Carbon Dioxide Separation from Cement Industry's Flue Gas by Cyclic Processes through Adsorbent Material from Natural Origins

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ABSTRACT

In the present case, the implementation of a Pressure Swing Adsorption – PSA – system was studied in order to separate carbon dioxide from a gaseous stream, containing 80% of nitrogen, originated from SECIL-Outão's plant. The design considers a recovery of CO_2 of 92% and a purity of 95%.

During the design, 3 adsorbents where considered: zeolite 13X and two pillared clays (PILCs), Zr Wyoming (Zr_W) and Al Wyoming (Al_W). It was also considered the existence of 3 cycle times of 3, 5 and 10 minutes.

A short economic balance is presented taking into account the material cost, the recovered carbon dioxide economic potential and the energetic cost associated to the process.

Keywords: Adsorption; PSA; Carbon Dioxide; Design; Zeolite; PILC;

INTRODUCTION

Emissions of pollutant gases, as CO_2, had been of great concern to populations and world government for several decades. The establishment of international protocols in order to contain and control emissions from this gas and its consequences to the environment have been considered insufficient in their primal goal. The use of CCS methods – Carbon Capture and Storage – have been presented as an innovating approach with space for improvement.[1]

SECIL, as a cement producer, is part of an industry where CO_2 emissions present themselves as a major issue due to its dependence on cement production processes.[2] Since 2010, CO_2 emissions from SECIL have been representing above 99% of all flue gas annually thus the urge to reduce the amount of CO_2 released.[3]

According to CCS there are 3 ways for control and reduce of CO_2 emissions: [4,5]

1. Reducing Energy Intensity – by using energy efficiently;
2. Reduce Carbon Intensity – by using cleaner energy sources;
3. CO_2 capture promotion – by using and develop CO_2 capture and storage technologies;

SEPARATION TECHNOLOGIES

Over the last decades a large number of technologies have been used to capture CO_2 from several flue gases and several industries. Among the vast spectrum of existing processes there are 3 that are considered of major interest: chemical absorption, membranes and physical adsorption. [6,7]

Chemical absorption, as absorption using amine solutions such as MEA, is considered the most mature technology and its used due to the high affinity between amine solutions and CO_2. However, the same affinity is responsible for the need of complex regeneration processes, where high temperatures are required, leading to amine solution's degradation. This technology presents a high energy consumption (and cost) and a high corrosion rate. [5,8,9]

Separation by membranes, such as polymeric membranes, has gain attention during the last years due to its large selectivity and space for innovation. However, it is still difficult to conciliate selectivity with permeability thus not being prepared for large flows. [5,10]

From the 3 technologies physical adsorption is considered the best choice due to its high mechanical and thermal resistance, high versatility of use and easy synthesis of adsorbents in order to manage a higher selectivity. The most common adsorption processes are Temperature Swing

Adsorption (TSA) and Pressure Swing Adsorption (PSA) where TSA is commonly used for purification processes due to its long cycle times, and PSA is the process of choice for separations. [11,12]

A simple PSA cycle is commonly composed by 4 steps: [13,14,15]

1. Feed;
2. Pressurization and Adsorption;
3. Purge;
4. Depressurization and Regeneration;

MATERIALS

From the large number of known adsorbents, 2 groups are presented: zeolites and pillared clays (PILC). These materials are well known for the high selectivity of CO_2 over N_2, and for their physical properties and the possibility of working under high temperature and low pressures (up to 10 bar). Both materials work as molecular sieves and the capture of a certain compound depends majorly on pore size and functional groups at the material surface. For those reasons 3 adsorbents where considered for the present work: zeolite 13X, PILC Zr-Wyoming (Zr_W) and PILC Al-Wyoming (Al_W). As their physical parameters are very similar these were considered equal among the 3 adsorbents. Materials properties are listed in table 1. [12]

Table 1 – Materials physical properties;

|	
d_{poro} *(nm)*	6
ε_p	0,35
S_g *(m²/g)*	284,4
$d_{partícula}$ *(mm)*	4
$r_{partícula}$ *(mm)*	2
ε_e	0,5

