

ENVIRONMENTAL CONSEQUENCES OF CCS TECHNOLOGY INTEGRATION IN THE CEMENT PROCESS CHAIN

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Abstract: The cement industry is one of the major sources of CO₂ emissions. The CO₂ emissions from manufacturing cement process are provided from the calcination of the raw materials, the fuel used in the rotary kiln and the electricity used in the process. The CO₂ emissions from calcination process cannot be avoided, a way to reduce them is the integration of CO₂ capture technology. In this study, we analyzed the integration of the chemical absorption process using monoethanolamine. Since the temperature of the exhaust gases from cement plant is higher than 350 °C, a HRSG (Heat Recovery Steam Generator) was used for electricity generation. Also, the steam at the outlet of the back pressure steam turbine was used for solvent regeneration. In the cases studied, considering a constant value of the CO₂ capture process efficiency, the MEA weight concentration varied in the range 15-35 %, while the CO₂ lean loading solvent varied in the range 0.17-0.25 mol_{CO₂}/mol_{MEA}. After the chemical absorption process integration in the cement plant, the CO₂ emission factor obtained was 0.067 kg_{CO₂}/kg_{cement} and the specific heat consumption varied between 1.41-3.19 GJ/t_{CO₂} and 0.89-1.93 GJ/t_{cement}. The heat usage factor varied in the range 72-165 %, which means that in some cases studied the thermal energy available does not cover the heat duty required. However, for higher mass concentrations of MEA and higher CO₂ lean loading solvent, the heat duty required for desorption process is achieved.

Keywords: cement plant, CO₂ capture, chemical absorption process, MEA

1 INTRODUCTION

The cement industry is characterized by a high energy consumption and therefore it is an important source of CO₂ emissions which contribute to GHG emissions rising associated with the anthropic activities. The cement production increased constantly over time, reaching in 2013 of 2840 million tons of cement produced [1]. The CO₂ emissions of the cement production are generated by two sources: fossil fuels combustion and raw materials calcination (limestone). For one tone of cement produced, the amount of CO₂ emitted is in the range of 600 - 1000 kg_{CO₂}[1-2]. The cement industry contributes to global CO₂ emissions generated with approximately 5 % [2]. In the worldwide context focused on GHG emissions reduction until 2020, more solutions need to be analyzed for integration in the cement industry. One of the recognized solution for reducing the carbon dioxide emissions consists in the CCS technologies integration. Over the years, due to the progress in the cement industry, the CO₂ emissions per ton of cement produced was reduced either by improving the energy efficiency or by using additives for increasing the amount of clinker [3]. However, for further reduction of CO₂ emissions due to the limitation of the existing solutions mentioned above, other techniques need to be integrated in the cement process.

The cement plants are relatively large point sources of CO₂ due to the CO₂ molar concentration in the flue gases which is higher comparing to fossil fuel power plants (14-33% against 5-15%) [1]. The CO₂ emissions produced by a cement plant are provided by 60 % from the clinker production, 30 % from fuel combustion used in kiln, and 10 % from other operations [4]. Thus, by replacing the fossil fuels with renewable energy sources, the CO₂ emissions cannot be entirely avoided. Taking into account the Gibbs free energy, it will be more feasible to separate the molar CO₂ emissions from a cement plant comparing to a power plant [5-6]. Today, there are several technologies for capturing carbon dioxide from cement plants: starting with oxy-fuel combustion, or post-combustion like chemical absorption process and calcium looping combustion [4-6], see Figure 1. In either post-combustion cases, the chemical absorption or CaO looping combustion processes integration in a cement plant has the advantage that no major changes are required [7]. The main drawback of the chemical absorption process consists in a higher amount of heat required for solvent regeneration [8]. Generally, the heat is provided by the steam extracted from the low pressure steam turbine (in the energy process case) or by the heat recovery from the exhaust flue gases but, in the last case, the amount of heat recovered is not enough for a complete regeneration (to reach 0.2 mol_{CO₂}/mol_{solvent}). Thus, taking into account the exhaust gases flow and its temperature, a HRSG (heat recovery steam generator) unit could be used for steam generation [9]. In the HRSG unit case used, a part of the total steam flow at 3.6 bar could be extracted for chemical solvent regeneration.

