

CO₂ capture by adsorption on activated carbons using pressure modulation

Mario Pellerano^{a*}, Pascaline Pré^a, Mariem Kacem^b, Laurence LE COQ¹, Arnaud Delebarre^c

¹EMN : Ecole des Mines de Nantes, 4 rue Alfred Kastler. B.P. 20722 44307 NANTES Cedex 3 – France

²ENISE : 58, rue Jean PAROT - 42023 ST-ETIENNE Cedex 02 - FRANCE

³ESSTIN : 2, rue Jean Lamour, F-54519 Vandoeuvre Lès Nancy Cedex – France

* *Corresponding author. Tel.: +33-2-51-85-85-63; fax: +33-2-51-85-82-99.*
E-mail address: Mario.Pellerano@emn.fr.

Abstract.

In order to reduce greenhouse gases emissions, CO₂ release due to human activities should be better controlled. CO₂ Capture by adsorption is considered as one of the potential options. However, the success of this approach is dependent principally on the use of a low cost adsorbent with a high CO₂ selectivity, high adsorption capacity and not material aging. In this work, different commercialized Activated Carbons (AC) were evaluated as a potential adsorbent for CO₂ capture by pressure modulation and were compared with commercialized zeolites. AC with different physical properties were chosen to analyze in order to understand the different implications with adsorption. The main advantage of AC is the fully reversibility after regeneration by pressure modulation. The mass of gas captured in an AC sample represents at least 3 times the quantity compressed in the same volume, at identical pressure and temperature conditions. At pressure above 4 bar, the adsorption capacities of the AC are larger than for zeolites. Moreover aging studies showed that AC materials keep their initial adsorption capacities even after 15 adsorption-desorption cycles.

1. Introduction

The increase in the CO₂ emissions is one of the major environmental problems. In addition to efforts to reduce energy consumption and develop renewable energy sources, CO₂ capture and storage emerge as an option insofar as fossil fuels will continue to be exploited.

CO₂ capture involves a gas separation process of the industrial combustion effluents. In pre-treatment processes, synthetic fuel gases (H₂, CH₄) are purified in order to reduce CO, CO₂ concentration levels. Among the various technologies such as absorption, membranes, adsorption may be considered as a competitive solution. Its major advantage is the ease of the adsorbent material regeneration by thermal or pressure modulation.

In this work, we examine most adapted materials for CO₂ adsorption. Comparison between these materials was made based on the following criteria: adsorption equilibria, regeneration capacity and aging.

Adsorption can be applied for gas separation systems and for CO₂ emissions reduction. For example, Cavenati [1] adopted a VSA process in purification obtaining a refined methane gas with a reduced concentration of CO₂ conformed at the law (lower than 2%). Otherwise, results by Chue [2] shown that a concentration of 99% of CO₂ can be obtained using a VSA on flue gases for CO₂ capture.

The first stage was characterization Activated Carbons (AC) and zeolites properties. Specific area, porosity, pore size distribution and particle size distribution were measured. The adsorption equilibria were determined in a temperature range of [0°C, 75°C] and pressure range of [0.4 bar, 8 bar] using an experimental device.

In the present work relations between physical properties and adsorption capacities are founded. These relations are used in order to determine the adsorbent demonstrating the best adsorption regeneration capacities depending on the operating conditions applied.

2. Experimental

2.1. Experimental apparatus

The equipment used for adsorption test consists of a bottle of CO₂ sourced from AIRLIQUIDE linked through a pipe to the system (fig. 1). A cylindrical cell stainless steel reactor is equipped with an internal thermocouple that allowed to know the temperature within the bed of the adsorbents, the cell is immersed in a regulated thermosystem in order to control the adsorption temperature. A pressure monitoring system which gives the

