

The comparison of CO₂ capture processes

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Abstract. The multitude of methods can be grouped into three: absorption procedures (the majority), adsorption procedures, and diffusion procedures (the fewest). Most of the industrial applications of the capture procedures of CO₂ were in the installations of ammonia producing and the chemical absorption procedures had them, and when the gas is under pressure, the physical absorption ones are applied, or the combined ones - chemical and physical absorption. This study demonstrates that the use of the best available technology for post-combustion CO₂ capture, namely the chilled ammonia process (CAP), is closest to being commercialized.

Key Words: capture processes, CO₂, gas, post-combustion with chilled ammonia, post-combustion with amines.

Introduction. The idea of capturing CO₂ from the flue gas of power plants did not start with concern about the greenhouse effect. Rather, it gained attention as a possible economic source of CO₂, especially for use in enhanced oil recovery (EOR) operations where CO₂ is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. Several commercial CO₂ capture plants were constructed in the late 1970s and early 1980s in the US (Arnold et al 1982). Several more CO₂ capture plants were subsequently built (Barchas & Davis 1992) to take advantage of some of the economic incentives in the Public Utility Regulatory Policies Act (PURPA) of 1978 for "qualifying facilities" and to provide CO₂ for sale commercially.

The energetic industry, the chemical industry, metallurgy, concrete production, transports, waste burning are the most important emission sources of the gases having a greenhouse effect, contributing to global warming. Nowadays, at a global level, 22 bill. tones of CO₂, out of which 8 bill. tones come from coal burning, are released into the atmosphere (Crutzen & Lelieveld 2013).

The energetic system based on coal is mostly responsible for polluting emissions. At the same time nonetheless, we remain dependent to coal for the following years: coal is cheaper and more available.

Nigel Yaxley, ex president of the Euracoal Association, says that the fastest growing energy source at a global level is still coal (3,1 % increase in 2008). Therefore, the technologies which allow the clean extraction and exploiting of coal are indispensable: „The capture and storage of coal must be a part of the solution for emission reduction" (Maroto-Valer et al 2002).

The European Union has adopted ambitious objectives for the reduction of gas emissions that produce the greenhouse effect, which cannot be fulfilled without a significant reduction of CO₂ emissions produced by the usage of fossil fuels (Omer 2004).

From a technical point of view, this reduction is also possible by applying three measurement types:

- the improvement of energetic efficiency;
- the usage of energy sources which can be regenerated;
- the capture and storage of carbon dioxide currently released.

The energetic efficiency and the energy sources that can be regenerated represent, on the long term, the most abiding solutions for the safety of energy supplying and for the climate conservation.

The European Union had to reduce by 10% the gas emission causing the

greenhouse effect between 2012-2020, and, on the long term, these emissions must be diminished by approximately 72% in comparison to the year 2012. The established targets cannot be achieved without the capture and storage of the carbon dioxide within the geological formations (<http://heionline.org/HOL/LandingPage>).

The annual global emissions of CO₂ escalate to the amount of 30 Gt. out of which approximately 2/3 are released by the developed countries: SUA (20%), China (20%), the UE countries (16%) and Russia (9%). The difference between countries in reference to the CO₂ emissions of power stations, in grams/kwh, is also interesting. Therefore, in the UE, these have the average of 341 g/kwh, in the USA it is 573 g/kwh, and in China 788 g/kwh (Da Silva & Svendsen 2007).

Out of all the known gases, CO₂ holds most of the separation procedures, some of them being applied at an industrial scale, and some at a smaller scale, inside the pillars, or just in the laboratory. As a consequence of the past development of chemical fertilizers industry, which is currently declining, and also of the attention that environmental protection now enjoys, a continuous development of the separation procedures for CO₂ is noticed.

Global capacity for storage of carbon dioxide is presented in Table 1 (Constantin et al 2008).