ADSORPTION ISOTHERM

The adsorption isotherm represents the kinetic behaviour of a material regarding a compound. It gives a representation of how adsorption proceeds with the increase of pressure. In the present work the adsorption of CO_2 and N_2 follows the Langmuir type isotherm described by *Brunauer et al.*.[16]

$$q = \frac{Kq_mP}{1 + KP} \qquad (1)$$

where q_m represents the maximum amount of adsorbed compound and K corresponds to the equilibrium constant. The isotherm choice falls on the following assumptions:

1. The adsorption process occurs in a monolayer;
2. The forces between the species are neglected;
3. Adsorption only takes place when there is physical contact between a specie and the adsorbent surface;
4. The process is reversible;

The isotherms were determined using the data available in *Cavaneti et al.*[17] and *Pires et al.*[18] and the parameters are listed in table 2. Graphs 1 to 3 represent the adsorption isotherms for each specie on the 3 materials.
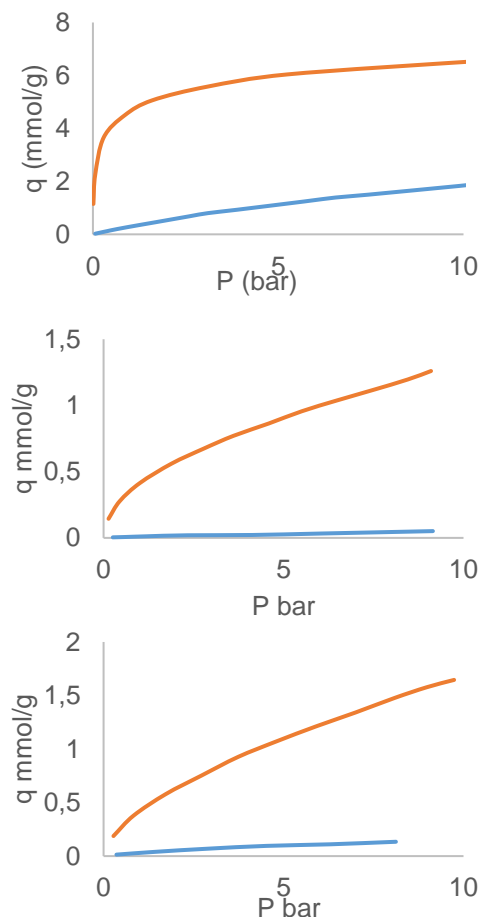
Graph 1 – Isotherms of adsorption for (a – up) zeolite 13X; (b – middle) PILC Zr_W and (c – down) PILC Al_W for CO_2 (orange) and N_2 (blue);

		q_m (mmol/g)	K (bar^{-1})
Z 13X	CO_2	7,358	1,417
	N_2	5,652	0,052
PILC Zr$_W$	CO_2	1,712	0,252
	N_2	0,169	0,045
PILC Al$_W$	CO_2	2,797	0,138
	N_2	0,250	0,125

The work capacity, q_w, gives the real adsorption capacity of a certain material for a given scale of pressure.

$$q_w = q_{HP} - q_{LP} \qquad (2)$$

where HP and LP corresponds to high and low pressure. Given by tables 3 and 4.

SELECTIVITY

Gives a measure of the material's affinity to a specie over others.[19] It considers the amount of specie in the fluid phase and in the adsorbed phase.

$$\alpha_{AB} = \frac{X_A/Y_A}{X_B/Y_B} \qquad (3)$$

where X_A and Y_A corresponds to the molar fractions of A in the adsorbed phase and in the fluid phase, respectively. This factor changes with the chosen material and for all 3 materials an increase variation with pressure is observed.

PROCESS DESIGN

In the present work a simple PSA system was considered for the recovery of 60.000t of CO_2 annually at Outão's plant. The process is composed by 2 parallel columns according to illustration 1, and the following operational assumptions were considered:

- Feed Pressure: 1 bar;
- Feed Temperature: 298K;
- Feed composition of CO_2/N_2: 20%/80%;
- Recovery of 92%;
- Purity of 95%;

Process	PSA
Feed	65.217,4 t
Feed composition	20/80 %v/v (CO_2/N_2)
Feed pressure	1 bar
Feed temperature	25 ºC
Recovery	92%
Purity	95%

Table 5 shows the initial assumptions on the process.

