

## **CARBON DIOXIDE CAPTURE BY ADSORPTION (REVIEW)**

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*Received 13 May 2016*

*Accepted 01 September 2016*

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### **ABSTRACT**

*The present paper reviews the different types of adsorbents that could be used for CO<sub>2</sub> capture from flue gases. They include carbon-based adsorbents, zeolites, molecular sieves, metal-organic frameworks, hydrotalcite-like compounds and advanced adsorbents. Their possibilities are described and confronted. In particular, it has been demonstrated that classical adsorbent materials need further functionalization or impregnation with different nitrogen-containing species in order to become suitable for CO<sub>2</sub> capture. The different methods for CO<sub>2</sub> capture by adsorption cyclic processes such as Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (PSA), Thermal Swing Adsorption (TSA), Electric Swing Adsorption (ESA) as well as the combination of TSA and chemical reaction, known as Thermal Swing Sorption-Enhanced Reaction (TSSER), are also mentioned in the cited literature.*

*Keywords: carbon dioxide, adsorption.*

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### **INTRODUCTION**

Carbon dioxide is the main greenhouse gas and anthropogenic CO<sub>2</sub> emissions are almost entirely caused by the fossil fuels used to produce energy. In the quite near future, it seems necessary to reduce the CO<sub>2</sub> emissions by 30 - 60 % by 2050, compared to 2000 levels, in order to keep CO<sub>2</sub> concentration in the atmosphere below 450 parts per million by volume in order to keep the temperature raise between 2.48 and 2.88°C, compared to pre-industrialized levels [1 - 2]. Carbon dioxide capture and storage stands therefore as a CO<sub>2</sub> abatement option that can contribute substantially

to these still ambitious targets.

Largest quantities of CO<sub>2</sub> are emitted from thermo-electric power plants. There are essentially three approaches for reducing emissions associated with coal combustion [3 - 4]: the pre-combustion CO<sub>2</sub> capture, the oxy-combustion CO<sub>2</sub> capture, and the post-combustion CO<sub>2</sub> capture.

The pre-combustion CO<sub>2</sub> capture refers to the removal of carbon from fuel prior to combustion, so that the combustion does not generate CO<sub>2</sub>. The process involves converting fossil fuel or biomass into a mixture of CO<sub>2</sub> and hydrogen through the reforming of natural gas or the gasification of coal. Carbon dioxide is then

removed and captured whereas hydrogen can be used as fuel. The advantage of this approach is that it is much less expensive than the post-combustion capture process. It is characterized by relatively high pressure (up to 4 MPa) and CO<sub>2</sub> concentrations ranging from 15 to 40 %. In the pre-combustion capture, it may be preferable to use different physical solvents that combine less strongly with CO<sub>2</sub>. The advantage of such solvents is that CO<sub>2</sub> can be separated from them in the stripper mainly by reducing the pressure, which results in a lower energy consumption. The main physical solvents that can be used for CO<sub>2</sub> capture are methanol (Rectisol process), dimethyl ethers of polyethylene glycol (Selexol process), propylene carbonate (Fluor process), and sulfolane. Physical solvent scrubbing for separation of sulfur compounds is already used in large-scale integrated gasification combined cycle (IGCC) plants [5].

The process of oxy-combustion capture of CO<sub>2</sub> involves burning fossil fuels in pure oxygen as opposed to air and results in a more complete combustion. The exhaust stream consists of almost pure CO<sub>2</sub> (typically 90 %) and water vapor. In the oxy-firing process, the air is separated in oxygen and nitrogen. The main difficulty of this method lies with the separation of oxygen from the air. This is usually carried out cryogenically, which requires a lot of energy.

Gas absorption is the primary technology in post-combustion capture. Flue gases leaving a power station are cooled then fed into a CO<sub>2</sub> absorber, where they pass through an absorbing solution containing a chemical that captures CO<sub>2</sub>. Approximately 85 % of the CO<sub>2</sub> from flue gas is captured by the absorber. The CO<sub>2</sub> is then removed from the absorbing solution by steam, which allows the absorber to be reused. This process is characterized by low pressure of the flue gas (about 0.1 MPa) and the CO<sub>2</sub> concentration is typically 10 - 20 %. Currently, the prevailing methods for post-combustion removal of CO<sub>2</sub> from flue gases use chemical solvents. Historically, the first method of carbon dioxide capture was based on chemical absorption by monoethanolamines (MEA), diethanolamines (DEA) and methyldiethanolamines (MDEA). This type of storage has been used in the ammonia synthesis plants for separation of carbon dioxide from hydrogen in the synthesis gas. The amines

react rapidly, selectively, and reversibly with CO<sub>2</sub>, and are relatively nonvolatile and inexpensive but they are corrosive and require more expensive construction materials.

The chemical-looping combustion is a new technology of unmixed combustion with inherent capture of CO<sub>2</sub> that uses metal oxide particles like Fe<sub>2</sub>O<sub>3</sub>, NiO, CuO or Mn<sub>2</sub>O<sub>3</sub>, for the transfer of oxygen from the combustion air to the fuel. The system is composed of two reactors: an air reactor and a fuel one. The reduction of the metal oxide particles occurs in the fuel reactor, which allows the oxygen from the metal oxide to react with the fuel. The reduced metal oxide particle is routed, or looped, to the air reactor where oxidation of the reduced metal particle occurs thanks to an incoming stream of air. The oxidized metal particle is then looped back to the fuel reactor where it reacts again with the fuel to repeat the reduction and oxidation cycle. The reactors can be designed in a variety of ways, but two interconnected fluidized beds offer a marked advantage over alternative designs, because the process requires a good contact between gas and solids as well as a significant flow of solid material between the two reactors [6]. A promising route for post-combustion CO<sub>2</sub> capture from coal-fired power plants is to use a lime carbonation/calcination cycle called "Carbonate Looping". This process involves the separation of CO<sub>2</sub> from the flue gas of a coal-fired power plant at high temperatures (873 - 973 K) by using the reversible exothermic CaO carbonation reaction and the endothermic calcination reaction of CaCO<sub>3</sub>. This process is economically feasible when compared to other alternatives.

Membrane gas absorption provides also an efficient way for carbon dioxide recovery or removal. Membrane contactors offer a much larger contact area per unit volume than the conventional bubble columns, packed towers, Venturi scrubbers or sieve trays. The main advantage of this method is that the available contact area remains undisturbed even at high or low flow rate because the two fluid flows are independent.

Separation membranes are thin barriers that allow selective permeation of certain gases. Differences in permeation rates are generally due to the relative sizes of the permeating molecules or their solubility and/or

diffusion coefficients in the membrane material. There are different types of gas separation membranes: polymers, inorganic membranes, microporous hollow fibers.

Although chemical absorption methods actually prevail for CO<sub>2</sub> capture, the degree of absorption is always limited by the fixed stoichiometry of the chemical reaction. As a consequence, the use of this process for CO<sub>2</sub>-rich gas streams will lead to high solvent circulation flow rates and high energy requirements. Physical sorption techniques such as gas-solid adsorption permit treating gases with a low concentration of CO<sub>2</sub> and therefore assuring a high degree of gas separation that is not reachable by using any other method of CO<sub>2</sub> capture. In regard to the yet small mass transfer rate in the gas-solid system compared to the gas-liquid system, efforts are made to increase this rate. The adsorbent choice also depends on the type of combustion process. In the case of post-combustion, the gas temperature is relatively low (~ 573 K) and carbon-based adsorbents can be used. In the case of pre-combustion process, the gas formed after the fuel conversion has a high temperature (up to 973 K) and heat-resistant adsorbents must be used. Both natural and synthetic porous adsorbents are used for the separation of CO<sub>2</sub> from various gas mixtures.

