CO_2 Capture on Zeolites for Sustainable Energy Production

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In the context of the global warming, which is unanimously considered to be determined by the increasing of greenhouse gases emission, CO_2 capture and sequestration is one of the possible ways to lower emissions resulted in fossil fuel combustion for industrial energy production. Most of the emissions of CO_2 to the atmosphere from the electricity generation and industrial sectors are currently in the form of flue gas from combustion, in which the CO_2 concentration is typically 4-14 % by volume, although CO_2 is produced at high concentrations by a few industrial processes. Different technologies for CO_2 capture are currently under research and development: physical/chemical absorption, adsorption, membrane separation. Today, chemical absorption is a typically process, with an energy cost ranging from 280 up to 960 kcal/kg CO_2, depending on the sorbent type and the process configuration. Different types of zeolites with low Si/Al ratio, i.e., high aluminium content (zeolites NaA and NaX), high Si/Al ratio, i.e. low aluminium content (zeolite ZSM-5) and mesoporous silica MCM-41, respectively have been synthesized to check their CO_2 adsorption capacity. Some data regarding zeolites synthesis, their characterisation, the experimental setup description and CO_2 adsorption results will be presented in this paper.

Keywords: zeolite, CO_2 capture, pressure swing adsorption

The burning of fossil fuels for energy generation for industrial and domestic use accounts for the emission of huge quantities of CO_2 in the atmosphere, which lead to a high degree of pollution by supporting the greenhouse effect. An evaluation of the CO_2 concentration in the environment has concluded that 70 % of the emissions result from the energy industry mainly because of fossil fuels combustion.

In order to reduce CO_2 emissions in the atmosphere the present tendencies are the following: the development and the implementation of feasible economic technologies to capture CO_2. There are three main directions for CO_2 emissions reduction:

- increasing of processes efficiency;
- replacement of present energy sources with others with less carbon or new technologies (unconventional energy sources);
- CO_2 capture and sequestration.

The sorbents materials designated to be used in CO_2 capturing are the synthetic zeolites. Gas adsorption on zeolites gains remarkable attention in the nanotechnology era, since it has importance in many industrial processes (Ruthven D.,1998, [1]; Delmas M. P. et al., 1995, [2]; Mac Dougall et al 1990, [3]; D. W. Breck, 1984, [4]).

The post-combustion technology for capturing the carbon dioxide has as main goal a selective mass transfer of one or more components to a stationary layer of solid porous materials, the adsorption process taking place simultaneously by chemical reactions or by forming physical bonds between the captured component and the adsorbent solid surface. In this way the gases are purified, the harmful components – in this case, the carbon dioxide, being eliminated.

Experiments part

Industrial flue gas characteristics

In our case study flue gas used to prove CO_2 capture on zeolites was collected from an industrial power plant, located nearly Black Sea Coast refinery and petrochemical plant named Midia Navodari (a Rompetrol Society Subsidiary). Midia Power Plant produces power for national energy system and steam for the refinery and petrochemical total site and uses for combustion feed also fuel oil and also natural gas or both of them. In order to characterise the flue gas composition generated by burning of mentioned fuel laboratory tests and measurements have been conducted in a steam boiler of the plant, with a 105-t/h capacity of steam generated, adequate adapted to supply the needed information and data for our studies. The flue gas resulted from the combustion process are evacuated in atmosphere through the funnels for dispersion. The tests and experiments have been conducted for different charges of the boiler: between 70 and 90 t/h by using fuel oil and natural gases in different proportions of volumetric flow rates. The analysis of component concentration in the flue gas which was evacuated in the vent has been carried out with a high sensitive sensor (TESTO 350 XL). Table 1 presents the flue gas component concentrations recorded at their evacuation in the atmosphere when the two types of fuel were used.