During the process design 3 cycles were studied of 3, 5 and 10 minutes and 2 cases of pressure range were also considered:

- Case 1: from 1 to 5 bar considering the 3 materials;
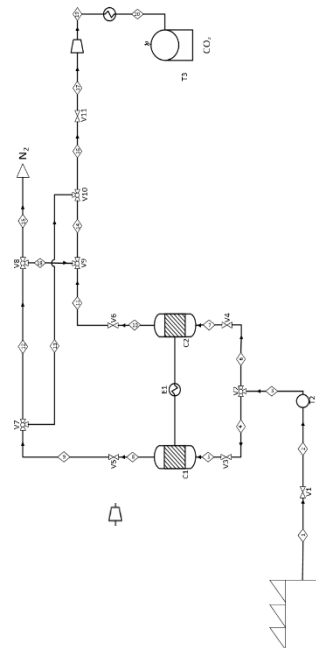- Case 2: from 1 to 10 bar considering only the PILCs;

Illustration 1 – Process diagram;

Table 4 – Work capacity from 1 to 5 bar;

	CO$_2$			N$_2$		
	q_{1bar}	q_{5bar}	q_w	q_{1bar}	q_{5bar}	q_w
	(mmol/g)	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*
Zr_W	0,344	0,954	0,610	0,007	0,031	0,024
Al_W	0,339	1,141	0,802	0,029	0,100	0,071
13X	4,314	6,448	2,134	0,281	1,171	0,890

Table 5 – Work capacity from 1 to 10 bar;

	CO$_2$			N$_2$		
	q_{1bar}	q_{10bar}	q_w	q_{1bar}	q_{10bar}	q_w
	(mmol/g)	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*	*(mmol/g)*
Zr_W	0,344	1,225	0,881	0,007	0,052	0,045
Al_W	0,339	1,621	1,282	0,029	0,145	0,116

GLOBAL BALANCE

Although the process within the columns is considered as a batch due to the steps of pressurization and depressurizations that occurs, the overall process is considered continuous.

$$Feed = CO_{2\,product} + N_{2\,product} \quad (4)$$

The determination of the columns dimensions depends on the materials properties, weight and volume according to equations:

$$S_g = 4\frac{\varepsilon_p}{\rho_p d_p} \quad (5)$$

$$M_{ads} = \frac{n_{CO_2}}{q_{w\,CO_2}} \quad (6)$$

$$V_{ads} = \frac{M_{ads}}{\rho_p} \quad (7)$$

The quantity of CO$_2$ in the process depends on the cycle time as the feed is 205,8kmol/h of CO$_2$, the longer the cycle, the bigger the amount of CO$_2$ to adsorb leading to higher columns. On the other hand, higher working capacities contribute to lower material quantity thus, lower bed volume.

The bed volume is given by:

$$V_{leito} = \frac{V_{ads}}{1 - \varepsilon_e} \quad (8)$$

Where the heuristic rule of $h = 3D$ ∴ $h_{leito} = 3D_{leito}$ was considered.

Aside from the bed volume, the volume occupied by the N$_2$ inert must also be taken into account as it remains untouched inside the column during adsorption. Once again, as the cycle time increases, the amount of N$_2$ also increases and it occupies the bed void volume and the extra volume on the top and bottom of the column.

$$V_{void} = V_{bed} \times \varepsilon_e \quad (9)$$

The void volume depends on the bed volume so for higher volume, such as the ones observed for PILCs comparing to the zeolite, the void volume is also higher and the extra volume of the column tends to decrease.

Overall, the columns dimensions are listed in table 6.

Where H corresponds to the height of the column and D to its diameter.

Table 6 – Overall columns dimensions for the 3 materials, time cycles and for each case;

	Case 1			Case 2	
	Zr_W	Al_W	13X	Zr_W	Al_W
H_{Column} (m) 3 min	40,2	47,2	86,2	26,7	32,9
D_{Column} (m) 3 min	2,7	2,4	1,8	2,4	2,1
H_{Column} (m) 5 min	47,7	55,9	102,2	31,7	39,0
D_{Column} (m) 5 min	3,2	2,9	2,1	2,8	2,5
H_{Column} (m) 10 min	60,1	70,5	128,7	39,9	49,1
D_{Column} (m) 10 min	4,0	3,7	2,6	3,5	3,1

CO$_2$ STORAGE

As the CO_2 is separated from the N_2 mixture it needs to be storage. According to the global balance the volume of CO_2 produced from the process corresponds to 218,3m^3/h, which in a daily basis it's equivalent to 395,9 m^3, considering the storage conditions of 273K and 80 bar. The gaseous product must be storage in Horton spheres as they are specially design for gases. The dependence of its dimensions with the number of spheres needed is presented in table 7.

