Exhaust gas treatment technologies for pollutant emission abatement from fossil fuel power plants

E. David, V. Stanciu, C. Sandru, A. Armeanu & V. Niculescu
Department of Research,
National Research Institute of Cryogenics & Isotopic Technologies,
Rm Valcea, Romania

Abstract

The emission of carbon dioxide (CO_2) and other pollutants which result from burning fossil fuels has been identified as the major contributor to global warming and climate change. However, for the immediate term, over the next 10 – 20 years at least, the world will continue to rely on fossil fuels as the source of primary energy. The challenge for the fossil fuel industry is to find cost-effective solutions that will reduce the release of CO_2 and other pollutants into the atmosphere.

The focus of this paper is on the ability to treat the exhaust gas from fossil fuel power plants in order to capture and store the CO_2 and remove other pollutants such as SO_x and NO_x which are released in the atmosphere.

In summary, capture/separation costs represent the largest financial impediment for these types of plants. Hence, efficient, cost-effective capture/separation technologies will need to be developed to allow their large-scale use.
Keywords: exhaust gas, fossil fuel, treatment technologies, carbon dioxide, separation process, pressure swing adsorption, pollutant reduction.

1   Introduction

Carbon dioxide capture and storage (CCS) is gradually becoming an important concept to reduce greenhouse gas emissions, next to other options, such as the use of renewable energy, the use of nuclear energy, energy efficiency

improvements and switching from coal to gas firing [1]. CO_2 accounts for over eighty-two percent of all greenhouse gas emissions [2]. Nearly sixty percent of CO_2 is emitted by utility or industrial power systems, which are based on fossil fuel combustion [1,2]. Future power generation technologies such as fuel cells or gasification need to mature and to lower costs to gain widespread application. Consequently, it is likely that for the next several decades the bulk of the CO_2 will be emitted from the fossil fuel-based energy infrastructure, both existing and that likely to be added in the near term. Carbon sequestration would enable the continual use of carbon-based fuels to meet the world's growing energy demand without further increasing the atmospheric concentration of CO_2. Because carbon-based technologies dominate about 75% of the world [3], and because they will likely maintain their dominance for the foreseeable future, an effective CO_2 emission control strategy should target power systems.

The flue gas effluents of the corresponding medium to large point sources present a desirable control point due to their centralized location and large scale [4]. CO_2 capture technology retrofitted to the existing energy infrastructure offers the potential to meaningfully reduce worldwide CO_2 emissions in the near term in a practical manner.

Some of the emerging technologies e.g. oxyfuel combustion with CO_2 recycle will require unconventional combustion systems. As such, as they become more cost effective, they will mainly find applications in new energy installations [5]. This paper describes the technology development efforts focused on the recovery of CO_2 from existing flue gases without having to modify the current infrastructure.

The challenge for fossil fuel industry is to find cost-effective solutions that will reduce the release of carbon dioxide into the atmosphere.

2   Carbon dioxide emissions

Figures 1 and 2 present trends in CO_2 emissions for past 150 years [6] in Romania. Prior to 1850, in pre-industrial times, the average emissions of CO_2 was about 280 parts per million as seen in Figures 1 and 2. The emission levels of CO_2 in the atmosphere are now approaching 360 parts per million and continue to increase steadily at a rate of about 0.3–0.4% per year [6].

This increase in CO_2 in the atmosphere is primarily due to the societal changes brought about by the industrial revolution. When fossil fuels are burned, the carbon content is oxidized and released as CO_2; every tonne of carbon burned produces 3.6–3.7 tonnes of CO_2.