The basic topic of the present study is the review of different materials which can be used as adsorbents for CO<sub>2</sub> capture.

### **Carbon-based adsorbents**

Carbon dioxide may be recovered from flue gas by using non-reactive sorbents like carbonaceous materials and zeolites. High porous materials such as activated carbons and charcoals exhibit CO<sub>2</sub> capture capacities ranging from 10 to 15 % by weight. However, the CO<sub>2</sub>/N<sub>2</sub> selectivity is relatively low. Therefore the CO<sub>2</sub> capture costs are such that the carbon-based systems can be applicable when CO<sub>2</sub> purity is not more than 90 % [7 - 8]. Zhu et al. [9] examined the adsorption on high-surface-area porous carbons synthesized by chemical activation using petroleum coke as precursor and KOH as activation agent. The maximum CO<sub>2</sub> adsorption uptake of 15.1 wt. % together with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 9.4 at 0.1 MPa were obtained for a sample activated at 973 K, which indicates its high potential for the capture

of CO<sub>2</sub>. Gil et al. [10] used phenol–formaldehyde resins and a low-cost biomass residue, olive stones, to prepare five activated carbons for CO<sub>2</sub> separation at atmospheric pressure. As a result of their study the authors obtained optimum values of activation temperature and burn-off degree that maximize CO<sub>2</sub> uptake by the activated carbons at 308 K and atmospheric pressure. The CO<sub>2</sub> adsorption capacity reached 9.3 wt. %.

Many works are based on improving the adsorptive properties of porous adsorbents by modifying their surfaces, which generally improves their basic feature. Such modifications include exchange or substitution of cations within the metal framework, chemical treatment of the surface or functionalization of the pores. The modifications usually result in a decrease of the surface area but increase the adsorptive selectivity and capacity for CO<sub>2</sub>.

Z. Yong et al. [11] studied the adsorption equilibrium of CO<sub>2</sub> on chemically modified active carbons by introducing MgO and S-CaO-MgO. The commercial superactivated carbons MSC-30 and G08H with surface areas of 3370 m<sup>2</sup>.g<sup>-1</sup> and 2250 m<sup>2</sup>.g<sup>-1</sup> respectively were used as basic activated carbon. The authors showed that the BET surface area of the chemically modified carbon samples was lower than the one of the original carbon. The results indicate that it is difficult to enhance the adsorption capacity of CO<sub>2</sub> on carbon-based adsorbent at high temperature (573 K) and relative high pressure (0.1 MPa) by introducing calcium oxide-magnesium oxide mixture only. However, the introduction of a heteroelement “S” and the increase of the polarity of carbon-based adsorbent is very favorable for the adsorption of carbon dioxide on carbon-based adsorbents at high temperature.

The high-temperature ammonia treatment of commercialized carbon CWZ-35 activated carbon was studied by Przepiorski et al. [12]. The treatment was performed for two hours at elevated temperatures (from 473 to 1273 K). The surface groups were determined by Fourier Transform Infrared Spectroscopy of solid. It was demonstrated that in comparison with pristine activated carbon, all the carbons treated with ammonia showed an enhanced ability to adsorb CO<sub>2</sub>. The authors found that the increase of adsorption capacity depends

on the treatment temperature. The sample treated at 673 K exhibited the highest ability ( $0.076 \text{ g} \cdot \text{CO}_2 \cdot \text{g}^{-1}$ ). At higher temperature, the treatment did not result in additional enhancement in adsorption and samples treated at temperatures above 673 K even showed a gradual decrease of their ability.

The use of ammonia impregnation and microwave irradiation in  $\text{N}_2$  or  $\text{H}_2$  atmosphere in order to modify the activated carbons can also enhance their  $\text{CO}_2$  adsorption capacity [13]. Plaza et al. [14] investigated the effect of the oxidation upon the  $\text{CO}_2$  capture performance with a phenolic resin carbon as the base material. Oxygen surface groups were introduced through liquid and gas phase oxidation treatments, using ammonium persulfate, nitric acid and air, respectively. They observed that the oxidized samples are easily regenerated. The authors concluded that the oxidation is a plausible modification technique for developing easy-to-regenerate carbon adsorbents with enhanced  $\text{CO}_2$  capture performance.

J. Wang et al. [15] developed a sorbent by loading polyethylenimine (PEI) on mesoporous carbons which possessed well-developed mesoporous structures and large pore volumes. The authors reported that the sorbent capture capacity with  $\text{CO}_2$  concentration was ranging from 5 % to 80 %. The optimal PEI loading was determined to be 65 wt. % with a  $\text{CO}_2$  sorption capacity of  $4.82 \text{ mmol} \cdot \text{CO}_2 \cdot \text{g}^{-1}$ -sorbent in 15 %  $\text{CO}_2/\text{N}_2$  at 348 K.

The above presented active carbons are well adapted to the carbon dioxide storage in high pressure and ambient or medium temperature when the heat effect of adsorption is important and where it is therefore necessary to eliminate the heat from the bed. But their application for the  $\text{CO}_2$  capture from the flue gas of power plants is limited.

In two articles, Menard et al. [16 - 17] reported a development of carbon monoliths, used as adsorbent media in the bed, with higher thermal conductivity than granular adsorbents. The monolith represents a composite of intensified overall thermal conductivity ( $10 \text{ W m}^{-1} \text{ K}^{-1}$ ), made of activated carbon in situ elaborated within a consolidated expanded natural graphite matrix. It was tested for  $\text{CO}_2$  adsorption both experimentally and numerically according to the adsorption step and the desorption one, respectively.

The used column was composed of an adsorbent bed packed with the tested material and of a peripheral heat exchanger. First, the authors tested the adsorption of pure  $\text{CO}_2$  at low pressures with ordinary fixed bed in order to generate the highest thermal effect close to the one encountered in the case of gas storage processes. In this case, the use of a peripheral heat exchanger presents a poor efficiency. Comparatively and under the same conditions, the composite conductive packing presents very homogeneous radial and axial temperatures and is able to withdraw the heat of sorption in a very relevant manner. With such a packing, the use of a peripheral heat exchanger leads to an increase of the storage capacity of 20 %. At intermediate  $\text{CO}_2$  concentrations and under external heat transfer, the conductive packing presents the best dynamic behavior but a lower storage capacity. However, for diluted gas streams, conventional beds of adsorbents present better performances.

In the second article, thermal regenerations of the two adsorptive beds by peripheral heating were presented. It was demonstrated that the use of the conductive composite leads systematically to enhanced performances in terms of reduced step duration, reduced radial thermal gradient (avoiding hot spots and increasing selectivity), and high desorbed gas stream concentrations. This material allows thermal regeneration without purge gas and consequently without dilution of the desorbed species. Moreover, in situ activation of the adsorbent within the graphite matrix leads to a very efficient thermal transfer between the activated carbon fraction and its conductive support. By using the proposed material, the main thermal resistance, which in conventional beds is located inside the bed, is moved from the adsorptive bed to the heat exchanger. Considering that all adsorption process is composed of the two steps, namely saturation and regeneration, the conductive composite clearly presents a general interest.

