Environmental Engineering and Management Journal

January 2019, Vol.18, No. 1, 47-58 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



"Gheorghe Asachi" Technical University of Iasi, Romania



INFLUENCE OF DESULPHURIZATION IN THE CARBON DIOXIDE ABSORPTION PROCESS USING MONOETHANOLAMINE

Cristian Dincă^{*}, Adrian Badea

Energy Generation and Use Department, University of Politehnica of Bucharest, Romania

Abstract

The aim of this paper is to determine the influence of desulphurization on process efficiency and monoethanolamine (MEA) absorption capacity. The experiment was conducted on a circulating fluidized bed combustion (CFBC) which uses indigenous coal from Jiu Valley. We determined the absorption capacity of MEA considering three values of concentrations in the solution: 20%, 30% and 40%. It was noticed that the higher the concentration of MEA is in the solution, the greater is the influence in the efficiency of the desulphurization process on the absorption capacity of MEA. Therefore, the increase in the efficiency of the desulphurization process from 68 to 98% leads to the increase of the amount of CO₂ rich loading solvent by 0.172 g CO₂/gMEA for a concentration of 40%. Considering an optimal desulphurization (1 % NaOH), the efficiency of the CO₂ capture process was of 85% irrespective of the MEA concentration in the solvent. However, the minimum energy consumption is obtained for the optimal concentration of 40% (3 GJ / tonne of CO₂).

Keywords: CO2 capture, MEA degradation, post-combustion capture, SO2 removal

Received: February, 2014; Revised final: May, 2015; Accepted: May, 2015; Published in final edited form: January, 2019

1. Introduction

Thermo-electric power plants represent the main source which generates macro pollutants such as dust (PM10 and PM2.5), NO_x , CO_2 , and SO_x . The amount of pollutants depends on the composition of the elemental fuel. Sulphur oxides are mainly generated in the combustion processes of the different coal types. Therefore according to the current researches we found that monoethanolamine degrades in a sulphur dioxide environment (Bello and Idem, 2005, 2006; Idem et al., 2006). The energy processes are responsible for GHG emissions generated in atmosphere (Călămar et al., 2017; Cioca et al., 2017; Dinca et al., 2009).

The negative influence of sulphur dioxide on the amine behavior in the CO_2 capture process was emphasized in numerous scientific literature articles such as (Badea et al., 2004; Dinca, 2013; Idem et al., 2006; 2004; Kather and Oexmann, 2007; Norișor et al., 2012; Rau and Rubin, 2002; Strazisar, 2003; Smit et al., 2002). One of the negative effects which results from the reaction between monoethanolamine (MEA) and SO_x consists in the formation of thermally stable salts such as sulphates and tiosulphates (Ibid et al., 2006; Smit et al., 2002; Veldman, 2000). The formation of thermally-stable salts reduces the absorption capacity of the amine which was used. In order to maintain the same absorption capacity it is necessary to add fresh amine, which leads to increased costs in purchasing the amine. Therefore, so as to avoid the large solvent loss, we have to limit the SO₂ concentration in the flue gases stream before entering the absorption unit to maximum 10 ppm (Rau and Rubin, 2002). It is not necessary to have an expensive desulphurization process as long as the SO₂ concentration in the flue gases does not exceed 150 ppm. In the papers (Barchas and Davis, 1992; Gao et al., 2011) there was analyzed the amine degradation on a pilot installation, and the conclusion was that the

^{*}Author to whom all correspondence should be addressed: e-mail: crisflor75@yahoo.com

sulphur dioxide amplifies the amine degradation and cannot be removed in the same conditions as those in the unit for the CO_2 which regenerates from the amine /for the CO_2 amine regeneration (Ibid et al., 2006).

Even if we have low concentrations in flue gases, sulphur dioxide can dissolve and can be transported to the regeneration unit where at high temperatures of the process it can react with the amine (MEA) thus triggering strong degradation reactions. In the paper (Uyanga and Ditto, 2007) there was studied the kinetics of the MEA reaction with the SO₂ and so there was determined the rate of amine degradation in the presence of sulphur dioxide both for the coal plants and for the natural gas ones; we noticed that sulphur dioxide is an accelerator of the amine degradation, especially in the presence of a high oxygen concentration in the flue gases.

The dual alkaline treatment of the flue gas represents a third desulphurization process which uses an alkaline solution based on sodium. In this process we use alkaline solutions such as NaOH, Na₂CO₃ and Na₂SO₃ which react with SO₂ to form mainly Na₂SO₃ and NaHSO₃. The alkaline solution absorbs the sulphur dioxide and the slurry which forms is regenerated by using calcium oxide or calcium carbonate. This is the reason why the process is a dual alkali one or double wash. The resulted products such as calcium sulphite are precipitated and collected while the regenerated sodium solution is recycled in the absorption column. By utilizing such processes we can obtain a very high efficiency of up to 99%.