The aim of this paper consists in the energetically assessment of the CO₂ capture post-combustion technology by chemical absorption process integration in a modern cement factory. In the whole process, the heat of the exhaust gasses is recovered in different steps in order to optimize it.

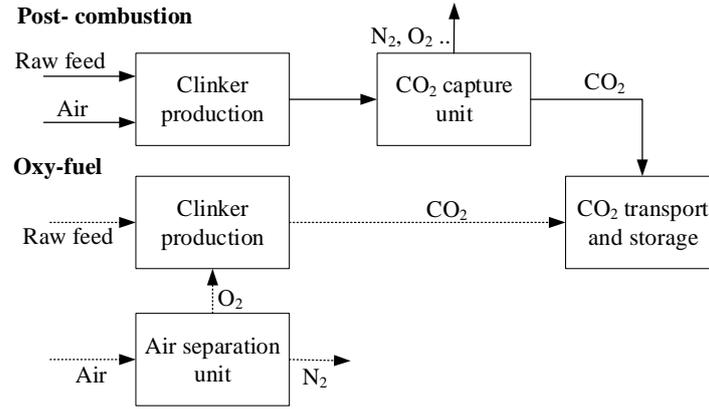


Figure 1: CO₂ capture technologies for cement industry [4]

2 METHOD

2.1. Cement manufacturing process description

The manufacturing cement process consists in three principal stages (Figure 2): the raw materials preparation, clinker production and cement preparation. In the first stage, the raw materials used are crushed, grinded and blended forming a raw feed. The principal raw material used to produce clinker is limestone (CaCO₃). For producing 1 kg of clinker, 1.5-1.6 kg raw feed dry is required [2], due to the chemical reactions that take place in the kiln (calcination of limestone). In the clinker production stage, the raw feed is introduced in kiln for a gradually heated up to approximately 1500 °C. The final stage consists of the grinding clinker with additives (gypsum, blast furnace slag, fly ash) and forming the final product. The clinker factor represents the ratio between the amount of the clinker produced and the amount of the additives introduced in the process. The clinker factor varies between the 0.5-0.95 [2]. For lower value of the clinker factor, the amount of the carbon dioxide produced is smaller, but the cement produced has a poor quality.

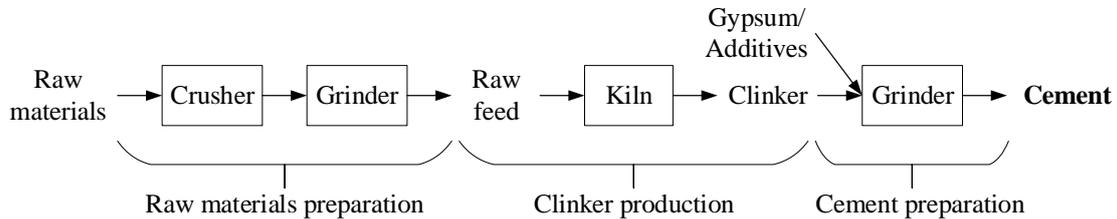


Figure 2. Simplified scheme of manufacturing cement process [1]

The processes applied in the cement production are divided in four categories: wet process, semi-wet process, semi-dry process and dry process. These processes are differentiated by the moisture content of the raw feed that enters the kiln. The dry process is the most efficient process from the fuel consumption point of view, due to the heat recovery in the preheater and pre-calciner unit. In the dry process the moisture content of the raw materials is reduced up to <1 % [1-2]. In the pre-calciner, the temperature reach up to 900 °C and approximately 80-90 % of the limestone calcination takes place here [2-3]. In the pre-calciner chamber approximately 60 % of the fuel is used [2].