The global consumption of fossil fuels is estimated to release over 22 billion tonnes of CO_2 into the atmosphere every year – and the amounts are still climbing [7]. In CCS, CO_2 is extracted at some point in the energy conversion train, depending on the type of energy technology used. It is then prepared for transport and stored in a suitable geological sink, where it is kept for a sufficiently long period. As it is seen in Table 1, the flue gases emitted from medium to large point sources are generally at, or slightly above, atmospheric pressure.
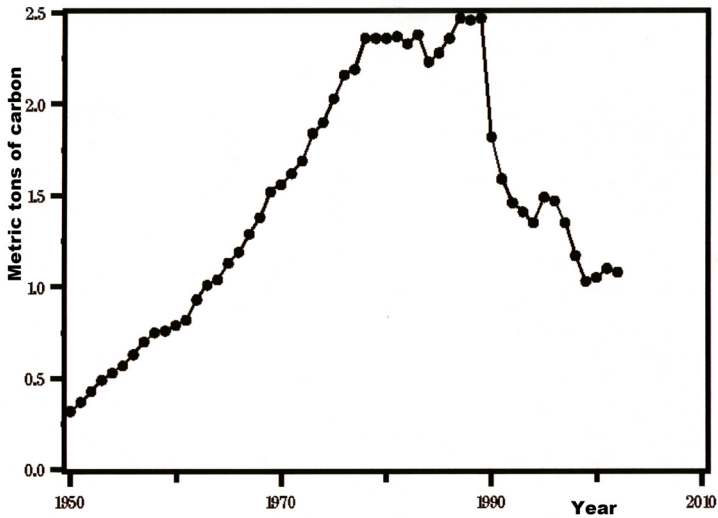
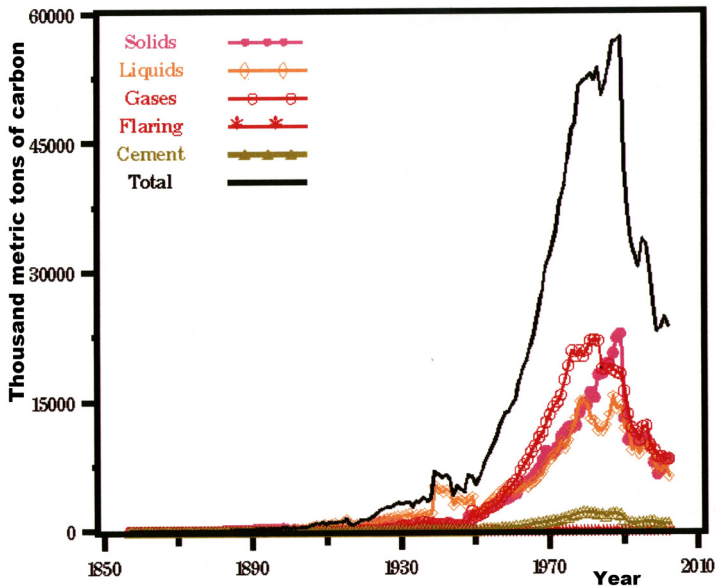Figure 1:   Estimated CO_2 emissions in Romania [6].

Figure 2:   Evolution in time of the global CO_2 emissions in Romania [6].

They typically contain 3–15%(by volume) of CO_2. For example, flue gas from a coal fired power plant typically contains about 13% CO_2, 5% O_2, and 82% N_2. Flue from a natural gas turbine is lower in CO_2, but higher in O_2, with a typical composition of 4% CO_2, 14% O_2 and 82% N_2. Typical trace contaminants

include sulfur oxides (SO_x), nitrogen oxide (NO_x) and particulates. Their levels vary widely, depending on fuel composition, combustion system and operating conditions.

Table 1:   Some sources of CO_2 emissions.

Source	CO_2	Impurities	Pressure
Natural gas turbine exhaust	3–4.5%	Low SO_x and NO_x levels, 10-15% O2	1 atm
Coal/oil fired boilers	3–15%	High SO_x and NO_x levels, 3-6% O2	1 atm
Singas turbine exhaust	4.5–6.5%	Low SO_x and NO_x	1 atm
Cement off-gas	20–30%	Could have many other impurities	1 atm
Blast furnace gas	15–35%	SO_x and NO_x are presented	1 atm

3 Types of carbon dioxide separation technology

Most of carbon dioxide separation technologies are not new, but the selection of a technology for a given separation application depends on many factors, i.e. pressure of CO_2 in the gas stream, extent of CO_2 recovery required, types and sensitivity to impurities, purity of desired CO_2 product, costs of the process, environmental impacts and so one.