In this article we aimed to maximize the absorption capacity of the monoethanolamine by increasing the SO₂ removal. We also noted the effects which the SO₂ concentration in the flue gases has on the absorption capacity of the monoethanolamine at different concentrations in the solution (20 wt.%, 30 wt.% and 40 wt.%).

One of the main problems that the energy sector has to face is the reduction of greenhouse gases and in particular the reduction of the CO₂ emissions. At present, there are more solutions for reducing the CO₂ emissions generated by the processes of burning fossil fuels (especially coal): to increase the efficiency along the entire energy chain so that the required primary energy should be reduced (Dinca et al., 2007); to use renewable energy sources (at present there are no advanced or well-developed technologies to produce energy in optimal technical and economic conditions); and to use CCSs (carbon capture and storage) technologies. The existing studies seem to show that only the concomitant implementation of the three solutions could contribute to reducing greenhouse gases. However, the CCS technologies could be the most efficient in diminishing CO₂ emissions (Badea and Dinca, 2012; Cottrell et al., 2009). At present, there are several technological possibilities for reducing the CO₂ emissions, among which:

• Post-combustion technologies (chemical and physical absorption processes, adsorption processes, membranes etc.);

• Pre-combustion technologies (physical absorption processes, membranes etc.);

• Oxy-combustion technologies (chemical looping combustion).

Nowadays, the most developed technology is post-combustion, and the chemical absorption process is already applied in numerous pilot or lab installations (Dinca et al., 2018; Meuleman et al., 2010; Oyenekan, 2007). The chemical absorption process which uses various chemical solvents has some advantages over the other processes, which led to its major development (Jassim and Rochelle, 2005). The most important advantage of this process resides in its integration in the new thermo-electrical power plants and especially in the existing ones. But the integration of this process in a thermo-electric plant requires high energy consumption for regenerating the chemical solvent which is used. The energy consumption is estimated by specialists to be of 35% from the energy production depending on the chemical solvents which are used (Dinca et al., 2007). The most frequent chemical solvents are amines, ammonium, piperazines, etc. (Puxty et al., 2010; Rochelle, 2003). Depending on their absorption capacity, amines are classified into primary, secondary and tertiary (Simon et al., 2011). The best known amines are: the primary one: MEA (monoethanolamine), the secondary one: DEA (diethanolamine) and the tertiary one: TEA. Piperazine is often used as an activator for enhancing blended amines such as MEA/PZ, etc. The cost of the separation of a CO₂ tonne (for a 90% efficiency) from the flue gases which result from burning lignite varies between 30÷50 € (Dinca, 2013). However, if we use MEA we have the following disadvantages:

• low loading capacity (kg absorbed CO₂/ kg absorbing CO₂);

• high degree of equipment corrosion;

• degradation of the amines due to the following compounds in the flue gases: SO_2 , NO_2 , HCl, HF and O_2 (Davis, 2009). This makes it necessary to add MEA in order to maintain the same CO_2 separation rate;

• high energy consumption for regenerating the solvent at high temperatures.

When using MEA we need to separate the sulphur dioxide from the flue gases in order to avoid the formation of irreversible compounds. In the absorber unit, fresh MEA is added in the solvent for maintaining the CO₂ removal rate from the flue gases. One of the disadvantages of having sulphur dioxide in the flue gases is the decrease in the absorption capacity of the mono-ethanolamine. The absorption capacity is determined as the difference between the degree of the CO₂ rich solution loading and the degree of the CO₂ lean solution loading. In the specialized literature, the value of MEA absorption capacity is of 0.5 mole CO₂/mole amine (Abu-Zahra et al., 2007; Dinca and Badea, 2013; Davis, 2009).

The aim of this paper was to determine the negative effects that sulphur dioxide has on the chemical process of the CO_2 absorption. In order to find out the negative effects of sulphur dioxide (SO₂)

on MEA, we determined the rich and lean loading solution (mole CO_2 /mole amine) experimentally, for various values of the MEA concentration in the solution.

2. Description of fluidized bed combustion pilot installation

In order to analyze the effects of sulphur dioxide on the mono-ethanolamine absorption capacity, we used the experimental CFBC (coal fluidized bed combustion) pilot installation provided with the chemical absorption process for the retention of the CO_2 from flue gases by using primary, secondary and tertiary amines or alkanolamines solvents. These solvents include water and amines in different concentrations but, considering the strong corrosive effect of amines, especially of the primary amine, the amine concentration did not exceed 40% during the experimental processes.

The pilot installation is located in the Renewable Energies and Environmental Assessment Laboratory within the Power Plant Department. In order to determine the mass flow rate of the coal combustion, we need the elemental composition (Table 1). The coal (lignite) is extracted from Jiu Valley.