The calcination process (limestone conversion) is the main carbon dioxide emission generator due to the chemical reaction that takes place [5]:



The amount of CO₂ generated by the cement production is influenced by the following parameters: type of fuel used (coal, petcoke, natural gas, heavy fuel oil etc.), type of the process applied and its efficiency, and the clinker factor. Another source of the CO₂ emissions is from electricity consumption. The grinding of raw materials and of clinker takes place in the stages with the largest electricity consumption. The electricity consumption reported by the IEA is of 90-120 kWh/t_{cement} [1].

In this study, we considered a dry process with rotary kiln, five stage preheater, pre-calciner and grate cooler. The fuel used was petcoke 100 % with a low heating value (LHV) of 33.5 MJ/kg. The main parameters of the cement manufacturing process are presented in Table 1, as well as the mass balance for producing of 1 kg of cement.

Table 1. Main design of cement process [2]

<i>Parameters</i>				
Type of process	Dry			
Fuel	Pet coke 100 %			
Low heating value of fuel	33.5 MJ/kg			
Clinker factor	0.8			
Raw materials factor	1.52 kg/kg _{clinker}			
Moisture	5 %			
Air moisture	1 %			
Heat consumption	3.3 MJ/kg			
<i>Mass balance</i>				
<i>Inputs</i>				
Raw materials	1214 g			
Petcoke	79 g			
Air	2605 g			
H ₂ O	71 g			
Additives	200 g			
<i>Outputs</i>				
Clinker	800			
Cement	1000			
Emissions	CO ₂	O ₂	N ₂	H ₂ O
	672 g	389 g	1975 g	132 g

The total amount of CO₂ generated to produce a 1 kg of cement is 672 g of which 421 g (63 %) comes from calcination of the raw materials and 251 g (37 %) from the combustion fuel. The CO₂ factor for production a 1 kg of clinker is of 0.84 kg_{CO₂}/kg_{clinker}. The CO₂ emissions factor of fuel used for produced electricity is of 1140.7 kg_{CO₂}/MWh.

2.2. Chemical absorption process integration into cement plant

As it is known, the CO₂ capture by chemical absorption process using amine is considered the most mature technology. The chemical absorption process consists in passing the gases through an absorption column. The absorption process takes place at temperature of ~ 50 °C [10]. The exhaust gases after the preheater unit have a temperature between 350-450 °C which allows producing steam in a HRSG unit [9, 11, 12]. In this study, we considered the temperature of exhaust gases of 400 °C as the average of the limits found in the scientific literature. Prior to the exhaust gases entering in the absorption column, a HRSG recovers the heat of the exhaust gases in order to reduce its temperature to around 50 °C. The rich chemical solvent in CO₂ comes out at the bottom of the absorber column and the clean exhaust gases exits at the top of the column. The desorption process takes place at a temperature of 120 °C [13]. Before the regeneration stage, the heat of the lean chemical solvent is transferred to the reach chemical solvent into a heat exchanger. After increasing its temperature, the lean chemical solvent in CO₂ is evacuated at the bottom of the desorption column for recirculated to absorption column. Due to the chemical solvent degradation in the desorption process, a fresh amount of chemical solvent is added for maintaining the mass concentration imposed in the absorption process [14]. The CO₂ separated leaves the desorption column at the top being compressed and transported to the storage site. In figure 3, the diagram of the chemical absorption process is presented.

In figure 4, the manufacturing cement process with CO₂ capture technology is presented. It can be seen that the heat is recovered for maximizing the process efficiency. The parameters of the steam extracted for solvent regeneration are: pressure is 3.6 bar and temperature is about 140 °C. The chemical solvent used in this study was monoethanolamine (MEA) in different concentration. The simulation of chemical absorption process was performed in ChemCAD, version 6.0.1. The thermodynamic package used in simulations was Amine packed. The main data of the simulated process is summarized in the Table 2. The CO₂ capture efficiency was calculated after the following equation:

$$\eta_{CO_2} = \frac{CO_2^{in} - CO_2^{out}}{CO_2^{in}} \cdot 100 [\%] \quad (2)$$

where: η_{CO_2} is the CO₂ capture efficiency, in %, CO_2^{in} is the amount of CO₂ from exhaust gases prior to chemical absorption process, CO_2^{out} is the amount of CO₂ from clean gases after chemical absorption process, in mol CO₂.

