CO$_2$ CAPTURE FROM POST-COMBUSTION GAS BY EMPLOYING MEA ABSORPTION PROCESS – EXPERIMENTAL INVESTIGATIONS FOR PILOT STUDIES

Adrian Alexandru BADEA[1], Cristian Florian DINCĂ[2]

Post-combustion CO$_2$ capture and storage (CCS) presents a promising strategy to capture, compress, transport and store CO$_2$ from a high volume–low pressure flue gas stream emitted from a CFBC pilot plant. The focus consists in determining the heat of absorption required to regenerate the solvent. The solvent used for CO$_2$ capture was MEA pure 99 % wt. Major energy savings can be realized by optimizing the lean solvent loading and the amine solvent concentration. A minimum thermal energy requirement was found at a lean MEA loading of 0.42, using a 40 wt. % MEA solution, resulting in a thermal energy requirement of 3.1 GJ/tonne CO$_2$.

Keywords: CCS technology, lignite combustion, MEA, post-combustion

1. Introduction

The atmospheric concentration of greenhouse gases GHGs (e.g. carbon dioxide, methane, nitrous oxide and chlorofluorocarbons) has increased gradually in the last century. The Intergovernmental Panel on Climate Changes (IPCC) has evaluated the size and impact of this increase. One of the conclusions is that the reasons behind the increased concentration of the greenhouse gases in the atmosphere are the human activities [1]. As a result, the global atmospheric concentration of CO$_2$ increased from a pre-industrial value of about 280 parts per million by volume (ppmv) to 384 ppmv in 2007(see Figure 1) [2]. Moreover, the GHGs concentration is expected to increase to about 600 ppmv by 2050 if no mitigation and emissions reduction options are applied [3]. The emissions of the different greenhouse gases have been monitored and measured all around the globe. It is evident that carbon dioxide is the most important anthropogenic GHG. Its annual emissions have grown between 1970 and 2004 by about 80%, from 21 to 38 gigatonnes, and represented 77% of total GHGs emissions in 2004 (Figure 2) [3].

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[1] Prof., Power Engineering Faculty, University, POLITEHNICA of Bucharest, Romania
[2] Lecturer, Power Engineering Faculty, University, POLITEHNICA of Bucharest, Romania
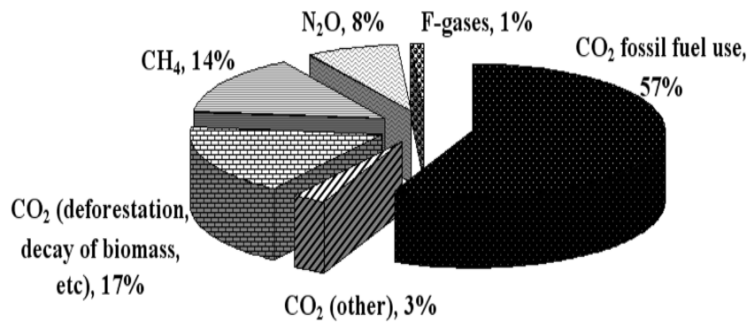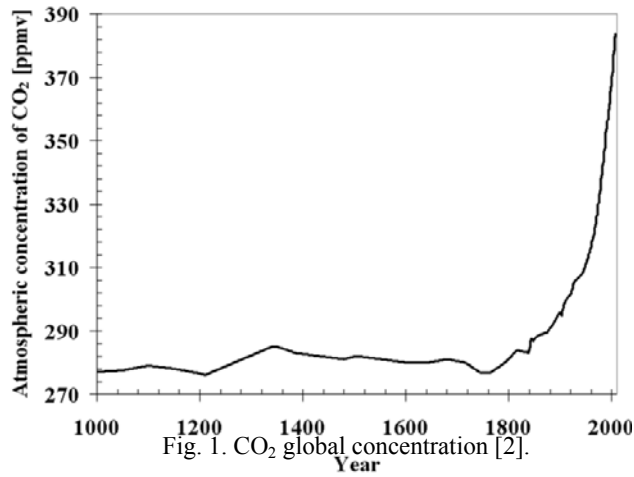
Fig. 1. CO_2 global concentration [2].