Table 1. The elemental composition of the lignite (W – moisture; A- ash; daf – dry and ash free basis)

Γ	Ultimate analysis (wt. %, daf)							
	С	Н	0	N	s	W	А	LHV (kJ/kg)
	21.55	1.25	2.55	0.65	1	36	37	8 918

All the processes of the circulating fluidized bed combustion are shown in Fig. 1. The pilot installation was designed for a mass fuel flow up to 20 kg /h, which can be analyzed for both the lignite combustion and the co-combustion biomass processes. As it is equipped with desulphurization equipment and post-combustion separation of carbon dioxide from flue gases, the CFBC pilot installation allows us to study the sulphur dioxide from the flue gases at different concentrations of MEA in the solvent. Besides, the subject is interesting from the perspective of maintenance costs, if we consider the CO₂ capture process, especially when we analyze the chemical absorption process which uses alkanolamines.



Fig. 1. The complete process of the circulating fluidized bed combustion

(1. Air cooling fan, 2. Natural gas combustion initiation process, 3. Fuel supply system, 4. Circulating fluidized bed combustion,
 5. Flue gases recirculation, 6. Flue gases cooling system, 7. Plate heat exchanger unit 8. The second system for flue gases cooling,
 9. De-dusting, 10. CO₂ Stripper (Economizer), 11. CO₂ flushing, 12. Desulphurization unit, 13. CO₂ Absorber, 14. NaOH solution reservoir, 15. MEA solution reservoirs)

For a better understanding of the absorptiondesorption process integrated in the CFBC pilot installation, Fig. 2 shows in a detailed manner the stepwise solvent regeneration which uses the heat recovery from the flue gases and an electric boiler. In order to separate the CO₂ from the flue gases generated by the lignite combustion process, we used the mono-ethanolamine solvent with different concentrations in water. The CO₂ capture through the process of chemical absorption is based on the absorption and desorption processes so that the chemical solvent which is used should separate the CO₂ from the flue gases and then eliminate it during the regeneration process (desorption).

In the experimental study, the chemical absorption process uses an absorber unit with a Raschig rings package. Before reinserting the amine solvent in the absorption unit, the latter is heated in an electric boiler up to a temperature of 110°C. During the first stage of the regeneration process, the solvent temperature may increase due to the heat recovery from the flue gases in the economizer (see equipment 10 in Fig. 1). The solvent temperature at the economizer outlet is insufficient for advanced regeneration and therefore it is introduced in the second regeneration step which uses two 2 kW electrical resistances. The temperature of the solvent in the electrical boiler is around 110°C.

One of the main problems of the chemical absorption process which uses amines as solvent refers to/deals with the flue gases of the SO_x compounds. Amines react very easily with acid gases and form thermally stable salts and consequently generate the degradation of the amine solution (Kothandaraman, 2010; Rochelle, 2002). In principle, in order to avoid amine degradation, we should use, at the inlet absorber for the flue gases, a SO_x concentration of maximum 10 ppm (Dinca, 2016; Sharma et al., 2012). The absorber packed column is defined by the following

parameters: column bed height - 0.86 m; column diameter -0.105 m; the solution temperature of the absorber process: 40-45 °C; the stripper pressure -2atm; the inlet CO₂ concentration of the flue gases: 10-13 %. The packing material which we used in the absorber unit was the Raschig material. In the experimental installation we made a 20 stages desorption unit in order to improve the contact between the flue gases and the solvent. So as to determine the carbon content in the rich and lean amine, we used the TOC analyzer Siever 900. The methodology which is employed is described by Dinca (2013). We also used the Testo 350 analyzer in order to monitor the composition of the flue gases before and after going through the absorber unit and circulating through the desulphurization unit.

3. Experiments and process simulation of CFBC with the process of CO₂ chemical absorption

One of the main issues dealing with the CO₂ chemical absorption process integrated in the power plant refers to the steam required for solvent regeneration. According to Kvamsdal et al. (2011) the penalty of the global efficiency for a power plant with sub-critical parameters is about 12-15%. In this respect, one of the objectives for this process optimization is to minimize the thermal energy consumption by recovering the heat from the flue gases. It is obvious that the thermal energy needed for solvent regeneration depends on the amine solvent which is used. Table 2 shows the exhaust emissions before their treatment through the wet desulphurization procedure which uses the NaOH solution; it also shows the exhaust emissions before their treatment by means of the CO₂ retention procedure through chemical absorption which uses MEA, when the flue gases pass through a cyclone in order to retain the solid particles.



