Model Development for CO_2 Capture in the Cement Industry

Udara S.P.R. Arachchige, Dinesh Kawan, Lars-André Tokheim, and Morten C. Melaaen

Abstract—**Climate change has become a prominent global issue due to human activities. One of the major green house gas emitting sources (CO_2) to the environment are considered as flue gases, which generated from process industries (coal and gas fired power plants, cement industry, etc.). In this study, a flue gas emission from a cement manufacturing process is considered for development of CO_2 capture plant. The cement industry emits approximately 5% of global man-made CO_2 emissions. Aspen Plus simulation tool is used for the development of the carbon capture model for three different removal efficiencies, 85%, 90% and 95%. Flue gas data related to the cement industry as well as process development parameters are taken from the literatures. Solvent concentration is varied from 25 to 40 (w/w %) and lean loading is varied from 0.15 to 0.35 (mole CO_2/mole MEA) for 85- 95 (mol %) CO_2 removal efficiency. Required re-boiler duties are calculated as 3229, 3306, and 3365 kJ/kg CO_2 (74, 80 and 86 MW) for 85%, 90% and 95% removal efficiencies, respectively.**

Index Terms—**Cement industry, carbon capture, Aspen Plus, post combustion, re-boiler duty**

I. INTRODUCTION

The cement industry is considered as one of the major contributors of global anthropogenic carbon dioxide emissions [1]. The cement industry emits approximately 900kg of CO_2 per ton of cement produced, and the global cement demand is expected to increase by 60-110% by 2020 [2].

Typically 40% of the CO_2 comes from fossil fuel combustion in the kiln process, about 50% is due to de-carbonation of limestone ($CaCO_3$) to calcium oxide (CaO), and the remaining 10% is related to transportation and handling [3]. The process flow diagram of a typical cement manufacturing process is shown in Fig. 1.

The first section of the cement manufacturing process is the raw material (raw meal) preparation. The limestone from the quarry is transported to the raw meal processing area, where the limestone is first pre-crushed, whereupon the pre-crushed raw material is transferred to the grinding section to make a fine raw meal by dry or wet grinding. Most of the cement industry is currently using ball mills for this processing step. Raw meal homogenization, typically by air fluidization, is required before the meal is sent to the kiln section.

After homogenization (and intermediate storage), the raw meal is transferred to the second section, which is the kiln process. In the kiln system, the raw meal is first preheated in the pre-heater unit, consisting of several (typically 4-5) cyclones in series, to raise the temperature of the raw meal. The most modern kiln systems will also be equipped with a pre calciner which de-carbonates most of the calcium carbonate in the raw meal before it enters the rotary kiln at a temperature close to 900 °C. The pre-calciner will be located in-between the penultimate and the ultimate cyclone stage, and typically 60% of the supplied fuel will be combusted in the calciner, whereas about 40% will be combusted in the rotary kiln outlet. In a kiln system without a pre-calciner, most of the de-carbonation will take place in the rotary kiln instead. In the rotary kiln, the material temperature rises to about 1400 °C, and clinker minerals are formed. Finally, the hot clinker is cooled in a clinker cooler. Ambient air is used for cooling in the clinker cooler. Hot air from the cooler is then used as preheated combustion air in the rotary kiln, and in the pre-calciner, and the exhaust gas from the rotary kiln and the pre-calciner is further used to counter currently preheat the raw meal in the pre-heater tower. Downstream of the tower the exhaust gas is cooled and cleaned before being released to the stack.

The clinker produced in the kiln system is passed on the third section of the manufacturing process, the cement grinding plant. There, the clinker is mixed with gypsum and other additives and ground to the fine powder which is known as cement. Finally, the cement is packed and stored before being shipped to customers.

The global cement production has increased from 1043 to 2840 million tonnes per year in the last 20 years [5], see Table I [6].

TABLE I: AMOUNT OF CEMENT PRODUCTION PER YEAR [6].

Country	Amount of cement production per year (million tonnes)
Brazil	51.9
China	1390
India	177
Japan	62.8
South Korea	53.9
Russia	53.6
Turkey	51.4
United states	87.6
Other countries	911.8
Total	2840

It can be seen from 1 that it is chemically impossible to create CaO from $CaCO_3$ without generating CO_2. Hence, primary measures to reduce CO_2 emissions from the cement manufacturing process are reduction in specific emissions by

increasing the energy efficiency [7] and replacing fossil fuels with CO_2-neutral fuels [8].