Fig. 2. Share of different greenhouse gases in total global emissions in 2004 [3]

There is a growing consensus that temperature increase due to climate change should be limited to around 2-3 degree celsius. There are many scenarios presented and discussed to evaluate the required level of CO_2 emissions reduction to achieve this target [1,3,6,8]. The International Energy Agency (IEA) has considered two climate policy scenarios corresponding to long term stabilization of greenhouse gas in the year of 2030 at 550 (an increase in global temperature of approximately 3 ^{o}C) and 450 (a rise of around 2 ^{o}C) ppm of CO_2 [8]. This can be achieved by combining different solutions (renewable, energy efficiency, CCS, nuclear) to cut down the CO_2 emissions by 50-65% in 2030 comparing to the reference case level in 2006 [8]. The European Union (EU) emphasis the necessity to reduce CO_2 emissions by developed countries by 30% in 2020 compared to 1990 levels [3,4]. In addition, the EU is committed to achieve a 20% reduction of its greenhouse gas emissions by 2020 compared to 1990 [5]. To reach this ambitious goal, the focus is mainly on the CO_2 emissions from the consumption of

fossil fuel, which is responsible of around 57% of the global GHGs emissions (see Figure 2). The global intention is directed toward the fossil fuels that are used for electricity generation, which are responsible for 41% of the global CO$_2$ emission in 2004 [6] (see Figure 3). The transportation sector is the second largest CO$_2$ emitter and can contribute in reducing CO$_2$ emissions (e.g. by the development of more efficient engines and by switching to more environmental friendly fuel like hydrogen, which is connected to an earlier CO$_2$ separation step).
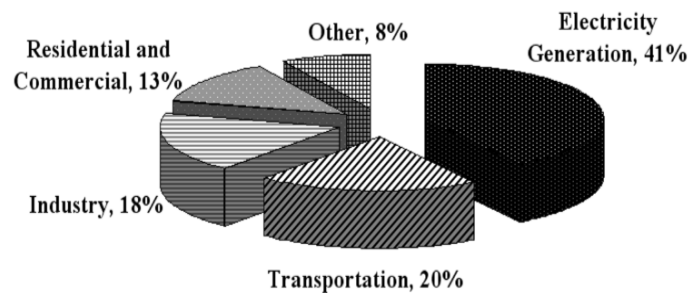

Fig. 3. World fossil fuel-energy related CO$_2$ emissions by sector 2004 [6]

Currently, fossil fuels provide around 80% of the world's total energy demand. Coal is playing a major role as the main source of electrical power (38% of the total electricity generation) [7]. The large dependency on fossil fuels makes it difficult to switch completely to other energy sources. Moreover, the international energy agency scenarios have expected the world energy demand to expand by 45% between now and 2030.

2. CFBC – pilot plant experimental studies

The CFBC pilot installation was designed and commissioned in the Laboratory of Renewable Energy Sources, Power Engineering Department – University Politehnica of Bucharest (UPB), and represents the only facility of this type and scale in Romania. The main particularity is the CO$_2$ capture system integrated in the last section of flue gas cleaning stage that uses the flue gases to heat and regenerate the rich MEA (monoethanolamine) flux.

CFBC main operating parameters are:
- Thermal load 75 kWt;
- Feed-in flow: up to 20 kg/h (depending of fuel type and particles size);
- Combustion air: up to 175 m^3/h;
- Temperature flue gas in the combustor: 850°C-1000°C.

