velocity to stabilize the fluidization bed while the bed temperature was raised up to 75°C. Upon reaching the temperature set point, the feed gas was switched to the simulated flue gas (~18% CO₂ and ~10% H₂O in balance with N₂) and the adsorption stage started. After few minutes, the CO₂ concentration in the effluent started rising and the adsorption stage was complete when the CO₂ concentration in the effluent approached an asymptote. After steady-state achieved, the temperature of the fluidization column was elevated to 110°C for the regeneration stage. In parallel, the feed gas composition was slowly changed by adding more steam and reducing CO₂ and N₂. As temperature reached a setting point, the feed gas was completely replaced by the steam and the CO₂ concentration observed in the effluent was 100 vol% - indicating that the sorbent regeneration was occurring. Finally, the feed gas was slowly switched to N₂ at the same temperature for about 20 min to dry the adsorbent and begin another cycle. Variation in the CO₂ concentration in the effluent and CO₂ removal efficiency in a typical adsorption-regeneration cycle is presented in **Figure 17**.

Within the early stage of the adsorption, no CO₂ was detected in the effluent and the removal efficiency was 100 %, indicating that the sorbent worked well in the fluidized bed

reactor. After the breakthrough point (approximately 5 min), the CO₂ concentration in the effluent increased and nearly reached equilibrium after 30 min. In the regeneration stage, as temperature was elevated, the CO₂ concentration in the effluent increased until 100 % CO₂ was detected. This result confirms that the prepared sorbent is suitable for CO₂ capture from flue gas using the fluidized-bed reactor.

Previous study on technical and economical evaluation of a CO₂ capture process based on PEI-impregnated adsorbent indicated that a process based on fluidized-bed reactors helps reduce capital cost (21%), cost of electricity (81.7 compared to 85 \$/kWh), and cost of CO₂ avoided (62 compared to 69.8\$/ton) in comparison with a conventional process based on aqueous ethanolamine (MEA) 30 wt% [73]. Fluidized-bed reactors were designed to capture 90% of CO₂ in the NGCC flue gas operating at 70 and 110 °C for adsorption and regeneration, respectively. The obtained results based on the assumption that the sorbent should be fluidizable and have CO₂ adsorption capacity of 8 wt%. The sorbent prepared in the current study has CO₂ loading above 8 wt% at the same adsorption and regeneration temperatures of previous research [73] and fluidize well in both flue gas and steam. This suggests that PEI-impregnated silicagel could be a promising adsorbent, which may help reduce the cost of CO₂ capture in comparison with a conventional aqueous amine solution (MEA 30 wt%).

4. Conclusion

An advanced solid CO₂ sorbent has been successfully prepared by the impregnation of PEI onto mesoporous silica. The obtained sorbent is relatively stable under the heat treatment and starts decomposing at a temperature of ~170°C. The sorbent CO₂ capacity can be improved by increasing the PEI impregnated content up to 40 wt%. However, above this concentration, the CO₂ loading is not improved.

The CO₂ adsorption-regeneration performances are greatly affected by the operation temperature in both SCF and NGCC flue gases. The optimal adsorption temperatures are from 50 to 80°C for NGCC flue gas and from 70 to 90 °C for SCF flue gas, while the optimal regeneration temperatures are from 110 to 130°C for both flue gas. At this condition, the sorbent also has an optimal CO₂ adsorption kinetics with longer breakthrough time and higher CO₂ loading at the breakthrough.

The sorbent exhibits a relatively stable CO₂ adsorption performance for multiple adsorption-regeneration cycles. The loss in CO₂ loading was 16.6 % for 335 cycles operating with the SCF flue gas and 7.6 % for 265 cycles operating with the NGCC flue gas. The lifetime of the sorbent is, however, significantly affected by SO₂ impurity in the flue gas. SO₂ at a concentration of 50 ppm caused 43.4 % CO₂ loading capacity loss after 108 cycles and a concentration of 200 ppm resulted in 60.1 % CO₂ loading capacity loss after 88 cycles.

Regardless of the operating temperature, the sorbent displays a bubbling fluidization regime under dry N₂ gas, but it exhibits a dependence on temperature and PEI impregnated concentration while fluidizing with a humid gas. Sorbent with 30 wt% PEI fluidized well at temperatures from 75 to 110°C, however, sorbent containing 35 wt% PEI, only fluidized at temperatures above 90°C. The effect of having higher PEI concentration becomes more severe when fluidizing with water vapor, in fact, no fluidization was observed on a sorbent containing 37.5 wt % PEI.

