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## Feasibility assessment of CO<sub>2</sub> capture retrofitted to an existing cement plant: post-combustion vs. oxy-fuel combustion technology

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### Abstract

This research presents a preliminary techno-economic evaluation of CO<sub>2</sub> capture integrated with a cement plant. Two capture technologies are evaluated, monoethanolamine (MEA) post-combustion CO<sub>2</sub> capture and oxy-fuel combustion. Both are considered potential technologies that could contribute to reduction of CO<sub>2</sub> emissions in the cement industry. The study compares these two technologies in terms of technical performance, investment costs, and operational costs. The case study is applied to the one of the largest cement plants in Portugal, Alhandra. The results show that the amount of CO<sub>2</sub> avoided using the post-combustion MEA technology is lower due to additional emissions from reboiler steam production. Moreover, the total capital investment of the post-combustion CO<sub>2</sub> capture system is estimated at 260 M€<sub>2014</sub> and the annual operation and maintenance costs of around 43 M€<sub>2014</sub>; whereas the oxy-fuel combustion CO<sub>2</sub> capture requires a capital investment of about 217 M€<sub>2014</sub> and 37 M€<sub>2014</sub> annually for operation and maintenance. This indicates that the oxy-fuel CO<sub>2</sub> capture technology may be a better choice in terms of costs. However, this technology implies higher technical uncertainties concerning integration with the cement plant.

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## 1. Introduction

Cement is one of the most important building materials and its production is a highly energy intensive process. Limestone calcines at temperatures between 900 and 1000 °C and kiln temperatures are kept at 1500 °C to achieve calcination [1]. To produce the heat, mostly fossil fuels are used in the combustion system, leading to large amount of anthropogenic CO<sub>2</sub> emissions. The amount of CO<sub>2</sub> produced by decomposition of limestone in the raw mix is even larger than the CO<sub>2</sub> from the combustion process. This ranks the cement manufacturing sector as the second most relevant industry in terms of CO<sub>2</sub> emissions in Portugal, following electricity production. It is responsible for approximately 13 % of CO<sub>2</sub> emissions in the Portuguese energy system [2].

Although the cement industry is yet to deploy a large commercial capture project, CO<sub>2</sub> capture could significantly reduce its CO<sub>2</sub> emissions. Among the three types of CO<sub>2</sub> capture technologies (post-, pre-, and oxy- combustion) post-combustion and oxy-fuel combustion are the most suitable methods for capturing CO<sub>2</sub> at cement manufacturing plant. Pre-combustion CO<sub>2</sub> capture is less suitable because it does not capture the significant amount of CO<sub>2</sub> emission from the limestone calcinations process [3].

The objective of this research is to analyze the performance of the two capture methods when integrated in the cement plant. The case study is applied to the Alhandra cement plant, which uses a dry process with a 5 stage preheater and has a production capacity of around 5000 tonne per day. The feasibility assessment quantifies performance and cost impacts of retrofitting the plant with both CO<sub>2</sub> capture technologies. The objective is accomplished as follows:

- Simulation of the pyro-processing unit of the cement process;
- Technical evaluation of the MEA post-combustion CO<sub>2</sub> capture applied to the Alhandra cement plant;
- Technical evaluation of the Alhandra cement plant using oxy-fuel combustion;
- Preliminary cost analysis of both CO<sub>2</sub> capture methods, post-combustion and oxy-fuel combustion, for the designed systems.

### Nomenclature

AACE	Association for the Advancement of Cost Engineering
ASU	Air Separation Unit
CCS	Carbon Capture and Storage
CEPCI	Chemical Engineering Plant Cost index
CHP	Combined Heat and Power
DCC	Direct Contact Cooler
DF	Dust Filters
FGD	Flue Gas Desulphurization
IECM	Integrated Environmental Control Model
M	Millions
MEA	Monoethanolamine
O&M	Operation and Maintenance
SCR	Selective Catalytic Reduction
TCR	Total Capital Requirement

## 2. Methodology

### 2.1. Reference case study

The Alhandra cement plant is one of the largest cement plants operating in Portugal. It produces 1,8 Mt of clinker per year and started its production in 2005. The composition of the mix of fuels burned in the pyro-processing unit of the Alhandra plant is presented in Table 1, as well as the composition of the raw materials and the final clinker product.