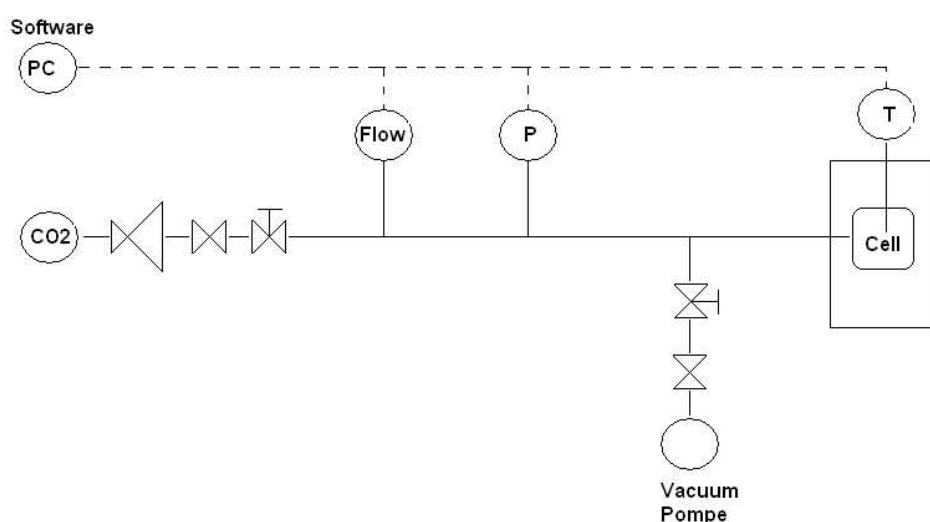


Figure 1 Schematic experimental

pressure within the system and a mass flowmeter Brooks 5850S allowed knowing the input mass of the gas. Experiments were carried out at 0, 25, 75 °C and the pressure was increased step by step up (0.4, 1, 2, 4, 8 Bar) to 8 Bar. Prior to adsorption measurements the sample was passed for 12h at 100 °C and after inserted in the cell. Before charging the system the gas inside the circuit was extracted using a vacuum pump to reach a pressure around 0.02 Bar. The loading process was started by opening main input valve and regulated with a manual fine valve in order to respect the max flow imposed by the flowmeter. The gas flow rate, the time to reach the equilibrium, and the gas mass input were continuously recorded. The data were acquired by means of the Test Point software and the acquisition frequency for temperature, pressure and carbon dioxide mass flow is of 1Hz. The apparatus was previously tested for leak absence and for accuracy through calibration with the empty tank.

To know the effective adsorbed mass on the adsorbents materials Q_{eff} , two quantities was defined : Q_{tot} that is the mass containing on the total circuit composed of the pipeline and the cell containing the adsorbents and Q_{dead} the mass containing only on the pipeline or dead volume. The Q_{eff} was calculated with the follow equation :

$$Q_{\text{eff}} = Q_{\text{tot}} - Q_{\text{dead}}$$

Once the Q_{eff} was determined the adsorption isotherms was obtained. These isotherms are generally described through the amount of CO_2 on the adsorbent in function of the pressure. But the adsorbent can be considered in terms of mass or volume. Thus, the isotherm can be defined as moles of CO_2 on kilograms of adsorbent (Q_m) or as moles of CO_2 on liters of adsorbent (Q_v). The difference between Q_m and Q_v stay on the bulk density. The bulk density determines the material mass that can to fill a determined volume. Thus, if the bulk density is high more material mass fills the cell at the same volume than other material with lower density. This concept will be interesting for the isotherms results chapter.

2.2. Materials

Activated carbon and zeolites are the most discussed adsorbents for CO_2 capture by adsorption. Four activated carbons(AC) and two zeolites were used in this study. The samples are named *AC1*, *AC2*, *AC3* and *AC4* for AC, *Z1* and *Z2* for zeolites. Sample *AC4* was used as tissue (*a*) or as fiber (*b*). We chosen activated carbon with different parameters and we compared them with zeolites (table 1).

2.3. Characterization of the adsorbents properties

Surface areas and information about micropores were determined using a Micrometrics model ASAP 2010 micropore-volume reactor. The sample was evacuated at 350 °C for 24h. Nitrogen adsorption measurements were conducted at liquid nitrogen temperature (77 K). The size pore distribution was obtained utilizing the t-plot method and Horvath-Kawazoe method to determine micropore volume, BJH method to determine mesoporosity and BET method to obtain surface area. The porosity type is based on IUPAC classification.