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

The typical flue gas compositions are given in the following Table II [9].

TABLE II: TYPICAL FLUE GAS COMPOSITION IN CEMENT INDUSTRY FLUE GAS STREAM [9].

Component	Concentration
CO_2	14-33% (w/w)
NO_2	5-10% of NO_x
NO_x	<200-3000 mg /Nm3
SO_2	<10-3500mg/Nm3
O_2	8-14% (v/v)

Post combustion chemical absorption is the well known technology for CO_2 capture in process industries. Post combustion capture studies have been performed for several applications related to the power generation. However, there are relatively few studies carried out for cement manufacturing processes.

Installing a CO_2 capture plant will generally not require significant modifications of an existing cement plant. However, the SO_x and NO_x have to be removed from the flue gases before sending it to the CO_2 capture plant. Otherwise, these pollutants will react with amines and form heat stable salts, which result in solvent degradation. The maximum NO_x amount is around 20 ppmv, and SO_x is indicated as 10 ppmv for successful CO_2 capturing [9]. A simplified process flow diagram of cement production process which includes CO_2 capture is shown in Fig. 2. The De-NO_x process is typically carried out by selective non-catalytic reduction (SNCR) in the pre-calciner. The Electrostatic precipitator is indicated by ESP and should be prior to the De-SOx unit.

Since there are two sources for the CO_2 in the kiln exhaust gas (the de-carbonation and the combustion), the CO_2 concentration in the flue gas is quite high. Depending on where the exhaust gas is extracted or on the false air in leakage in the process, it will be in the range 14-33%. This is high compared to a coal fired power plant (around 12-15%) and indeed a gas fired power plant (around 4%). Therefore, CO_2 capture in the cement industry may as well give a correspondingly lower energy requirement. The main objective behind this study is to develop the model for CO_2 capturing in cement manufacturing process.

II. MODEL DEVELOPMENT

In this paper, post combustion amine absorption of CO_2 in a cement manufacturing process is modeled with Aspen Plus. Amine concentrations and CO_2 lean loadings are varied to simulate the capture process with 85%, 90% and 95% removal efficiencies. After careful evaluation of the simulated results, suitable CO_2 concentrations and lean CO_2 loadings are selected for different operating efficiencies for the cement flue gas treating process. The amine concentration and CO_2 lean loading, which will give the lowest re-boiler duty are then selected. Absorber and stripper packing

conditions and operating parameters related to the simulations are selected from the literature [10, 11]. Some of the information related to the absorber and stripper models are given in the Table III.

The flue gas data related to the cement manufacturing process for this study is taken from the literature [12] and given in the Table IV. The data is originated from one of the largest cement plants in Ontario, Canada.

The Aspen Plus simulation tool is used to simulate the CO_2 capture. The electrolyte NRTL model is used, and equilibrium and kinetic data, as well as, relevant chemical reactions are selected from the literature [15, 16] and implemented in the model.

TABLE III: INFORMATION RELATED TO THE ABSORBER AND STRIPPER MODELS [10, 11].

Specification	Parameter values	
	Absorber	Stripper
Number of stages	15	15
Operating pressure	1 bar	1.9 bar
Re-boiler	None	Kettle
Condenser	None	Partial-vapour
Packing type	Mellapak, Sulzer, Standard, 350Y	Flexipac, Koch, metal,1Y
Packing height	12m	8m
Packing diameter	6m	4m
Mass transfer coefficient method [13]	Bravo et al. (1985)	Bravo et al. (1985)
Interfacial area method [13]	Bravo et al. (1985)	Bravo et al. (1985)
Interfacial area factor	1.5	2
Heat transfer coefficient method	Chilton and Colburn	Chilton and Colburn
Holdup correlation [14]	Billet and Schultes (1993)	Billet and Schultes (1993)
Film resistance	Discrxn for liquid film and Film for vapour film	Discrxn for liquid film and Film for vapour film
Flow model	Mixed	Mixed

TABLE IV: FLUE GAS STREAM DATA USED FOR SIMULATION STUDIES [12].