Table 1. Summary of the main input and output streams used for the simulation of the reference case [4,5].

Input				Output			
Raw materials		Fuels		Final product		Pre-treated flue gas	
Composition		Composition		Composition		Composition	
CaCO <sub>3</sub>	90.28 %	Petroleum coke	77 %	Al <sub>2</sub> O <sub>3</sub>	0,7 %	CO <sub>2</sub>	16.5 mol%
SiO <sub>2</sub>	4.8 %	Alternative fuels	15 %	C <sub>2</sub> S	27,1 %	H <sub>2</sub> O	13.2 mol%
Al <sub>2</sub> O <sub>3</sub>	1.9 %	Biomass	6.6 %	C <sub>3</sub> S	51,5 %	N <sub>2</sub>	62.4 mol%
Fe <sub>2</sub> O <sub>3</sub>	1.61 %	Fuel oil	0.15 %	C <sub>3</sub> A	9,4 %	O <sub>2</sub>	7.9 mol%
Others	1.3 %	Gas oil	0.5 %	C <sub>4</sub> AF	2,7 %	Total flow	35720 kmol/h
Total flow	392235 kg/h	Natural gas	0.005 %	CaO	8.5 %	Temperature	128 °C
Temperature	25 °C	Total flow	25600 kg/h	Total flow	230570 kg/h		
		Temperature	25 °C	Temperature	50 °C		

The pyro-processing unit of the cement process was simulated in AspenPlus [6]. The process flow diagram includes a 5-stage preheater, a calciner, a kiln and a clinker cooler. Its simplified layout is shown in Fig. 1. Streams into the system are raw material, fuel inlet into the calciner and kiln and air for combustion and cooling. Streams that go out are the produced clinker and exhaust gases. The simulation was optimized in such manner that out-coming flows were in agreement with actual data from the Alhandra plant.

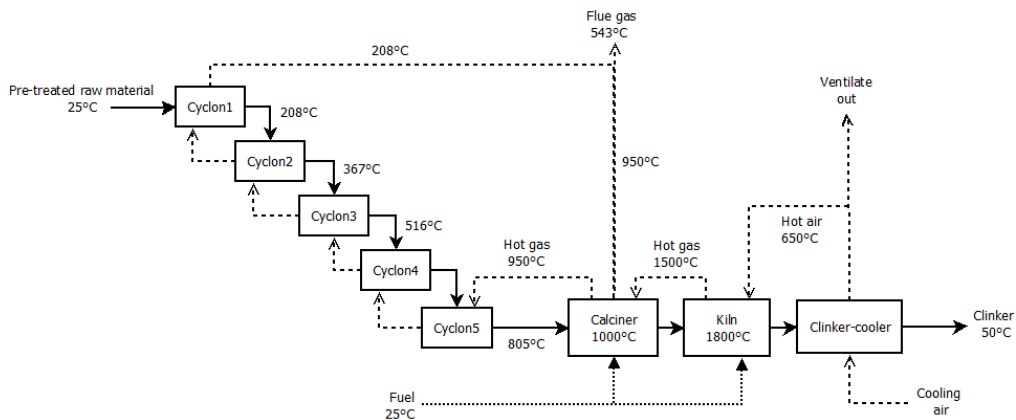


Fig. 1. Simplified diagram of the simulated reference cement plant.

## 2.2. Post-combustion CO<sub>2</sub> capture

Post-combustion systems separate CO<sub>2</sub> from the exhaust gases of the system by adding an additional unit to the tail-end of the clinker process where the CO<sub>2</sub> is separated from other combustion flue gases. The amine systems are currently the closest to commercial application and therefore are considered as the most mature technology to be applied on existing plants. The flue gases coming from the combustion process and the calcination reaction were considered as inlets into the MEA post-combustion unit. Unlike many coal power plants, cement plants are generally not equipped with SO<sub>2</sub> and NO<sub>x</sub> controls. Therefore, dust filter bags, FGD, and SCR facilities need to be additionally installed to avoid unnecessary solvent degradation. It is assumed that the pretreated flue gas entering the CO<sub>2</sub> capture process consists primarily of CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub> (Table 1). Fig. 2 shows the simplified flowsheet of the simulated CO<sub>2</sub> capture unit. It was simulated using ProTreat software [7].