Materials (sample)	BET surface m^2/g	Microporosity (cm^3/g)		Mesoporosity cm^3/g	Bulk Density g/ml	Adsorbent information
		0.35-0.5 nm	0.5-1.6 nm			
<i>AC1</i>	2187	0	0.82	0.82	0.28	AC in grain
<i>AC2</i>	1468	0.07	0.56	0.67	0.18	AC in grain
<i>AC3</i>	1087	0.3	0.44	0.03	0.58	AC in grain
<i>AC4(fiber a, tissue b)</i>	989	0.3	0.41	0.04	0.27	AC in fiber
<i>Z1</i>	550	0.22	0.24	0.02	0.75	Zeolites molecular sieves
<i>Z2</i>	499	0.20	0.21	0.02	0.73	

Table1 Physical properties of adsorbents.

The BET surface area of the sample *AC1* is the highest of the considered sample. A high surface area is characterized by an elevated microporosity. Zeolites *Z1* and *Z2* are characterized by a microporosity type despite their low surface area. Difference in the physic properties generates difference in the adsorptive characteristics of the gas considered.

3. Results and discussion

3.1. Adsorption isotherms of pure CO₂

One criterion for adsorbent selection to use in pressure modulation process is the adsorption capacity of the material for the considered gas. The adsorption isotherms of pure CO₂ on the samples mentioned are shown in Figures 2a and 2b, in the two ways mentioned before. The best adsorbent in terms of capacity depends on the considered parameter. In the two cases the best adsorbent in terms of capacity is not the same. The bulk density of the material makes the difference.

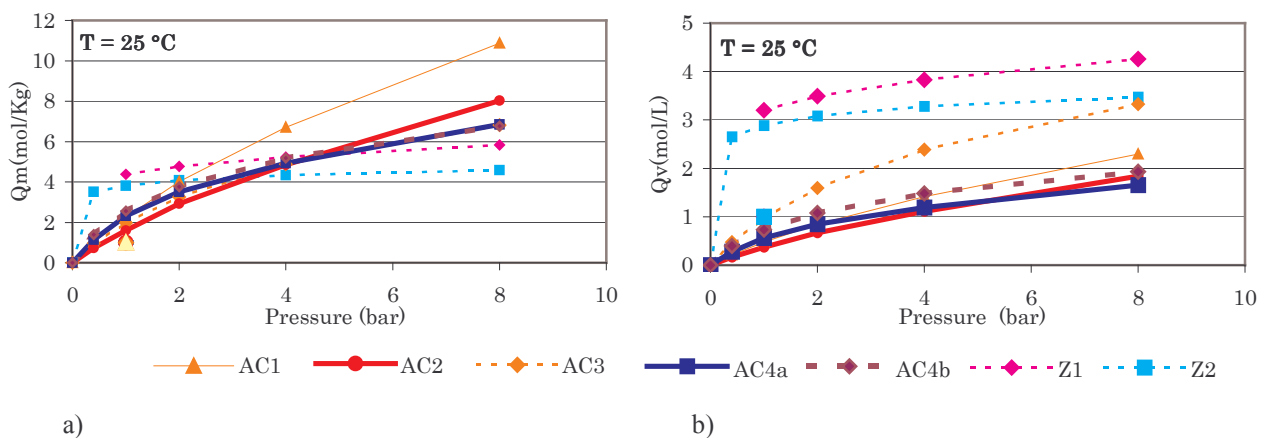


Figure 2 Adsorption isotherms moles CO₂ : a) on adsorbent mass Q_m and b) on adsorbent volume Q_v at 25 °C

Figure 2a and b shows that for the zeolites **Z1** and **Z2** when the pressure was increased up to 1 Bar the adsorption capacity increases almost at the plateau value. After 1 Bar till up to 8 Bar the adsorption is almost constant. For activated carbon the adsorption increases moderately till up 8 Bar. After 8 Bar seems to grow up again. This last supposition is confirmed by results from Sircar et al.[3], where is indicated that AC adsorption capacity increases till 30 Bar and becomes steady after 30 - 35 Bar.