In the work of Py et al. [18], an optimization of the storage capacities of active carbons was carried out by change of carbon structure. The textural modification of conventional commercial active carbon was achieved through an original technique that consists in a series of cumulative cyclic mild-oxidation/carbonization treatments. This gives rise to a gradual erosion of the

carbonaceous structure. It was found that the materials obtained after each of the 7 first cycles present increasing mean pore sizes and microporous volumes while the subsequent 5 cycles lead to a decrease of those two parameters. Simultaneously, it was observed that the particle density decreases during the 6 first cycles and increases slightly after. Those two antagonistic behaviors of the microporous volume and of the density during the successive treatments lead to an optimal value of the whole storage capacity per volume of adsorbent bed with respect to the number of cumulated cycles. The optimal extend in textural modification was found to depend strongly on the temperature–pressure working ranges of the concerned storage application. At low temperature levels such as 273 K, the storage capacity was found to be enhanced for all considered loading pressure levels within the range from 1 to 3 MPa. The optimal number of cycles and enhancement factor increase with the loading pressure level. For example, an enhancement factor of 75 % in storage capacity was obtained at 3 MPa in the case of the RB2 (manufactured by the NORIT Company) modified by eight successive oxidative treatments [18]. At higher working temperatures (333 K), the enhancement was severely reduced but still observed for the highest loading pressure levels and very first oxidative cycles.

Thiruvengkatachari et al. [19] evaluated experimentally the possible application of large-sized honeycomb-structured monolithic carbon fiber composites (HMCFC) to CO<sub>2</sub> capture. They used simulated flue gas in 2 m long, large-sized adsorption columns. The average adsorption capacity of pure CO<sub>2</sub> on the HMCFC at ambient temperature and pressure was reported to be 11.9 wt. %.

Jang and Park [20] studied the adsorption behaviors of nickel-oxide-loaded activated carbons in the case of carbon dioxide capture. The authors showed that the implantation of nickel oxide on activated carbons led to an increase in the carbon dioxide adsorption capacity of the activated carbons.

Bezerra et al. [21] studied the impregnation of commercial adsorbents with monoethanolamine (MEA) and triethanolamine (TEA) in order to investigate the effect of the modified surface chemistry on CO<sub>2</sub> adsorption, especially above the room temperature. They compared

an impregnated carbon and 13X zeolite. The obtained results are promising and indicate that CO<sub>2</sub> adsorption may be enhanced despite high process temperatures (e.g. 348 K), if convenient impregnation and drying methods are applied.

Chen et al. [22] obtained the nitrogen-rich carbon with a hierarchical micro-mesopore structure through pyrolysis of a porous polymer prepared from terephthalaldehyde and melamine. They investigated this adsorbent as regards CO<sub>2</sub> capture. This nitrogen-rich porous carbon exhibited a CO<sub>2</sub> uptake of 141 mg g<sup>-1</sup> at 298 K, 0.1 MPa, which is one of the highest CO<sub>2</sub> capture capacities among carbons.

Cho et al. [23] investigated the possible modification of carbon molecular sieves (CMS) through oxyfluorination. Authors have found that at 298 K, the CO<sub>2</sub> adsorption capacity increased from 1.61 mmol g<sup>-1</sup> for an unmodified CMS to 2.07 mmol g<sup>-1</sup> for the oxyfluorinated CMS.

Z. Zhang et al. [24] synthesized nitrogen-containing porous carbon from an ocean pollutant, *Enteromorpha prolifera*, via hydrothermal carbonization and potassium hydroxide activation. The carbon manifested high CO<sub>2</sub> capacity and facile regeneration at room temperature.

Xia et al. [25] prepared an ordered sulfur-doped microporous carbon material by a nanocasting method. The modified carbon possesses tunable sulfur content in the range of 1.3 - 6.6 wt. %, a surface area of 729 - 1627 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.60 - 0.90 cm<sup>3</sup> g<sup>-1</sup>. The obtained results suggest that S-doped microporous carbons are potentially promising adsorbents for hydrogen and CO<sub>2</sub>.

Deng et al. [26] synthesized mesoporous carbon nitride (MCN) and carbon nitride-carbon (MCN/C) composites with a partly graphitized structure using mesoporous silica SBA-15 as a hard template and ethylenediamine and carbon tetrachloride as precursors. The synthesized MCN and MCN/C composites were used as adsorbents for CO<sub>2</sub> capture, showing both a high adsorption capacity and a good reusability.

Multiwalled carbon nanotubes (CNTs) fabricated and modified by 3-aminopropyl-triethoxysilane (APTS) solutions were also used to study thermodynamics and regeneration of CO<sub>2</sub> adsorption from gas streams [27]. The thermodynamic analysis indicated that the CO<sub>2</sub> adsorption on CNTs and CNT(APTS) is exothermic and

relates to typical physical adsorption. The cyclic CO<sub>2</sub> adsorption on CNT(APTS) showed that the adsorbed CO<sub>2</sub> can be effectively desorbed at 393 K for 25 min while the CO<sub>2</sub> adsorbed due to physical interaction can be effectively desorbed at 14600 Pa for 30 min. The adsorption capacity, the pore structure, the crystal phase, and the surface functional groups of CNT(APTS) were preserved in the 20 cycles of adsorption and regeneration. This suggests that the CNT(APTS) can be used in prolonged cyclic operation. The CNT(APTS) are thus possible cost-effective CO<sub>2</sub> sorbents in the predictable future.

Kong et al. [28] prepared the micro-nano carbonaceous composite activated carbon fiber/carbon nanotube (ACF/CNTs) by chemical vapor deposition and further modified it with branched polyethyleneimine. The CO<sub>2</sub> adsorption capacities of ACF/CNTs and ACF/CNTs-PEI proved to be 66.2 mg g<sup>-1</sup> and 98.8 mg g<sup>-1</sup>, respectively, at 303 K, which are much higher values than that of unmodified ACF (42.4 mg g<sup>-1</sup>).

Other interesting carbon-based materials with potential for CO<sub>2</sub> storage are the anthracites and the coals. In the work of Maroto-Valer et al. [29], the possible use of activated anthracites was investigated. A Pennsylvania anthracite was used for their experiments. The activation temperature was varied between 973 K and 1163 K for periods of 2 - 3.5 h. Two surface treatment methods were applied: NH<sub>3</sub> treatment and polyethylenimine impregnation. The adsorption capacity of treated anthracite samples was measured at 303; 323 and 348 K. It was shown that the NH<sub>3</sub> treatment increases the surface area of the activated samples, especially at lower temperatures of impregnation (923 K). The chemical impregnation with PEI results in a dramatic decrease of the surface area of the activated anthracite, probably due to pore blockage and surface coverage by PEI. Both the NH<sub>3</sub> treatment and the PEI impregnation increase the CO<sub>2</sub> capture capacity of the activated anthracites at higher adsorption temperature, due to the introduction of alkaline nitrogen groups on the surface. The highest CO<sub>2</sub> adsorption capacity was 65.7 mg CO<sub>2</sub> g<sup>-1</sup> for the anthracite activated at 1073 K for 2 hours.

In the paper of Di Federico et al. [30], the possible use of coal for CO<sub>2</sub> sequestration and simultaneous

production of methane was studied. The sequestration process was controlled by the maximum adsorption capacity. It was found that the tested coal adsorbs more strongly CO<sub>2</sub> than methane and nitrogen at 388 K. The obtained sorption isotherms follow the Langmuir equation.