Fig. 2. Advanced mono-ethanolamine regeneration process

The paper aims to determine in what way the SO_2 concentration influences the MEA absorption capacity. To this purpose, we measured the concentration of SO_x , and CO_2 , respectively, in the flue gases, after the cyclone of retention of solid particles. These values were obtained for a lignite flow of approximately 5.6 kg/h, and, respectively, for an air excess which varied between 1.5 and 1.66 (the O_2 concentration in the flue gases varied between 7 and 8%). For an average value of 990 ppm, the mass concentration of SO_2 in the flue gases was of approximately 2 800 mg/m³N. The experimental study was carried out in the following conditions:

• MEA concentration in the solution: 20 wt.%, 30 wt.%, 40 wt.%;

The temperature of the cooling agent (the water from the drinking water network) was of approximately 13°C;

• The cooling water flow recirculated through the heat exchanger varied between 5 and 7 L/min;

• The power of the electrical resistances used by the electric boiler varied between 3 and 4 kW;

• The fuel flow was maintained at 5.6 kg/h (the frequency of the mixing spindle was established at 11 Hz);

• The temperature of the CO₂ lean solution varied between 30 and 50°C depending on the network cooling water flow in the heat exchanger;

• The temperature of the NaOH solution varied between 25-35 °C;

• The concentration of the NaOH in the solution was of 1, 5, 10, 15, 20 and of 25 %.

We did not study, in this article, the effects of the O_2 concentration in the flue gases on the amine degradation. It is so due to the fact that in the paper we considered the O_2 content (7 – 8 %) as being the value specific to the ASFC installation so as to minimize the CO concentration in the flue gases (<50 ppm). On the other hand, taking into account the fact that the regeneration process temperature did not exceed 100°C, the role of the O_2 content in the MEA degradation is low (Pinto et al., 2013). In what regards the NO_x concentration, this was below 50 ppm in the flue gases as a consequence of using low-NO_x burners. In order to retain the SO_2 from the flue gases, we used a blend of NaOH and water solution in different concentrations. We should note that the countercurrent absorption allows us to reduce the mass flow of solution introduced into the desulphurization unit for the same contact surface of the package. The efficiency of the desulphurization unit is determined with the Eq. (1):

$$\boldsymbol{\varepsilon}_{\boldsymbol{SO2}} = \frac{c_{\boldsymbol{SO2_in}} - c_{\boldsymbol{SO2_out}}}{c_{\boldsymbol{SO2_in}}} \cdot 100 \% \tag{1}$$

where: $c_{SO_2_{in}}$, $c_{SO_2_{out}}$ – represents the SO₂ concentration in the flue gases before and after the desulphurization process, in ppm.

In order to verify the experimental results which we obtained, the CO_2 capture – chemical absorption process was simulated in Aspen Plus. The schema of the process is presented in Fig. 3.

The data used for the CO₂ capture section simulation in Aspen Plus was the following:

- the elemental analysis of the flue gas in different points of the CO_2 capture process (before and after going through the desulphurization unit, and also before and after circulating through the absorber unit);

- the carbon content in the amine solvent before and after the absorption and desorption process; we used the total carbon organic equipment so as to determine the carbon content in the solvent;

- the model which we employed is described by means of the thermodynamic properties package for the amines available in Aspen HYSYS. We selected the Kent Eisenberg model (Kent and Eisenberg, 1976), from the amines package properties.

4. Results and discussion

The aim of this experimental study is to monitor the efficiency variation of the desulphurization process as resulting from modifying the NaOH concentration in the solution, and also, as resulting from the variation of the solution temperature, respectively by varying the temperature of the solution at the desulphurization installation inlet between 25 and 35 $^{\circ}$ C.

European aim	Fuel flow, B	Flue gases density, p	Flue gases flow, mga	Flue ga	ses comp	osition, i	n ppm
Excess air, x	(kg/h)	(kg/m^3)	(m^{3}/h)	CO2, %	SO_2	NO_x	O 2, %
1.51	5.6	1.2713	23.987	9.87	996	40.7	7.2
1.5	5.6	1.2709	23.494	9.63	998	42.3	7.4
1.53	5.6	1.2701	22.26	9.55	999	44.8	7.1
1.6	5.6	1.2708	23.247	9.67	975	40.2	7.4
1.57	5.6	1.27	22.136	9.82	978	40.6	7.5
1.62	5.6	1.271	23.617	9.61	983	38.6	6.99
1.53	5.6	1.2721	25.345	9.74	985	38.78	7.2
1.59	5.6	1.271	23.617	9.55	992	41	7.6
1.64	5.6	1.2718	24.851	9.82	1002	40.8	8.02
1.66	5.6	1.2715	24.357	9.87	998	46.1	7.7

Table 2. Flue gases concentration before desulphurization



Fig. 3. The simulation of the CO₂ capture process in ASPEN Plus

In Table 3 we determined the influence of the NaOH concentration (for a concentration of 1% wt.) on the solvent pH. We can note that following the reaction between the NaOH and the SO₂, the solution becomes acidic after about 50 minutes.