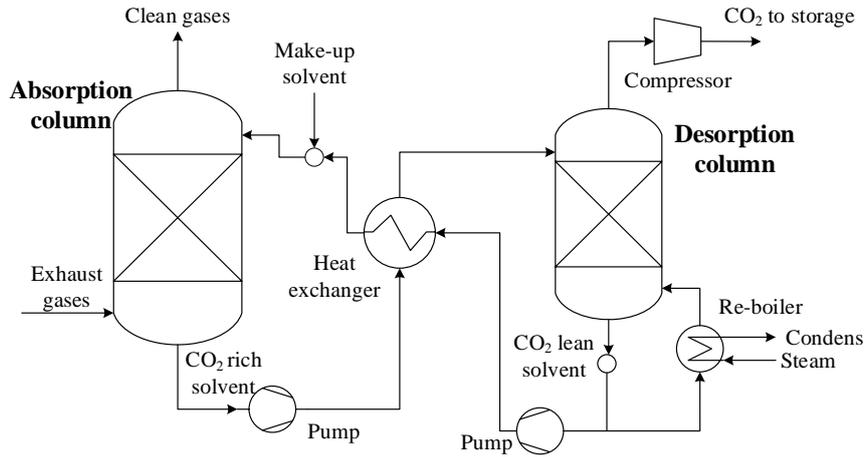


Figure 3. Chemical absorption process [15]

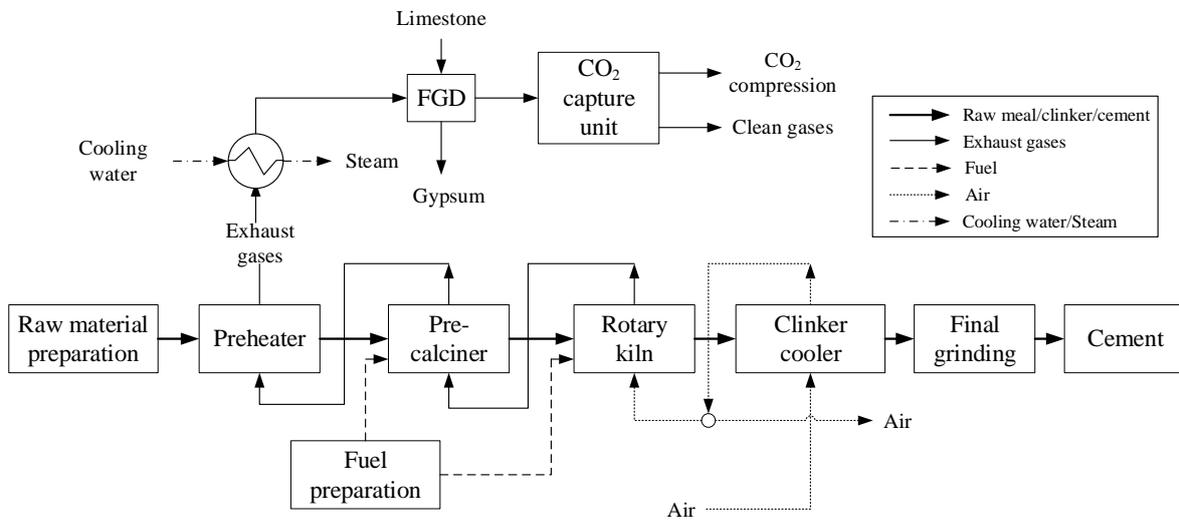


Figure 4. Cement plant with CO₂ capture [6]