Table 7 – Dependence of Horton spheres with the number of spheres;

Number of spheres	Volume sphere (m^3)	Radium sphere (m)	Diameter sphere (m)
1	396	4,6	9,11
2	198	3,6	7,23
3	132	3,2	6,32
4	99	2,9	5,74

MATERIAL COSTS

For the material cost was considered an average price per ton of adsorbent of 1,70€. As a column requires more adsorbent material, its cost become higher. However, the increase of material does not change linearly rather tends to present an exponential growth with time cycle, as seen in graph 2. As the cost changes linearly with material weight, material costs also presents the same behaviour. Comparing the 2 cases, case 1 presents higher costs than case 2 as it requires a bigger amount of adsorbent, as seen in table 8.
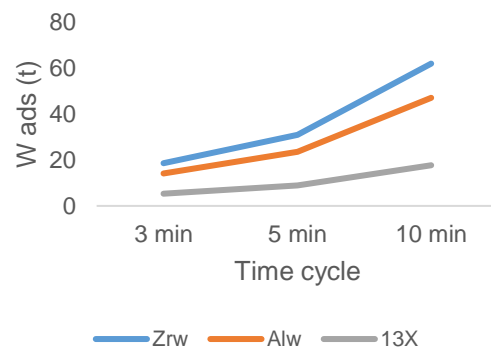
Graph 2 – Evolution of material weight with time cycle;

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Table 8 – Total cost of material for Case 1 (top) and Case 2 (bottom);

Cost $_{Total}$ (€)	3 min	5 min	10 min
Zr_W	63.071,28 €	105.118,80 €	210.237,59 €
Al_W	47.914,43 €	79.857,39 €	159.714,78 €
13X	18.015,95 €	30.026,58 €	60.053,17 €

Cost $_{Total}$ (€)	3 min	5 min	10 min
Zr_W	43.646,43 €	72.744,05 €	145.488,09 €
Al_W	29.983,39 €	49.972,32 €	99.944,64 €

ENERGY CONSUMPTION

There are 2 stages in the process where the most energy is consumed: during the adsorption and during the storage. During the adsorption the mixture of CO_2 ad N_2 is compressed to 5 bar, or to 10 bar, however the two species don't follow the same compression law[20]. As N_2 is an inert its compression follows a reversible adiabatic compression:

$$W = \frac{(P_f V_f - P_i V_i)}{\gamma - 1} \qquad (10)$$

with

$$\gamma = \frac{C_P}{C_V} \qquad (11)$$

The volume of N_2 is determined by knowing the density of the gas at initial and final pressure and the calorific capacities are intrinsic to each compound.

On the other hand, the amount of compressed CO_2 decreased with pressure thus being considered a reversible isothermal compression. Expressed by:

$$W = -nRT \ln \frac{P_i}{P_f} \qquad (12)$$

During the adsorption stage the amount of work needed changes with the cycles, as longer cycles contains higher amounts of gas thus requiring more work, nevertheless the amount of work in an hour does not change with the cycle as the amount of gas compressed in that time is the same for every cycle. During the storage stage, the mixture of mainly CO_2 is also treated as a reversible adiabatic compression.

As a result, the energetic consumption and cost regarding case 1 and case 2 are listed in table 9, considering the unitary price for energy consumption of 0,11€/kWh.

Table 9 – Energetic consumption and overall cost;

	Case 1	Case 2
E Total (kWh)	384,6	525,8
Cost €/h	42,31 €	57,84 €
Cost €/day	1 015,39 €	1 388,05 €
Cost €/year	304 617,29 €	416 414,59 €

CONCLUSION

- Smaller cycles require smaller equipments, consume less energy individually and are more productive. However, a smaller cycle needs sufficient time to avoid equipment and equipment control malfunction;
- Materials with higher work capacities lead to smaller bed volumes but also require a larger extra volume for inerts as they present a smaller void volume;
- The amount of adsorbent changes exponentially with time cycle;
- The increase of pressure leads to smaller equipments and lower amount of adsorbent but requires a higher energy consumption;

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