Table 3. The variation of the NaOH concentration a	and the
pH of the solvent	

Experiment time (minutes)	pH of NaOH solution	NaOH concentration (%)
0	12.51	100
5	11.89	64.2
10	11.29	47.7
15	10.7	35.5
20	10.13	26.3
25	9.57	19.6
30	9	14.5
35	8.48	10.8
40	7.96	8.03
45	7.44	6
50	6.94	4.4
55	6.46	3.3
60	5.99	2.5
65	5.53	1.8
70	5.1	1.4
75	4.66	1

The variation of the NaOH concentration and the pH solution is presented in Fig. 4. The influence of the NaOH solution temperature on the desulphurization process efficiency is presented in Table 4. The efficiency of the desulphurization process is strongly influenced by the solvent

Table 4. The influence of the temperature of the NaOH solution on the efficiency of the desulphurization process

Sample no.	Temperature (°C)	Initial SO ₂ concentration (ppm)	Final SO ₂ concentration (ppm)	Efficiency (%)
1	20	998	58	94.2
2	25	998	159	84.1
3	30	998	195	80.5
4	35	998	212	78.8



Fig. 4. The variation of the NaOH concentration and the pH of the solvent

temperature. As the process temperature increases, the SO₂ absorption of the NaOH solution decreases.

We analyzed the effects which the efficiency of the SO₂ retention has on the absorption capacity of monoethanolamine (ΔX_{CO_2}) . The absorption capacity of the MEA solution was determined as the difference between the rich loading solvent $(X_{CO_2}^{rich})$ and the lean loading solvent $(X_{CO_2}^{lean})$ in the CO₂ in accordance with the Eq. (2):

$$\Delta X_{CO_2} = X_{CO_2}^{rich} - X_{CO_2}^{lean}, [\text{mol CO}_2/\text{mol MEA}] \quad (2)$$

The values which we obtained for the efficiency of the sulphur dioxide retention (Fig. 5) correspond to the NaOH mass concentration in the solution of 1, 5, 10, 15, 20 and 25%. Consequently, we can notice that at a low NaOH concentration in the solution (1 wt.%), the absorption capacity of monoethanolamine is of 0.24; 0.27; and of 0.31 mole CO_2 /mole MEA depending on the MEA concentration in the solution: 20 wt.%; 30 wt.% and 40 wt.%.

Table 5 shows the experimental results concerning the influence of the Na OH concentration in the solution on the efficiency of desulphurization. By analyzing Table 5 we see that whenever the NaOH concentration in the solution increases, the efficiency of the desulphurization process decreases.

 Table 5. The effects of the NaOH concentration on the efficiency of desulphurization

Concentration of NaOH, %	Initial concentration of SO ₂	Concentration of SO ₂	Efficiency of desulphurization process, %
1	998	12	98.79
5	998	58	94.19
10	998	112	88.78
15	998	231	76.85
20	998	266	73.34
25	998	312	68.73

We also determined the CO_2 absorption capacity of MEA for the concentrations of NaOH in the range of 1-25 %. We did not study how the CO_2 absorption capacity of MEA is reduced for a NaOH concentration in the solution of up to 1%. We determined over time the loading degree of the CO_2 rich, and lean solution, respectively, in order to find out the CO_2 absorption capacity of MEA. The absorption capacity was determined as the difference between the values of the loading degree of the CO_2 rich solution, and lean solution, respectively (see Eq. (2)). We determined the MEA concentration experimentally by means of the FT-IR and TOC equipment (Dinca and Badea, 2013; Jackson et al., 2009).

The influence of the NaOH concentration on the efficiency of the desulphurization process and on the absorption capacity of MEA was presented in Fig. 6. We observed that the concentration increase of the NaOH in the solution from 1 to 25% led to the decrease of the absorption capacity of the monoethanolamine solution irrespective of the MEA concentration. For example, in the case of 40 wt. % MEA, the absorption capacity (ΔX_{CO2}) decreases from about 0.3 to 0.05 mol CO₂/mol MEA. We explain this by the fact that there is a decrease in the efficiency of the desulphurization process when the NaOH concentration in the solution increases which allows a degradation of the MEA solvents in reaction with the SO_2 in the absorber unit. When the concentration of NaOH in the solution is higher than 1%, it is necessary to add fresh MEA in the solution in order to keep the efficiency value of the CO₂ capture process constant (85%). On the other hand, we should not increase the concentration of MEA in the solution over 30% due to its corrosiveness.

In addition, the decrease of the MEA concentration in the solution leads to the increase of the thermal energy consumption for solvent regeneration. This is not recommended because in the case of thermal power plants the increase of thermal energy consumption means a reduction of the overall efficiency. So, keeping a low concentration of NaOH in the solution (1%) has a double advantage: the increase both in the efficiency of the desulphurization process and in the CO_2 absorption capacity of the MEA solution.



