POST-COMBUSTION CO$_2$ CAPTURE FROM COAL-FIRED POWER PLANTS

BY

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Abstract

Post-combustion capture process involves the separation of CO$_2$ from the flue gas produced by combustion. The concentration of CO$_2$ in the flue gas of a typical coal-fired power plant is less than 15% (by volume) and the flue gas is present at almost atmospheric pressure. These two have a significant impact on the CO$_2$ capture process. However, post-combustion carbon capture is the most developed concept and has the greatest near- to middle-term potential for reducing CO$_2$ emissions, because it can be retrofitted to existing coal-fired power plants with only minor modifications. Chemical solvents are currently the most preferred option for post-combustion systems, offering a relatively high capture efficiency and selectivity. Three post-combustion systems are discussed and presented in this paper: amine-, carbonate- and ammonia-based process.

1. Introduction

Today, it is widely known that the major greenhouse gas is carbon dioxide (CO$_2$). Most researchers and scientists consider that an increase in atmospheric loading of CO$_2$ will lead to global warming. According to data from Mauna Loa Observatory, the concentration of CO$_2$ in the atmosphere has reached approximately 390 ppm (February 2010) [1]. It is about 39% higher than the CO$_2$ level of the pre-industrial era (~280 pm).

Fossil fuels are the dominant source of the global primary energy demand, and will likely remain so for the next decades. Currently, fossil fuels supply over 80% of all primary energy [2]. Since the Industrial Revolution, the emissions of CO$_2$ from fossil fuel combustion dramatically increased. In 2007, about 29 billion tonnes of CO$_2$ were from fossil fuel combustion (more than 47% as compared to 1990) [2,3]. As seen in Figure 1, energy sector produced

nearly 41% (~11 Gt) of the global CO_2 emissions in 2007, followed by transport (~23%) and industry (~20%). Fossil fuels provided over 70% of the world electricity and heat generation, of which coal supplied 41% of the generation.
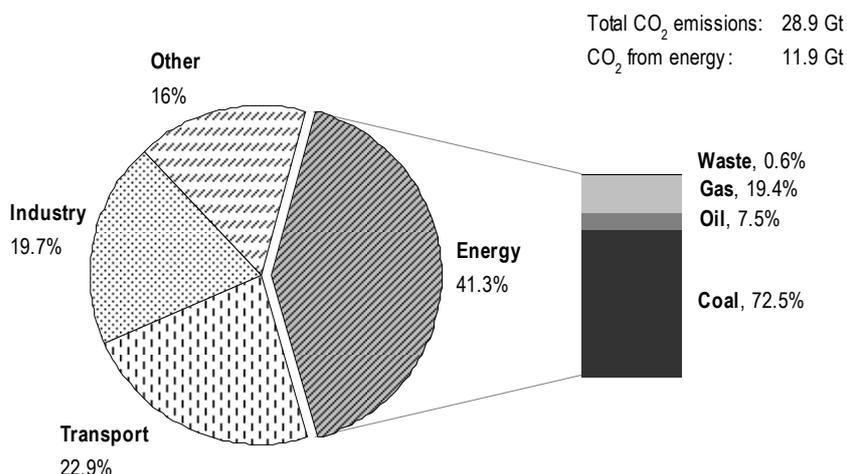

Total CO_2 emissions: 28.9 Gt
CO_2 from energy: 11.9 Gt

Other 16%

Industry 19.7%

Energy 41.3%

Transport 22.9%

Waste, 0.6%
Gas, 19.4%
Oil, 7.5%

Coal, 72.5%

Fig. 1 – World CO_2 emissions by sector, in 2007.

Romania emitted nearly 92 Mt of CO_2 in 2007 from fossil fuel combustion (with 51% less than in 1989) [3]. About 29% of these emissions came from the use of coal for electricity generation.

Emissions of CO_2 resulting from fossil fuels can be reduced by means of several measures: (i) to improve/increase the efficiency of power plants and production processes; (ii) to reduce the energy demand; (iii) to use low carbon content fuels and to increase the use of renewable energy source; and (iv) to apply CO_2 capture and storage.