Table 1

Global capacity for storage of carbon dioxide

No.	CO ₂ storage	Global capacity Gt CO ₂	Global capacity percentage of total emissions between 2000-2005
1	Depleted oil or natural gas reservoirs	920	45%
2	Unexploited coal layers	>15	>1%

CO₂ caption processes. Since 1913, when the first ammonia factory was made functional in Germany, the CO₂ absorption from the synthesis gas has been done through different procedures, the main objective being the reduction of energy consumption to the regeneration of the absorbing solution. For the increase of ammonia installations capacity, the pressure for the preparing of synthesis gas was increased, and, in these conditions, the passing from chemical absorption to combined absorption - chemical and physical, or just physical absorption - has been done (CO₂ elimination is only done through detente). At the same time, the evolution of absorbents has happened. For chemical absorbents, the choice was towards the absorbents that had a small reaction enthalpy (to obtain a reduced energy consume in regeneration), the absorbents with low volatility and viscosity, high physical and thermic stability, noncorrosive, non toxic and, surely, taking into consideration the cost of the absorbent. Therefore, after nearly a century of ammonia production, the absorption procedures are perfecting, and currently, when the problem of CO₂ caption from burnt gas has been raised, the energy specialists are addressing chemists to analyze the difference between synthesis gas and burnt gas, in order to select the best procedures, out of the multitude of existing possibilities.

The chemical absorption of CO₂. The oldest chemical absorption procedures of CO₂ were aqueous basic ammonia solutions of mono ethanolamylene (MEA), diethanolamylene (DEA), followed by aqueous solutions of K₂CO₃, activated by various activators, such as AS₂O₃ (Giammarco-Vetrocoke procedure), or activated by DEA and using V₂O₅ as passiver (the Benfield procedure - also applied to ammonia installations of the Kellogg type), or with amines borates (the Catacarb procedure). Later on, there appeared procedures based on methildiethanolamylene (MDEA), based on diisopropilamylene (DIPA). The basic reaction is the passing of CO₂ as a bicarbonate, followed by the reverse reaction, as such: CO₂ + OH⁻ = HCO₃⁻.

It is understandable how the enthalpy absorption/desorption evolved in these procedures: it has dropped from 83kJ/mol CO₂ in the MEA solution, to 63 kJ/mol CO₂ in the processes of hot solutions activated by K₂CO₃. More recently, polygamine processes

have been developed (where an amine mode absorbs 3 mols of CO₂), where the enthalpy has lowered to 44 kJ/mol CO₂ and, even more recently, the raw formula of amine C₈H₂₂N₄ (APEDA) makes 41,9 kJ/mol CO₂. In a power station, in the case of the MEA process usage, approx. 40% of its power is consumed, and in the case of new processes, the consume is reduced to half.

CO₂ physical absorption. When in the gas mixture a large content of CO₂ appears or when the gases are under pressure (more than 40 tam), the physical processes are applied. The most famous processes are: the Rectisol process (with methanol); the Purisol process (with N-methyl-pyrrolidone); the Fluor process (with propylene carbonate); the Estasolvan process (with tributylephosphate); the Sulfinol process (DIPA and tetrahydrotyophene mixture). The most known and used process is the Selexol, that uses the dimethyletherpolyethylenglicole compound). The Selexol solvent is the best from a technical point of view; it has large chemical and thermic stability, it is not toxic, noncorrosive, it has viscosity and tension of small vapors, and, also, it has small absorption heat and it is biodegradable (and also ecological). In the 80's, at U.P.G. Ploiesti, it was synthesized, but it was not industrially applied in an ammonia installation. The absorbent for this type of absorption is characterized by its selectivity towards CO₂, the other gases of this mixture (H₂, CH₄, CO, N₂, O₂, etc.) being little dissolved in the absorbent. Generally, the absorbents for CO₂ dissolve the other acid gases, like H₂S, Sox, COS, CH₃SH, etc. Therefore, in the purifying of burnt gas, first the gas desulphuration and then the CO₂ absorption is done.