Fig. 5. The effects of SO2 removal on the absorption capacity of MEA



Fig. 6. The effects of NaOH concentration on the efficiency of the desulphurization process and on the absorption capacity of MEA



Fig. 7. Variation of the lean and rich loading solvent for a 1% NaOH concentration in the solvent

Figs. 7-9 shows the variation of the MEA (30 wt.%) absorption capacity according to the NaOH concentration in the solvent (1, 10 and 15 % in the solvent). Thus, we observed that the higher the NaOH concentration is the lower is the MEA absorption capacity.

We can notice that while the concentration of Na OH in the solution increases, the absorption capacity of MEA decreases, but the values for the degree of loading become stable after a period which is almost as longer for cases analyzed. Considering the optimal value for the NaOH concentration in the solvent (1 %), we studied the CO_2 capture process using MEA in different concentration in the experimental and simulation protocol. In the CO2 capture process, we noticed that there was a decrease of approximately 20 % (Fig. 10) in the energy required for solvent regeneration when the solvent temperature increased from 87.7 to 92 °C, irrespective of the efficiency of the CO₂ capture process. For the constant value of the efficiency of the CO₂ capture process, we obtained the minimum of the necessary energy for the inlet solvent temperature of approximately 92 °C; this energy varied according to the efficiency of the CO_2 capture process from 3.1 GJ/tCO₂ for the efficiency of 85% to 5.5 GJ/tCO₂ corresponding to an efficiency of 92% in the CO₂ capture process.

When analyzing Fig. 3 we observe that the CO₂-rich amine, before entering the stripper, enters an economizer from where it recovers some of the heat flue gases (before they are desulphurization) a reason for which the amine temperature, (at the top of the stripper), increases by several degrees. The purpose of using economizer is to reduce the thermal energy consumption in the stripper unit. By inserting this heat exchanger, the heat consumption for the amine regeneration is reduced by approximately 6% (Dinca and Badea, 2013). The increase in the temperature for the process of desorption favors the increase in the absorption capacity of the CO₂ solvent which allows the reduction of the thermal energy consumption for the same efficiency of the CO₂ capture process. When we use a 30 % MEA concentration solution, (Fig. 11) we can notice another trend in the variation of the heat necessary for solvent regeneration compared with the case discussed above.



Fig. 8. Variation of the lean and rich loading solvent for a 10% NaOH concentration in the solvent



Fig. 9. Variation of lean and rich loading solvent for a 15% NaOH concentration in the solvent



Fig. 10. The stripper inlet temperature influence on the energy required of the 20% wt. MEA solvent regeneration for various CO₂ capture efficiency

Moreover, we can notice that the increase of the solvent temperature from 87 to approximately 91 $^{\circ}$ C led to the decrease of the necessary regeneration energy by approximately 27% to 3.1 GJ/tCO₂, according to the CO₂ capture process efficiency of 85%.

We can notice that, irrespective of the efficiency value of the CO_2 capture process, the necessary regeneration energy increases sharply at solvent temperatures which are smaller than 88 °C, while for solvent temperatures which are higher than 88 °C, there is a plateau in the value of the necessary energy. Consequently, the increase of the solvent temperature over values which are higher than 88 °C does not have a technical and economic justification, as the decrease of the necessary energy is insignificant.

Fig. 12 shows the variation of the necessary energy according to the stripper inlet temperature for a 40% MEA concentration. In this case, we can notice that the increase of the temperature from 86 to 88 °C led to a decrease of the necessary energy by 46% up to 3 GJ/tCO₂ for an efficiency of 85% of the CO₂ capture process.

Therefore, it is not efficient to use solution temperatures which are higher than 88 °C, since the necessary energy remains constant, according to the efficiency of the CO₂ capture process. The analysis of the influence which the MEA concentration has on the necessary energy for the same stripper inlet temperature (88.5 °C) showed that there is a slight decrease in the necessary energy from approximately 3.4 GJ/tCO₂ (20% MEA concentration) to 3 GJ/tCO₂ (40% MEA concentration).



Fig. 11. The stripper inlet temperature influence on the energy required of the 30% MEA solvent regeneration for various CO₂ capture efficiencies



Fig. 12. The stripper inlet temperature influence on the energy required of the 40% MEA solvent regeneration for various CO₂ capture efficiencies

5. Conclusions

The goal of the paper consisted in determining the influence of the desulphurization process on the absorption capacity of MEA for different MEA weight concentrations in the solvent. Considering the same elemental composition of the lignite, we measured the lean and the rich loading MEA solvent before and after entering the absorber unit. By using the NaOH solution in different concentrations (1-25 wt. %), we obtained a variation in the efficiency of the desulphurization process. The smaller NaOH concentration is in the solution, the higher is the efficiency of the desulphurization process. On the other hand, the increase of the MEA concentration in the solvent leads to an increase in the efficiency of the CO₂ capture process. But, taking into account the amine corrosiveness, it is preferred to have a 30 wt. % MEA concentration in the solvent. Thus, for a 30 wt.% MEA concentration in the solvent, we studied the effects of the absorption capacity of MEA, considering the 1, 10 and 15 wt. % NaOH concentrations in the solution. For each case (the 1, 10 and 15 wt. % NaOH concentrations in the solution) the absorption capacity of MEA for the CO_2 was of 0.27; 0.15 and 0.08 mol CO2/mol MEA. For a MEA concentration in the solution of 20 wt.%, the absorption capacity of MEA was reduced to 0.24 mol CO₂/mol MEA for a concentration of 1 wt.% NaOH in the solution.