The capture of CO_2 from fossil fuel-fired power plants offers the possibility to reduce the CO_2 emissions on a medium time scale. CO_2 can be captured either from flue gases or from process streams before combustion [4-7]. Among the types of fossil fuel used, coal has the highest carbon content, resulting in coal-fired power plants having the highest output rate of CO_2 per kilowatt-hour produced (e.g., 743 g CO_2/kWh for pulverized coal, 379 g CO_2/kWh for natural gas combined cycle) [3,4,8]. The CO_2 concentration in power station flue gas, for coal-fired boilers is about 15% by volume, while for natural gas combined cycle power plants is 4% and for natural gas-fired boilers is around 8%. The removal of CO_2 from the flue gas is best known as post-combustion capture. The concentration of CO_2 in flue gas can be increased by using pure oxygen instead of air for combustion, resulting in a flue gas that has a CO_2 concentration higher than 80%. This is known as oxy-combustion. Also, carbon dioxide can be removed from the power cycle before combustion applying pre-combustion CO_2 capture systems. The concentration of CO_2 in the CO_2/H_2 mixture will be 40-60% (by volume) for coal gasification, and around

20% for natural gas partial oxidation. The major advantage of a post-combustion CO_2 capture system over oxy- and pre-combustion is that it can be applied to existing power plants with minimal modification to the power station itself, or easily integrated into new ones [8].

In this work post-combustion capture systems (amine-, carbonate- and ammonia-based process) applied to coal-fired power plants are discussed.

2. Post-combustion capture concept

Capture of CO_2 from flue gases produced by combustion of fossil fuels (e.g. coal) in air is referred to as post-combustion capture. Figure 2 shows a block diagram of a coal-fired power plant with post-combustion capture. As can be seen, the CO_2 capture unit is integrated to the power plant as a flue gas post-treatment unit after the removal of pollutants in order to prevent plugging and fouling, and to minimize degradation of CO_2 capture solvents.
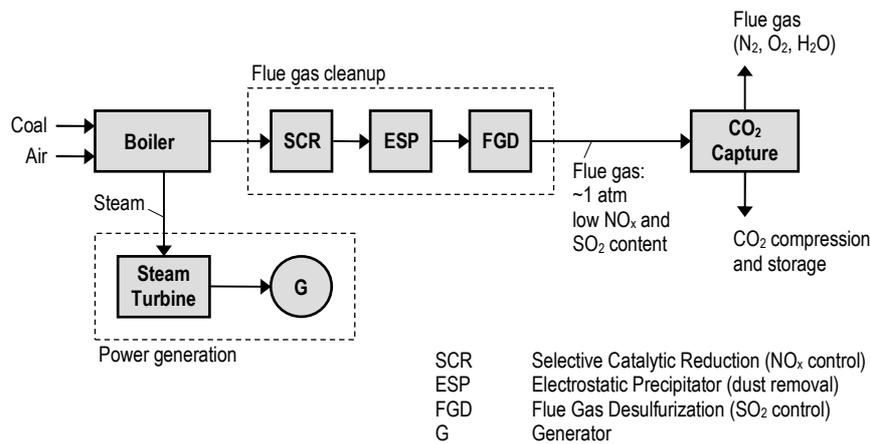

Fig. 2 – Coal-fired power plant with post-combustion CO_2 capture.

Before discharging to the atmosphere, flue gases, with low pollutant emissions content (NO_x, SO_2, particulate), are passed through equipment which separates most of the CO_2. The captured CO_2 is then compressed and further collected in a storage reservoir. Remaining compounds of flue gases, such as N_2, O_2 and vapors are discharged directly to the atmosphere.

The major drawback of this method is that the CO_2 partial pressure is very low due to the low CO_2 concentration in the flue gas (typically up to 15% by volume for coal-fired boilers) and hence large and expensive equipment is needed to extract the CO_2 [6,8]. Taking this into account, there have been proposed a variety of techniques for removing CO_2 from flue gases (e.g. using chemical or physical absorption, or adsorption, membrane separation). The study of them has shown that absorption processes based on chemical solvents

are currently the most preferred option for post-combustion systems, offering high capture efficiency and selectivity.

