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ACACIA Project – Development of a Post-Combustion CO₂ Capture Process. Case of the DMXTM Process

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PART 2

Post Combustion CO₂ Capture Captage de CO₂ en postcombustion

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ACACIA Project – Development of a Post-Combustion CO₂ Capture Process. Case of the DMXTM Process

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Abstract — *The objective of the ACACIA project was to develop processes for post-combustion CO₂ capture at a lower cost and with a higher energetic efficiency than first generation processes using amines such as MonoEthanolAmine (MEA) which are now considered for the first Carbon Capture and Storage (CCS) demonstrators. The partners involved in this project were: Rhodia (Solvay since then), Arkema, Lafarge, GDF SUEZ, Veolia Environnement, IFP Energies nouvelles, IRCE Lyon, LMOPS, LTIM, LSA Armines. To validate the relevance of the breakthrough processes studied in this project, techno-economic evaluations were carried out with comparison to the reference process using a 30 wt% MEA solvent. These evaluation studies involved all the industrial partners of the project, each partner bringing specific cases of CO₂ capture on their industrial facilities. From these studies, only the process using demixing solvent, DMXTM, developed by IFPEN appears as an alternative solution to the MEA process.*

Résumé — **Projet ACACIA – Développement d'un procédé de captage du CO₂ post-combustion – Cas du procédé DMXTM** — L'objectif du projet ACACIA était de développer des procédés de captage du CO₂ en postcombustion à moindre coût et plus efficaces que les procédés de première génération utilisant des amines de types monoéthanolamine (MEA) qui sont actuellement envisagées pour les premiers démonstrateurs industriels de captage du CO₂ en vue de son stockage géologique. Les partenaires impliqués dans ce projet étaient : Rhodia (depuis Solvay), Arkema, Lafarge, GDF SUEZ, Veolia Environnement, IFP Energies nouvelles, IRCE-Lyon, LMOPS, LTIM, LSA, Armines. Afin de valider la pertinence des procédés de rupture étudiés dans ce projet, des travaux d'évaluation technico-économiques ont été réalisés avec comparaison au procédé de référence mettant en œuvre comme solvant une solution

aqueuse de MEA à 30 % poids. Ces études ont été réalisées avec les partenaires industriels du projet, chacun apportant des cas concrets de captage du CO₂ sur leurs installations industrielles. De ces travaux, seul le procédé liquide de lavage des gaz par solvant demixant, DMXTM, qui est en cours de développement à IFPEN apparait comme une solution de rupture alternative au procédé de lavage à la MEA.

ABBREVIATIONS

MEA	MonoEthanolAmine
DMX TM	2 nd generation of chemical solvent using a novel demixing solvent
MDEA	MethylDiEthanolAmine
TEG	Tri Ethylene Glycol used for CO ₂ stream dehydration
OPEX	OPerating EXpenses, or operating cost
CAPEX	CAPital EXpenditure, investments
PC plant	Pulverised Coal plant
NGCC plant	Natural Gas Combined Cycle Plant

INTRODUCTION

The ACACIA project, which was launched by the AXELERA cluster (AXELERA is one of the 71 French “competitiveness cluster” initiated by the French government in September 2004), is dedicated to the development of new processes for CO₂ capture on industrial facilities before geological storage. As considered by IEA [1], Carbon Capture and Storage (CCS) is one of the possible pathway in order to mitigate greenhouse gases emissions; it thus requires the development of high efficiency CO₂ capture technologies.

The ACACIA project partners have chosen to consider only the post-combustion capture pathway for which the CO₂ is extracted directly from the industrial flue gases [2]. The main objective of the project was the research and development of new technologies to reduce the cost of capture per ton of CO₂ and the impact of CO₂ capture on the cost of electricity or industrial products (cement, chemicals). It is known from process studies [3] or from pilot demonstration [4], that the energy penalty reduction, especially due to the energy required at reboiler, estimated about 3.7 GJ/ton_{CO2} for the MEA (MonoEthanolAmine) 30 wt% process, is the key issue for making CO₂ capture an attractive solution for carbon mitigation.

Conventional processes for CO₂ capture are based mostly on absorption by a chemical solvent. Chemical solvents used are primary amines, and in particular MEA. If the MEA can recover up to 98% CO₂ and obtain a purity of 99.9%, its use leads to high operating

costs. In the medium term, to make CCS deployment possible, it is necessary to develop new capture processes with lower energy costs further reducing the cost of carbon capture. The purpose of the ACACIA project was to develop new processes with a cost of capture 50% lower than the cost of existing processes while allowing to capture at least 90% CO₂ in the treated gas and obtain a CO₂ purity near 95%. Such a purity level is necessary for transport and storage.