It can be noted that at low pressure the best adsorbent resulted zeolites **Z1** and **Z2** despite their reduced surface area. Thus, it can be supposed that for zeolites the surface area is not the determining factor. However, it can be noted that the homogeneous structure and chemical affinity in zeolites can be important factors for adsorption capacity. At higher pressure activated carbons **AC1** and **AC3** are more efficient than zeolites. Thus, for AC surface area can be considered as an important factor for adsorption capacity denoted in moles on mass adsorbent. For AC, Fig. 2a shows that the higher is the surface, the higher is the adsorption capacity. In fact at 8 bar the adsorbents are classified as their BET surface value. These first considerations show that in AC and in zeolites a different adsorption mechanism operates on.

When the isotherms adsorption are denoted in moles of gas on volume of adsorbent Q_v , the best adsorbents are zeolites, exactly sample **Z1**. The adsorption capacity of activated carbons **AC3** is almost the same of the zeolite **Z1** at 8 Bar and his seems to increase after this pressure. This affirmation is reported and confirmed in results by Siriwardane [4] for activated carbons in general. Although those zeolites have a small BET surface resulted to be a better adsorbent than AC at small pressure. Chue [2] affirmed that zeolites are the best adsorbent for PSA process when adsorption pressure is near to the atmospheric pressure. When adsorption pressure becomes higher, AC can be better than zeolites. Because of this different operating conditions it should be noted that the zeolite have a different CO_2 adsorption mechanism from AC. For adsorbent selection operating condition is an important element to consider.

3.2. Adsorption and physical parameters relation

The CO_2 adsorption capacity versus adsorbents physical parameters (surface BET, microporosity, mesoporosity, average diameter and bulk density) were observed at high relative pressure (8 Bar). The CO_2 adsorption was denoted in the two ways before mentioned. The most interesting results are shown in figure 3a and 3b. It is noted that there is a relation between the adsorption denoted in moles/Kg and the surface BET (fig 3a). The **AC1** sample with the largest BET surface resulted the best sorbent.

In figure 3b is shown that bulk density is a determining factor when adsorption is denoted in moles/L. It must be noted that often a large BET surface implies a reduced bulk density. So it needs to find a correct balance between these parameters. Once more, it can be found the interest to define the adsorption capacity expression. For example, for a reactor volume dimensioning (where volume can be the limiting factor for selection adsorbent) adsorption in moles/L is the more convenient expression. When the weight shows interest, for example in CO_2 transport by adsorption phase, CO_2 moles on adsorbent mass it's more interesting to analyze energy cost.

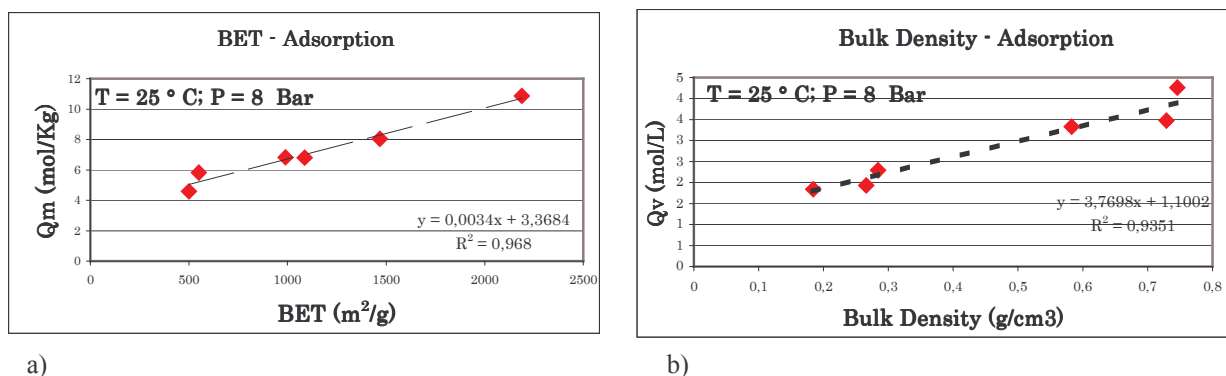


Figure 3 Relations between adsorption capacity and physical parameters.