Table 1

FLUE GAS COMPONENT CONCENTRATION INTERVALS, IDENTIFIED FROM THE EXPERIMENTS

		Natural gas		Fuel oil	
Component	Units	minim	maxim	minim	maxim
excess of combustion air	% vol.	35.6	47.3	12.9	14.3
t_{ga}	^{o}C	157-160		186-189	
O_2	% vol.	5.51	6.74	2.4	2.63
CO2.	% vol.	8.08	8.78	14.96	15.15
CO	mg/Nm^3	0	2	2	2
NO_x	mg/Nm^3	213	214	487	505
SO_2	mg/Nm^3	0	0	1832	1926

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Syntheses of zeolite adsorbents (molecular sieves type) for carbon dioxide capture

The structure of zeolite we had to be synthesized was of molecular sieve type and selective for CO_2 and it had to have the following characteristics: large pore structure, medium pore structure, small pore zeolite structure and ordered mesoporous material in order to establish the relation between adsorption process performances and zeolite structure.

Different types of zeolites with low Si/Al ratio, i.e., high aluminum content (NaA and NaX zeolites), high Si/Al ratio, i.e. low aluminum content (ZSM-5 zeolite) and mesoporous MCM-41 silica, respectively have been synthesized to check their CO2 adsorption capacity (C. Zhang et al, 2003, [5]; J. Weitkamp, 2000, [6]; J. S. Beck et al., 1992, [7]).

Generally, the synthesis of zeolites involves a few elementary steps in which a mixture of silica and alumina precursors, alkaline cations and water is converted into microporous crystalline aluminosilicates {R. M. Barrer, 1987, [8]). Zeolites A and X were synthesized in an inorganic system: SiO_2-Al_2O_3-Na_2O-H_2O. The high silica containing ZSM-5 zeolite was synthesized using 1, 6-diaminohexane (HDA) as structure directing agent (template). The synthesis of mesoporous MCM-41 silica involves the use of a surfactant aqueous solution. The cationic surfactant assisted synthesis of the MCM-41 (sample 07ZEC$_6$) has been performed according to reported procedures using cetyl trimethylammonium bromide (C_{16}TMABr) as surfactant (G. D. Stucky et al., 1994, [9]). Sodium silicate, tetramethylammonium hydroxide and fumed silica were used as reagents.

For all zeolite syntheses the crystalline solid materials were recovered by successive operations of filtration, washing with distilled water to *p*H of 7.5-8.0 followed by drying in air at 100°C. The preparation process of the MFI-type material included several successive hydrothermal post synthesis stages to obtain the hydrogen form of ZSM-5 zeolite as follows:

- calcination in air at 600°C for 6 hours to remove the organic template;
- ion exchange with 1M NH_4NO_3 solution at 90°C, followed by washing with distilled water and drying at 100°C;
- calcination at 550°C to convert NH_4-ZSM-5 into H-ZSM-5.

Table 2 gathers the synthesis conditions of sodium form of zeolites A and X and ZSM-5 zeolite, respectively and mesoporous MCM-41 silica.

Structural characterization of adsorbents

The synthesis of the designed molecular sieves was checked by X-ray diffraction (XRD). The samples were recorded on a computer-controlled DRON DART UM2 diffraction meter equipped with a graphite monochromatized Cu anode.

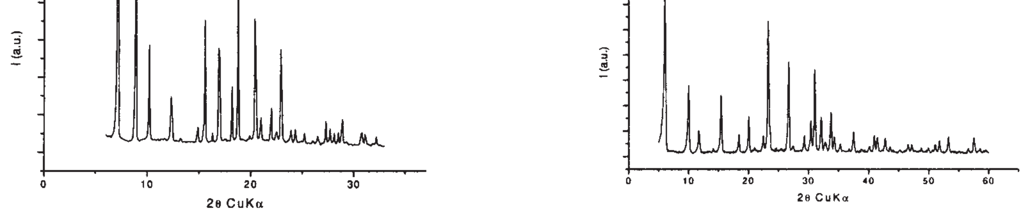
The XRD patterns confirm the formation of the desired zeolite structure: A zeolite, X zeolite and ZSM-5 zeolite and of ordered mesoporous MCM-41 respectively. Figures 1 (a,b) and 2 (a) display the XRD patterns of well-crystallized zeolites exhibiting the crystalline structure of zeolite A (framework type LTA), zeolite X (framework type FAU) and ZSM-5 (framework type MFI), respectively (M.M.J. Treacy et al., 2001, [10]).