Five types of processes were studied in the ACACIA project:

- demixing solvents: use of amine solvents which either for high CO₂ loadings or for high temperature form two non-miscible phases. With this type of solvents, only the heavy CO₂-rich phase is regenerated which reduces the energy cost of carbon capture [2];
- hydrates: research on thermodynamic additives to improve the operating conditions of CO₂ capture by hydrates; the objective being to capture CO₂ at low temperature and moderate pressure and deliver CO₂ at high pressure with low energy inputs which would reduce the cost of regeneration and CO₂ compression;
- enzymes: use of enzymes, which are immobilized in porous materials, to enhance CO₂ absorption with in particular an increase in CO₂ absorption kinetics and an associated investment reduction;
- ionic liquids: optimizing the absorption of CO₂ by the use of some ionic liquids offering high solubilities;
- innovative chemistry: development of new solvents with innovative chemical routes for CO₂ capture with low enthalpy of formation requiring less energy at regeneration step.

Through these lines of research, the ACACIA project aimed to develop solutions applicable in priority to the industry (power plants, cement plants, incinerators, and chemical industry). To validate the relevance of the new processes studied in this project, a benchmark based on a techno-economical study between MEA technology and new processes was undertaken by the industrial partners of the project, each bringing specific cases of CO₂ capture corresponding to an industrial case. The pooling of these cases and appropriate technological solutions was a very important part of this project because it allowed the identification of viable pre industrial study technological solutions: a validation process