In combustion process of fossil fuel for to produce thermique energy results exhaust gases, that contain until 15% vol. CO_2. This amount can be separated by different methods and then stored and used. Figure 3 gives an idea about CO_2 capture pathways in a broad spectrum of fossil energy conversion processes including power generation.
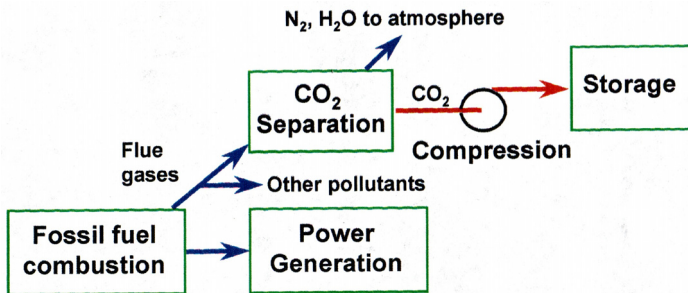

Figure 3: CO_2 capture from a conventional power plant.

Based upon the process of CO_2 separation, capture technologies can be classified into the following approaches (see Figure 4):
   1. Chemical and physical absorption;
   2. Membrane separation
   3. Low temperature separation-cryogenics processes
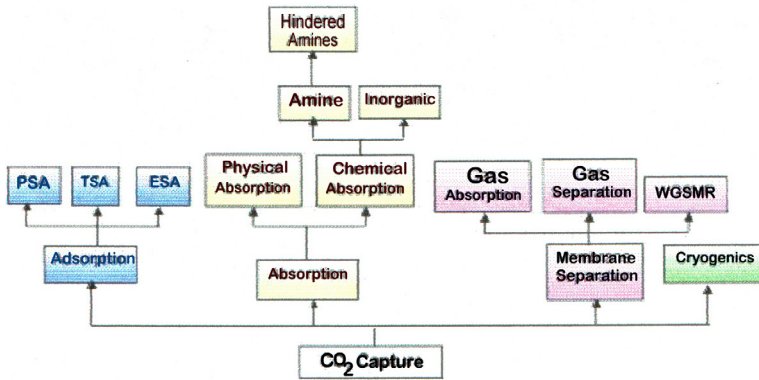   4. Physical adsorption on selective adsorbent materials;

Figure 4:   Approaches of CO_2 capture and separation technologies.

After CO_2 separation, by one of above process (see Figure 4), this needs to be compressed to achieve the right transport and storage conditions. CO_2 separation processes can be divided into three main categories: post-combustion processes, pre-combustion processes and oxy-combustion/de-nitrogenation processes. These process categories are applicable to both fossil fuel and biomass.

3.1 Chemical and physical absorption

The chemical absorption process for separating CO_2 from exhaust gases is taken over from the gas processing industry. Amine based processes has been used commercially for the removal of acid gas impurities such as CO_2 and H_2S, from process gas streams. Alkanolamines remove CO_2 from gas stream by the exothermic reaction of CO_2 with the amine functionality of the alkanolamine.

Different amines have different reaction rates with respect to the various acid gases. In addition, different amines vary in their equilibrium absorption characteristics for the various acid gases and have different sensitivities with respect to solvent stability and corrosion factors. Alkanolamines can be divided into three groups: 1) primary amines whose members include monoethanol amine (MEA); 2) secondary amines whose members include diethanolamine (DEA), and 3) tertiary amines whose members include triethanolamine (TEA).

It may be pointed out that corrosion has been a serious issue in amine processes. In general, alkanolamines themselves are not corrosive to carbon steel, but the dissolved CO_2 is the primary corroding agent. As such, the alkanolamines indirectly influence rate due to their absorption of CO_2. The observed corrosivity of alkanolamines to carbon steel is generally in the order:

primary amines > secondary amines > tertiary amines

To date, all commercial CO_2 capture plants use processes based on chemical absorption. Typically the size of the commercial plant is relatively small (maximum 800 t/d), compared to that required for processing power plant flue gas (>5,000 t/d). The greatest limitation for CO_2 capture from flue gas is the low pressure of the flue gas (see Table 2).