Parameter	
Temperature, °C	160
Pressure, bar	1.013
Mass flow, kg/hr	304996
Mole fraction	
H_2O	0.072
CO_2	0.224
N_2	0.681
O_2	0.023

III. OVERVIEW OF CAPTURE PROCESS

The amine based carbon capture process implemented in Aspen Plus is illustrated in Fig. 3. Basically, it consists of two unit operation blocks, an absorber column and a stripper column. The flue gas, which has been de-dusted in a bag filter before entering the CO_2 capture unit, is at a temperature of around 160°C. However, the suitable temperature for

absorption of CO_2 in MEA is around 40°C. Therefore, the flue gas stream is cooled before entering the absorber. The COOLER-1 block is used for reduction of the temperature of flue gas stream to 40°C, and water generated during cooling is separated using a SEP (separator) unit as SEP-OUT.

A primary amine, monoethanolamine (MEA), is used as absorbent (solvent). MEA counter-currently reacts with the flue gas stream in the absorber column to capture the CO_2 in

the flue gas- Next, the rich solvent is routed to the stripper column, where the CO_2 is released, and the solvent is regenerated. The main drawback of the MEA based CO_2 capture process is the high energy consumption in regenerating process. Hence, optimization of the regeneration process is required to obtain carbon capture with a lower energy usage.
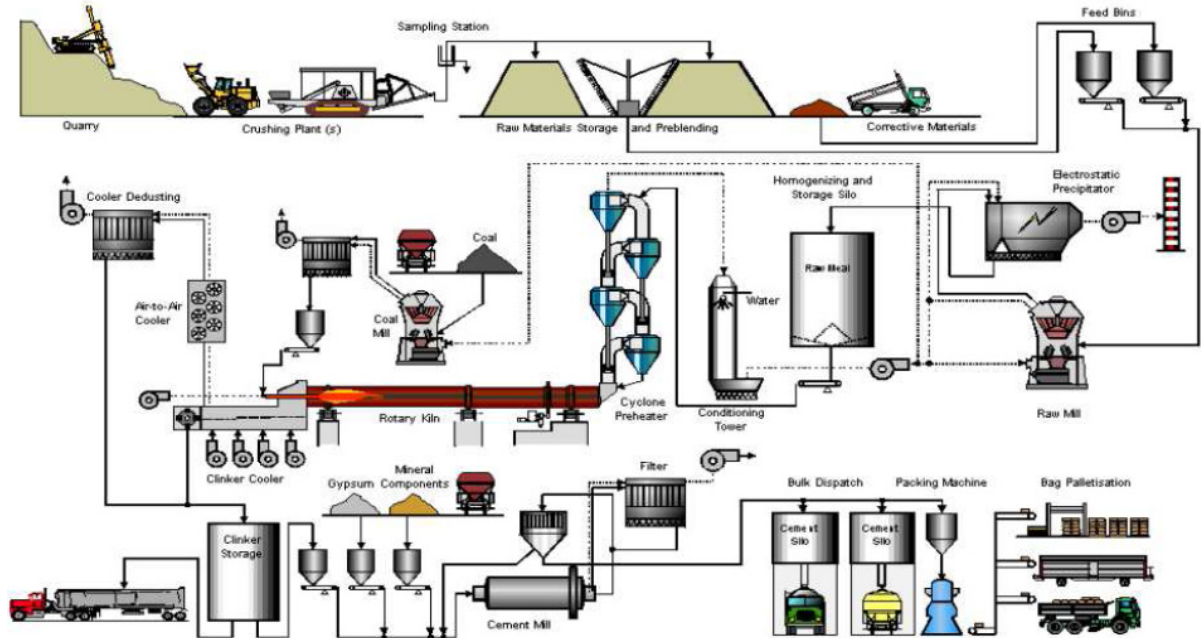

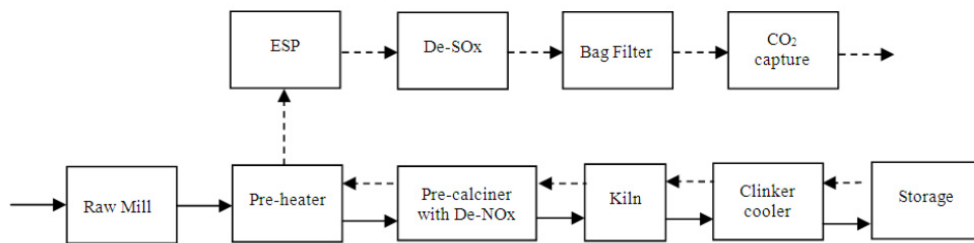Fig. 1. Typical cement manufacturing process flow diagram [4].