We analyzed the CO_2 capture process by chemical absorption using MEA from the viewpoint of the required thermal energy. Thus, for a 1 wt.% NaOH concentration and a 30 wt. % MEA concentration in the solution, the heat duty was of 3.1 GJ/tCO₂ (considering the CO₂ capture process efficiency of 85 %). The heat necessary for the process was diminished by increasing the temperature of the solvent before entering the stripper unit. In this case, the heat of the flue gases is recovered in a heat exchanger, while the temperature of the solvent increases with 3-4°C depending on the MEA concentration in the solvent.

This study is very useful in practice when we need to determine correctly the quantity of MEA required for a certain efficiency of the CO₂ capture process, especially for power plant revamping.

Acknowledgements

The study has been funded by the UEFISCDI within the National Project number 38/2012 with the title: "Technical-Economic and Environmental Optimization of CCS Technologies Integration in Power Plants Based on Solid Fossil Fuel and Renewable Energy Sources (biomass)" CARBOTECH.

References

Abu-Zahra M.R.M., Schneiders L.H.J., Niederer J.P.M., Feron P.H.M., Versteeg G.F., (2007), CO₂ capture from power plants. Part I: a parametric study of the technical performance based on monoethanolamine, International Journal of Greenhouse Gas Control, 1, 37-46.

- Badea A., Apostol T., Dincă C., (2004), Environmental Impact Evaluation by Using the Life Cycle Assessment, (in Romanian), Polytechnic Publishing House, Bucharest, Romania.
- Badea A., Dincă C., (2012) CO₂ capture from postcombustion gas by employing MEA absorption process experimental investigations for pilot studies, *University Politehnica of Bucharest Scientific Bulletin*, 74, 21-32.
- Barchas R., Davis R., (1992), The Kerr–McGee/ABB Lummus Crest technology for the recovery of CO₂ from stack gases, *Energy Conversion and Management*, **33**, 333-340.
- Călămar A.N., Găman G.A., Pupăzan D., Toth L., Kovacs I., (2017), Analysis of environmental components by monitoring gas concentrations in the environment, *Environmental Engineering and Management Journal*, 6, 1249-1256.
- Cioca L.I., Moraru R.I., Rada E.C., Toretta V., Stelea, M.P., (2017), Greenhouse effect reduction through mine methane valorization: overview and feasibility study, *Environmental Engineering and Management Journal*, 6, 1257-1262.
- Cottrell A.J., McGregor J.M., Jansen J., Artanto Y., Dave N., Morgan S., Pearson P., Attalla M.I., Wardhaugh L., Yu, H., Allport A., Feron P.H.M., (2009), Postcombustion capture R&D and pilot plant operation in Australia, *Energy Procedia*, 1, 1003-1010.
- Davis J., (2009), *Thermal degradation of aqueous amines* used for carbon dioxide capture, PhD Thesis, University of Texas at Austin, USA.
- Dinca C., (2013), Technical, Environmental and Economic Assessment of CO₂ Absorption Chemical Process Integration in the Power Plant Technology, In: Materials and Processes for Energy: Communicating Current Research and Technological Developments, Méndez-Vilas A. (Eds.), Formatex Research Center, 935-945.
- Dinca C., (2016), Critical parametric study of circulating fluidized bed combustion with CO₂ chemical absorption process using different aqueous alkanolamines, *Journal of Cleaner Production*, **20**, 1136-1149.
- Dinca C., Slavu N., Badea A., (2018), Benchmarking of the pre/post-combustion chemical absorption for the CO₂ capture, *Journal of the Energy Institute*, **3**, 445-456.
- Dinca C., Badea A., (2013), The parameters optimization for a CFBC pilot plant experimental study of postcombustion CO₂ capture by reactive absorption with MEA, *International Journal of Greenhouse Gas Control*, **12**, 269-279.
- Dinca C., Badea A.A., Apostol T., Lazaroiu Gh., (2009) GHG emissions evaluation from fossil fuel with CCS, *Environmental Engineering and Management Journal*, 1, 81-89.
- Dinca C., Badea A., Rousseaux P., Apostol T., (2007), A multi-criteria approach to evaluate the natural gas energy systems, *Energy Policy*, 35, 5754-5765.
- Gao J., Wang S., Zhao B., Qi G., Chen C., (2011), Pilotscale experimental study on the CO₂ capture process with existing of SO₂: degradation reaction rate, and mass transfer, *Energy Fuels*, **25**, 5802-5809.
- Idem R., Wilson M., Tontiwachwuthikul P., Chakma A., Veawab A., Aroonwilas A., Gelowitz D., (2006), Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology

development plant and the Boundary Dam CO₂ capture demonstration plant, *Industrial & Engineering Chemistry Research*, **45**, 2414-2420.