Table 2: CO_2 separation technologies capabilities.

Parameters	Absorption	Adsorption	Membrane	Cryogenics
Feed pressure	medium to high	Low to high	medium to high	medium to high
CO_2 pressure	low	low	low	low to medium
CO_2 purity	medium to high	medium to high	low to medium	high
CO_2 capture	high	high	low	high

CO_2 is absorbed much easily into solvents at high pressure. A typical flue gas contains some amount of NO_x. NO_x generally consists of NO and NO_2 in a ratio of from 95:5 to 90:10. The main component NO performs as inert gas and will not affect the solvent. However, NO_2 will partially lead to form heat stable salt.

3.2 Separation by permeation membranes

A membrane is a barrier film that allows selective and specific permeation under conditions appropriate to its function. With regards to CO_2 capture, two types of membranes systems are considered: gas separation and gas absorption membranes. Gas separation membranes rely on differences in physical or chemical interactions between gases and a membrane material, causing one component to pass through the membrane faster than another.

Gas absorption membranes are micro-porous solid membranes that are used as contacting devices between gas flow and liquid flow. The CO_2 diffuses through the membrane and is removed by the absorption liquid, which selectively removes certain components from a gas stream on the other side of the membrane.

3.3 Cryogenic separation

Cryogenic separation is widely used commercially for purification of CO_2 from streams that already have high CO_2 concentrations (typically > 50%). It is not normally used for dilute CO_2 streams such as flue gas from coal/natural gas fired boilers as the amount of energy required for refrigeration is uneconomic for plant. Cryogenic separation has the advantage that it enables direct production of liquid CO_2 which is needed for economic transport. The most promising applications for cryogenics are expected to be for separation of CO_2 from high pressure gases, such as in pre-combustion capture processes, or oxyfuel combustion in which the input gas contains a high concentration of CO_2.

4 Separation of CO_2 by pressure swing adsorption process

The intermolecular forces between gases such as CO_2 and the surface of certain solid materials permit separation by adsorption. Selective adsorption of the gases depends on temperature, partial pressures, surface forces and adsorbent pore size. The solid adsorbents, such as activated carbon and molecular sieves are normally arranged as packed beds of spherical particles.

In pressure swing adsorption (PSA), the adsorbent is regenerated by reducing pressure. In temperature swing adsorption (TSA), the adsorbent is regenerated by raising its temperature and in electric swing adsorption (ESA) regeneration takes place by passing a low-voltage electric current through the adsorbent.

Both PSA and TSA are commercially available technologies and are used in commercial process for to remove CO_2 from natural gas [2]. A combination process of pressure and temperature swing adsorption (PTSA) tested for a power station burning coal/oil mix and a flue gas with a concentration of 11.7% CO_2 generated a recovery of 90% CO_2 [3].

We present a case that was studied by us, for CO_2 removing from flue gases released from fossil power plant, using PSA process. The main parameters are presented in Table 3.

Table 3:   Flue gas characteristics.

Parameters	Gas flue			
Temperature ^{o}C	160			
Pressure, bar	1.013			
Volume flow, m^3/day	350×10^3			
Components	H$_2$O	CO$_2$	N$_2$	O$_2$
Mass flow kg/day	1528	45733	250024	10769
Volumic fraction	0.005	0.150	0.820	0.035

The plant was operated at highest capacity. The experimental system used for PSA separation process of CO_2 from this flue gas is presented in scheme from Figure 5.

Carbon dioxide is separated from exhaust gases that contain 15% vol. CO_2, such as presented in Table 3, by an adsorption process using ambient temperature, when the adsorption step of the process is conducted by passing exhaust gases through an adsorption zone (adsorption column, see Figure 5) containing carbon molecular sieve (CMS). CO_2 is adsorbed on CMS and all other components pass through the adsorption column, without being adsorbed. The CO_2 production is obtained on desorption process.