The combined absorption. When the gas is under pressure, for the chemical absorption with water, the gas also dissolve physically, and through detente they desorb, then the solution is boiled for regeneration (the bicarbonates decompose into carbonates). In the chemical absorption, the CO₂ is absorbed reaching small concentrations, comparing it to the physical absorption, and the CO₂ purity is greater, allowing the usage of CO₂ in the synthesis of other products (urea, methanol, carbonates etc.). By comparing the two procedures, from this point of view, the chemical absorption is superior to the physical absorption, which cannot absorb CO₂ to low concentrations and cannot reach a high purity for the CO₂. Therefore, in the physical absorbents some substances that must chemically connect the CO₂ are to be added. In the Selexol process, DIPA was added, in this way improving the performances of the process, resulting into a combined absorption (physical-chemical). The selection of the CO₂ absorption procedure is done by taking into consideration the chemical composition of the gas mixture, their pressure and debit. In the case of the synthesis gas containing CO₂ in a 17-18% proportion, combined processes, if the gas has pressure (20 tam), or chemical ones, if it doesn't have pressure, can be applied.

The burnt gas from the power stations, with large debits and low pressure (the compressing of large debits means a large energetic consume) where the main gas is nitrogen (up to 80%), the content of CO₂ is below 13%, and the gases also contain O₂ (up to 6-7%), the choice of the process is more difficult. In addition, the separated CO₂ is compressed, transported and stored in the subterranean (where it is non purified), meaning it doesn't need to have high purity as in the case of its usage for chemical synthesis. In these conditions, the chemical processes would be more suitable compared to physical ones, because the CO₂ content is smaller than in the case of synthetic gas and the pressure is reduced. In the speciality literature, three main directions for CO₂ caption in the energy field, have been outlined: post-combustion fulfills the realization of burnt gas that appear by fuel burning in power stations (Wilcox 2012). The composition of these gases differs from fuel to fuel, they having in common only the large content of nitrogen (due to the air excess); the content of sulphur oxides is determined by the fuel's content of carbon, more accurately by its quality; the oxygen content determined by the air excess is important, because it can degrade the amines; the content of solid impurities also depends on the fuel quality. Therefore, first of all the mechanic impurities are retained by the aid of electro-filters and then the gas de-sulfuring and the CO₂ caption are to be achieved (through the cold ammonia process and the amine process).

In Romania, at the Turceni power station, the cold ammonia process has been imported. Globally, the cold ammonia process was generally applied in the Northern countries, where the climate is colder. This process involves additional expenses regarding work protection (gas masks for ammonia, antidote), typical for the chemical industry. The oxy-combustion applies the burning of fuels with oxygen, and the burnt gases will not contain nitrogen, meaning that the gas debit is much lower, while the CO₂ content is larger (80-85%), this helping for the absorption phase. Therefore, as the debit is small, the option of gas compression and combined or physical absorption are taken into consideration. A part of the CO₂ is recirculated in the boiler for lowering the temperature, the separate CO₂ having a great purity (more than 99%). The disadvantage of this process is represented by the high cost of the oxygen obtained through cryogenic separation. The electric energy consume for the production of oxygen usually represents about 15% out of the power station's production. The pre-combustion acts by eliminating the sulphur from the fuels, so that later the fuel burning with oxygen is achieved. A new process for obtaining oxygen with lower costs is being elaborated. This thing has held back for many decades the application on a large scale of the coal gasifying processes.

Material and Method. This article presents conclusions regarding the CO₂ capture method, through local coal use, for two natural gas compressing stations, equipped with wet flue gas desulfurization (GDI) and with an evacuation plant for ash and slag as thick slurry. The choice of the best post-combustion capture technologies should be made according to each respective case. To take measurements at the two compressing stations, the chilled ammonia process (CAP) was used, as well as the advanced capture with amines (AAC), as they represent the most reviewed and closer to commercialization technologies. The CAP is a promising technology, with a high degree of innovation and performance potential. This process is presented in Figure 1 (Morris 2007). It is based on the use of water and ammonia solutions, at temperatures below those of the environment. CO₂ is recovered in extremely concentrated states and high pressure.

The main processes of the chilled ammonia capture method are:

Cooling of flue gas → flue gas treatment → CO₂ absorption → water scrubbing → low pressure stripping → stripping column → high pressure regeneration → cooling (refrigeration) system → CO₂ compression → CO₂ product dehydration.

Companies in the field have been involved in the common development and commercialization of the advanced capture with amines process (AAC) in order to capture CO₂ from flue gas. Two main directions have been followed: improving the performance and formula of the amine solution – Dow, and improving the procedure itself – Alstom (Amararene & Bouallou 2004). The advantages of AAC compared to the MEA scrubbing procedure consist of (Aboudheir et al 2003):

- a more energy-efficient capture;
- a lower solvent degradation level, leading to a reduced consumption of chemicals and less effluents and waste produced;
- reduced corrosion leading to cheaper installations;
- more advanced and flexible schematics, with a potential for energy saving.