- Jackson P., Robinson K., Puxty G., Attalla M., (2009), In situ Fourier Transform-Infrared (FT-IR) analysis of carbon dioxide absorption and desorption in amine solutions, *Energy Procedia*, **1**, 985-994.
- Jassim M.S., Rochelle G.T., (2005), Innovative absorber/stripper configurations for CO₂ capture by aqueous monoethanolamine, *Industrial & Engineering Chemistry Research*, **45**, 2465-2472.
- Kather A., Oexmann J., (2007), Optimization and Integration of CO₂-Capture by Wet Chemical Absorption Process, 10th Workshop of the Int. Network for CO₂ Capture, 24th May, 2007, Lyon, France.
- Kent R.L., Eisenberg B., (1976), Better data for amine treating, *Hydrocarbon Processing*, **55**, 87-90.
- Kothandaraman A., (2010), Carbon dioxide capture by chemical absorption: a solvent comparison study, PhD Thesis, Massachusetts Institute of Technology, USA.
- Kvamsdal H.M., Chikukwa A., Hillestad M., Zakeri A., Einbu A., (2011), A comparison of different parameter correlation models and the validation of an MEA-based absorber model, *Energy Procedia*, 4, 1526-1533.
- Meuleman E., Artanto Y., Jansen J., Osborn M., Pearson P., Cottrell A., Feron P., (2010), CO₂ Capture Performance of MEA and Blended Amine Solvents in CSIRO's Pilot Plant with Flue Gas from a Brown Coal-Fired Power Station, 35th Int. Technical Conference on Clean Coal and Fuel Systems: the Clearwater Clean Coal Conference: Clearwater, Florida, USA, 6 - 10 June 2010.
- Norişor M., Badea A., Dincă C., (2012), Economical and technical analysis of CO₂ transport ways, University Politehnica of Bucharest Scientific Bulletin, 74, 127-138.
- Oyenekan B.A., (2007), *Modeling of strippers for CO₂ capture by aqueous* amine, MSc Thesis, University of Texas at Austin, USA.
- Pinto D.D., Brodtkorb, T.W., Vevelstad S.J., Knuutila H., Svendsen F.H., (2013), Modeling of oxidative MEA degradation, *Energy Procedia*, **63**, 940-950.

- Puxty G., Rowland R., Attala M., (2010), Comparison of the rate of CO₂ absorption into aqueous ammonia and monoethanolamine, *Chemical Engineering Science*, 65, 915-922.
- Rao A.B., Rubin E.S., (2002) A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control. *Environmental Science and Technology*, **36**, 4467-4475.
- Rochelle G.T., (2002), Modeling of CO2 Absorption/Stripping with MEA, CO2 Capture Test Network Workshop, Kyoto, Japan.
- Rochelle G.T., (2003), *Innovative Stripper Configurations* to Reduce the Energy Cost of CO₂ Capture, 2nd Annual Carbon Sequestration Conference, May 5-8, 2010, Alexandria, Greece.
- Simon L.L., Elias Y., Puxty G., Artanto Y., Hungerbuhler K., (2011), Rate based modeling and validation of a carbon-dioxide pilot plant absorption column operating on monoethanolamine, *Chemical Engineering Research and Design*, 9, 1684-1692.
- Sharma A.K., Prasad D.S.N., Acharya S., Sharma R., (2012), Utility and application of FGD System (Flue Gas Desulphurization) in chemical and environmental engineering, *International Journal of Chemical Engineering and Applications*, 3, 129-135.
- Smit C.J., Van Heeringen G.J., Van Grinsven P.F.A., (2002), Degradation of Amine Solvents and the Relation with Operational Problems, Proc. of 52nd Annual Laurance Reid Gas Conditioning Conference, Oklahoma University, Norman, UK.
- Strazisar B.R., Anderson R.R., White C.M., (2003), Degradation pathways for monoethanolamine in a CO₂ capture facility, *Energy Fuels*, **17**, 1034-1039.
- Uyanga I.J., Idem R.O., (2007), Studies of SO₂ and O₂ induced degradation of aqueous MEA during CO₂ capture from power plant flue gas streams, *Industrial* &*Engineering Chemistry Research*, **46**, 2558-2566.
- Veldman R.R., (2000), Alkanolamine Solution Corrosion Mechanisms and Inhibition from Heat Stable Salts and CO₂, Corrosion 2000: NACE International Annual Conference and Exposition, Orlando, USA.