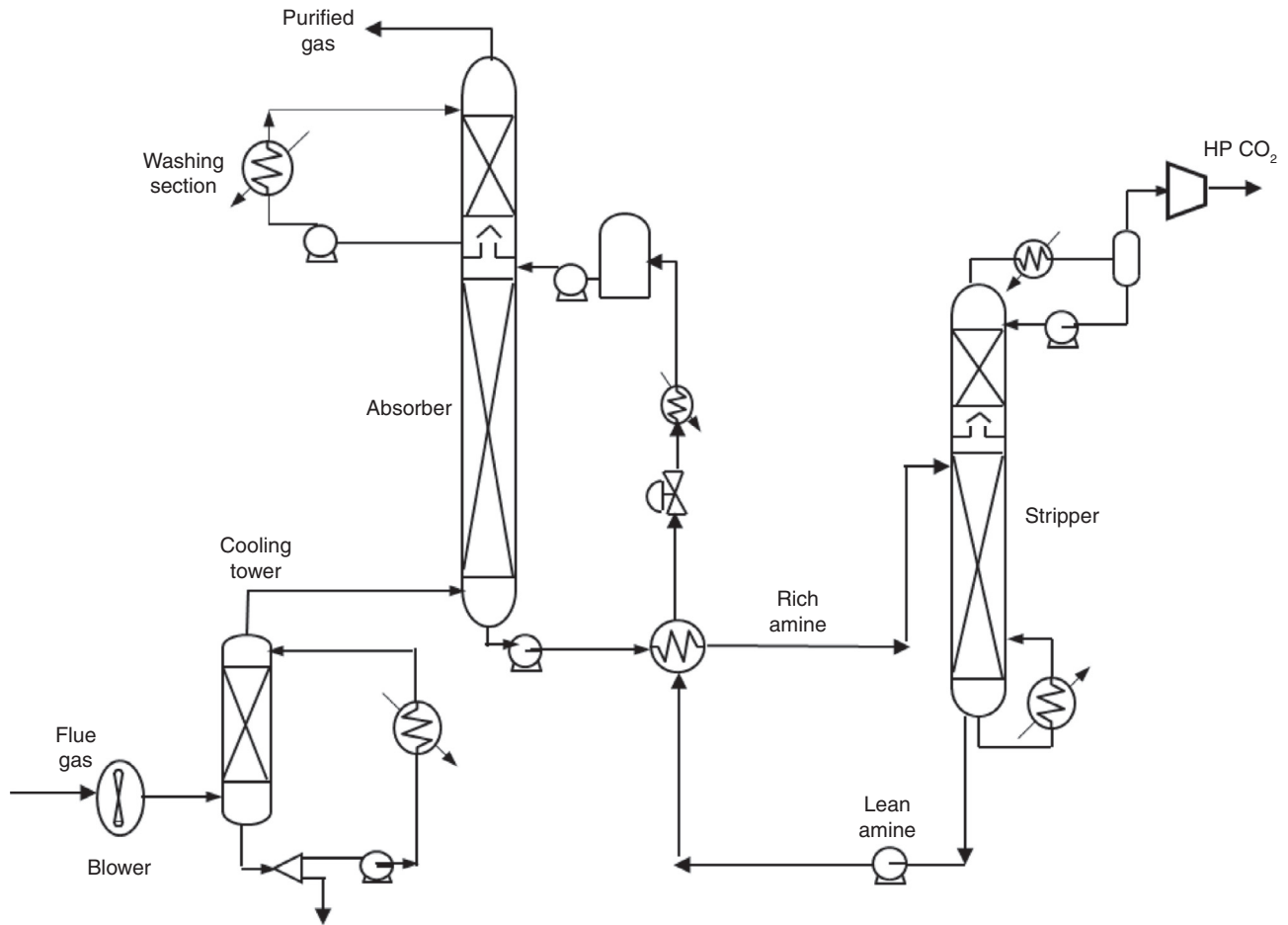


Figure 1
Simplified process flow diagram of the MEA post-combustion capture process.

pilot type being envisaged only after the end of ACACIA depending of the results obtained.

In this paper, we present the results of the techno-economical study carried out on the DMXTM process and the comparison with the reference process using 30 wt% MEA. For all other original routes studied (hydrates, enzymes, ionic liquid), it has not been possible to obtain sufficient data for performing process evaluation and techno-economic evaluation.

In a first part, a description of the operating conditions for the MEA (1st generation of chemical solvent) and DMXTM (2nd generation of chemical solvent) processes is provided. A second part is dedicated to a description of the emission case studies, the study methodology and economic assumptions. In the last part, a comparative analysis between the MEA and DMXTM processes is presented.

1 CO₂ CAPTURE PROCESS: 1ST GENERATION VERSUS 2ND GENERATION WITH DMXTM SOLVENT

1.1 MEA Process Description

To separate CO₂ from the flue gas (low pressure, low CO₂ content), the reference process is a chemical absorption process using 30 wt% MEA as solvent. It is widely admitted that this process is the reference for CO₂ capture on flue gases [3]. Within the CASTOR and CESAR FP7 European projects, this process has been demonstrated at pilot plant scale on real power plant flue gas [4-6] and some companies are able to commercialize such a process with already some large scale references existing in the food industry [7, 8]. Figure 1 shows a typical process flow diagram for a first generation process such as the reference MEA 30 wt% process.

- The capture process is composed of five main sections:
- a cooling tower which purpose is first to cool down the flue gas issued at 140°C and second to perform a pre-conditioning of the flue gas (washing of ash, impurities, etc.);
 - an absorber, operated at ambient pressure and moderate temperature, where CO₂ is separated from the flue gas by being contacted with the solvent;
 - a washing section which ensures that the decarbonized flue gas sent to the stack does not contain any unwanted pollutants (amines, degradation products or any other volatile compounds);
 - a regenerator operated at moderate pressure and high temperature, where CO₂ is separated from the solvent, the latter being regenerated;
 - a compression section needed to deliver high-pressure pure CO₂ ready for storage.

All these five sections are specific to a given process and are interconnected. As an example, the cooling tower, using a first washing section, can be more or less important depending on the solvent sensitivity towards impurities contained in the flue gas such as SO_x or NO_x. In the same idea, a process using a volatile solvent may require a large washing section downstream the absorber, while a small section may be enough for others. Similarly, the operating conditions in the regeneration section, in particular in terms of pressure may impact the compression section. It is thus mandatory to consider all the needed sections for the process at constant boundary limits, inlet flue gas and outlet CO₂ and treated gas as shown in Figure 1, when making comparison.

1.2 DMXTM Process Description

The DMXTM process has been developed and patented by IFPEN (see [9] or [10] for process or physical and chemical basic information respectively). It has been described with further details in [11, 12] and only a quick description is given hereafter. The main objective being to present the techno-economic comparison with the MEA process.