It is necessary to stress that the diffraction pattern of faujasite zeolites showed that the zeolite synthesized in our laboratory (sample 07ZEC5) is structurally similar to commercial 13X-UOP zeolite.

Note that the LTA and FAU frameworks types described structures build from three-dimensional channels intersecting large cavities. The channels are of 0.41x0.41 nm for LTA framework type and of 0.74 x 0.74 nm for FAU framework type, respectively. The MFI framework has a particular structure characterized by a void space of three-dimensional interconnecting channels of 10-rings of 0.51x 0.55 nm and 0.54 x 0.56 nm respectively (Ch. Baerlocher, et al., 2001, [11]). The MCM-41 structure is not a genuine crystalline structure because the atomic arrangement of walls is not crystalline.

Table 2
SYNTHESES OF ZEOLITES A, X AND ZSM-5 AND MESOPOROUS SILICA MCM-41

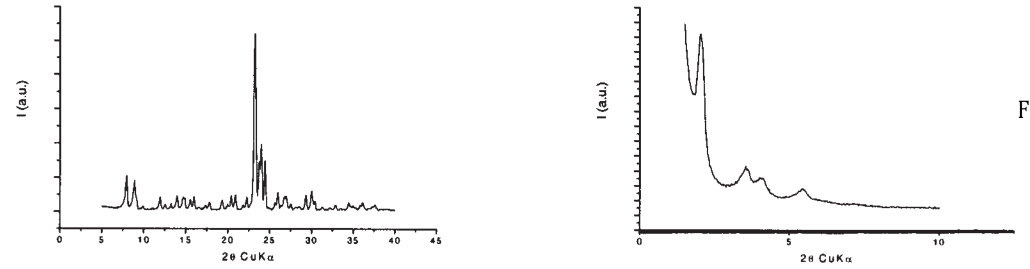
Synthesis type	Gel - molar composition	Hydrothermal synthesis
NaA 07ZEC$_1$ Zeolite	$2.0SiO_2 \cdot 1.0Al_2O_3 \cdot 2.2Na_2O \cdot 70H_2O$	Dynamic system, 1 L Parr reactor, pH=13, 80°C, 4 h
NaX 07ZEC$_5$ Zeolite	$1.0SiO_2 \cdot 1.0Al_2O_3 \cdot 3.5Na_2O \cdot 120H_2O$	Static system, 10 mL autoclave, pH=13, 100°C, 4 h
Na-ZSM-5 07ZEC$_3$ Zeolite	$1100.0SiO_2 \cdot 1.0Al_2O_3 \cdot 1.2Na_2O \cdot 0.22HDA \cdot 60H_2O$	Dynamic conditions, 1 L Parr reactor pH 12.2,170°C, 48 h
MCM-41 07ZEC$_6$	$SiO_2 \cdot 0.07Na_2O \cdot 0.08TMAOH \cdot 0.15C_{16}TMABr \cdot 60H_2O$	Dynamic conditions 1 L Parr reactor pH 12,100°C, 48 h



(a) As-synthesised A-zeolite specimen (07ZEC1)

(b) XRD pattern of as-synthesised X-zeolite specimen (07ZEC5)

Fig. 1. XRD patterns for A- and X- zeolites



(a) As-synthesized ZSM-5 zeolite specimen (07ZEC$_3$)

(b) As-synthesized ordered mesoporous MCM-41 specimen (07ZEC$_6$)

Fig.2. XRD patterns for ZSM and MCM zeolites

The typical XRD pattern exhibits in the wide-angle region only a broad peak around 2θ=23°, indicative for amorphous silica including the intrinsic contribution of wall disorder structure (F. Schuth, 1996, [12]) (not shown here). In the low-angle region 4 to 5 Bragg reflections appears revealing the regular disposition of pore systems and can be indexed according to a 2D hexagonal *p6mm* symmetry (fig. 2b). The MCM-41 structure is an assemblage of 3-5 nm size parallel hexagonal channels developing a so-called "honeycomb" motif.