Table 2. Main data of chemical absorption process

Parameters	Value			
Cement flow, [kg/h]	100			
Exhaust gases flow, [kg _{fg} /h]	316.8			
Exhaust gases composition, [wt. %]	CO ₂	O ₂	N ₂	H ₂ O
	21.21	12.28	62.34	4.17
Temperature exhaust gases, [°C]	400			
Temperature of chemical absorption process, [°C]	50			
Pressure of chemical absorption process, [bar]	1.013			
Temperature of desorption process, [°C]	120			
Pressure of desorption process, [bar]	2			
Steam temperature for solvent regeneration, [°C]	140			
Steam pressure for solvent regeneration, [bar]	3.6			
Number of stages absorption column	10			
Number of stages desorption column	10			
MEA weight concentration, [%]	15-35			
CO ₂ lean loading solvent, [mol _{CO2} /mol _{MEA}]	0.17-0.25			
CO ₂ capture efficiency, [%]	90			

3 RESULTS AND DISCUSSION

In this study, we analyzed the integration of chemical absorption process into a cement plant with heat recovery for steam generation used in the chemical solvent regeneration process. The CO₂ efficiency was maintained constant of 90 %. Due to the corrosiveness of the chemical solvent, the MEA weight concentration was considered of 35 %, 30 %, 25 %, 20 % and 15 %. The CO₂ lean loading solvent was varied between 0.17-0.25 mol_{CO2}/mol_{MEA}. In Figure 5, the variation of the ratio between the chemical solvent and exhaust gases (L/G) was represented. The L/G ratio varies with the weight concentration of MEA in the chemical solvent considering the same CO₂ capture process efficiency. For lower concentrations of MEA, the L/G ratio is higher to maintain the same CO₂ capture efficiency. The higher value of L/G ratio obtained was of 3.11 kg_{sol}/kg_{gas} for the MEA concentration of 15 % and the lower value was of 1.43 kg_{sol}/kg_{gas} for MEA of 35 %.

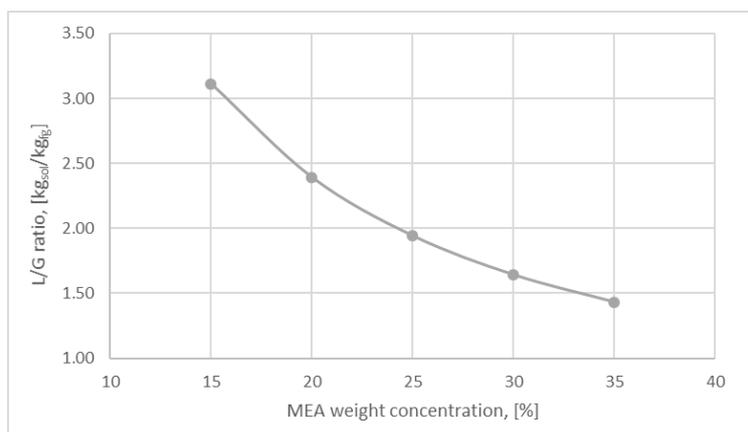


Figure 5. L/G ratio according to MEA concentration

The heat duty for capturing one ton of carbon dioxide is represented in Figure 6 according to the CO₂ lean loading solvent and MEA concentration. The heat duty for solvent regeneration decreases with increases of the CO₂ lean loading solvent for maintaining at a lower value of the CO₂ partial pressure in the gaseous phase. With increasing of the weight concentration of MEA, the values obtained for heat duty was lower. Because at the lower concentration of MEA the L/G ratio is higher, and a higher flow is passed through the desorption column. In this study, the stages number of absorption and desorption column was maintained constant. The values obtained for heat duty varied between 1.41-3.19 GJ/t_{CO2} according to the solvent flow taking into account different values of lean loading solvent. For a specific value of lean loading solvent (0.21 mol_{CO2}/mol_{MEA}), the heat duty is reduced due to a higher amount of amine solvent and a higher amount of CO₂ emissions captured (as we can see in Figure 7).