Results and Discussion. At the investment level, the costs for CAP are higher than those for AAC, due to technological differentiation, which involves more equipment. This is an advantage for the advanced amine capture process (AAC). Regarding operational costs, the inverse is true, the costs of amine based reagents being higher than ammonia, which allows an independent and timely supply from local sources. The chilled ammonia process is a new technology with encouraging possibilities regarding performance and emissions, based on complex laboratory pilot tests.

Measurements conducted at two stations belonging to S.N.G.N. compression Romgaz Medias S.A.

For obtaining the values of measured parameters, a Multilyzer NG Series 213 measuring apparatus was used, proper for CO₂ concentrations measurements. In the case of Cristur natural gas compressing station, the CO₂ post-combustion storage with chilled ammonia is performed, after the compression of natural gas, with the help of

turbo compressors. There are literally hundreds of different equipment configurations for the processing required to separate natural gas condensate from a raw natural gas. The schematic flow diagram to the right depicts just one of the possible configurations, Figure 2 (Source: http://en.wikipedia.org/wiki/Natural_gas_condensate).

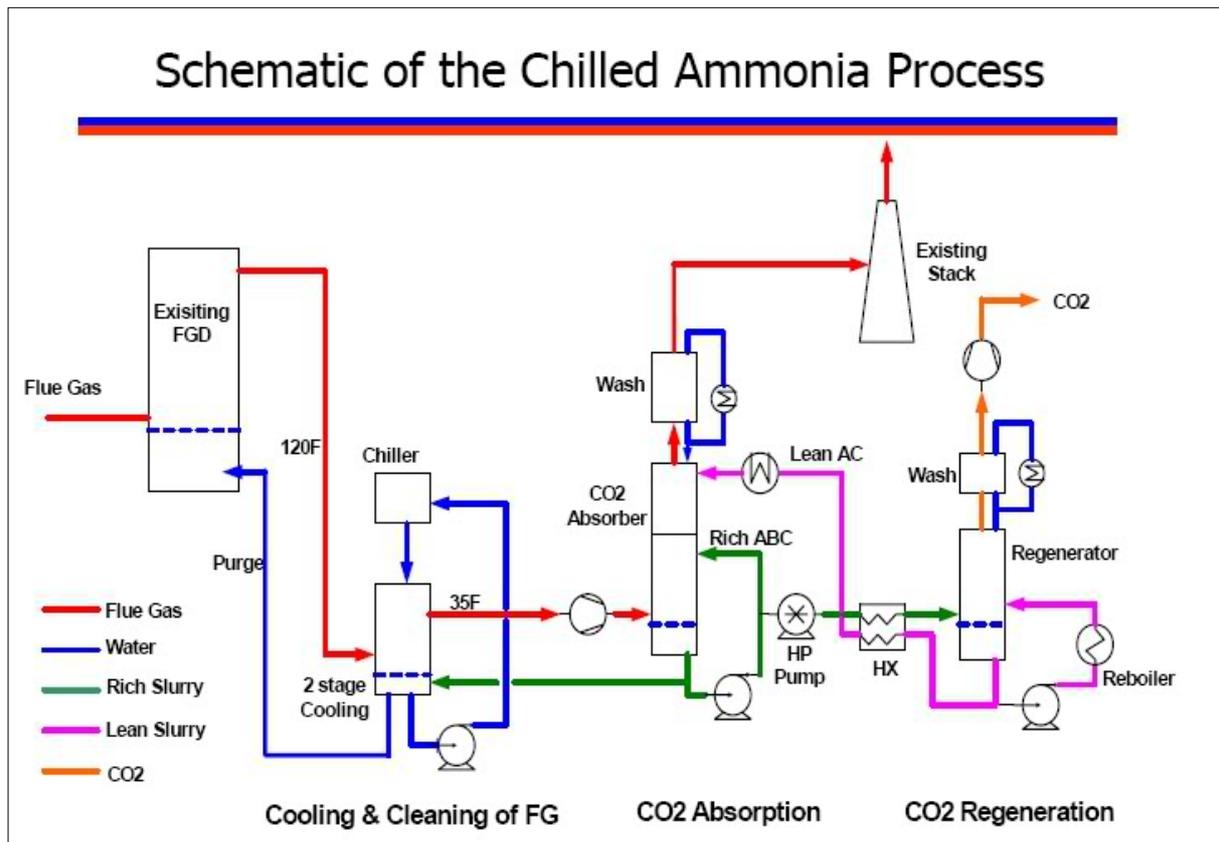


Figure 1. Schematic process for chilled ammonia post-combustion.