At present, there are a number of absorption solvents commercially available for CO_2 capture. Most of them are used for treating gas streams with low- to moderate-CO_2 partial pressure. The typical chemical solvents are alkanolamines, which are commonly used in the form of aqueous solutions. These chemical solvents include monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), etc. Aqueous monoethanolamine is often regarded as the first chemical solvent to be used for CO_2 capture from coal-derived flue gases. Today, there are two MEA-based absorption processes commercialized: Fluor's Econamine process and Kerr McGee/ABB Lumus Global's absorption/stripping process [9,10].

Mixtures between various single amines are also gaining a great deal of interest from the practitioners due to their process advantages over the single alkanolamines [4,11]. Most formulations of the blended amines are tertiary amine-based (e.g., MDEA). An addition of primary amine MEA or secondary amine DEA into the MDEA solution helps enhance rate of capturing CO_2.

There are also a large number of solvents currently proposed and being investigated. The Kansai Electric Company and Mitsubishi Heavy Industry developed a family of KS energy efficient proprietary solvents (sterically hindered amines) [12-14]. The performance of blends between potassium carbonate (K_2CO_3) and piperazine (PZ) has also been investigated [5,15]. The K_2CO_3/PZ system has been showing higher rate of CO_2 absorption and less sensitive to oxidative degradation than MEA. Ammonia (NH_3) has also been viewed as alternative to amine-based processes [16-18].

3. CO_2 capture from flue gas

3.1. Amine-based processes

The most commonly used absorbent for CO_2 absorption from low pressure flue gas is monoethanolamine. This amine was developed over 60 years ago as a general non-selective solvent to remove acid gases, such as H_2S and CO_2, from natural gas streams [19].

Figure 3 shows the process flow diagram of a typical chemical absorption system. The process consists of two major sections, an absorption section where CO_2 in the flue gas is absorbed into the liquid solvent and a regeneration section where the absorbed CO_2 is stripped out by means of heat.
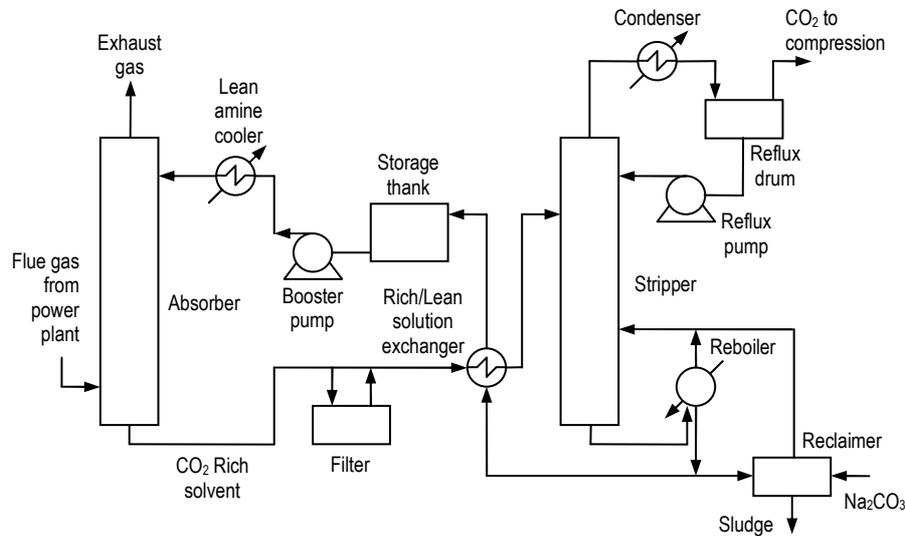
Fig. 3 – Process flow diagram of an amine-based system.