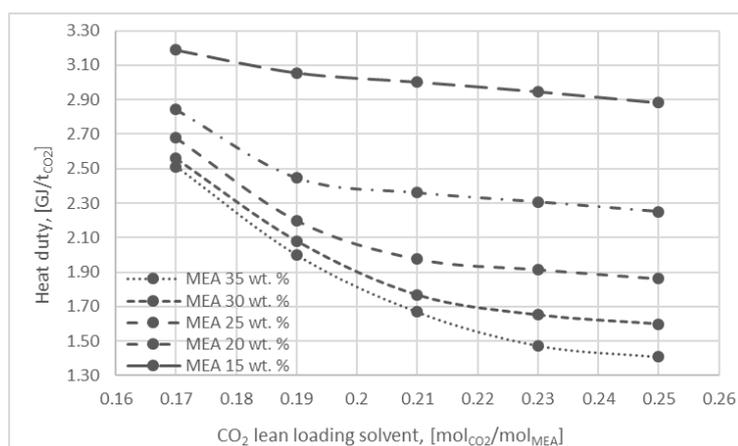


Figure 6. Heat duty according to CO₂ lean loading solvent and MEA concentration

In figure 8, the variation of the heat duty required for chemical absorption process for one ton of cement according to the CO₂ lean loading solvent is represented. The specific heat duty varied between 0.85-1.93 GJ/t_{cement} according to the CO₂ lean loading solvent and MEA concentration.

For all cases studied the thermal energy recovered from the exhaust gases was of 117.15 MJ/h. The exhaust gases from cement plant with a temperature of 400 °C was introduced in the HRSG for steam generation at 25 bars. The steam produced expands in back pressure steam turbine from 25 bars to 3.6 bar being then used for chemical solvent

regeneration. After the HRSG, the exhaust gases are cooled in heat exchanger up to 50 °C before entering the absorption column. The thermal energy amount required for solvent regeneration varied according the lean loading solvent. A higher value of the lean loading solvent allowed a small amount of heat duty.

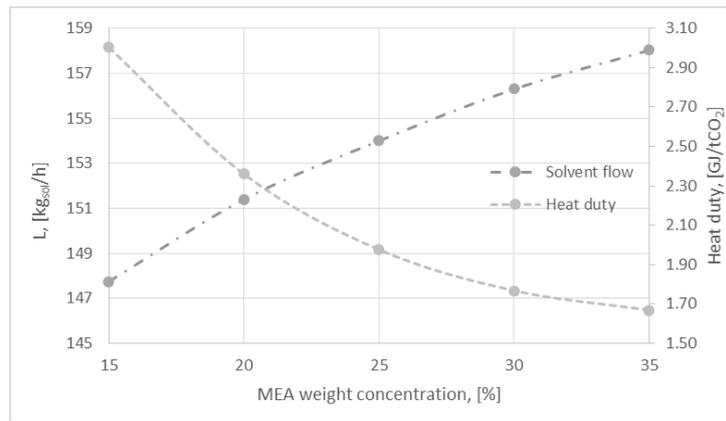


Figure 7. Heat duty and solvent flow variation according to MEA concentration

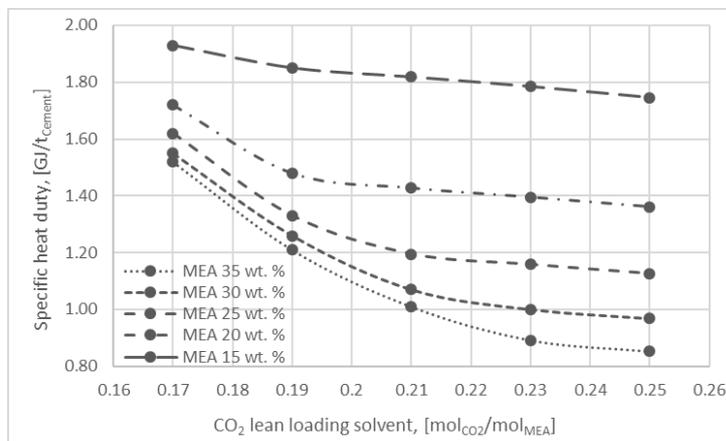


Figure 8. Specific heat duty according to CO₂ lean loading solvent and MEA concentration