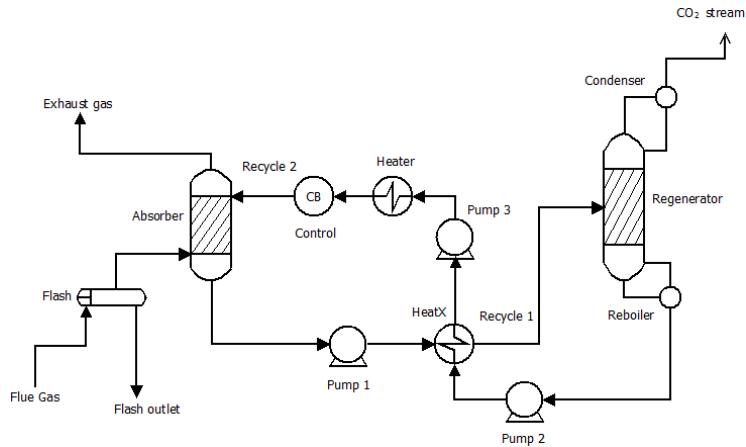


Fig. 2. Diagram of the simulated post-combustion CO<sub>2</sub> capture unit.

The exhaust gas from the cement plant is cooled down to 50 °C before it enters into the absorber, to improve the absorption of CO<sub>2</sub>. Also, the flue gas is pressurized in order to overcome a pressure drop when passing through the absorption column. The presented MEA scrubbing system consists of two main elements: an absorber where CO<sub>2</sub> is removed and a regenerator, where CO<sub>2</sub> is released and the original solvent is recovered. In this research, the main focus is minimizing the thermal energy requirement for the solvent regeneration and the solvent flow since these two parameters significantly lower the energy requirement and consequently reduce the total costs of the CO<sub>2</sub> capture process [8,9]. The representative solvent is 30% aqueous MEA, under lean sorbent loading 0.2 and the optimized sorbent flow was determined to be 50000 kmol/h, while capturing 90 % of CO<sub>2</sub>. Reboiler steam demand is assumed to be met with a dedicated auxiliary natural gas boiler. However, the additional boiler emits CO<sub>2</sub> itself which is released into the atmosphere. This offsets part of the CO<sub>2</sub> captured.

### 2.3. Oxy-fuel combustion CO<sub>2</sub> capture

Oxy-fuel combustion is gaining increasing interest from the cement industry. Wrampe and Rolseth showed several benefits, including increased clinker production, heat recovery, and combustion conditions [10]. With this technology, oxygen is used for combustion instead of air. It produces a flue gas mainly consisting of H<sub>2</sub>O and CO<sub>2</sub> and therefore allowing simple CO<sub>2</sub> purification. However, oxygen combustion increases the temperature profile in the kiln which can cause structural damage to the equipment [11,12]. It is therefore essential that a portion of the CO<sub>2</sub> rich flue gasses are recycled back to the combustion zone to moderate the flame temperature. This has a direct impact on the energy balance and the plant operation and yet the quality of the final product needs to be maintained. Another operational concern of an oxyfuel layout is corrosion from the flue gases in the recycle loop.

Fig. 3 presents a simplified simulated process diagram of the oxy-fuel combustion CO<sub>2</sub> capture system implemented into the reference cement plant. An ASU, recirculation duct and CPU were added to the simulation of pyro processing unit. The preheater, calciner and rotary kiln were kept unchanged. The effect of the flue gas recirculation rate was studied to obtain the desired oxy-fuel combustion capture process and was defined to be 0.595 in order to keep the temperature of the kiln at 1800 °C. The flue gas leaving the calciner consist of 88 % of CO<sub>2</sub>. Part of the flue gas enters the preheater and the remaining is cooled down and enters the CO<sub>2</sub> purification and compression. Additional modifications in the reference plant were considered, such as the adjustments in the burner and a proper sealing to avoid air leakage. Another important modification is the cooler improvement for the two-stage clinker-cooler. This layout is important to separately operate the two different gas atmospheres, the flue gas/oxygen mixture and the cooling air. The cooling air leaves the cooler at temperature of 485 °C and its heat is used for raw material drying. The overall quality of the final product is unchanged under oxy-fuel conditions.