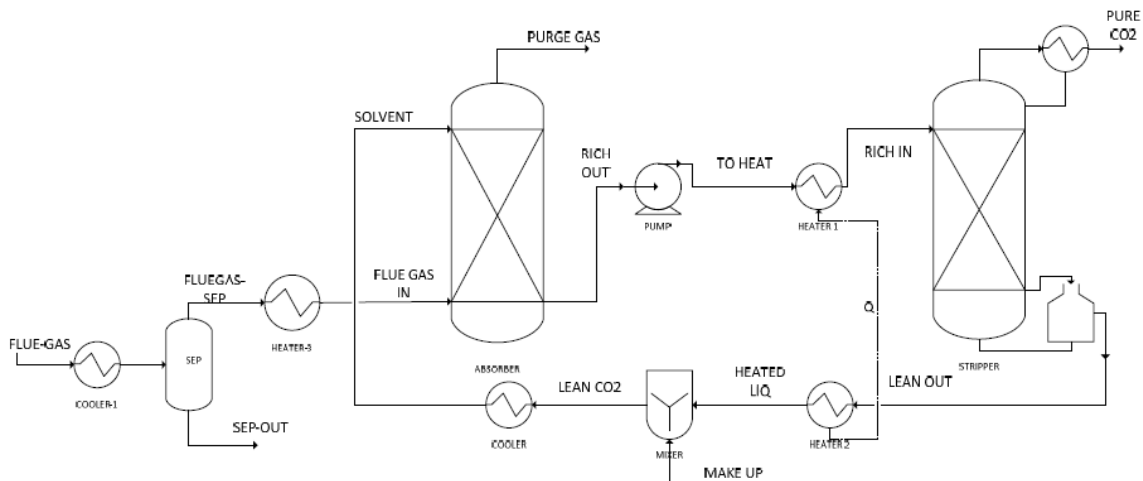Fig. 2. Cement plant with CO2 capture unit (material flow, gas flow).

Fig. 3. Process flow diagram.

IV. SIMULATIONS

Simulations are performed to select the suitable solvent concentration and CO_2 lean loading for different efficiencies. The solvent concentration is varied from 25 to 40 (w/w %), and the lean loading is varied from 0.15 to 0.35 mole CO_2/mole MEA for 85-95 CO_2 removal efficiency. Three different case studies are carried out to determine the best operating conditions. An open loop process flow diagram (without recycling back to the absorber) is used to develop the model with exactly 85, 90 and 95% removal efficiencies, respectively. The solvent flow rate is varied to get the exact amount of removal efficiency in the gas stream from the stripper.

Simulation results are given in the Fig. 4 (a, b, c represent the different removal efficiencies) with the variation of CO_2 lean loading.