The scheme of the CFBC pilot plant test unit, representing the main components of the installation, is shown in Fig. 1. The fuel, water and gas flow and as well the temperature, pressure and gas analysis sampling points are represented. The CFB bench installation is conceived as a modular structure: fuel feeding system; fan and air distributor system of primary and secondary air; natural gas burner for start-up; fluidized bed reactor; cyclone precipitator for separation of ash fraction; heat exchanger; bottom ash cooling screw; cyclone; CO_2 absorber; CO_2 scrubber; cooling system, pumps for MEA and NaOH.

Fluidizing air is introduced at the base of the fluidized bed through a nozzle distributor and used as both fluidization and combustion air. The fuel is introduced in the furnace above the air distribution plate.

After combustion the flue gases must be cleaned of impurities that affect the CO_2 capture solvent efficiency and contributes to its degradation. The dust particles are retained by the cyclone system. After the dust removal the flue gases pass through the desulphurization unit that has a triple role: (a) to remove the SO_x contaminants, that reacts with MEA and forms stable salts, (b) to cool the flue gases and (c) to wash the dust particles from flue gases. The desulphurization unit is a direct contact heat exchanger with reactions. The flue gases are passed in counter current with the NaOH solution. The contact surface area it is increased through a layer of ceramic RASCHIG rings. The gases from the desulphurization unit are introduced at the bottom of CO_2 absorption column. The absorber column has the same characteristics as the desulphurization unit.

The pilot plant is designed for measurements of pressure, temperature and air flow rates. The temperature variation and air flow variation values are recorded in continuous form and displayed on a synoptic board. During the experimental campaigns two samples are continuously extracted from flue gases and sent to the on-line flue gas analyzers (O_2, NO, CO_2, H_2S, SO_2, CO, NO_2, and excess air). The first flue gas composition sampling is before the desulphurization unit and the CFBC pilot installation with advanced flue gas purge system second one is after the absorber unit. Measurement points for temperature, pressure, air-flow and flue gas composition are presented also in Figure 4.
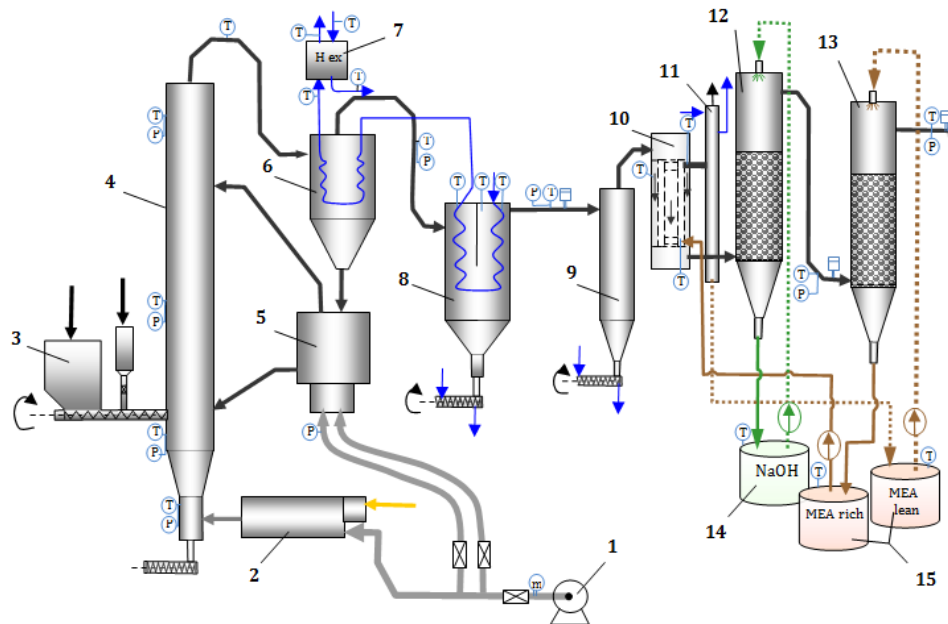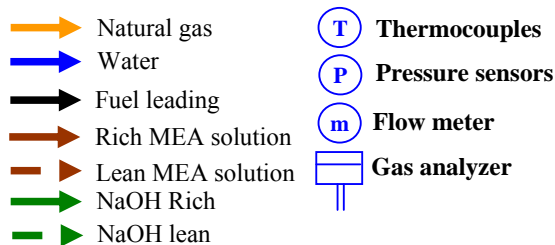
Fig. 4. Schematic diagram of experimental pilot CFBC installation