The DMXTM process is based on the use of very specific solvents which, for given loading and temperature conditions, can form two immiscible liquid phases. These phases have sufficient density differences that they can be separated by decantation. The light liquid phase is such that it contains almost no CO₂, the latter being concentrated in the heavy phase. This result is similar to what could be obtained with a high capacity. The DMXTM solvent is also characterized by an easy separation which can be performed in a standard decanter placed downstream the lean/rich heat exchanger,

downstream the absorption column, as can be seen in Figure 2. The decanter is preferably positioned after the amine/amine heat exchanger and before the regenerator in particular to make decantation easier *via* the reduction of liquid viscosity associated with the increase of temperature. Only the CO₂ rich loaded heavy phase is sent to the stripper, the CO₂ lean light phase being directly sent back to the absorber. Note that depending on the operating conditions chosen at stripper and at decanter, one may observe an important CO₂ gas release at decanter. The compression section is then modified turning into a possible supplementary energy reduction when the decanter is operated at a pressure higher than the pressure at stripper.

Figure 3 shows a picture of a transparent decanter that has been used on a mini-pilot at IFPEN. The flow goes from left to right as indicated by the plain arrow. As can be seen in the close view, the inlet flow contains CO₂ gas bubbles and droplets of the light phase dispersed in the heavy phase. On the right-hand-side, one observes that, very quickly, a clear separation of the phases is reached, the interface being indicated with a dashed line.

Such a process presents a significant decrease of solvent mass flow and of captured CO₂ sent to the regeneration column requiring less energy input. It can thus offer a significant cost reduction compared to the reference case that is the MEA 30 wt% based process.

The choice for the formulation of the demixing solvent DMX-1, was firstly based on its thermodynamic capacity which comes in addition to demixtion for reducing the solvent flow rate going to the stripper. Secondly, we paid a particular attention towards degradation performances. As shown in Raynal *et al.* [11], the DMX-1 degradation performances are much better than those of MDEA (MethylDiEthanolAmine), a commercial amine known as being much more stable than MEA. As discussed by Raynal *et al.* [12], degradation impacts many costs and not only solvent make-up; it makes possible the operation of the stripper at higher pressure/temperature operating conditions enabling CO₂ compression cost reduction. Last, kinetics performance and operability issues were considered.

2 CASE DESCRIPTION STUDY METHODOLOGY AND ECONOMIC EVALUATION: MEA VERSUS DMXTM PROCESS

2.1 Case Description

Each industry has defined the gas to be treated by the CO₂ capture process considered within the ACACIA project.