In conclusion, PEI impregnated mesoporous silicas are promising sorbents for CO₂ capture from both coal-fired power and natural gas combined cycle power plants. These materials have significant scalability potential due to a simple wet impregnation method as well as cheap raw materials. These sorbents have a relatively high adsorption capacity that can be

maintained for a long-term operation. Also, they are fluidizable with both simulated flue gas (adsorption stage) and steam (regeneration stage) indicating that they could be suitable for a CO₂ capture process using a fluidized bed reactor.

Nomenclature

ASAP 2020	Micromeritics Surface and Porosity Analyzer
BJH	Barrett-Joyner-Halenda method
BT	Breakthrough time
CCS	Carbon Capture & Sequestration
DI	Deionized water
MeOH	Methanol
EtOH	Ethanol
<i>i</i> PrOH	Isopropanol
MEA	Ethanolamine
NGCC	Natural gas combined cycle power plant
PBR	Fluidized-bed reactor
PBR	Packed-bed reactor
PEI	Polyethyleneimine
SCF	Coal fired power plant
TGA	Thermal Gravimetric Analysis
μ_{mf}	Minimum fluidization velocity
μ_{ms}	Minimum slugging velocity

Acknowledgement

This study was supported by grant from Abu Dhabi Clean Energy, Masdar Company, UAE (12KZOA1) and Department of Energy, USA (DE-FE0007707).

References

[1] A.B. Rao, E.S. Rubin, A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control, *Environmental Science & Technology*, 36 (2002) 4467-4475.

- [2] A.M. Wolsky, E.J. Daniels, B.J. Jody, CO₂ Capture from the flue gas of conventional fossil-fuel-fired power plants, *Environmental Progress*, 13 (1994) 214-219.
- [3] B.P. Mandal, A.K. Biswas, S.S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine, *Chemical Engineering Science*, 58 (2003) 4137-4144.
- [4] B.P. Mandal, S.S. Bandyopadhyay, Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine, *Chemical Engineering Science*, 61 (2006) 5440-5447.
- [5] G. Maurin, P.L. Llewellyn, R.G. Bell, Adsorption Mechanism of Carbon Dioxide in Faujasites: Grand Canonical Monte Carlo Simulations and Microcalorimetry Measurements, *The Journal of Physical Chemistry B*, 109 (2005) 16084-16091.
- [6] R. Serna-Guerrero, Y. Belmabkhout, A. Sayari, Modeling CO₂ adsorption on amine-functionalized mesoporous silica: 1. A semi-empirical equilibrium model, *Chemical Engineering Journal*, 161 (2010) 173-181.
- [7] Z.-l. Liu, Y. Teng, K. Zhang, Y. Cao, W.-p. Pan, CO₂ adsorption properties and thermal stability of different amine-impregnated MCM-41 materials, *Journal of Fuel Chemistry and Technology*, 41 (2013) 469-475.
- [8] S.-T. Yang, J.-Y. Kim, J. Kim, W.-S. Ahn, CO₂ capture over amine-functionalized MCM-22, MCM-36 and ITQ-2, *Fuel*, 97 (2012) 435-442.
- [9] M. Bhagiyalakshmi, L. Yun, R. Anuradha, H. Jang, Synthesis of chloropropylamine grafted mesoporous MCM-41, MCM-48 and SBA-15 from rice husk ash: their application to CO₂ chemisorption, *J Porous Mater*, 17 (2010) 475-484.
- [10] D.V. Quang, A.V. Rabindran, N. El Hadri, M.R. Abu-Zahra, Reduction in the regeneration energy of CO₂ capture process by impregnating amine solvent onto precipitated silica, *European Scientific Journal*, 9 (2013).
- [11] Y. Fan, R.P. Lively, Y. Labreche, F. Rezaei, W.J. Koros, C.W. Jones, Evaluation of CO₂ adsorption dynamics of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption, *International journal of greenhouse gas control*, 21 (2014) 61-71.