Table 2. Prices used for the cost estimates.

Parameter	Unit	Value*	Source
Activated carbon	€/tonne	1282	[17]
Caustic soda	€/tonne	331.6	[17]
Limestone	€/tonne	50.86	[17]
Lime	€/tonne	260.5	[17]
Sorbent	€/tonne	1951	[18]
Reclaimer waste disposal CO <sub>2</sub> capture	€/tonne	192.8	[18]
Water	€/m <sup>3</sup>	1.547	[19]
Natural gas	€/GJ	13.04	[20]
Electricity	€/kWh	0.1802	[21]
Labour	€/h	11	[22]
FGD stacking	€/tonne	6.358	[18]
FGD waste disposal	€/tonne	10.9	[18]
NO <sub>x</sub> catalyst	€/m <sup>3</sup>	4515	[18]
Amonnia	€/tonne	113	[18]
Fabric dust filter bag	€/ks	97.16	[18]
Waste disposal dust filter	€/tonne	14.16	[18]
Misceallenous chemicals for CPU	€/tonneCO <sub>2</sub>	0.76	[18]

\*when necessary, currency conversion is applied.

### 3. Results and discussion

Table 3 presents the required modifications, CO<sub>2</sub> emissions balance, and the energy consumption when post-combustion CO<sub>2</sub> capture or oxy-fuel combustion is applied to the cement plant.

Table 3. Technical performance of the post-combustion and oxy-fuel combustion CO<sub>2</sub> capture process.

Parameter	Unit	MEA post-combustion CO <sub>2</sub> capture	Oxy-fuel combustion CO <sub>2</sub> capture
Modification to the reference plant		No	Kiln burner, two-stage clinker-cooler, sealing
Additional units installed to the reference plant		DF, SCR, FGD, DCC, CO <sub>2</sub> capture unit, compressor, CHP	ASU, DCC, CPU, CO <sub>2</sub> recycle, DCC, DF, fan, compressor
CO <sub>2</sub> capture rate	%	67.2	87.1
CO <sub>2</sub> in the flue gas	tonne/h	186.9	Total 459.2
	tonne/h	-	To recycle 273.2
	tonne/h	-	To CPU 186
CO <sub>2</sub> captured	tonne/h	161.9	161.9
CO <sub>2</sub> stack out	tonne/h	Total 61.26	24.06
	tonne/h	Primary stack 18.7	-
	tonne/h	CHP stack 42.56	-
Additional heat requirement	GJ/h	681.8	0
Electricity consumption	MW	9.56	30.93

The table shows that the amount of CO<sub>2</sub> captured is similar for the MEA and the oxy-fuel combustion case. However, under the MEA post-combustion option, a large amount of CO<sub>2</sub> emissions is caused by the additional CHP

(23 % of the total CO<sub>2</sub> emissions in the flue gas), which is vented to the atmosphere. Thus, oxy-fuel CO<sub>2</sub> capture has a larger direct CO<sub>2</sub> emission reduction potential, while producing the same amount of clinker as the reference plant. However, this figure only includes direct emissions, also including potential CO<sub>2</sub> emissions of electricity production might shift the balance away from oxy-fuel.

For the MEA case, the CO<sub>2</sub> emission reduction comes at the expense of 682 GJ/h of additional heat for solvent regeneration. In terms of electricity, the largest consumer is the CO<sub>2</sub> compressor. The oxy-fuel combustion process has higher consumption of electricity than the MEA case due to requirements from ASU and CPU.