The cyclic process includes adsorption-desorption steps and on desorption the steps are: purging-evacuation for purging, evacuation for production and regeneration by a vacuum system. As noted above, the pressure at which the adsorption step is carried out is typically in a range of about 1 to 25 bar. For PSA processes the adsorbent regeneration step is typically carried out at 10^{-6} bar.

We have experimented the pressure swing adsorption (PSA) for separation and recovery of CO_2 emitted by thermal power station. The energy costs for CO_2 separation from flue gases are accounted for approximately 70–80% of total cost for CO_2 sequestration. Therefore, it is important to develop new adsorbents to reduce the energy for CO_2 separation because the energy costs for CO_2

separation greatly depend on the performance of the adsorbents. The adsorbent used in these tests was a carbon molecular sieve (CMS) prepared as in reference [8], having appropriate pore size to separate CO_2 from the gaseous mixture.
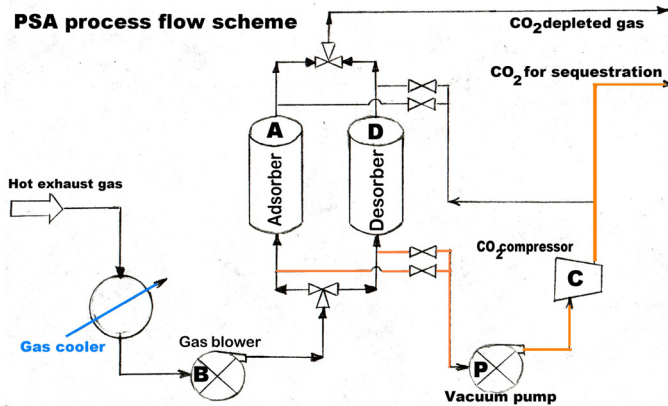

Figure 5: PSA process flow scheme used for CO_2 removing from flue gas.

4.1 Adsorption measurements and CO_2 separation.

Performance tests for CO_2 adsorption on CMS were performed using the above PSA system (Figure 5) and flue gas from fossil power plant, that contains 15% vol. CO_2 (see Table 2). The initial flue gas and after PSA adsorption process were analysed by the gas-chromatografy method, using a Hewlett Packard gas cromatograph, with thermal conductivity.

4.2 Results and discussions

Dynamic adsorption capacity for CO_2 was measured. The pressure swing adsorption process is usually used for CO_2 separation from different gaseous sources. This process consists of two major steps: adsorption and desorption. The technical feasibility of process is dictated by the adsorption step, whereas the desorption step controls its economic viability. Adsorption isotherms of CO_2, N_2, O_2 and water vapours on carbon molecular sieve (CMS) are shown in Figures 6 and 7.