### **Zeolites**

Zeolites, on their own, offer CO<sub>2</sub>/N<sub>2</sub> selectivity 5 to 10 times greater than those of carbonaceous materials. However, their CO<sub>2</sub> capacities are 2 to 3 times lower [31 - 33]. Moreover, zeolites performance is impaired when water vapor is present. To be competitive with liquid solvents, solid sorbents must be less sensitive to steam and must also offer substantially greater capacity and selectivity for CO<sub>2</sub> than currently available physical sorbents.

Vatalis et al. [34] studied the possible use of Greek natural zeolites for carbon dioxide capture and permanent storage.

Cheung et al. [35] investigated the carbon dioxide removal from flue gas by zeolite NaKA with a K<sup>+</sup>/(K<sup>+</sup> + Na<sup>+</sup>) ratio of 17 at. %. They concluded that this sorbent is highly selective as regards CO<sub>2</sub> over N<sub>2</sub> adsorption.

Due to their high surface area and a variety of pore sizes, zeolites are considered as good adsorbents. However, thermal destruction affects their stability at elevated temperatures and makes them useless for high-temperature CO<sub>2</sub> capture operations. In order to improve capture capacity and selectivity, chemically modified zeolites are considered as an option by using the advantage of high BET surface area and various pore sizes [36].

Introduction of alkali metals or alkaline earth on the surface of the adsorbent provides basic sites which have strong affinity for molecules of acidic gases such as carbon dioxide. J. Zhang et al. [37] studied the potential of modified chabazite zeolites by exchange with alkali cations (Li, Na, K) and alkaline-earth cations (Mg, Ca, Ba), for CO<sub>2</sub> capture from flue gas by Vacuum Swing Adsorption (VSA) for temperatures below 393 K. Equilibrium capacities of the samples had been examined by measuring isotherms for CO<sub>2</sub> and N<sub>2</sub> under

three different temperatures. The authors found that at high temperatures ( $> 370$  K), Na- and Ca-exchanged samples give the best adsorption potential for  $\text{CO}_2$  capture. The comparison with commercial Na-X zeolite showed that its adsorption potential is more significant at low temperatures ( $< 370$  K).

Many chemicals may be regarded as modification materials on zeolites. The hydrotalcite-like compounds are favorable ones and provide significant benefits.

In the paper of Othman et al. [38], the adsorption of  $\text{CO}_2$  on zeolite 5A coated by the Mg-Al hydrotalcite was studied. Authors compared the adsorption of  $\text{CO}_2$  on coated and non-coated zeolites in the temperature range between 303 K and 573 K. In both cases, they found that the coating of zeolite by hydrotalcite increases the adsorption capacity in all the temperature range.

#### **Advanced adsorbents**

Another way for carbon dioxide capture is to introduce in the porous structure of adsorbents different amines which react with  $\text{CO}_2$ . A variety of amines, sorbent supports and immobilizing techniques have been tested.

In the work of Gray et al. [39], a fly-ash carbon structure was enriched by 3-chloropropylamine-hydrochloride. The chemical  $\text{CO}_2$  capture capacities were determined by the combination of diffuse reflectance infrared transform spectroscopy, temperature-programmed desorption and mass spectroscopy analyses. Three types of enriched ash carbon structures were tested at 298 K for adsorption and at 393 K for desorption. It was found that the adsorption of  $\text{CO}_2$  increases with the amine chemical treatment. The maximum capacity achieved was  $174.6 \mu\text{mol g}^{-1}$  ( $140.6 \mu\text{mol g}^{-1}$  after regeneration) whereas the capacity of commercial carbons was 1800 to  $2000 \mu\text{mol g}^{-1}$ . Later, the same group examined the possibility of carbon dioxide capture by using immobilized and aminated mesoporous silica sorbents [40]. The initial mesoporous silica material, with a uniform pore size of 21 nm and a surface area of  $200 - 230 \text{ m}^2 \text{ g}^{-1}$ , was grafted with  $\gamma$ -aminopropyltriethoxysilane. The capacity of  $\text{CO}_2$  capture was determined by temperature-programmed desorption and mass spectroscopy analyses. The

obtained results showed that a higher amine loading and the use of secondary ethyleneamine based sorbents led to an improved  $\text{CO}_2$  capture capacity among immobilized amine sorbents. The initial capacity of reformulated immobilized amine sorbent achieved  $4188.1 \mu\text{mol g}^{-1}$ . This capacity is about two times higher than those of initial silica sorbents and classical immobilized silica sorbents. However, after the first regeneration, the capacity decreases to  $2690.2 \mu\text{mol g}^{-1}$  and after the second regeneration to  $2169.4 \mu\text{mol g}^{-1}$ .

Gray et al. [41] reported an improvement of the carbon dioxide capture by immobilization of tertiary amine 1,8Diazabicyclo-[5.4.0]-undec-7-ene (DBU) in porous polymer solid substrate - polymethylmethacrylate (PMMA) beds. Beads with 10; 5 and 2.5 weight ratios (bead/DBU) were tested as  $\text{CO}_2$  capture sorbents. The experimental results show that a decrease in the weight ratio, which corresponds to more DBU within the pore structure of the PMMA beads, leads to a decrease in the surface area and the pore volume of the sorbent. In the same time, the performance of these sorbents in capturing  $\text{CO}_2$  improves with an increase in DBU loading. At 298 K, it was  $0.0 \text{ mol CO}_2 \text{ kg}^{-1}$  for the initial PMMA, and  $3.02 \text{ mol CO}_2 \text{ kg}^{-1}$  for 2.5 bead/DBU weight ratio. Experiments were carried out to test the sorbent performance at higher capture temperatures (up to 338 K). The capacity was reduced to  $2.34 \text{ mol CO}_2 \text{ kg}^{-1}$  at 338 K. This sorbent can be used for post-combustion capture in the 298 to 360 K temperature range.

Zhou et al. [42] have prepared graphene- $\text{Mn}_3\text{O}_4$  (GMNO) hybrid porous material by a hydrothermal method and have investigated its performance in carbon dioxide adsorption. They found that as-prepared GMNO hybrid materials exhibit a specific surface area ranging from 140 to  $680 \text{ m}^2 \text{ g}^{-1}$  and a maximum carbon dioxide capacity of about 11 wt. %.

S. Dinda [43] proposed new alkali-impregnated mesoporous solid sorbents with porous-alumina-like support material. The author shows that the adsorbent with 20 wt. %  $\text{Na}_2\text{CO}_3$  loading has the best  $\text{CO}_2$  adsorption capacity among the studied adsorbents; it lies in the range of  $0.35 - 0.39 \text{ mmol g}^{-1}$  of adsorbent at a temperature of about 328 K. A similar study has been effected by S.C. Lee et al. [44]. They proposed

a new potassium-based sorbent using alpha-alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) as a support. The authors showed that this sorbent has good regeneration properties as well as a high  $\text{CO}_2$  capture capacity during multiple  $\text{CO}_2$  sorption and regeneration tests at 333 K and 473 K, respectively.

In the study of Shou-Heng Liu et al. [45], modified mesocellular silica foams were impregnated with Tetraethylenepentamine (TEPA) and then chemically grafted. The adsorption capacities of these sorbents were observed to be 26.4 - 193.6  $\text{mg-CO}_2\text{ g}^{-1}\text{-sorbent}$  under ambient pressure using dry 15 %  $\text{CO}_2$ .