Table 4 summarizes the direct capital and O&M costs of the designed CO<sub>2</sub> capture processes. The largest capital requirement for the post-combustion CO<sub>2</sub> capture process comes from the columns and the compression unit. Under the oxy-fuel combustion, the highest investments include the ASU and CPU (which includes the CO<sub>2</sub> compression), accounting for 68 % of the total investment costs. The cost estimates of the oxy-fuel configuration include an estimation of required modifications to the reference plant, such as adjustments to the burner and proper sealing to avoid air leakage.

In both configurations, the main operating costs are connected to the consumption of electricity. For the post-combustion CO<sub>2</sub> capture, the additional natural gas to the CHP also presents an important share of the O&M costs. Like the investment costs, the O&M costs of the oxy-fuel option are lower than those of the MEA option. This study hence suggests that also from an economic perspective oxy-fuel combustion may be preferable over MEA capture.

Table 4. Cost estimates of the post-combustion and oxy-fuel combustion CO<sub>2</sub> capture systems.

MEA post-combustion CO <sub>2</sub> capture		Oxy-fuel combustion CO <sub>2</sub> capture	
Capital investment	M€ <sub>2014</sub>		M€ <sub>2014</sub>
<i>Pretreatment of flue gases</i>		<i>Pretreatment of flue gases</i>	
Dust filters	10.12	Dust filters	10.54
Selective catalytic reduction	6.58	<i>Additional units</i>	
Flue gas desulphurization	45.4	Air separation unit	54.39
<i>CO<sub>2</sub> capture process area</i>		Flue gas recycle fan	1.08
Flash	10.52	Recycle flue gas pipeline	5.73
CO <sub>2</sub> absorber vessel	32.02	Flue gas cooler	14.61
Heat exchanger	1.95	Cryogenic purification unit	45.14
Sorbent circulation pumps	5.85	<i>Modification to the reference cement plant</i>	
Sorbent regenerator	21.48	Kiln burner	10.72
Reboiler	10.5	Two stage clinker cooler	3
Cooler of recycle	7.06	Sealing	0.07
Sorbent reclaiming	0.41	<i>CO<sub>2</sub> system process facilities capital</i>	
Sorbent processing	0.7	Engineering cost	10.71
<i>Additional heat supply</i>		General facilities capital	14.53
Auxiliary gas boiler	11.22	Project contingency cost	21.79
<i>Post-treatment of CO<sub>2</sub></i>		Process contingency cost	7.26
Drying and compression unit	21.67	Interest charges	10.31
<i>CO<sub>2</sub> system process facilities capital</i>		Royalty fees	7.26
General facilities capital	22.62	<i>Total capital requirement</i>	
Project contingency cost	15.83		216.6
Process contingency cost	33.93		
Interest charges	11.31		
Royalty fees	1.31		
<i>Total capital requirement</i>	260.25		

O&M costs	M€ <sub>2014</sub> /year		M€ <sub>2014</sub> /year
Variable	35.3	Variable	30.28
Fixed	8.03	Fixed	6.9
Total	43.33	Total	37.18

#### 4. Conclusions

This work presented a preliminary techno-economic assessment of CO<sub>2</sub> capture from a cement plant using A) MEA post-combustion technology with additional steam production in a NG boiler and B) oxy-fuel combustion technology. The results indicate that the oxy-fuel option is capable of achieving higher removal rates of the cement plants' direct CO<sub>2</sub> emissions (87 % versus 67 % for MEA). This is mainly due to the additional emissions of steam production which is required for the MEA post-combustion CO<sub>2</sub> capture unit, and the exclusion of secondary emissions from electricity use, which benefits the oxy-fuel case. Also from an economic perspective, the studied oxy-fuel configuration presents the lowest investment and operational costs. The TCR of the MEA and oxy-fuel case are 260 and 216 M€, respectively. The operational costs are 43 and 37 M€/a. The techno-economic results thus point towards oxy-fuel combustion as the preferable option for the studied cement plant. A drawback of the oxy-fuel case is that it requires more adaptations to the core clinker production process, increasing uncertainties in process performance and product quality. Post-combustion CO<sub>2</sub> capture could be readily implemented and may therefore be an easier option for retrofitting in the short term.

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