- [12] D.H. Jo, H. Jung, D.K. Shin, C.H. Lee, S.H. Kim, Effect of amine structure on CO₂ adsorption over tetraethylenepentamine impregnated poly methyl methacrylate supports, *Separation and Purification Technology*, 125 (2014) 187-193.
- [13] M.A. Alkhabbaz, R. Khunsupat, C.W. Jones, Guanidinylated poly(allylamine) supported on mesoporous silica for CO₂ capture from flue gas, *Fuel*, 121 (2014) 79-85.
- [14] Y.G. Ko, H.J. Lee, H.C. Oh, U.S. Choi, Amines immobilized double-walled silica nanotubes for CO₂ capture, *Journal of Hazardous Materials*, 250–251 (2013) 53-60.
- [15] Y.G. Ko, H.J. Lee, J.Y. Kim, U.S. Choi, Hierarchically Porous Aminosilica Monolith as a CO₂ Adsorbent, *ACS Applied Materials & Interfaces*, 6 (2014) 12988-12996.
- [16] K. Wang, H. Shang, L. Li, X. Yan, Z. Yan, C. Liu, Q. Zha, Efficient CO₂ capture on low-cost silica gel modified by polyethyleneimine, *Journal of Natural Gas Chemistry*, 21 (2012) 319-323.
- [17] D.W.F. Brilman, R. Veneman, Capturing Atmospheric CO₂ Using Supported Amine Sorbents, *Energy Procedia*, 37 (2013) 6070-6078.
- [18] G. Qi, Y. Wang, L. Estevez, X. Duan, N. Anako, A.-H.A. Park, W. Li, C.W. Jones, E.P. Giannelis, High efficiency nanocomposite sorbents for CO₂ capture based on amine-functionalized mesoporous capsules, *Energy & Environmental Science*, 4 (2011) 444-452.
- [19] G. Qi, L. Fu, B.H. Choi, E.P. Giannelis, Efficient CO₂ sorbents based on silica foam with ultra-large mesopores, *Energy & Environmental Science*, 5 (2012) 7368-7375.
- [20] C. Chen, W.-J. Son, K.-S. You, J.-W. Ahn, W.-S. Ahn, Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity, *Chemical Engineering Journal*, 161 (2010) 46-52.
- [21] Y. Labreche, R.P. Lively, F. Rezaei, G. Chen, C.W. Jones, W.J. Koros, Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture, *Chemical Engineering Journal*, 221 (2013) 166-175.
- [22] D.V. Quang, A. Dindi, A.V. Rayer, N.E. Hadri, A. Abdulkadir, M.R. Abu - Zahra, Effect of moisture on the heat capacity and the regeneration heat required for CO₂ capture process using PEI impregnated mesoporous precipitated silica, *Greenhouse Gases: Science and Technology*, (2014).
- [23] J.-Y. Kim, J. Kim, S.-T. Yang, W.-S. Ahn, Mesoporous SAPO-34 with amine-grafting for CO₂ capture, *Fuel*, 108 (2013) 515-520.

- [24] B. Dutcher, M. Fan, S. Cui, X.-D. Shen, Y. Kong, A.G. Russell, P. McCurdy, M. Giotto, Characterization and stability of a new, high-capacity amine-functionalized CO₂ sorbent, *International journal of greenhouse gas control*, 18 (2013) 51-56.
- [25] O. Cheung, Z. Bacsik, Q. Liu, A. Mace, N. Hedin, Adsorption kinetics for CO₂ on highly selective zeolites NaKA and nano-NaKA, *Applied Energy*, 112 (2013) 1326-1336.
- [26] N.A. Rashidi, S. Yusup, H.L. Lam, Kinetic studies on carbon dioxide capture using activated carbon, *Chemical Engineer Transaction*, 35 (2013) 361-366.
- [27] B. Guo, L. Chang, K. Xie, Adsorption of Carbon Dioxide on Activated Carbon, *Journal of Natural Gas Chemistry*, 15 (2006) 223-229.
- [28] T.L.P. Dantas, F.M.T. Luna, I.J. Silva Jr, D.C.S. de Azevedo, C.A. Grande, A.E. Rodrigues, R.F.P.M. Moreira, Carbon dioxide–nitrogen separation through adsorption on activated carbon in a fixed bed, *Chemical Engineering Journal*, 169 (2011) 11-19.
- [29] M.S. Shafeeyan, W.M.A.W. Daud, A. Houshmand, A. Shamiri, A review on surface modification of activated carbon for carbon dioxide adsorption, *Journal of Analytical and Applied Pyrolysis*, 89 (2010) 143-151.
- [30] M. Auta, N.D. Amat Darbis, A.T. Mohd Din, B.H. Hameed, Fixed-bed column adsorption of carbon dioxide by sodium hydroxide modified activated alumina, *Chemical Engineering Journal*, 233 (2013) 80-87.
- [31] C. Chen, W.-S. Ahn, CO₂ capture using mesoporous alumina prepared by a sol–gel process, *Chemical Engineering Journal*, 166 (2011) 646-651.
- [32] J.A. Thote, R.V. Chatti, K.S. Iyer, V. Kumar, A.N. Valechha, N.K. Labhsetwar, R.B. Biniwale, M.K.N. Yenkie, S.S. Rayalu, N-doped mesoporous alumina for adsorption of carbon dioxide, *Journal of Environmental Sciences*, 24 (2012) 1979-1984.
- [33] V. Nafisi, M.-B. Hägg, Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO₂ capture, *Journal of Membrane Science*, 459 (2014) 244-255.
- [34] T.O. Nelson, L.J.I. Coleman, A. Kataria, M. Lail, M. Soukri, D.V. Quang, M.R.M.A. Zahra, Advanced Solid Sorbent-Based CO₂ Capture Process, *Energy Procedia*, 63 (2014) 2216-2229.
- [35] X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO₂ Capture, *Energy & Fuels*, 16 (2002) 1463-1469.