Textural characterization of adsorbents

Textural characteristics of the samples including specific surface area, pore volume, pore size distribution and average pore diameter were evaluated from nitrogen adsorption measurements at 77K using an Automatic Volumetric Sorption Analyzer (Autosorb MP-1, Quantachrome).

The following samples were analyzed to evaluate the pore structure parameters: commercial 13X zeolite, NaX (07ZEC$_5$) zeolite, H-ZSM-5 (07ZEC$_3$) zeolite and calcined MCM-41 (07ZEC$_6$), respectively. All samples were degassed at 300°C for 4 h at 10^{-5} torr prior to nitrogen adsorption measurements. The adsorption isotherms corresponding to microporous materials are of type I having relatively small external surface in accordance to IUPAC classification. Some differences between the zeolite samples can be related to different pore structure accessibility.

For all samples adsorption isotherms showed a fast increase in the nitrogen amount adsorbed in the low pressure region (p/p < 0.1) followed by a long flat region at higher pressures. The difference appeared in the higher-pressure region (p/p_0>0.9) leads to the following order of large pore size: NaX (07ZEC$_5$) zeolite > commercial 13X zeolite > H-ZSM-5 zeolite. This result can be related to different factors as type framework structure, cationic composition, synthesis conditions, etc. Nitrogen adsorption-desorption isotherm of MCM-41 sample is of type IV according to IUPAC classification. The shape of the isotherm and the hystheresis loop associated with capillary condensation in mesopores are characteristic for cylindrical mesopores, which indeed form the MCM-41 structure.

Table 3 shows the textural data of different adsorbents. The surface area was calculated using the BET equation. The total pore volume was obtained by converting the amount adsorbed at a relative pressure of 0.999 to the volume of adsorbate liquid. The micro pore area and micro pore volume was evaluated by the t-plot method. The pore size distribution was determined by the BJH method using the desorption branch of the isotherm. In general the values obtained for X zeolite and ZSM-5 zeolite samples are in accordance to reported data. Data presented in table 3 shows that FAU-type structure offers some advantages in terms of surface area and pore volume, which can provide more space for adsorbate molecules to accumulate and adsorb inside the cage structure of diameter>0.11 nm. In general, high surface areas and large pore volumes are important parameters for the selection of a zeolite adsorbent. The MCM-41 sample has high specific surface area, high pore volume and large pore diameter that are typically for a highly ordered pore structure. In connection with reported data it can presume that good MCM-41 based adsorbents for carbon dioxide capture could be obtain by both exploiting the MCM-41 mesoporosity and applying a post synthesis chemically modified treatment (A. Macario et al., 2005, [13]; R. S. Franchi et al., 2006, [14]).

Adsorption process experiments and modeling

The equilibrium dates from adsorption CO_2 on zeolites were obtained with thermo gravimetric instrument *Du Pont 951*. The laboratory set-up consists of thermo gravimetric balance (TG) to determine the amount of CO_2 at a wide range of temperatures and pressures, and a modified differential scanning calorimeter. These determinations may represent a quantitative criterion for the pre-selection of synthesized zeolites, which will be used in the CO_2 capture technology The set-up is carried out as a closed system in which the sample is placed in an atmosphere of pure vapor of carbon dioxide. No other gas is present in the test cell during the measurements. The system is designed to work at a temperature range for the sample from 0 to 600°C. For each temperature step, one equilibrium point consisting of temperature, pressure and adsorbed amount mass of the sample is needed. The sample is completely desorbed as soon as its weight does not show any further change. During an adsorption process step and also