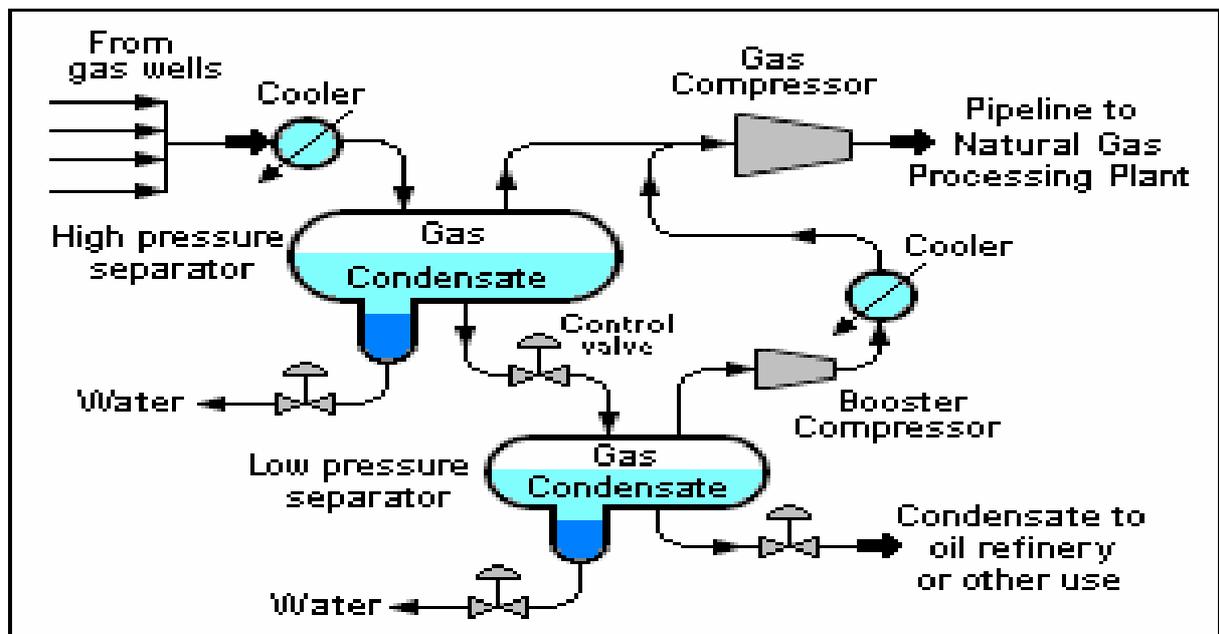


Figure 2. Schematic for a natural gas turbo compressor.

The raw natural gas feedstock from a gas well or a group of wells is cooled to lower the gas temperature to below its hydrocarbon dew point at the feedstock pressure and that

condenses a good part of the gas condensate hydrocarbons. The feedstock mixture of gas, liquid condensate and water is then routed to a high pressure separator vessel where the water and the raw natural gas are separated and removed. The raw natural gas from the high pressure separator is sent to the main gas compressor.

The gas condensate from the high pressure separator flows through a throttling control valve to a low pressure separator. The reduction in pressure across the control valve causes the condensate to undergo a partial vaporization referred to as a flash vaporization. The raw natural gas from the low pressure separator is sent to a "booster" compressor which raises the gas pressure and sends it through a cooler and on to the main gas compressor. The main gas compressor raises the pressure of the gases from the high and low pressure separators to whatever pressure is required for the pipeline transportation of the gas to the raw natural gas processing plant. The main gas compressor discharge pressure will depend upon the distance to the raw natural gas processing plant and it may require that a multi-stage compressor be used.