- [36] X. Xu, C. Song, J.M. Andrésen, B.G. Miller, A.W. Scaroni, Preparation and characterization of novel CO₂ “molecular basket” adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, *Microporous and Mesoporous Materials*, 62 (2003) 29-45.
- [37] C. Song, X. Xu, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel Nanoporous “Molecular Basket” Adsorbent for CO₂ Capture, in: J.-S.C. Sang-Eon Park, L. Kyu-Wan (Eds.) *Studies in Surface Science and Catalysis*, Elsevier 2004, pp. 411-416.
- [38] X. Xu, C. Song, B.G. Miller, A.W. Scaroni, Influence of Moisture on CO₂ Separation from Gas Mixture by a Nanoporous Adsorbent Based on Polyethylenimine-Modified Molecular Sieve MCM-41, *Industrial & Engineering Chemistry Research*, 44 (2005) 8113-8119.
- [39] C. Song, Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing, *Catalysis Today*, 115 (2006) 2-32.
- [40] X. Ma, X. Wang, C. Song, “Molecular Basket” Sorbents for Separation of CO₂ and H₂S from Various Gas Streams, *Journal of the American Chemical Society*, 131 (2009) 5777-5783.
- [41] X. Wang, V. Schwartz, J.C. Clark, X. Ma, S.H. Overbury, X. Xu, C. Song, Infrared Study of CO₂ Sorption over “Molecular Basket” Sorbent Consisting of Polyethylenimine-Modified Mesoporous Molecular Sieve, *The Journal of Physical Chemistry C*, 113 (2009) 7260-7268.
- [42] D.V. Quang, A. Dindi, A.V. Rayer, N.E. Hadri, A. Abdulkadir, M.R.M. Abu-Zahra, Impregnation of Amines Onto Porous Precipitated Silica for CO₂ capture, *Energy Procedia*, 63 (2014) 2122-2128.
- [43] A.D. Ebner, M.L. Gray, N.G. Chisholm, Q.T. Black, D.D. Mumford, M.A. Nicholson, J.A. Ritter, Suitability of a Solid Amine Sorbent for CO₂ Capture by Pressure Swing Adsorption, *Industrial & Engineering Chemistry Research*, 50 (2011) 5634-5641.
- [44] G.P. Knowles, J.V. Graham, S.W. Delaney, A.L. Chaffee, Aminopropyl-functionalized mesoporous silicas as CO₂ adsorbents, *Fuel Processing Technology*, 86 (2005) 1435-1448.
- [45] R.A. Khatri, S.S.C. Chuang, Y. Soong, M. Gray, Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO₂ Capture, *Energy & Fuels*, 20 (2006) 1514-1520.
- [46] G. Calleja, R. Sanz, A. Arencibia, E.S. Sanz-Pérez, Influence of Drying Conditions on Amine-Functionalized SBA-15 as Adsorbent of CO₂, *Top Catal*, 54 (2011) 135-145.
- [47] Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, Amine-bearing mesoporous silica for CO₂ removal from dry and humid air, *Chemical Engineering Science*, 65 (2010) 3695-3698.