Table 3
THE TEXTURAL CHARACTERISTICS OF ADSORBENTS

Sample	Surface area, m^2/g		Pore volume, cm^3/g		Average pore diameter, nm
	BET^a	micropore	total	micropore	
13X UOP Zeolite	906	719	0.667	0.210	1.41
NaX-07ZEC$_5$ Zeolite	692	501	1.035	0.164	1.42
H-ZSM-5-07ZEC$_3$ Zeolite	410.5	255	0.323	0.102	1.41
MCM-41 - 07ZEC$_6$	1113	-	1.437	0.37	2.52

Table 4
CO_2 ADSORPTION CAPACITY OF SEVERAL SORBENTS

Zeolite	Maximum adsorption capacity in g CO_2/ 100 g adsorbent, at 27 °C (nearly liquefaction pressure of pure CO_2 at this temperature)	
	99.99% CO2 purity	CO_2 with traces of H_2O
	Commercial zeolites	
13X- UOP	19.52	-*
07- UOP	19.37	-
13XE	14.39	9.71
5A balls	13.31	-
A 15	5.4	-
	Synthesized zeolites	
07ZEC 5	20.02	23.6
07ZEC 3	6.16	-
07ZEC 3E	4.6	-
07ZEC 1	4.2	-
07ZEC	1.6	-
A7 TUF	5.35	-
A5 TUF	12.7	-
CLN-Cu	5.43	-
CLN-Cu-La	4.1	-

* "- " no experimented

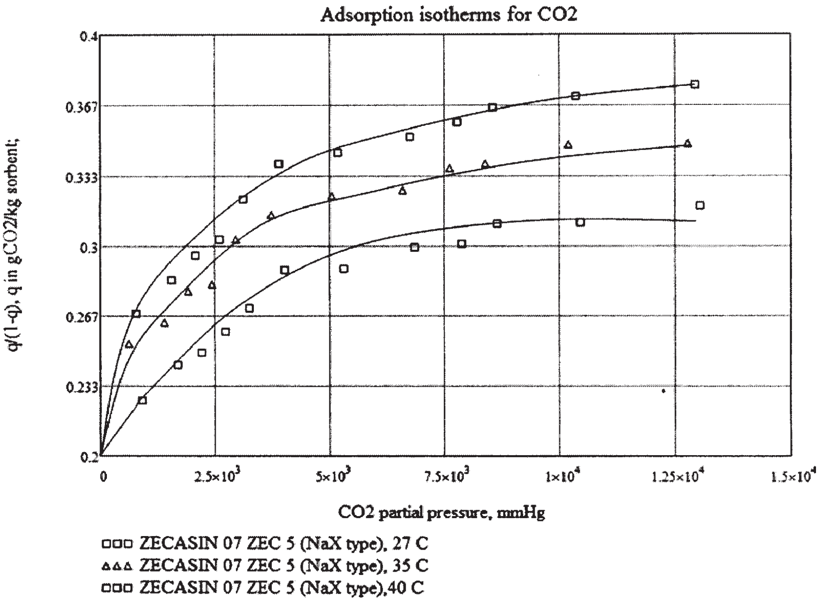


Fig.3. Equilibrium data of system CO_2 gas-solid phase of ZECASIN 07 ZEC 5 zeolite, at different temperatures