According to Fig. 4 specific energy requirement in the re-boiler decreases with an increase in CO_2 lean loading until the minimum is obtained. The point which gives the lowest re-boiler energy can be defined as the optimum CO_2 lean loading. At the same time, the inlet solvent flow rate is varied to achieve the specified CO_2 removal efficiency. The efficiency range from 85 to 95% can be considered as good values for the removal process.
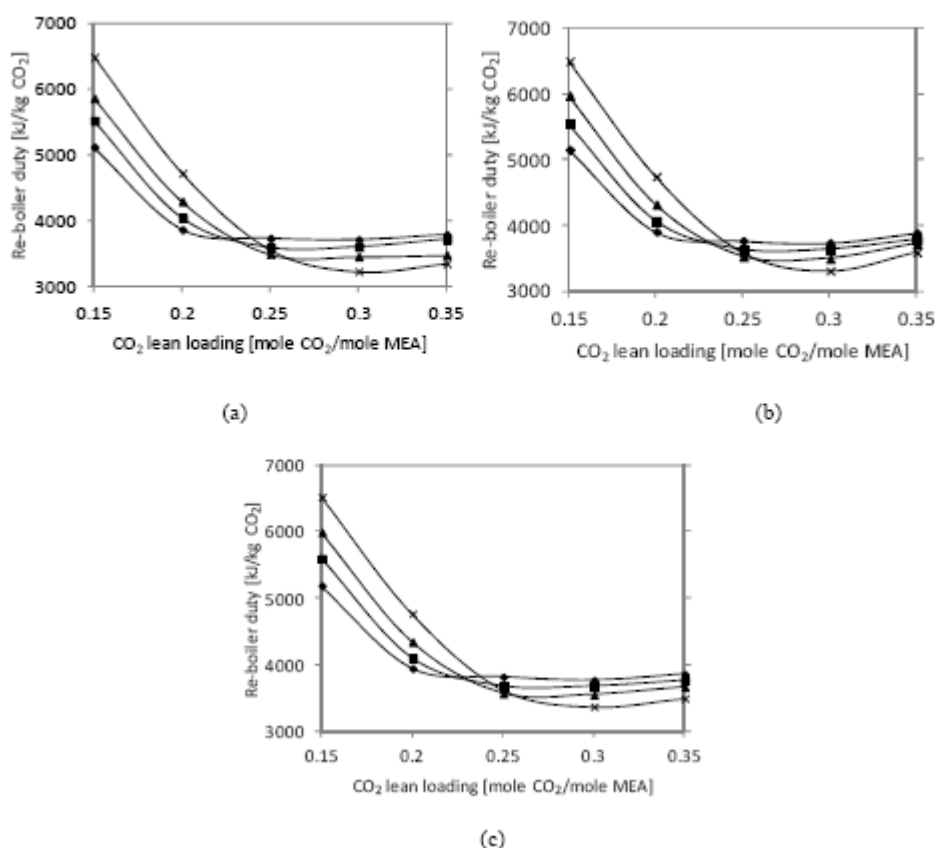

(a)

(b)

(c)

Fig. 4. Re-boiler duty variation with CO2 lean loading (a) 85% (b) 90% (c) 95% removal efficiencies, symbols refer to the MEA concentrations: ♦, 25; ■, 30; ▲, 35; ×, 40 w/w%.

The overall re-generation energy in the stripper section represents 3 sub sections: the energy required to liberate the bonded CO_2, the sensible heat required to heat up the solvent and the energy needed for water evaporation. The contribution of all these three parts is varied with CO_2 lean loading [11]. The energy required to release the CO_2 is almost constant due to fix removal efficiency in the process. At the low values of CO_2 lean loading, amount of steam required is dominant. It means that, re-boiler energy consumption is increasing to produce extra steam. Therefore, with low CO_2 lean loading, re-boiler duty reaches higher value. At the high CO_2 lean loading, heating up of solvent flow rate is dominant, and re-boiler temperature will be increased for fulfilling that purpose. It will be the reason for reducing re-boiler energy requirement. However, with higher amount of CO_2 lean loading, inlet solvent flow rate is increasing. Therefore, heat required to increase the temperature of the solvent stream to stripper temperature is increasing. Therefore, after a certain limit, the total amount of heat requirement (re-boiler energy demand) is increasing.

The simulation results indicate that 40% MEA concentration and 0.30 CO_2 lean loading are the most suitable operating conditions for 85%, 90% and 95% CO_2 removal efficiencies. Due to the limitations in Aspen Plus data banks for amines, 40% MEA concentration is selected as upper bound for simulation studies. It can be seen that amine solutions with a higher CO_2 lean loading easily can be regenerated in the stripper with a lower re-boiler duty than with a lower CO_2 lean loading.

The absolute re-boiler duty (in MW) variation with CO_2 lean loading is given in Fig. 5, for the three different efficiencies. In those simulations, MEA concentration is maintained at 40 %.