Legend Figure 4

1. Blower, 2. Pre-firing using natural gas, 3. Fuel feeding system, 4. Combustion chamber, 5. Recirculation system, 6. Cyclone, 7. H2O-H2O plate heat exchanger, 8. Convective heat exchanger, 9. Cyclone, 10. CO2 Scrubber, 11. H2O-MEA tubular heat exchanger, 12. Desulphurization unit, 13. CO2 Absorber, 14. NaOH solution tank, 15. MEA lean and reach solution tanks.

The UPB laboratory contributes in diverse research projects to the development of CO_2 capture by chemical scrubbing. Solvent screening and characterization is carried out in our laboratories as part of these investigations. An important parameter to determine the applicability of a solvent for CO_2 capture is its absorption capacity. The objective of this study was to examine and compare the performance of aqueous of MEA under diverse regeneration conditions. The final goal was to study the contribution of process and solvent optimization to the reduction of the energy demand for regeneration. The cyclic

capacity of solvent at different concentration was determined. The effects of diverse operational parameters, such as re-boiler energy input, solvent flow rate and amine concentration on the regeneration energy for the MEA solution were studied. The setup and procedure to determine the equilibrium loadings of amine solutions at diverse temperatures with synthetic flue gas has been already described elsewhere [12,13].

Energy for solvent regeneration comes from flue gas heat recovery and an electrical re-boiler that provides the supplement energy to completely regenerate of the MEA. Consequently, one of the main objectives of this article is to determine the contribution of the thermal energy consumption of re-boiler used to regenerate the solvent.

Figure 5 shows the picture of the power plant.

Fig. 5. Picture of the power plant

Parameter study

To assess the process, results regarding the experimental work using the coal - lignite. The lignite is an aboriginal coal from Schitu and Golesti, having a Low Heating Value (LHV) smaller than 9 000 kJ/kg. The particle size is smaller than 4 mm. The proximate and ultimate analysis values as well as the lower heating value (LHV) for lignite are presented in Table 1.

Properties of Romanian lignite used in the combustion tests: W-moisture; A-ash; daf – dry and ash free basis; LHV – lower heating value (proximate analysis)

Ultimate analysis (wt. %, daf)					Proximate analysis (wt.%)		LHV (MJ/kg)
C	H	O	N	S	W	A	
35.2	4.5	45.4	0.65	0.5	12.75	1	8.92

In this study, some of the main parameters affecting the capture process will be varied as an initial step towards an optimization of the process. Starting from the baseline case (no CO$_2$ capture) the following process parameters will be varied:

- The CO$_2$ lean solvent loading (mol CO$_2$/mol MEA), by varying the degree of regeneration (20, 30 and 40 % degree of regeneration);
- The amount of CO$_2$ removed (70, 75, 80, 85 and 90 % removal);
- The MEA weight percentage in the absorption solvent (20, 30 and 40 wt. %);
- The rich solvent temperature at the electrical re-boiler inlet by varying the electrical power of the re-boiler (3, 3.5, 4 and 4.5 kW);
- The thermal energy required in the stripper (GJ energy/tonne CO$_2$ removed);
- The solvent circulation rate need for the absorption (m3 solvent/tonne CO$_2$ removed);

These indicators were chosen because they present information on the operating process. Each experiment run began by introducing the rich solution into the desorber bottom and re-boiler and heating it up to re-boiler temperature. Once the re-boiler reached the desired set points, the rich amine solution was pumped continuously at a given flow rate to the top of the stripper. Several samples from the outlet liquid stream were taken during the experiments for analysis of CO$_2$ and amine content.