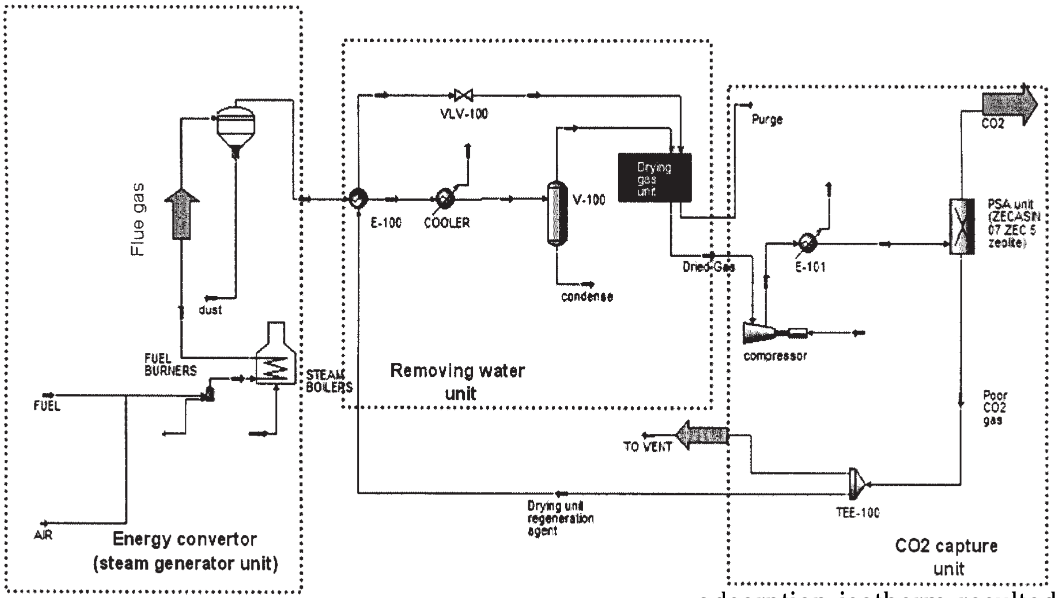


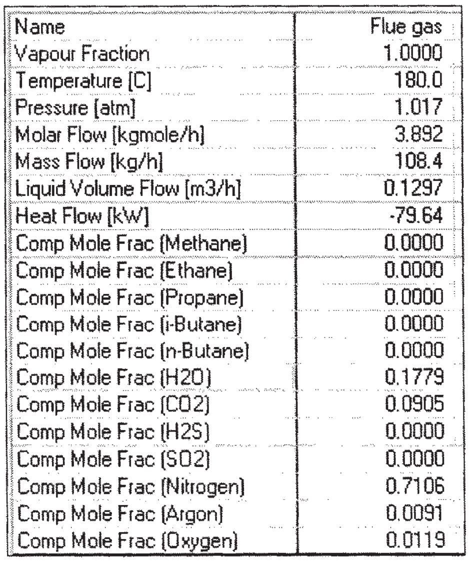
Fig.4. Process flow sheet for post-combustion CO_2 capture

desorption process step all equilibrium points are reached and the hysteresis diagrams are records.

Table 4 presents the adsorption capacity of the commercial and our synthesized zeolites, and figure 3 gives adsorption isotherm resulted from experiment data interpretation.

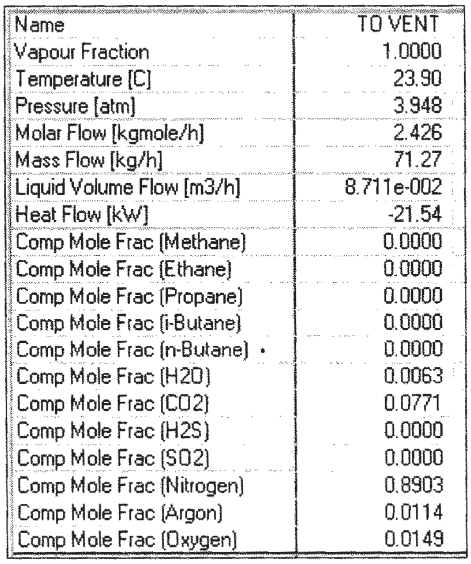
Post-combustion CO_2 capture process topology

Several operation techniques of the adsorption process are known: thermal swing adsorption (TSA) and pressure



Name	Flue gas
Vapour Fraction	1.0000
Temperature [C]	180.0
Pressure [atm]	1.017
Molar Flow [kgmole/h]	3.892
Mass Flow [kg/h]	108.4
Liquid Volume Flow [m3/h]	0.1297
Heat Flow [kW]	-79.64
Comp Mole Frac (Methane)	0.0000
Comp Mole Frac (Ethane)	0.0000
Comp Mole Frac (Propane)	0.0000
Comp Mole Frac (i-Butane)	0.0000
Comp Mole Frac (n-Butane)	0.0000
Comp Mole Frac (H2O)	0.1779
Comp Mole Frac (CO2)	0.0905
Comp Mole Frac (H2S)	0.0000
Comp Mole Frac (SO2)	0.0000
Comp Mole Frac (Nitrogen)	0.7106
Comp Mole Frac (Argon)	0.0091
Comp Mole Frac (Oxygen)	0.0119