Fig. 5 shows the effect of CO_2 lean loading on re-boiler

duty for given flue gas data. The re-boiler duty decreases from 150 to 75 MW when the CO_2 lean loading is changed from 0.15 to 0.35 (85% removal efficiency). Simulations were performed for 85%, 90% and 95% CO_2 recovery with 98% CO_2 purity in the stripper exit gas. The specific re-boiler energy requirement is given in Table V for all the simulation studies. When calculating the cement-specific energy consumption, a literature value of 0.9 kg CO_2 per kg cement [2] has been applied.
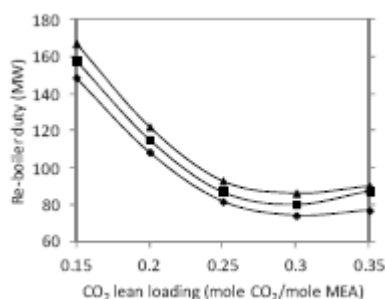

Fig. 5. Re-boiler duty variation with CO_2 lean loading, symbols refer to the 3 different efficiencies: ♦ , 85%; ■, 90%; ▲, 95%.

TABLE V: RE-BOILER ENERGY REQUIREMENT.

	(40% MEA concentration and 0.30 CO_2 lean loading)	
	Removal efficiency	Re-boiler duty
kJ/kg CO2	85%	3229
	90%	3306
	95%	3365
kJ/kg Cement	85%	2470
	90%	2678
	95%	2877

\ The re-boiler energy requirement for carbon capture process in the cement industry is 3229, 3306, and 3365 kJ/kg CO_2 for 85%, 90% and 95% removal efficiencies, respectively (40% MEA concentration and 0.30 CO_2 lean loading). A pinch analysis has to be performed for the cement industry, to find the excess energy availabilities through the process. It may be feasible to use some amount of excess energy to replace part of the re-boiler energy requirement.

The waste heat in the exhaust gas from cement kiln (outlet of the pre-heater tower) may be utilized by installing waste heat boilers downstream of the pre-heater. The temperature in the pre-heater outlet gas stream is around 350-450°C. This high temperature flue gas stream can, in some plants, be used to produce steam using waste heat boilers. The steam can then be used for solvent regeneration in an amine-based carbon capture plant. The waste heat in the cooler exhaust air may be utilized as well. The amount of available waste energy is mainly a function of gas flow rates and temperatures, and whether this heat is utilized for other purposes at the given plant. There are two main options for installing the carbon capture plant; either use the existing waste heat to replace part of the energy requirement in the stripper regeneration section while cleaning the entire exhaust gas stream; or clean only part of the exhaust gas while supplying all the energy required in the stripper. Waste heat utilization will reduce the investment and operational

costs of the CO_2 capture plant. This scheme will be considered in future work.

It can be seen that the required solvent inlet flow rate is decreasing with an increase in MEA concentration for all cases. The solvent flow rate is increased to achieve higher removal efficiencies. When considering the removal efficiency, the lowest solvent requirement is given for the highest MEA concentration. Increasing the amine concentration may increase the corrosion in different sections of the capture plant. However, this can be counteracted by adding a small amount of corrosion inhibitor to the solvent stream and/or by using corrosion resistant materials instead of carbon steel. The presence of these inhibitors is supposed to have negligible effect on the CO_2 removal process.

V. CONCLUSION

The Aspen Plus process simulation tool has been used with the electrolyte NRTL property method, to simulate CO_2 capture applied to a cement kiln flue gas. The CO_2 content in the cement flue gas was 22%, and 85%, 90% and 95% removal efficiencies were simulated. The optimum MEA concentration and CO_2 lean loading were selected as 40 w/w % and 0.30 (mol CO_2/mol MEA), respectively. The required re-boiler duty decreased with an increase in CO_2 lean loading. The re-boiler energy requirement for the carbon capture process was calculated to 3229, 3306, and 3365 kJ/kg CO_2 for 85%, 90% and 95% removal efficiencies, respectively. A De-NOx unit and a De-SOx unit must be installed upstream of the capture plant in order to reduce the concentrations of NO_x and SO_x, respectively. Because of the relatively high CO_2 concentration in the in the cement kiln flue gas, CO_2 capture in the cement industry may be one of the most favorable solutions for reduction of CO_2 emissions and reduced global warming.

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