Adsorbents lying on the basis of silica hollow fiber loaded with PEI were proposed by Labreche et al. [46]. After amine infusion, the 51 wt. % silica hollow fiber sorbents have demonstrated to have a nitrogen loading of 0.52  $\text{mmol g}^{-1}\text{-fiber}$  and a  $\text{CO}_2$  uptake of 1.2  $\text{mmol g}^{-1}\text{-fiber}$ , at equilibrium.

Ma et al. [47] produced zeoliteX/activated carbon composites with different ratios of zeolite and activated carbon. An additional surface modification was achieved in diluted  $\text{NH}_4\text{Cl}$  solution. Both before and after modification, all composites exhibited a remarkable preferential adsorption of  $\text{CO}_2$  compared to  $\text{N}_2$ .

Qian et al. [48] produced microporous polyamide networks through the interfacial polymerization of piperazine and acyl chloride monomers containing tetrahedral carbon and silicon cores. These sorbents have BET surface areas ranging between 488 and 584  $\text{m}^2\text{ g}^{-1}$ . They show a  $\text{CO}_2$  uptake of up to 9.81 wt. % and a  $\text{CO}_2/\text{N}_2$  selectivity of up to 51 at 0.1 MPa and 273 K.

W. Wang et al. [49] prepared a new sorbent for  $\text{CO}_2$  capture through the immobilization of a branched PEI onto porosity-enhanced naturally abundant clays. The authors showed that at the optimal PEI loading of 50 wt. % on clay support, the  $\text{CO}_2$  sorption capacity of sorbent reached 112  $\text{mg-CO}_2\text{ g}^{-1}\text{-sorbent}$  at 348 K under dry condition, which can be further enhanced to 142  $\text{mg-CO}_2\text{ g}^{-1}\text{-sorbent}$  with moisture addition (ca. 3 vol. %).

Linneen et al. [50] developed a new  $\text{CO}_2$  sorbent which consists of high porosity hydrophilic and hydrophobic silica aerogel impregnated with tetraethylenepentamine. The 80 wt. % TEPA loaded hydrophilic sorbent achieved the largest capacity of 6.1  $\text{mmol g}^{-1}$  in pure  $\text{CO}_2$  while also attaining 3.5  $\text{mmol g}^{-1}$  under a dry 10 %  $\text{CO}_2$ /

Ar stream. The sorbent also showed excellent cyclic stability having a working  $\text{CO}_2$  sorption capacity of 5.1  $\text{mmol g}^{-1}$  over 10 cycles.

### Hydrotalcite-like compounds

Hydrotalcite-like compounds (HLC) have recently attracted significant attention because of their  $\text{CO}_2$  capture ability at elevated temperatures. HLC, also known as layered double hydroxides, are bidimensional basic solids. Their structure consists of positively charged brucite (magnesium hydroxide)-like layers with interlayer space containing charge-compensating anions and water molecules. Hydrotalcite-like compounds have been reported as having high adsorption capacity at elevated temperatures [51 - 53]. On the other hand, it has an abnormal adsorption behavior with temperature-related changes following a  $\text{Q300} > \text{Q20} > \text{Q200}$  trend (where QT is the adsorption capacity at atmospheric pressure and temperature T in Celsius degrees) [51].

The possible reason for this unexpected behavior is suggested, on the one hand, through a decrease of the interlayer spacing between room temperature and 473 K, which would result in less available spacing for the target molecule that inhibits the carbon dioxide adsorption, followed on the other hand, at 573 K, by the dehydroxylation and decarbonization of the HLC, which would result through a structural modification to an increased porosity that could consequently enhance the adsorption capacity of carbon dioxide [51].

### Molecular sieves

Molecular sieves are a series of specially designed sieves that separate molecules, based on their molecular mass or molecular size. Molecular sieves have been used for separating gas mixtures in various industrial applications. However, for  $\text{CO}_2$  separation, molecular sieves without chemical modification will stand ineffective when the molecular diameters are close.

MCM-41 is a well-known mesoporous molecular sieve first synthesized by Mobil Company researchers [54]. A possible route to improve capture ability of the molecular sieves is to modify them with polymers. Xu et al. [55] studied a novel  $\text{CO}_2$  "molecular basket" adsorbent for separation of carbon dioxide from a flue

gas of natural gas-fired boilers. This adsorbent is based on mesoporous molecular sieve MCM-41 impregnated with polyethylenimine. The CO<sub>2</sub> “molecular basket” can selectively store CO<sub>2</sub> in a condensed form and therefore exhibits a high CO<sub>2</sub> adsorption capacity and a high CO<sub>2</sub> separation selectivity. The adsorption capacity was tested in adsorption columns with fixed bed. It was shown that the adsorption capacity increases from 8.6 mg g<sup>-1</sup>-adsorbent for the pure MCM-41 to 112 mg g<sup>-1</sup>-adsorbent for the “molecular basket”. Adsorption separation performance and structure analysis indicated that the adsorbent was stable in cyclic adsorption/desorption operations.

In the paper of Knowles et al. [56], the immobilization of 3-aminopropyltrimethoxysilane on mesoporous silica was studied. Hexagonal mesoporous silicas with approximately 2 or 5 silanol groups per nm<sup>2</sup> were first prepared. Aminopropyl-functionalized products were obtained by treatment with different quantities of aminopropyl-trimethosilan and different times of treatment. The products were characterized by BET analysis. The capacity for CO<sub>2</sub> adsorption was determined by differential thermal analysis and thermo gravimetric analysis. The maximum specific surface (1195 m<sup>2</sup> g<sup>-1</sup>) and maximum CO<sub>2</sub> adsorbed (7 wt. %) were obtained for the treated samples. These values were much higher than those of the non-treated silica substrates (567 m<sup>2</sup> g<sup>-1</sup> and 1.8 wt. %, respectively). The authors also show that the CO<sub>2</sub> capacity of the produced adsorbents is enhanced by the presence of water and that the overall rate of desorption (at 293 K) is diminished.

In the work of Chafee [57], a molecular dynamic study was performed in order to optimize the structures of hexagonal mesoporous silicas (MCM-41, SBA-15, etc.). The simulations based on the experimental data of Knowles et al. [56] give the possibility to determine the mechanism of interactions between the pore surface atoms and the trimethoxyaminopropyl-silane introduced into the mesopores. The interaction between the hybrid surface and the CO<sub>2</sub> molecules has also been studied. The comparison between numerical results and experimental data shows a satisfactory agreement. The obtained results give the possibility to determine some strategy for new material synthesis with improved carbon dioxide

sorption capacities.

Hicks et al. [58] reported the first use of covalently tethered hyperbranched aminosilica material capable of adsorbing CO<sub>2</sub> reversibly from simulated flue gas with very high capacities of 3.1 mmol CO<sub>2</sub> g<sup>-1</sup> material at 298 K. The authors conceived these materials as practical CO<sub>2</sub> adsorbents due to their simple synthesis, covalent inorganic-organic linkage, and low cost.

Sharma et al. [59] synthesized two types of mesoporous silica, MCM-41 and MCM-48, and impregnated them with 30, 50 and 70 wt. % of polyethylenimine. The authors show that the material with a 50 wt% loading of PEI on MCM-48 has the maximum adsorption of 248 mg g<sup>-1</sup>-PEI at 353 K, which is about 30 times higher than that of MCM-48 and about 2.3 times that of pure PEI.