3. CFBC – Results and discussion

The lean solvent loading of the MEA solution representing the degree of regeneration, was varied to find the optimum solvent loading for a minimal thermal energy requirement. This can be achieved by changing the electrical re-boiler energy input. For a given degree of regeneration, to achieve the same CO$_2$ removal capacity, the absorption solvent circulation rate was varied. While studying the effect of the different lean loading on the capture process, the re-boiler temperature was varied to change the values of the lean loading. At the same time, the solvent flow rate has been changed to achieve the target CO2

removal percentage. On the other hand, the rest of the process conditions were kept constant (e.g. stripper pressure: 200 kPa, MEA concentration, heat exchangers conditions).

At low values of lean solvent loading, the amount of electrical energy for the electrical re-boiler required to achieve this low solvent loading is dominant in the thermal energy requirement. At high values of lean solvent loading, the heating up of the solvent at these high solvent circulation flow rates is dominant in the thermal energy requirement. Therefore, a minimum is expected in the thermal energy requirement. From Figure 6 it is indeed clear that the thermal energy requirement decreases with increases lean solvent loading until a minimum is attained. The point at which the energy requirement is lowest will be defined to be the optimum lean solvent loading.
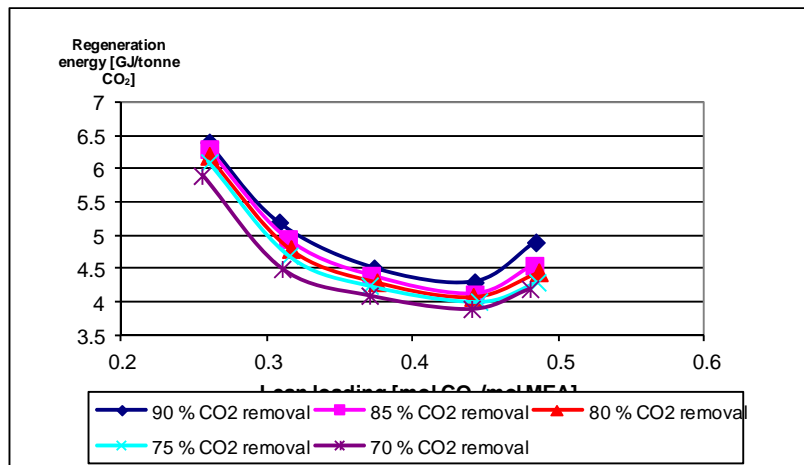

Fig. 6. Thermal energy requirement at various lean solvent loadings for different CO_2 removal

Figure 7 presents an example of the various contributions to the regeneration energy at 90 % CO_2 removal. It can be seen that the energy required to release CO_2 is almost constant because of the constant CO_2 removal percentage. Lower lean loading means higher re-boiler temperature. At higher lean loading, larger amount of solvent is needed to achieve the same CO_2 removal. This higher solvent quantity requires larger sensible heat to heat up the solvent to the re-boiler temperature
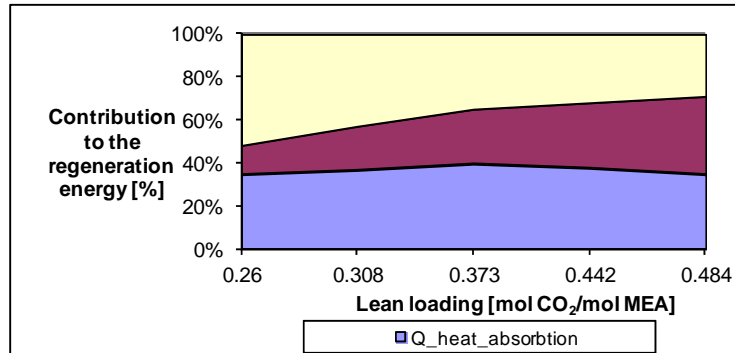
Fig. 7. Various contributions to the regeneration energy as function of lean loading (for 90 % CO$_2$ removal and 30 wt. % MEA solution)