3.3. Materials aging

An other criterion for adsorbent selection is the material aging. In order to study this factor the adsorption capacity for repeated cycles was analyzed. Each cycle consists of an adsorption phase started at 0.02 Bar and

stopped at 4 Bar and a regeneration phase started at 4 and stopped at 0.02 Bar. Cycles were repeated three times at 25 °C for each sample. After each cycle no treatment was made at the sample. Sample **Z1** was chosen as representative for zeolites and sample **AC1** for activated carbons and shown in figure 4.

In Fig 4a and 4b it can see that the behavior of the two adsorbents is different. For **AC1** the adsorption capacity for repeated cycles is similar and larger (fig.4a) than zeolites. It showed that the adsorption is fully reversible and a complete regeneration can be obtained by evacuation of the material after adsorption. This is the principal advantage of activated carbon, in fact the same result is obtained for the others samples **AC2**, **AC3**, **AC4** too.

For sample **Z1** the highest adsorption capacity is shown on the first cycle. It must be noted that if adsorption capacity is denoted in Q_v , **Z1** yielded greater efficiency than **AC1** for the all three cycles. After each cycle the adsorption decrease sensibly and it seems that only a reversible part is present every cycle. This reversible part is almost 60% of the first cycle.

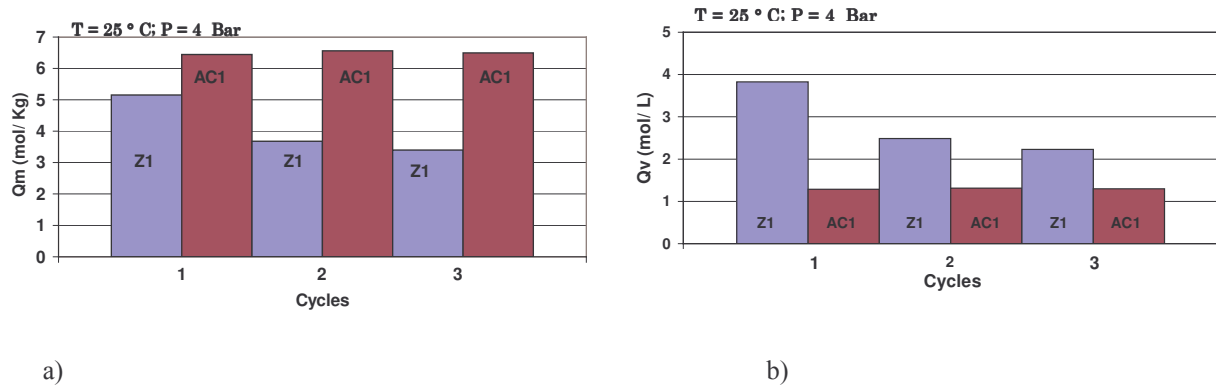


Figure 4 Three adsorption – desorption cycles on zeolite Z1 and on AC1a. at 25°C

This indicated that for zeolites no full reversibility is possible with only pressure modulation. The main reason of this decrease in adsorption capacity is due at the stronger bounds than in AC. This strong bound is expected because of interactions between the CO_2 molecule and the elements in the surface of the zeolites.

Results by Chue et al.[2] indicate, in fact, that average values of heat adsorption on zeolites (36 kJ/mol) is larger than for AC (30 kJ/mol), confirming the mentioned affirmation. Moreover, Siriwardane [4] affirmed that heat of adsorption decrease from 50 to 11 kJ/mol from 1 to 5 mol/kg in coverage surface and for AC decrease from 28 to 11 kJ/ mol with the same increasing coverage. These bounds are of chemical way, stronger and more difficult to cut than in physisorption. In fact 40 kJ/mol is the edge between physique and chemical adsorption type. In order to cut these bounds, zeolites need some kind of energy (for example thermal energy). For AC the adsorption is mainly of physic type and easily to cut with only pressure modulation.

Further analysis of material aging on the sample **AC1** were evaluated. Each cycle was started at 0.02 Bar and stopped at 0.4 Bar in adsorption phase. In regeneration phase the test was started at 0.4 Bar and stopped at 0.02 Bar. The test consisted of 15 adsorption-desorption cycles at 75 °C. and after each cycle no treatment was made at the sample. The figure 5 shows that the last cycle is similar at the first and that not aging of the material is presented.