- [48] P. Bollini, S. Choi, J.H. Drese, C.W. Jones, Oxidative Degradation of Aminosilica Adsorbents Relevant to Postcombustion CO₂ Capture, *Energy & Fuels*, 25 (2011) 2416-2425.
- [49] A. Heydari-Gorji, A. Sayari, Thermal, Oxidative, and CO₂-Induced Degradation of Supported Polyethylenimine Adsorbents, *Industrial & Engineering Chemistry Research*, 51 (2012) 6887-6894.
- [50] C.S. Srikanth, S.S.C. Chuang, Spectroscopic Investigation into Oxidative Degradation of Silica-Supported Amine Sorbents for CO₂ Capture, *ChemSusChem*, 5 (2012) 1435-1442.
- [51] A. Sayari, Y. Belmabkhout, Stabilization of Amine-Containing CO₂ Adsorbents: Dramatic Effect of Water Vapor, *Journal of the American Chemical Society*, 132 (2010) 6312-6314.
- [52] A. Sayari, A. Heydari-Gorji, Y. Yang, CO₂-Induced Degradation of Amine-Containing Adsorbents: Reaction Products and Pathways, *Journal of the American Chemical Society*, 134 (2012) 13834-13842.
- [53] T.C. Drage, A. Arenillas, K.M. Smith, C.E. Snape, Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies, *Microporous and Mesoporous Materials*, 116 (2008) 504-512.
- [54] F. Rezaei, C.W. Jones, Stability of Supported Amine Adsorbents to SO₂ and NO_x in Postcombustion CO₂ Capture. 2. Multicomponent Adsorption, *Industrial & Engineering Chemistry Research*, 53 (2014) 12103-12110.
- [55] M.W. Hahn, M. Steib, A. Jentys, J.A. Lercher, Mechanism and Kinetics of CO₂ Adsorption on Surface Bonded Amines, *The Journal of Physical Chemistry C*, 119 (2015) 4126-4135.
- [56] R. Sanz, G. Calleja, A. Arencibia, E.S. Sanz-Pérez, CO₂ adsorption on branched polyethyleneimine-impregnated mesoporous silica SBA-15, *Applied Surface Science*, 256 (2010) 5323-5328.
- [57] D.V. Quang, A.V. Rayer, N. El Hadri, M.R.M. Abu-Zahra, Preparation of Polyethylenimine Impregnated Mesoporous Precipitated Silica for CO₂ Capture, in: M.J.A.-M.T. Eljack (Ed.) *Proceedings of the 4th International Gas Processing Symposium*, Elsevier, Oxford, 2015, pp. 21-37.
- [58] A. Heydari-Gorji, Y. Belmabkhout, A. Sayari, Polyethylenimine-Impregnated Mesoporous Silica: Effect of Amine Loading and Surface Alkyl Chains on CO₂ Adsorption, *Langmuir*, 27 (2011) 12411-12416.

- [59] A. Zhao, A. Samanta, P. Sarkar, R. Gupta, Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study, *Industrial & Engineering Chemistry Research*, 52 (2013) 6480-6491.
- [60] A. Heydari-Gorji, A. Sayari, CO₂ capture on polyethylenimine-impregnated hydrophobic mesoporous silica: Experimental and kinetic modeling, *Chemical Engineering Journal*, 173 (2011) 72-79.
- [61] E.R. Monazam, J. Spenik, L.J. Shadle, CO₂ Desorption Kinetics for Immobilized Polyethylenimine (PEI), *Energy & Fuels*, 28 (2013) 650-656.
- [62] R.K. Iler, *The chemistry of silica*, Wiley, New York, 1979.
- [63] E.F. Vansant, P. Voort, K.C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier 1995.
- [64] Y. Tan, E. Croiset, M.A. Douglas, K.V. Thambimuthu, Combustion characteristics of coal in a mixture of oxygen and recycled flue gas, *Fuel*, 85 (2006) 507-512.
- [65] D. Geldart, Types of gas fluidization, *Powder Technology*, 7 (1973) 285-292.
- [66] D. Kunii, O. Levenspiel, *Fluidization Engineering*, Butterworth-Heinemann 1991.
- [67] W. Zhang, H. Liu, C. Sun, T.C. Drage, C.E. Snape, Performance of polyethyleneimine-silica adsorbent for post-combustion CO₂ capture in a bubbling fluidized bed, *Chemical Engineering Journal*, 251 (2014) 293-303.
- [68] J.A. Quevedo, J. Flesch, R. Pfeffer, R. Dave, Evaluation of assisting methods on fluidization of hydrophilic nanoagglomerates by monitoring moisture in the gas phase, *Chemical Engineering Science*, 62 (2007) 2608-2622.
- [69] F. Raganati, V. Gargiulo, P. Ammendola, M. Alfe, R. Chirone, CO₂ capture performance of HKUST-1 in a sound assisted fluidized bed, *Chemical Engineering Journal*, 239 (2014) 75-86.
- [70] Q. Guo, Y. Li, M. Wang, W. Shen, C. Yang, Fluidization Characteristics of SiO₂ Nanoparticles in an Acoustic Fluidized, *Chemical Engineering & Technology*, 29 (2006) 78-86.
- [71] P. Ammendola, F. Raganati, R. Chirone, Effect of operating conditions on the CO₂ recovery from a fine activated carbon by means of TSA in a fluidized bed assisted by acoustic fields, *Fuel Processing Technology*, 134 (2015) 494-501.
- [72] F. Raganati, P. Ammendola, R. Chirone, Effect of acoustic field on CO₂ desorption in a fluidized bed of fine activated carbon, *Particuology*, 23 (2015) 8-15.