Recently, some authors studied adsorbents based on the modification of the mesoporous silica Santa Barbara Adsorbent – 15 (SBA-15). Yan et al. [60] prepared mesoporous silica SBA-15 samples and impregnated them with polymer amine. These samples were evaluated for their ability to adsorb CO<sub>2</sub> through equilibrium adsorption isotherms using volumetric adsorption at three different temperatures of 273 K, 278 K and 283 K. The authors found that the SBA-15 sample with the higher microporosity displayed a higher CO<sub>2</sub> uptake when amine-modified. They explain this result by a blockage of the micropores by the amines group.

Sanz-Pérez et al. [61] prepared carbon dioxide adsorbents by functionalization of SBA-15 mesostructured silica with amino groups. The authors tested the adsorbent capacities for carbon dioxide uptake with a gas mixture similar to that of a coal-fired thermal power plant. They showed that moisture improves the CO<sub>2</sub> uptake of impregnated adsorbents by about 50 - 60 %, therefore obtaining an adsorption capacity of 16.2 wt. % CO<sub>2</sub>.

X. Zhang et al. [62] have prepared the CO<sub>2</sub> sorbent by impregnating SBA-15 with acrylonitrile- modified tetraethylenepentamine. The results of test experiments showed that the solid base-impregnated SBA-15 demonstrated a high CO<sub>2</sub> adsorption capacity (180.1 mg g<sup>-1</sup>-adsorbent for a 70 % amine loading level).

Yu Jing et al. [63] have synthesized new adsorbents by functionalizing SBA-15 through stepwise growth of

melamine-based and acrylate-based amine dendrimers. CO<sub>2</sub> adsorption performance was then determined in fixed bed flow system under simulated flue gas (12 % CO<sub>2</sub> and 88 % N<sub>2</sub>) at 303 K, 323 K and 348 K, respectively.

### **Metal-organic frameworks**

Arstad et al. [64] used metal organic framework (MOF) as matrix for amine implantation. MOF were built up by metal atoms (ions) linked together by multifunctional organic ligands. Three different metals were studied: aluminum, nickel and indium. Samples have been prepared with and without uncoordinated amine functionalities inside the pores. Both adsorption and desorption isotherms were measured at low and high pressures. It was shown that introduction of amino groups in the MOF porous structure leads to a decrease in the specific surface area and in the pore volume for all three metal structures. At low partial pressure (0.1 MPa) of CO<sub>2</sub>, the highest CO<sub>2</sub> adsorption capacities were obtained with the MOF adsorbents having uncoordinated amine functionalities within the pores. Such functionalities increase the adsorption energy of carbon dioxide. At elevated CO<sub>2</sub> pressures (2.5 MPa), the adsorption capacities show a linear relationship to the specific surface area and pore volume of the adsorbents.

Ramsahye et al. [65] presented a molecular dynamic study using the Grand Canonical Monte Carlo simulation in order to compare different CO<sub>2</sub> adsorption mechanisms between Materials of the Institut Lavoisier (MIL) hybrid metal-organic framework materials MIL-47 (V) and MIL-53 (Al). The results confirm the presence of a structural interchange between large-pore and narrow-pore forms of MIL-53 (Al), which is not seen with the MIL-47 (V) material since it is a consequence of the presence of  $\mu_2$ -OH groups. The authors proposed a distinct microscopic mechanism for CO<sub>2</sub> adsorption for each system investigated, which is consistent with the evolution of the differential adsorption enthalpy as a function of the coverage.

Munusamy et al. [66] studied the application of metal organic framework material, MIL-101(Cr), synthesized by hydrothermal method and granulated by using starch and sodium salt of carboxyl methyl cellulose as a binder. The authors found that the selectivity of CO<sub>2</sub>

over N<sub>2</sub> in MIL-101(Cr) is 12.6 higher than those for CO<sub>2</sub> over CH<sub>4</sub> (5.69) and CO (2.90).

Das et al. [67] studied the use of post-synthetic modification of 1,3,5-tris(1H-1,2,3-triazol-5-yl) benzene(Cu<sub>4</sub>Cl) with piperazine (pip) for CO<sub>2</sub> uptake at pressures pertinent to post-combustion flue gas capture and compared it with the non-grafted material.

Abid et al. [68] proposed the new nanosized Zr-metal organic framework (Zr-MOF, UiO-66) with a uniformed particle size around 100 nm for carbon dioxide and hydrogen storage.

### **Sorbent regeneration processes**

In pressure swing adsorption, the adsorbent is regenerated by reducing the pressure and, in temperature swing adsorption, by raising its temperature. The classical PSA and TSA techniques have been modified and adapted for removing CO<sub>2</sub> from gas streams. During the last decade, researchers have described several new PSA concepts that improve the process performance. Very promising results have also been reported with CO<sub>2</sub> removal from flue gas by using a combination of PSA and TSA (PTSA) [69].

Belmabkhout et al. [70 - 71] investigated high-pressure CO<sub>2</sub> adsorption up to 2.5 MPa and ambient temperature on MCM-41 silica samples prepared at different temperatures. The results showed a fairly linear correlation of the CO<sub>2</sub> excess uptake to the BET surface area and pore ordering. The material prepared at 373 K, which was optimal in terms of both structural properties and pore ordering, had a higher volumetric uptake in comparison to benchmark CO<sub>2</sub> adsorbents like 13X, MaxsorbAC and NoritAC at 4.5 MPa. Based on the volumetric CO<sub>2</sub> adsorption capacity per unit of surface area, the sample prepared at 373 K was also found to be one of the most effective materials in comparison to all physical CO<sub>2</sub> adsorbents. The authors conclude that this material is a promising candidate for CO<sub>2</sub> storage and separation at high pressure in dry conditions. Furthermore, it was shown that in comparison to well-known CO<sub>2</sub> adsorbents, MCM-41 exhibited enhanced CO<sub>2</sub> selectivity over N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> at high pressure. Based on its efficiency for CO<sub>2</sub> removal from N<sub>2</sub>-, CH<sub>4</sub>-, and H<sub>2</sub>-rich mixtures, MCM-41 was found to be a

competitive material for CO<sub>2</sub> separation from industrial gases such as flue gas, biogas and syngas compared to other CO<sub>2</sub> physical adsorbents.

In the study of Reynolds et al. [72], a rigorous PSA process simulator based on the model developed by Y. Liu et al. [73] was used. The adsorbent is the K-promoted hydrotalcite. The results for isotherms and the mass transfer coefficients were obtained elsewhere [52, 74]. The periodic-state PSA process performance was evaluated through CO<sub>2</sub> recovery (R), CO<sub>2</sub> enrichment (E), and throughput ( $\theta$ ). Thirteen simulations were carried out at the base case conditions, i.e. purge-to-feed ratio  $\gamma = 0.75$ , cycle step time  $t_s = 300$  s and pressure ratio  $\pi_T = 8$ . Finally, the results from 125 simulations, carried out at five different purge-to-feed ratios, cycle step times, and pressure ratios showed that R increased with increasing  $\gamma$  and  $\pi_T$  and decreasing  $t_s$ , while E increased with increasing  $t_s$  and  $\pi_T$  and decreasing  $\gamma$ . The highest E of 3.9 was obtained with R = 87 % for  $\gamma = 0.5$ ,  $\pi_T = 12$  and  $t_s = 500$  s under apparent optimum conditions for E, but not for R. In contrast, at R = 100 %, the highest E of 2.8 was obtained for  $\gamma = 1.5$ ,  $\pi_T = 12$  and  $t_s = 500$  s, under apparent optimum conditions for R. Different feed flow rates, i.e., different  $\theta_s$ , will result in different sets of optimal, possibly better, conditions. The results show the potential of high-temperature cycling for CO<sub>2</sub> capture.