Fig,5. Flue gas characteristics at outlet of boilers unit



Name	TO VENT
Vapour Fraction	1.0000
Temperature [C]	23.90
Pressure [atm]	3.948
Molar Flow [kgmole/h]	2.426
Mass Flow [kg/h]	71.27
Liquid Volume Flow [m3/h]	8.711e-002
Heat Flow [kW]	-21.54
Comp Mole Frac (Methane)	0.0000
Comp Mole Frac (Ethane)	0.0000
Comp Mole Frac (Propane)	0.0000
Comp Mole Frac (i-Butane)	0.0000
Comp Mole Frac (n-Butane) •	0.0000
Comp Mole Frac (H2O)	0.0063
Comp Mole Frac (CO2)	0.0771
Comp Mole Frac (H2S)	0.0000
Comp Mole Frac (SO2)	0.0000
Comp Mole Frac (Nitrogen)	0.8903
Comp Mole Frac (Argon)	0.0114
Comp Mole Frac (Oxygen)	0.0149

Fig. 6. Flue gas discharged in vent

swing adsorption (PSA). In both techniques, components adsorption and desorption are carried out through an adequate temperature change or pressure change in the adsorption system. Based on experimental data (especially adsorption equilibrium and adsorption capacity) we used process simulation to synthesize a process for post-combustion CO_2 capture. In figure 4 is given process flow diagram of the synthesized unit. This process unit corresponds to an experimental micro pilot.

Flue gas stream characteristics are presented in figure 5. This stream leaves steam boilers of the power plant unit (the energy converter) and enters in a solid separator in order to remove its content of solid particles. After a succession of operations of cooling and condensed water advanced removing flue gas is dried in a molecular sieves process unit. Then, dried flue gas enters in the adsorption unit, equipped with ZECASIN 07 ZEC 5 zeolite, after a pre-compression at 6 atm pressure. Superheated steam is used to regenerate zeolite sorbent in the adsorption unit. Poor in CO_2 flue gas, in adequate quantities, at an adequate temperature, is used to regenerate molecular sieve drier unit. Figure 6 gives characteristics of poor gas discharged in the vent.

Adsorption unit considered in flow sheet simulation was a PSA device with 2 cylinders. This PSA system was modeled and simulated by using MATLAB, according process data given in flow sheet scheme(fig. 5). 200 kg was the quantity of zeolite required to fit the mass balance of the process flow sheet.

In other paper was studied the conversion of light hydrocarbons from petroleum refining processes over Zn-H-HZSM-5 and ZnO / HZSM-5 catalysts [15].

Conclusions

CO_2 on zeolites post-combustion capture process was studied to estimate adsorption capacities and to synthesize and economic evaluate the process. A NaX type zeolite (*ZECASIN 07 ZEC 5*) was prepared and characterized. There have been also synthesized and morphological and structural characterized a series of different type of zeolites LTA, FAU and MFI. From all the synthesized zeolites, the 07 ZEC C5 adsorbent has shown a structural and morphological similitude with the commercial zeolites 13 X-UOP and 07 UOP. The 07 ZEC C5 type synthetic zeolite has indicated the higher CO_2 adsorption capacity after the conducted tests by using the thermo desorption technique.

Based on this zeolite adsorption experiments were developed in order to modeling the process from thermodynamic and kinetic point of view. A post-combustion capture of CO_2 unit was then modeled and simulated in order to evaluate the technical-economic characteristics of a pilot plant.

It was found that the 200 kg of zeolite are capable to capture 5 kg/h CO_2 from the flow rate of approximate 108 kg/h burned gasses containing initially a concentration of 14.3%(wt) CO_2. The operating costs for this capture were estimated to correspond to a theoretical consumption of 7 kW electric energy and 2 kW thermal energy (superheated steam).

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