It is clear that there is preferential adsorption of CO_2 on this carbon molecular sieve, indicating that it is suitable for separation of CO_2 from flue gases. The desorption isotherm, shown also in Figure 6, was very similar to that of the adsorption isotherm. This indicates that there is not substantial hysteresis during desorption and CO_2 can be almost fully recovered during desorption. For increasing the recovery efficiency it is good to use a vacuum pump as a carbon molecular sieve can be fully regenerated by evacuating adsorbed gas to 5×10^{-6} bar.
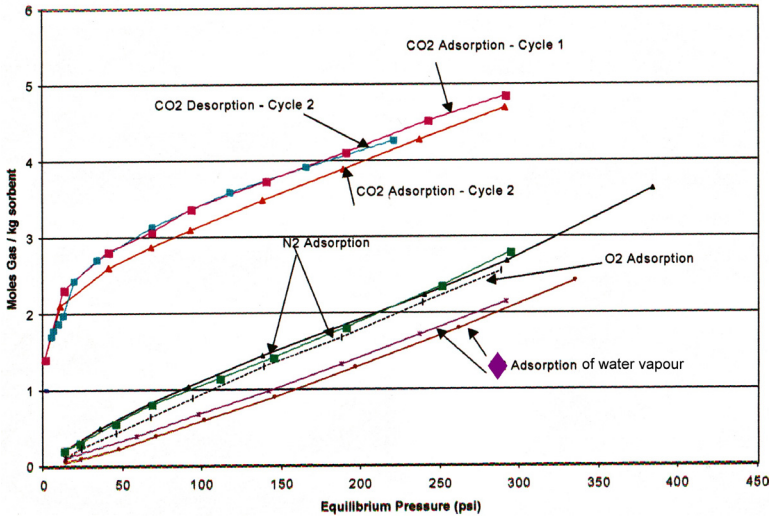
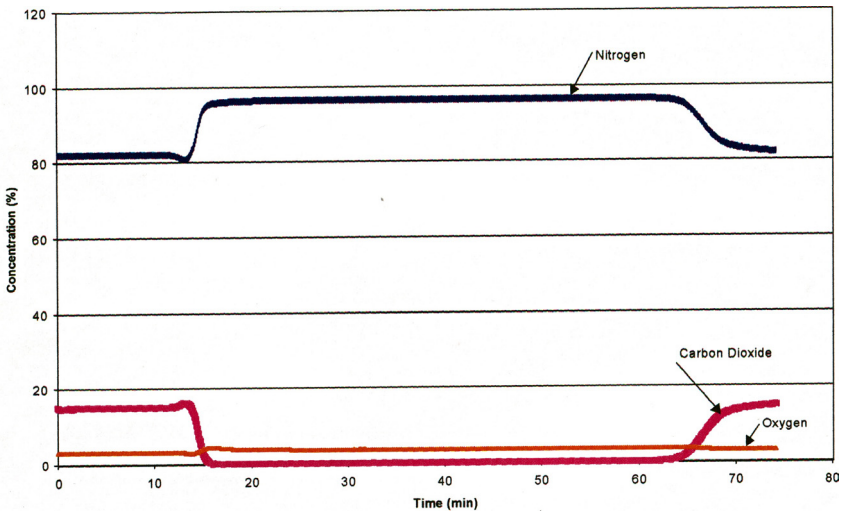Figure 6:   Adsorption-desorption isotherms of carbon molecular sieve-CMS [8].

Figure 7:   Adsorption curves of CO_2, N_2, O_2 and water vapour on CMS [8].

5   Conclusions

The main advantage of physical adsorption over other separation and capture technologies is its simple and energy efficient operation and regeneration, which can be achieved with a pressure swing cycle. The concerns over this technology are scale up and the need to develop CO_2 specific adsorbent materials.

Based on these circumstances, we plan to develop a new adsorbent based on amine-modified carbon molecular sieve with higher adsorption capacity for CO_2, to reduce the energy and costs for CO_2 capture and the sequestration process.

In the longer term, CO_2 capture technologies would not be limited to some of the presented processes. Separation technologies such as hydrate formation, various membranes, biomimetic route based on enzymatic catalysis, electrical swing adsorption and many others that are currently in the developmental stage, offer the promise of significantly reduced costs.

References

[1] Burchell, T.D., Judkins, R.R., Rogers, M.R. and Williams, A.M., *Carbon*, 35(9), pp 1279-94, 1997.

[2] Gunter, W.D., Wong, S., Cheel, D.B. and Sjostrom, G., *Applied Energy* 61, 209- 227, 1998.

[3] Mimura, T., Satsumi, S., Iijuma M., Mitsuoka S., *Proceedings of the Fourth International Conference on Greenhouse Gas Control Technologies*, Interlaken, Switzerland, pp.71-76, 1999.

[4] MacLean, H and L Lave , *Environmental Science & Technology* **34**:pp. 225-231,2000.

[5] Jasra R.V, Choudary N.V and Bhat G.T, in *Separation and Science Technology*, 26,pp. 885-930, 1991;

[6] Trends emissions on : http://cdiac.esd.ornl.gov/ftp/trends/emissions/rom.dat

[7] Johnson J., *Chemical & Engineering News*, 79 (1),18,2001.

[8] Stanciu V, David E, Stefanescu D., Separation of CO_2 and CH_4 from landfill gases by selective adsorption on CMS in *Advances in Materials and Processing Technologies*, AMPT'97, Edited by M. Andritschky, Vol.II, pp. 636-642, 1997.