In the work of Delgado et al. [75], the separation of carbon dioxide/methane mixtures by PSA using a basic resin (Amberlite IRA-900) at ambient temperature was studied. The choice of adsorbent was based on the results presented by R.T. Yang [76]. The fixed-bed experiments were carried out in devices including a column. The results show that the adsorption capacity initially decreases slowly with the number of adsorption-desorption cycles. After about 16 cycles, the adsorption capacity decreases by 28 %, and reaches a constant value. The adsorption capacity can be recovered by treating the resin with NaOH. The value of the adsorption enthalpy for CO<sub>2</sub> (19 kJ mol<sup>-1</sup>) suggests that this gas is physisorbed on the basic resin. In addition, a one-dimensional study with axial dispersion was developed to describe the fixed bed and PSA dynamics. The internal mass transfer rate was expressed by Linear Driving Force (LDF) model. For the equilibrium

description, the extended Langmuir isotherm was used. The model reproduces well the breakthrough curves obtained experimentally with carbon dioxide-helium and methane-helium mixtures. The model is also valid for simulating the breakthrough curves obtained with carbon dioxide-methane mixtures.

In order to simulate the PSA performance, the appropriate boundary conditions for the pressurization and blow-down steps were introduced. A product with 97 % of methane was obtained experimentally from a feed containing 35 % CO<sub>2</sub>. For a feed with 56 % of carbon dioxide, this was not possible. According to model simulations, a product with 97 % of methane could however be obtained with the same PSA configuration by increasing the bed length or reducing the low pressure in the cycle and reducing the feed flow rate.

Takamura et al. [77] studied dual-bed PSA at higher temperatures ranging from 993 to 1033 K. The authors' objectives were to obtain high recovery efficiency and high CO<sub>2</sub> concentration of the recovery gas by applying a dual-bed to the CO<sub>2</sub> PSA process for CO<sub>2</sub> recovery from boiler exhaust gas. The study was based on experiments and mathematical modeling. Two adsorbents for a dual-bed were selected: X-type zeolite (particle size: 0.002 m and specific surface area: 430 m<sup>2</sup>.g<sup>-1</sup>), substituted with Na<sup>+</sup>, Ca<sup>2+</sup>, Li<sup>+</sup> or Ba<sup>2+</sup> and A-type zeolite (particle size: 0.002 m and specific surface area: 380 m<sup>2</sup>.g<sup>-1</sup>), substituted with Na<sup>+</sup>, Ca<sup>+</sup> or K<sup>+</sup>. Breakthrough tests were done using a small column. The experimental study showed that Na-A type zeolite has the highest relative volatility for CO<sub>2</sub> (440) as a separator in test adsorbents, but the capacity for CO<sub>2</sub> adsorption is lower than with X-type zeolites.

In addition to these experiments, a modeling approach based on the one dimensional plug flow equations for mass balances has been developed. The assumption of isothermal process has been used. The mass transfer rates were approximated by a linear driving force model. The mass transfer coefficient kept into account both the molecular and Knudsen diffusions inside the adsorbent particle. Langmuir isotherm was applied for equilibrium. For the evaluation of the performance of dual-bed PSA process, simulations were made using two kinds of adsorbents in the bottom and the top of the bed. Na-X type zeolite was selected

for the adsorbent packed in the half bottom of the bed because of its large CO<sub>2</sub> adsorption capacity. Since Na-A type zeolite showed the highest relative volatility in the test, it was packed in the half top of the bed. According to the simulated results, the optimal Na-X to Na-A ratio has been confirmed to be present to obtain the high CO<sub>2</sub> concentration gas without the decrease of the recovery efficiency. The authors proved that the dual-bed CO<sub>2</sub> PSA process leads to higher recovery efficiency and a higher CO<sub>2</sub> concentration in the recovery gas than for the single-bed CO<sub>2</sub> PSA under the same operating conditions.

The utilization of hydrotalcite adsorbent for CO<sub>2</sub> capture by PSA-based process at 1033 K, which corresponds to the temperature of steam gases, was studied in the paper of Ding and Alpay [52]. Hydrotalcite is an anionic clay consisting of positively charged layers of metal oxide (or metal hydroxide) with inter-layers of anions, such as carbonate. A semi-technical and bench-scale elution apparatus were used to study the equilibrium and kinetics of CO<sub>2</sub> adsorption. A dynamical model based on the assumption of one-dimensional plug flow with axial dispersion and linear driving force for the internal mass transfer based on pore diffusion was developed. An adsorption model based on instantaneous local adsorption equilibrium between the gas and the adsorbed phases was also developed to further assess the importance of intraparticle mass transfer during different steps of operation. Measured adsorption saturation was respectively 0.65 and 0.58 mol kg<sup>-1</sup> at 673 and 753 K, under wet feed conditions. Under dry feed conditions, ~10 % reduction of the saturation capacity was observed. Experimental data indicated the degradation of the adsorbent under dry feed conditions, resulting in reduction in capacity of about 30 - 40 % at 673 K and in higher losses at higher temperatures. The comparison of breakthrough curves calculated by the dynamic model and the experimental data shows a satisfactory agreement. This work illustrates the complexities of CO<sub>2</sub> adsorption on hydrotalcite. For adsorbent previously not contacted with steam or CO<sub>2</sub> feed, observations suggest an initial strong adsorption of material, depicting a chemisorption mechanism.

G. Li et al. [78] used Na-X zeolite for CO<sub>2</sub> capture by VSA. This technology is promising because it has

relatively low power consumption. The study was focused on carbon dioxide removing in the presence of water vapors. Experiments were carried out in VSA apparatus, including a single packed adsorbent bed made of a stainless steel column and a humidifier. The results of experiments with dry carbon dioxide were compared with those obtained using humidified CO<sub>2</sub>. It was shown that the capacity of zeolite to adsorb CO<sub>2</sub> decreases by 99 % in presence of water vapor in the gas. The formation of the water zone creates multilayers resulting in a thermal regeneration and the occurrence of a “cold spot”, which changes the thermal profiles in the bed and hence the system performance. In addition, the presence of a water-saturated zone and its subsequent slow desorption during evacuation results in a vacuum level above its value for dry CO<sub>2</sub> feed.

Electric Swing Adsorption (ESA) process is mentioned in several reports as one possible technique to capture CO<sub>2</sub> from flue gases. ESA is an adsorption process where the regeneration is performed by increasing the temperature of the adsorbent using the Joule effect of passing electricity through a conductor.

An et al. [79] reported a parametric study in order to optimize ESA process for CO<sub>2</sub> capture using activated carbon fiber materials. Grande et al. [80] studied the adsorption dynamics of CO<sub>2</sub> in an activated carbon honeycomb monolith column. Desorption rate of CO<sub>2</sub> was enhanced by direct Joule effect by passing electric current through the honeycomb. ESA experiment was performed to test the cyclic operation of the process. It was determined that recoveries higher than 89 % can be obtained but with purities of CO<sub>2</sub> of 16 %. The same group later used a new cycle configuration with a partial recycling of CO<sub>2</sub>, and achieved a CO<sub>2</sub> rich stream with 89.7 % purity and 72 % recovery of the CO<sub>2</sub> from the inlet flue gas [81].