Taking into account that the amount of the thermal energy available depends on the flue gas temperature, a critical assessment was done. The scope of the assessment consisted in the evaluation of the thermal energy amount available comparing to the heat duty required for solvent regeneration. The thermal energy available depends on the steam flow and on its temperature and pressure parameters. For all cases, the steam was extracted at the outlet of the back pressure steam turbine, in order to avoid the eventually additional costs. Thus, in Figures 9-13, the amount of thermal energy available, and effectively used for chemical solvent regeneration are comparing on the graphs. For lower values of the lean loading, the heat duty required for solvent regeneration was higher than the thermal energy available. In this case, an additional heat source is necessary for reducing the lean loading value. On the contrary, for higher values of the lean loading solvent, the thermal energy available exceeds the heat duty required. In this case, the additional heat could be used either for increasing the electricity by reducing the pressure of the steam extracted or for own consumption.

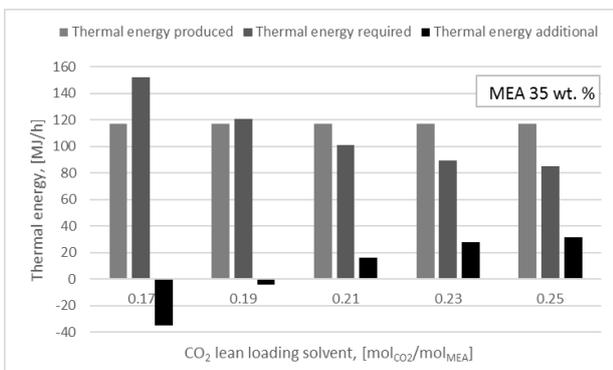


Figure 9. Thermal energy for MEA 35 wt. % according to CO₂ lean loading solvent

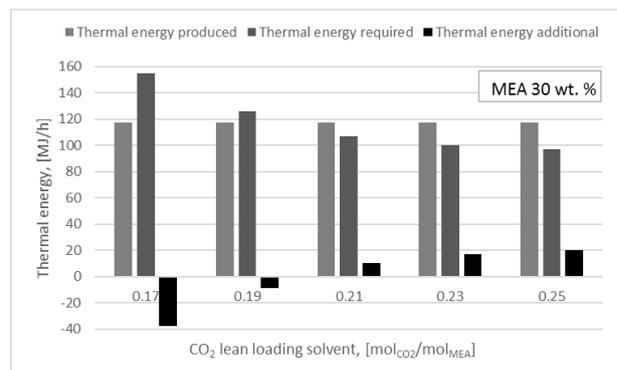


Figure 10. Thermal energy for MEA 30 wt. % according to CO₂ lean loading solvent

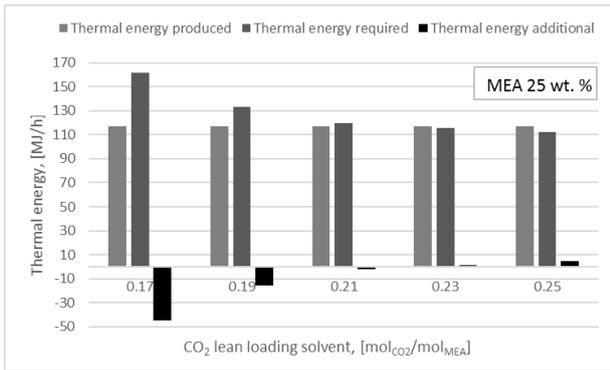


Figure 11. Thermal energy for MEA 25 wt. % according to CO₂ lean loading solvent

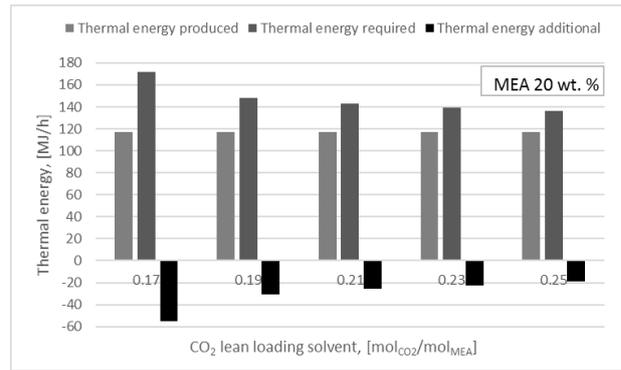


Figure 12. Thermal energy for MEA 20 wt. % according to CO₂ lean loading solvent

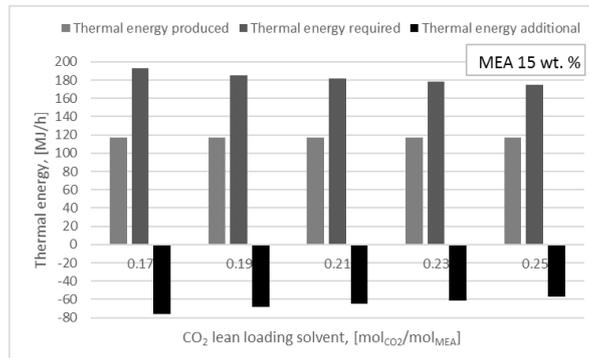


Figure 13. Thermal energy for MEA 15 wt. % according to CO₂ lean loading solvent