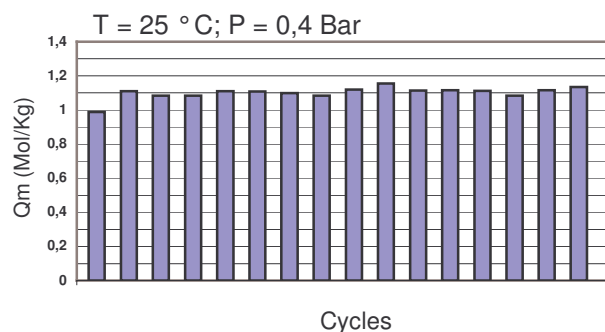


Figure 5 Fifteen adsorption-desorption cycles on sample AC1 at 75 °C

4. Possible application: CO₂ transport

As it has been seen in the preceding paragraph about results, that activated carbons had good adsorption and desorption capacities. In fact at high pressures activated carbons have larger adsorption capacities quantity than other adsorbents and during desorption they are fully regenerated with a simple pressure reduction and all of the adsorbed CO₂ is degassed. Thus, activated carbons were taken into account as possible adsorbent for CO₂ transport in adsorbed phase. The technico - economical analysis costs by ship, train and truck cistern the proposed methodologies by Ozaki [6], Öztürk [7], Edwards [8] were considered respectively. Calculations hypothesis was based on a transport in adsorbed phase, with capacities extrapolated from the empirical results presented above at conditions 0°C et 10 bar. The assessment of the CO₂ transport cost includes different stages: adsorption, storage, transport and load and unloading [5, 9, 10, 11, 12].

CO₂ is commonly transported from the production site to the storage site by pipelines or reservoir (tank or cistern) in supercritical or liquid phase. The liquefaction step is an expensive operation that requires a lot of energy which is not necessary if CO₂ is transported in the adsorbed phase by the means of tanks or cistern equipped with activated carbons filling. Moreover, the operating conditions to keep CO₂ in adsorbed phase (0°C, 10Bar) are cheaper and less radical than for liquid phase (-50°C and 7 Bar, -25°C and 15 Bar).

So, CO₂ transport method in adsorbed phase with activated carbons in reservoirs, was evaluated and compared with CO₂ transported in liquid phase. The results have shown that the CO₂ emissions generated by CO₂ transport in adsorbed phase are much smaller than the ones generated by liquid phase transport, because of the less drastic conditions of CO₂ conditioning and less severe pressure and temperature to be controlled in the transport reservoirs. Moreover, CO₂ transport in adsorbed phase is generally competitive compared to liquid phase transport: it is for transportation by boats excepted in case of very high distances, for all distances in case of train provided the adsorbent is well chosen. It is not competitive in case of transportation by trucks..

5. Perspectives

Once collected information about pure CO₂ adsorption on our materials we will analyze CO₂ separation from simulated gas mixtures on a adsorption system with swing pressure on considered adsorbents.

5.1. Future separation system

A system for adsorption with pressure modulation it was dimensioned. This system allows: a range pressure from almost 0 to a max of 25 Bar, keeping constant temperature during adsorption and desorption phase and to analyze gas concentration coming out from reactor.

5.2. Gas mixtures

Three gas mixture was synthesized to treat in our system. A first one composed of 20% CO₂ in N₂ representing a possible flue gas mixture to treat in post combustion, a second one composed of 50% CO₂ and 50% CH₄ representing a possible natural gas for a treatment in pre combustion and a third gas composed of 6% CO₂, 12% O₂ and 82% of N₂. This last one gas simulate a real gas coming out from a combustion system of wasting animal fat named ValorFat® process property of the S3d enterprise. S3d offers a fatty by-product energy recovery unit for agri-foodstuff industrialists (slaughterhouses, meat curing plants, prepared meat product plants etc.). The innovative ValorFat® process consists in simultaneously producing electricity and heat using vegetable or animal fat [5].