Prior to CO_2 removal, flue gases (usually at near atmospheric pressure and temperatures above 100°C) from power plant are cooled down to the temperature levels required for absorption, and treated for contaminants. After cooling, the flue gas is passed through an absorption vessel where it comes into contact with the chemical solvent, which absorbs much of the CO_2 by chemically reacting with it to form a loosely bound compound. The MEA/CO_2 reaction is as follows:

(1) $$C_2H_4OHNH_2 + CO_2 + H_2O \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^-$$

Then, the CO_2-rich solvent from the bottom of the absorber is pumped to another column (stripper or regeneration vessel), via a heat exchanger. In the stripper, the CO_2-rich solution is heated (to about 100-140°C) to release almost pure CO_2. Water vapors are condensed in the condenser and fed back to the stripper, whereas the net CO_2 gas leaves the unit with a purity over 99%. The lean solvent, containing far less CO_2 is cooled down to 40-65°C, and recycled to the absorber. The CO_2 recovery rates of about 98% can be achieved using an amine based chemical absorption process.

Although amine processes can remove CO_2 at low concentrations, large amounts of energy are required for solvent regeneration [6,8-10,20-22]. Moreover, contaminants typically found in flue gases from coal-fired power plants (e.g., SO_2, NO_x, hydrocarbons, and particulates) usually need to be removed prior to capture, as they can inhibit the ability of solvents to absorb CO_2.

At present, there are three amine-based processes commercially available for CO_2 capture in post-combustion systems: (i) the Kerr-McGee/ABB

Lummus Crest process, which uses for CO_2 separation a 15-20 wt% aqueous monoethanolamine solution [10]; (ii) the Fluor Daniel Econamine process (30 wt% MEA) [9]; and, (iii) the KEPCO/MHI process, which is an improved process based upon sterically-hindered amines (KS-1, KS-2 and KS-3) [12-14]. This kind of amines are amines in which a bulky alkyl group is attached on the amino group. The advantage of sterically-hindered amines over alkanolamines is that only 1 mol of the sterically-hindered amine is required to react with 1 mol of CO_2 (as compared to 2 mol of alkanolamine).

The first process requires a regeneration energy of 5-6.5 GJ/t CO_2 [6]. The Econamine process needs less thermal energy for solvent regeneration (4.2 GJ/t CO_2) [21] as compared to the first one. This high energy requirement makes the capture process energy-intensive and costly. Several researches have studied the possibility to reduce this energy requirement, especially for the MEA process [20,22]. Alie et al. [20] have found that the lowest energy requirement of 4 GJ/t CO_2 can be achieved at lean solvent loading (0.25-0.30 mol CO_2/mol MEA). Abu-Zahra et al. [22] have carried out an optimization and technical parameter study for a CO_2 capture process from flue gas of a 600 MWe coal-fired power plant, based on MEA solutions of 30 and 40 wt%. They found that: (i) the energy requirement decreases as MEA concentration increases (3 GJ/t CO_2 for a 40 wt% MEA solution); and, (ii) the optimum lean solvent loading is 0.30 and 0.32 mol CO_2/mol MEA for 40 and 30 wt% MEA solutions, respectively.

3.2. Carbonate-based process

CO_2 removal with potassium carbonate has been widely used in high pressure applications such as natural gas sweetening or the production of pure hydrogen for ammonia synthesis [19]. The commercial processes Benfield and Catacarb use 20 to 30 wt% aqueous K_2CO_3 solutions for CO_2 removal. However, under the conditions present in coal-fired power plants these processes are limited by selectivity and slow rates of absorption.

One possibility to improve the performance of CO_2 capture using potassium carbonate is the promotion with piperazine [5,15]. Theoretically, PZ can react with 2 mol of CO_2 per mol of amine. Researchers from the University of Texas at Austin have found that the K_2CO_3/PZ system has an absorption rate 10-30% faster than a 30 wt% MEA solution [5]. There should be also noted that oxygen is less soluble in potassium/piperazine solutions. However, piperazine is more expansive than MEA, so the economic impact of oxidative degradation will be probably the same. Oexmann et al. [15] have shown that the use of K_2CO_3/PZ (2.5 molar K; 2.5 molar PZ) in a CO_2 capture process may reduce the required heat duty for solvent regeneration (2.4 GJ/t CO_2) in comparison to MEA. Their study also indicates that the overall energy requirement may reduce as well.

3.2. Aqueous ammonia processes

Aqueous ammonia processes have been proposed as alternatives to traditional amine-based processes for post-combustion capture of CO_2.