For 90 % removal and a 30 MEA wt. % solution the optimum lean solvent loading was around 0.43 – 0.44 mol CO$_2$/mol MEA, with a thermal energy requirement of 4.4 GJ/tonne CO$_2$. The thermal energy requirement is provided from the flue gases (Qflue_gas) (eq. 3) and from electrical re-boiler (Q$_{boiler}$). Figure 5 presents the various contributions for the thermal energy requirement from flue gases and from electrical re-boiler.

By analyzing the Figure 5 can be noticed the contribution of the recovered heat from the flue gas on the total energy used for regenerating the solvent. For the optimal lean loading (0.43 – 0.44 mol CO$_2$/mol MEA), the contribution of heat recovered from the flue gas is around 22%.

The electrical energy consumed for the solvent regeneration for the optimum lean solvent loading was 3.5 GJ/tonne CO$_2$ that represents almost 80 % of the total heat requirement. Heat from flue gases contributes about 20 – 25 % of the total energy requirement.

The thermal energy requirement was found to decrease substantially with increasing MEA concentration (see Figure 6). It seems attractive to use higher MEA concentration. However, increasing the MEA concentration is expected to have pronounced corrosive effects. It is therefore required to use better corrosion inhibitors in order to realize the energy saving potential of higher MEA concentrations.

Moreover, at high MEA concentration, it is expected to have a higher MEA content in the vent gas, but a good washing section can overcome this problem keep the MEA content in the vent gas as low as possible. The wash section used in the process flow sheets always resulted in MEA content lower than 1 ppm. Upon an increase of the MEA concentration from 30 to 40 wt. %, the thermal energy requirement decreased with 7 – 10 %. The optimum lean solvent loading was for example around 0.42 mol CO$_2$/mol MEA for 40 MEA wt.% and

0.44 mol CO_2/mol MEA for 30 MEA wt.% solutions. The electrical energy consumed by the re-boiler for the solvent regeneration for the optimum lean solvent loading was 3.1 GJ/tonne CO_2.

4. Conclusions

An experimental study has been performed using indigenous lignite in a pilot plant technology, circulating fluidized bed combustion – CFBC, equipped with post-combustion CO_2 capture. In order to regenerate the MEA solution it was used in addition to re-boiler and the heat of the flue gases that represents about 20 – 25 % of the total energy requirement. This allowed us to effectively reduce the energy consumption per ton of CO_2 captured.

The lean solvent loading was found to have a major effect on the process performance parameters such as the thermal energy requirement. Therefore, it is a main subject in the optimization of solvent process. Significant energy savings can be realized by increasing the MEA concentration in the absorption solution. It is however still to be investigated if high MEA concentration can be used due to possible corrosion and solvent degradation issues.

Decreasing the lean solvent temperature would save energy in the process, but the amount of cooling water required would counter balance this effect.

From the optimization of the absorption/desorption cycle for CO_2 capture process, it can be concluded that a reduction of around 25 % in the thermal energy requirement seems realistic to be expected. For the optimum process, using a 30 MEA wt. % solution the energy requirement (used in the re-boiler) was found to be 3.3 GJ/tonne CO_2, which looks promising in reducing the costs and increase of the efficiency of the capture process. Moreover, when the absorption solution consisting of a 40 wt.% solution could be used, the energy requirement is 3.1 GJ/tonne CO_2, which is a substantial reduction compared with the values found in the literature.

Regarding the SO_x emissions, they were retained at a rate of 99 % with values of less than 6 ppm. We can conclude that the MEA solution it is not affected by the flue gas compositions.

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