CO₂ separation it will be realized at different pressures, the gas concentration coming out of the reactor will be analyzed for each analyzed pressure step till up the material saturation. During the desorption step the issued gas from adsorbents will be analyzed too. The pressure different pressure steps are 1, 5, 10, 15, 20, 25 Bar at different constant temperature of 0 or 25 or 75 °C.

5.3. Data

The obtained data will allow to show the recovered CO₂ from the treated gas and the CO₂ concentration during the desorption step. These two principal results will be put in function of different parameters as pressure, temperature, repeated cycles, adsorbents parameters characterization and their influence it will be analyzed.

6. Conclusions

Pressure modulation process can be a very interesting solution in comparison to CO₂ capture by thermal process. An adsorbent screening between samples of zeolites and activated carbons must be made in defined operation conditions. In fact, different ways of mechanism adsorption in the two types of adsorbents analyzed was showed. Zeolites was an efficacy adsorbent at small pressure where is BET surface is totally exploited. AC at higher pressure presented to be more convenient than zeolites and easier to regenerate. In fact, pressure modulation applied on zeolites does not achieve complete regeneration because of the chemisorption character of these adsorbents. It can be affirmed that the choice of the best adsorbent depending on the operating conditions of the process utilized.

The adsorption capacity expression is a determining factor for adsorbents selection. The adsorption can be denoted in CO₂ moles on mass or on volume of the adsorbent. The bulk density makes the difference between these ways to define adsorption and in the choice of the best adsorbent to use in pressure modulation.

A technico-economical evaluation of CO₂ transport in adsorbed phase with ACTIVATED CARBONS it was realized in ours laboratory. Results given that the transport by adsorbed phase thus appears to be an environmentally attractive and rather economical route, as compared to liquid one.

Analyses with different gas mixture containing CO₂ and a higher pressure than 10 Bar are the next steps of this work.

References

1. S. Cavenati, Carlos A. Grande, T.C. Drage, C.E. Snape, 2005, Removal of carbon dioxide from natural gas by vacuum pressure swing adsorption, *Fuel* Vol. 84, pp. 2204-2210
2. K.T. Chue, J.N. Kim, Y.J. Yoo and S.H. Cho, 1995, Comparison of activated carbon and zeolite 13X for CO₂ recovery from flue gas by pressure swing adsorption, *Ind. Eng. Chem. Res.* Vol. 34, pp. 591-598
3. S. Sircar and T.C. Golden, M.B. Rao, 1996, Activated carbon for gas separation and storage, *Carbon* Vol.34 No.1, pp.1-12,
4. V. Siriwardane, and M. Shen, E.P. Fisher, J.A. Poston, 2001, Adsorption of CO₂, N₂, and O₂ on Natural, *Energy & Fuels Zeolites Energy & Fuels*, 15, 279-284
5. <http://www.sol3d.com>
6. Ozaki, M., Davison, Minamiura J. [2005] Marine Transportation of CO₂. *Greenhouse Gas Control Technologies*, 2: 2535-2539.
7. Oztürk, Z. [2004]. Investigating Optimun speed in high-speed railway: Istanbul-Ankara Corridor. *The Bulletin of the Istanbul technical University*. 54: (3),78-89
8. Edwards W., Grain Wagon Transportation Cost, Iowa State University Extension, URL, www.extension.iastate.edu/AgDM/crops/xls/a3-29graintransportation.xls
9. Barrio M., Aspelund A., Weydahl T., Sandvik I.E. Wongraven, L.R.; Krogstad, H; Henningsen, R; Mølnvik, M; Eide, S.I. [2005] Ship-based transport of CO₂. *Greenhouse Gas Control Technologies*, II, 1655-1660.
10. Aspelund A., Sandvik T.E., Krogstad H., Koeijer G. [2005] Liquefaction of Captured CO₂ for ship-based Transport. *Green House Gas Control technologies*. 2: 2545-2549
11. STATOIL; Elsam; KM. [2003]. Delivery of CO₂ to Gullfaks - Tampen Area
URL, www.co2.no/download.asp?DAFID=17&DAAID=6,2003
12. Fujjoka Y.; Ozaki, M; Takeuchi, K; [1997] Cost comparison in various CO₂ ocean disposal options. *Energy conversion management*. 38: 273-277