For evaluating the cases analyzed, the heat usage factor was defined. The heat usage factor was defined as the ratio between the heat duty used for chemical solvent regeneration and the thermal energy available. According to this factor, all the cases were compared for different MEA weight concentration and CO₂ lean loading. In the cases in which an external heat source is required for achieving the chemical solvent regeneration, the heat usage factor was higher than 100 % (Figure 14). As we can observe in Figure 14, a higher value of the CO₂ lean loading solvent allows to have an amount of heat available for other processes.

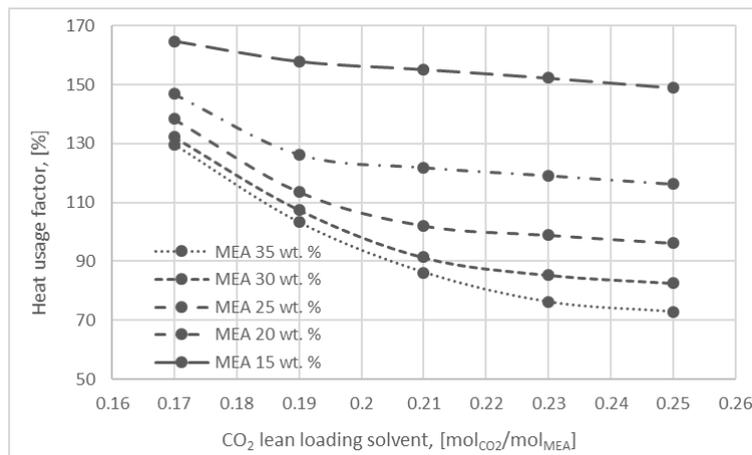


Figure 14. Heat usage factor according to CO₂ lean loading solvent and MEA concentration

4 CONCLUSIONS

In this study, we analyzed the integration of CO₂ capture technology by chemical absorption process into a cement plant with heat recovery facility. The high mass concentration of CO₂ in the exhaust gases from manufacturing cement process has a significant impact on the parameters of the chemical absorption process such as the L/G ratio and the heat duty required for solvent regeneration. The steam for solvent regeneration was produced in a HRSG due to the higher

temperature of the exhaust gases from cement plant. The heat duty required for solvent regeneration was analyzed according to the weight concentration of MEA and to the CO₂ lean loading solvent considering a constant CO₂ capture efficiency of 90 %. We noticed that the heat duty required increases with CO₂ lean loading solvent decreases for different MEA weight concentration. The thermal energy produced by steam boiler is the same in all cases studied since the exhaust gases flow is constant. Thus, the heat usage factor varied with the CO₂ lean loading solvent and the MEA weight concentration. However, for values of CO₂ lean loading solvent higher than 0.2 mol_{CO₂}/mol_{MEA} and MEA concentrations higher than 30 wt. %, the thermal energy produced covers entirely the heat duty required for solvent regeneration. For choosing the optimal parameters of chemical absorption process, an economic analysis is necessary.

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