Recently Ghougassian et al. [82] proposed a new heat-integrated pressure temperature swing adsorption process for the capture of CO<sub>2</sub> from the flue gas. The process involves a heat-pump, a refrigeration loop, a flash-separator train with inter-stage compression and cooling, and a heat exchange network.

In a series of papers, K.B. Lee et al. [83-85] proposed a novel concept called Thermal Swing Sorption-Enhanced Reaction that includes the following five

cyclic sequential steps:

1) Sorption enhanced reaction step: A feed gas containing a mixture of CO and H<sub>2</sub>O at a temperature of T<sub>R</sub> and a total gas pressure of P<sub>R</sub> was passed through a sorber-reactor column packed with the admixture of a water gas shift reaction catalyst and a high-temperature CO<sub>2</sub> selective sorbent. The sorber-reactor was filled with steam at temperature T<sub>R</sub> and pressure P<sub>R</sub> prior to this step. CO and H<sub>2</sub>O react to form CO<sub>2</sub> and H<sub>2</sub>. CO<sub>2</sub> was removed from the reaction zone by the sorbent and an essentially CO<sub>x</sub> free product gas containing H<sub>2</sub> and H<sub>2</sub>O was produced at pressure P<sub>R</sub> as the reactor effluent. An H<sub>2</sub> enriched product (~99.99%) was then produced at feed pressure by condensing out the water from the reactor effluent by cooling. The step was continued until the chemisorbent in the sorber-reactor was nearly saturated with CO<sub>2</sub> (short of CO<sub>x</sub> breakthrough).

2) CO<sub>2</sub> purge step: The sorber-reactor was purged with a stream of essentially pure CO<sub>2</sub> at pressure P<sub>R</sub> and temperature T<sub>R</sub> to purge out the left-over void gas from the sorber-reactor at the end of step (1). Some additional CO<sub>2</sub> was sorbed. The effluent gas may be rejected or recycled by mixing it with fresh feed gas to step (1). The chemisorbent was saturated with essentially pure CO<sub>2</sub> at pressure P<sub>R</sub> at the end of this step.

3) Batch heating step: The column was heated indirectly to a temperature of T<sub>H</sub> (> T<sub>R</sub>) in a batch fashion by raising the shell side temperature to T<sub>H</sub>. The column pressure reaches P<sub>H</sub> (>> P<sub>R</sub>) due to batch desorption of CO<sub>2</sub>. The column was saturated with pure CO<sub>2</sub> at pressure P<sub>H</sub> and temperature T<sub>H</sub> at the end of this step.

4) Regeneration by high pressure steam purge step: The sorber-reactor was counter-currently purged with superheated steam at pressure P<sub>H</sub> and temperature T<sub>H</sub> until a certain amount of the CO<sub>2</sub> was desorbed out of the column. The effluent gas was initially pure CO<sub>2</sub> at pressure P<sub>H</sub>, followed by a mixture of CO<sub>2</sub> and steam with decreasing partial pressures of CO<sub>2</sub>. The water was condensed out from the effluent gas by cooling in a constant pressure condenser. This produces a CO<sub>2</sub> enriched (~99.9%) product gas at pressure P<sub>H</sub>.

5) Multi-tasking regeneration step: The sorber-reactor pressure was reduced to a near ambient pressure level and counter-currently purged with super-heated

steam at temperature T<sub>R</sub>, while lowering the shell side temperature to T<sub>R</sub>, until most (> 95%) of the CO<sub>2</sub> was removed from the column. The effluent gas was rejected. The column was cooled down to T<sub>R</sub> at the end of this step and the column pressure was raised from near ambient to P<sub>R</sub> by counter currently introducing steam into the column at temperature T<sub>R</sub> and pressure P<sub>R</sub>. The cycle was then repeated starting from step (1).

Experiments were carried out using two adsorbents - promoted hydrotalcite [86] at 673 and 793 K and promoted alumina at 523, 623, and 723 K [87]. The isotherms of chemisorptions were fitted by classical Langmuir isotherms. The novel equilibrium isotherm model which accounts for simultaneous Langmuirian chemisorption of CO<sub>2</sub> on the sorbent surface and complexation of gaseous and chemisorbed CO<sub>2</sub> molecules which describes the isotherms on both chemisorbents at different temperatures was proposed. A constant stirred tank reactor in series with LDF approximation for internal mass transfer rate was applied to simulate the breakthrough curves.

## CONCLUSIONS

The physical sorption techniques such as gas-solid adsorption is not suitable for great amounts of flue gases but they give interesting possibilities for low CO<sub>2</sub> concentration assuring high degree of gas separation, which is not possible using the other capture methods. High porous materials such as activated carbons and charcoals exhibit CO<sub>2</sub> capture capacities ranging from 10 to 15% by weight. The CO<sub>2</sub>/N<sub>2</sub> selectivity is relatively low. Because of this point, the possible capture and compression costs are such that the carbon-based systems can be applicable when CO<sub>2</sub> purity is not more than 90%. Thus adsorbent surface modifications are required in order to improve their basic feature. Such modifications include cation exchange or substitution within the material framework, chemical treatment of the surface or functionalization of the pore structures. Another possible capacity improvement of commercial adsorbents consists in impregnation with amines. Other interesting carbon-based materials with potential for CO<sub>2</sub> capture/storage are coals and anthracites due to their

low price; these materials must be treated with nitrogen-containing compositions. The other type of classical adsorbents, i.e. the zeolites, offer CO<sub>2</sub>/N<sub>2</sub> selectivities 5 to 10 times greater than those of carbonaceous materials. However, their CO<sub>2</sub> capacities are 2 - 3 times lower due to their porosity structures. Another way for carbon dioxide capture is to introduce in the porous materials such as clay and porous silica, different amines that would react with CO<sub>2</sub>. The microporous polyamide networks also give promising results for high CO<sub>2</sub> uptakes and CO<sub>2</sub>/N<sub>2</sub> selectivities. Hydrotalcite-like compounds exhibit interesting CO<sub>2</sub> capture abilities at high temperatures. Molecular sieves have been used for separating gas mixtures in various industrial applications. However, for CO<sub>2</sub> adsorption, molecular sieves must be chemically modified by amines impregnation. The other adsorbents that could be used for CO<sub>2</sub> capture are the Metal Organic Frameworks with high specific surfaces. They can also be modified by amines impregnation.

The classical PSA and TSA techniques are modified and adapted for removing CO<sub>2</sub> from gas streams. During the last decade, several new PSA concepts that improve process performance have been described. Electric Swing Adsorption process is mentioned as one possible technique for CO<sub>2</sub> capture from flue gases. A novel concept based on the combination of adsorption and chemical reaction in packed column with an admixture of a catalyst and a high temperature CO<sub>2</sub> selective sorbent, known as Thermal Swing Sorption-Enhanced Reaction, can improve CO<sub>2</sub> capture efficiency. Promising results have also been reported with CO<sub>2</sub> removal from flue gas using PSA and TSA (PTSA) combination.

#### **Acknowledgements**

*The authors thank the Invited Professor protocol between Université Paris 13 and UCTM Sofia.*

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