[73] A. Seif El Nasr, T. Nelson, A. Kataria, M.R.M. Abu-Zahra, Benchmarking of a novel solid sorbent CO₂ capture process for NGCC power generation, International Journal of Greenhouse Gas Control, 42 (2015) 583-592.

Table captions

Table 1. Variation in adsorbent properties as a function of PEI concentration impregnated on silica (Silica I). PEI impregnation was conducted in MeOH. Adsorption and regeneration were carried out at 65°C in the SCF flue gas and 110°C in humidified N₂, respectively.

Table 2. Effect of adsorption temperature on CO₂ loading performance in SCF flue gas. Sorbent (Silica-I) contains 37.5 wt% PEI impregnated using EtOH. Regeneration were carried out at 110°C in humidified N₂.

Table 3. Effect of adsorption temperature on CO₂ loading performance in NGCC flue gas. Sorbent (Silica-I) contains 37.5 wt% PEI impregnated using EtOH. Regeneration were carried out at 110°C in humidified N₂.

Table 4. Properties of various silica substrates and their corresponding sorbents prepared by impregnation of PEI 37.5 wt% using EtOH.

Table 1.

PEI concentration (wt%)	CO ₂ loading (wt%)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)	N content (wt%)	Molar ratio of CO ₂ /N	Bulk density (g/cm ³)
0	0	300.0	1.15	150	-	-	0.39
30	8.48	115.0	0.49	109	8.77	0.31	0.56
35	9.08	88.4	0.39	113	10.20	0.28	0.61
37.5	9.59	76.0	0.32	110	11.20	0.27	0.62
40	10.50	56.0	0.30	113	11.86	0.28	0.65
45	10.47	38.8	0.17	110	13.16	0.25	0.70

Table 2.

Temperature (°C)	Breakthrough time (min)	CO ₂ loading percentage (%) at breakthrough	CO ₂ loading at breakthrough (wt%)	CO ₂ loading (wt%)
30	3.1	33.80	4.39	12.97
40	3.5	40.20	5.46	13.57
50	3.9	43.00	5.86	13.62
60	4.3	45.40	6.03	13.29
70	4.8	53.20	6.85	12.88
80	4.9	56.30	6.83	12.14
90	5.0	59.70	6.74	11.29
100	4.7	59.50	6.16	10.36

Table 3.

Temperature (°C)	Breakthrough time (min)	CO ₂ loading percentage (%) at breakthrough	CO ₂ loading at breakthrough (wt%)	CO ₂ loading (wt%)
30	16.9	71.60	6.00	8.38
50	23.3	76.33	7.35	9.63
65	22.4	79.93	7.08	8.86
80	23.7	83.79	6.56	7.83
100	19.0	76.43	4.46	5.84

Table 4.