At the raw natural gas processing plant, the gas will be dehydrated and acid gases and other impurities will be removed from the gas. Then, the ethane (C2), propane (C3), butanes (C4), and pentanes (C5) - plus higher molecular weight hydrocarbons referred to as C5+ - will also be removed and recovered as byproducts.

The water removed from both the high and low pressure separators may need to be processed to remove hydrogen sulfide (H₂S) before the water can be disposed of underground or reused in some fashion.

Some of the raw natural gas may be re-injected into the producing formation to help maintain the reservoir pressure, or for storage pending later installation of a pipeline.

CO₂ emissions resulting from the combustion of natural gas, are reproduced in the table below (Table 2).

Table 2

CO₂ capture with multilyzer NG series 213

<i>Location: Compression station Cristur</i>								<i>Date: 11.06.2013</i>
<i>Monitor Indicators</i>								
Fuel	O ₂ [100%]	CO [mg/m ³]	t gas [C°]	CO ₂ [%]	NO [mg/m ³]	NO _x [mg/m ³]	t air [C°]	Difference of temp. [C°]
Natural gas	7.6	13	234	0	35	55	25	190
<i>Location: Compression station Brateiu</i>								<i>Date: 11.06.2013</i>
<i>Monitor Indicators</i>								
Fuel	O ₂ [100%]	CO [mg/m ³]	t gas [C°]	CO ₂ [%]	NO [mg/m ³]	NO _x [mg/m ³]	t air [C°]	Difference of temp. [C°]
Natural gas	8.9	18	245	6.8	55	87	31.8	213.2

The Table 2 presents the CO₂ emissions from two natural gas compressing stations of S.N.G.N. Romgaz S.A., namely Cristur compressing station and Brateiu compressing station. The measurements were taken in June 2013. The temperature difference of the natural gas equals 23.2 degrees and the temperature difference of the air equals 6.8 degrees. As stated, there is an obvious difference between the measurement results of CO₂ emissions. In the case of Cristur compressing station, the emission level is 0 due to the fact that the CO₂ storage is implemented in an abandoned well, using chilled ammonia post-combustion.

Conclusions. The advantages of using ammonia solutions as CO₂ absorbents include:

- low reaction temperature;
- high CO₂ retention;
- high pressure regeneration;
- low sensibility to impurities;
- low absorbent cost;

- the application of CO₂ capture from the flow of gases generated by solid fuel burning and the application of de-dusting and desulfurization process of the gases prior to CO₂ absorption;
- the proposal to use flue gas as a heating agent for CO₂ rich absorbent used in MEA regeneration and reuse;
- the proposal for a purifying method of the regenerated agent.

Within the countries of the EU, the application of the three options is presented as such: Great Britain has adopted pre-combustion; Germany and France have chosen ox-combustion, and most of the countries around the continent have adopted post-combustion, acting towards the effect, just as Romania has acted, meaning the cold ammonia process, but for the price of 300 million euro (an old process at a novelty price). The feasibility study has been done by ISPE (with an energetic, not a chemical profile) without taking into consideration the IPROCHIM specialists' offer, that were collaborating with a well-known firm from the USA. For Romanian chemists, these environmental problems don't have a high degree of difficulty and could have been approached, as they had the experience of building a complex chemical installation.

The current global crisis has cut off the energy specialists' boost for applying expensive processes of CO₂ caption and storage.

The approach of the environment protection issue must be reevaluated in the current conditions; meaning an action towards the cause, and not towards the effect, the prevention of pollution and not its solving. In the case of post-combustion, for instance, the expenses for the burnt gases purifying (the caption of ash with electro-filters, non sulphation, the caption and storage of CO₂) go beyond the power station's value. Just as there is a thermodynamic limit (the energetic consume for the absorbent regeneration is determined by the reactive enthalpy), there also is a limit for the cost of burnt gas purification, that mustn't surpass the value of the power station's cost. In this manner, the other two options enter the competition, pre-combustion and ox-combustion, and according to the actual situations, the decision for adopting a suitable choice is taken.

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