Higher CO_2 loadings can be achieved with aqueous ammonia than with monoethanolamine [16]. This is mainly due to the aqueous ammonia/carbon dioxide system favoring bicarbonate over carbamate, particularly as CO_2 loading increases [23]. Yeh and Bai [16] reported that CO_2 absorption capacity of ammonia solution (28% concentration) decreased by 11% between reaction temperatures 10 and 40°C. Resnik et al. [17] confirmed that as the temperature approached the ammonium carbonate/bicarbonate decomposition temperature (~60°C), the CO_2 absorption rate decrease. Aqueous ammonia has also been shown to require less heat input for desorption than MEA [18]. This is due to the smaller reaction enthalpy for CO_2 absorption and higher CO_2 partial pressure at elevated temperature compared to MEA. Also, ammonia is resistant to oxidative degradation, which is a major benefit when treating oxygen containing gas streams such as those from coal-fired power stations. The other main attractive feature is that in the presence of sulfur and nitrogen oxides in the gas stream, the ammonium salts that form may have commercial value as fertilisers.

The reactions between NH_3 and CO_2 are:

$$(2) \qquad\qquad NH_3 + CO_2 + H_2O \leftrightarrow NH_4HCO_3$$

$$(3) \qquad\qquad 2NH_3 + CO_2 + H_2O \leftrightarrow (NH_4)_2CO_3$$

Another ammonia-based process is the chilled ammonia process. This process has been patented in 2006 by Gal [24]. The difference between those two is that the second process absorbs CO_2 at low temperatures (0-10°C).

Process description [24]: prior to absorption, the flue gas is cooled using chilled water and a series of direct contact coolers. After the cooling subsystem, the cold flue gas enters the absorber where most of the CO_2 is chemically absorbed in the lean solvent from the stripper. The absorber removes CO_2 from the flue gas mainly by the precipitation of ammonium bicarbonate and has a recirculation loop with refrigerated chilling that maintains it at a temperature of 0-10°C. The CO_2-rich stream flows to a heat exchanger where its temperature increases, and then flows to the desorber. The desorber temperature is in the range of 50-200°C, while the pressure is in the range of 2-136 atmospheres. Under those conditions, the vaporization of ammonia and water implied by the high temperature is reduced. The conditions cause CO_2 to evaporate from the solution. It leaves the top of the desorber as a relatively clean and high-pressure stream.

As mentioned, potentially exploitable advantage of ammonia process is that, unlike MEA, which is degraded by SO_2, ammonium carbonate reacts with

SO_2 to form ammonium sulfate and with NO_x to form ammonium nitrate, both of which are marketable as fertilizers. Thus, ammonia-based CO_2 capture may be carried out either separately from or simultaneously with the scrubbing of sulfur and nitrogen oxides [17,18].

4. Conclusions

In this paper, three processes for CO_2 separation and capture from flue gas of coal-fired power plants have been presented and discussed. The processes are based on aqueous solution of alkanolamines, potassium carbonate and ammonia. There has been also described a chilled ammonia process, which captures CO_2 at low temperatures.

The major disadvantage of the amine-based process is that a large quantity of energy is required for the CO_2 separation, regeneration, cooling and/or heating, etc. Although, carbonate-, ammonia- and chilled ammonia-based processes are less energy-intensive and more efficient than MEA, they are still under development and demonstration.

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CAPTAREA POST-COMBUSTIE A CO_2 DIN CENTRALE PE CĂRBUNE

(Rezumat)

Captarea dioxidului de carbon în faza de post-combustie este procesul de separarea CO_2 din gazele de ardere. Datorită concentraţiei joase a CO_2 în gazele arse, aproximativ 15% pentru centrale termoelectrice pe cărbune pulverizat, sistemele pe baza absorbţiei chimice reprezintă tehnologia cea mai dezvoltată la ora actuală. În această lucrare au fost prezentate şi discutate trei procese de captare CO_2 din gazele de ardere, şi anume, procesul de reţinere CO_2 prin absorbţie în soluţii de amine, carbonat de potasiu şi amoniac.