Silica substrates		<i>Silica-I</i>	<i>Silica-II</i>	<i>Silica-III</i>	<i>Silica-IV</i>	<i>Silica-V</i>	<i>Silica-VI</i>	<i>Silica-VII</i>	<i>Silica-VIII</i>	<i>Silica-IX</i>
PEI concentration (wt%)		37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
CO ₂ loading (wt%)*		11.38	11.79	10.65	9.75	10.92	11.69	11.52	11.79	10.03
Pore size (Å)	<i>Silica</i>	150	113.2	122.9	153	152	155	284	320	287
	<i>sorbent</i>	110	106.6	115.7	129.5	137.4	116.9	345	158	318
Pore volume (cm ³ /g)	<i>Silica</i>	1.15	1.19	1.23	1.11	1.16	1.12	1.24	1.24	0.81
	<i>sorbent</i>	0.32	0.36	0.38	0.31	0.35	0.27	0.40	0.34	0.22
Surface area (m ² /g)	<i>Silica</i>	300	345.4	353.3	290	305	290	175	155	98
	<i>sorbent</i>	76	86.27	85.5	63.8	67	61.9	34.2	58.9	20.1
Tap density of sorbent (g/cm ³)	<i>Silica</i>	0.39	0.36	0.36	0.43	0.39	0.44	0.38	0.39	-
	<i>sorbent</i>	0.63	0.56	0.57	0.66	0.61	0.67	0.6	0.61	-
Silica particle size (µm)		75-150	71-144	87-200	250-500	105-175	75-250	40-63	200-500	45-75
Silica pH (suspension 5 wt%)		-	-	-	7.1	7.2	7	7.5	7.3	-
Volatile content in silica (%, 160 °C)		-	-	-	4.5	4	4.8	3.3	2.9	-

*CO₂ loading was determined using SCF flue gas. Adsorption and regeneration were conducted at 65 and 110°C, respectively.

Figure captions

Figure 1. Packed-bed reactor (PBR) illustration. A, B, C, and D is humidifier, packed bed reactor, vapor condenser, and water collector, respectively.

Figure 2. Fluidized-bed reactor (FBR) illustration. A, B, C, D, and E is steam generator, fluidization column, cyclone, condenser, and water collector, respectively.

Figure 3. Variation in BET surface area and pore volume as a function of PEI concentration impregnated onto Silica-I

Figure 4. Variation in sorbent bulk density as a function of PEI concentration impregnated on Silica-I

Figure 5. TGA profiles of silica-I and prepared sorbents

Figure 6. CO₂ loading performance of sorbents as a function of PEI concentration impregnated on Silica-I. PEI impregnation was conducted in MeOH (Silica-I). Adsorption was conducted at 65°C in the SCF flue gas and regeneration was conducted at 110°C in humidified N₂.

Figure 7. The effect of different solvents on the CO₂ loading. Tests was conducted on sorbent containing 35 wt% PEI (Silica-I). Adsorption was conducted at 65°C in the SCF flue gas and regeneration was conducted at 110°C in humidified N₂.

Figure 8. Effect of adsorption temperature on a sorbent CO₂ loading. Tests conducted on sorbents containing 37.5 wt% PEI impregnated on Silica-I using EtOH as solvent and. Sorbent was regenerated at 110°C in humidified N₂.

Figure 9. Effect of regeneration temperature on a sorbent CO₂ loading. Adsorption was conducted at 65°C on sorbents containing 37.5 wt% PEI impregnated on Silica-I using EtOH as solvent.

Figure 10. CO₂ adsorption kinetics at 30°C, 60°C, 80°C and 100°C. Tests conducted with SCF flue gas on sorbents containing 37.5 wt% PEI impregnated on Silica-I.

Figure 11. CO₂ adsorption kinetics at 65°C. Tests conducted with NGCC flue gas on adsorbents containing 37.5 wt% PEI impregnated on Silica-I.

Figure 12. Long-term CO₂ adsorption performance stability of sorbents (Silica-I) containing 37.5 wt% PEI operating in SCF and NGCC flue gas environments.

Figure 13. Fluidization behavior of the adsorbent (Silica-VI) in N₂ gas at 75°C

Figure 14. Fluidization behavior of the adsorbent (Silica-VI) in N₂ gas at different temperatures.

Figure 15. Fluidization behavior of various PEI-loaded sorbents (**Silica-VI**) in simulated flue gas at 75°C

Figure 16. Fluidization behavior of various PEI-loaded adsorbents (**Silica-VI**) in steam at 110°C

Figure 17. A typical adsorption-regeneration cycle in the FBR. Test conducted on adsorbent containing 30 wt% PEI impregnated on Silica-VI.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Fi

gure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14.

Figure 15.

Figure 16.

Figure 17.

Investigation of CO₂ Adsorption Performance and Fluidization Behavior of Mesoporous Silica Supported Polyethylenimine