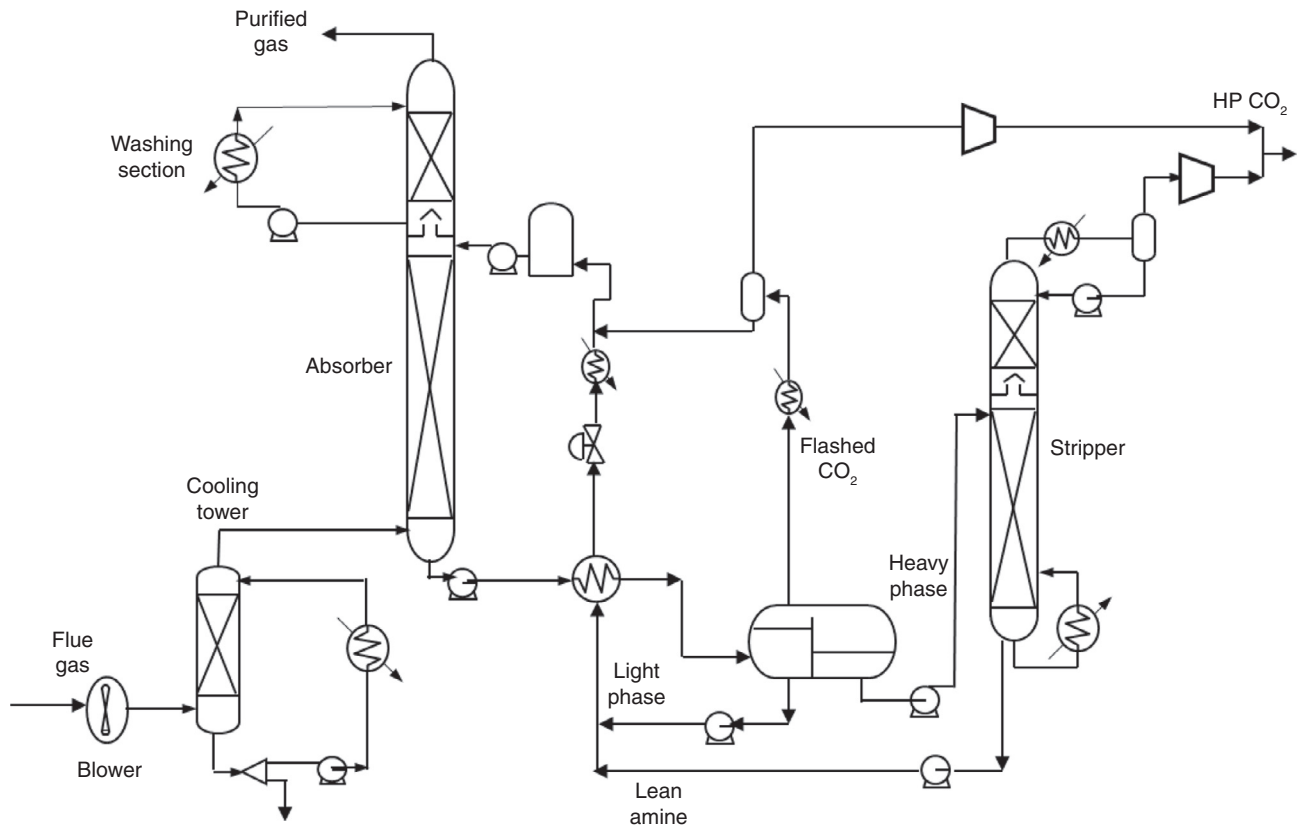


Figure 2
Simplified process flow diagram of the DMX™ post-combustion capture process.

The information on these gases, include:

- the flow rate, the density at standard conditions, the pressure and temperature;
- the molar composition;
- the expected impurities (dust, SO_x, NO_x).

This information is given for a nominal flowrate case of with a range of expected changes to account for the flexibility of the units.

The emitting industries concerned were the following:

- electricity production by gas-fired power plant (*GDF SUEZ*) and coal-fired power plant (*Electrabel GDF SUEZ*);
- production of cement (*Lafarge*);
- chemistry (*Rhodia Operations* and *Arkema*);
- incineration of household waste (*Veolia Environnement*).

Table 1 summarizes the characteristics of the flue gases to be decarbonized, which were given by these different industries.

For geological storage application, the CO₂ delivery pressure at battery limit was at 110 barg.

Compression energy to this pressure level was of course taken into account within the techno-economic evaluation.

2.2 Evaluation Methodology

The economic assessment methodology implemented in the ACACIA project allowed to establish a strong synergy between academic and industrial partners.

The stakeholders were as follows:

- For the MEA process:
 - *IFPEN* conducted the process studies and economic evaluation for *Veolia Environnement*, *Arkema* and *Rhodia* cases;
 - *GDF SUEZ* has completed the design of facilities for the collection for PC and NGCC plants;
 - *Rhodia* generated sizing and quantification of the *Lafarge* plant;
 - *Lafarge* got his own experience of the design of the system and has estimated the cost of the MEA

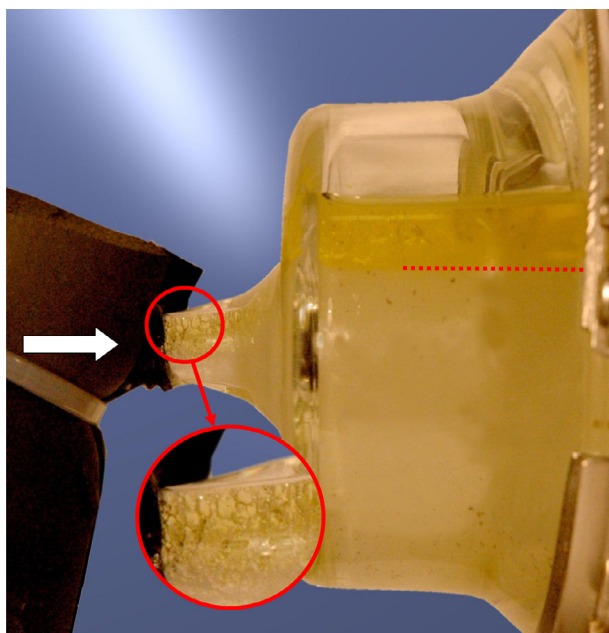


Figure 3

Picture of the decanter inlet of the mini-pilot of *IFPEN*. The three-phase flow, G/L/L, enters the decanter on the left-hand-side, the decantation being achieved in the large diameter section on the right-hand-side.

solution and proposed the cost estimation derived from that produced by *Rhodia*, for the purposes of *Solvay* (without compression step);

- For the DMXTM process:

Among the available demixing solvents *IFPEN*, proposed to consider the DMX-1 system which is currently the best solvent for the DMXTM process.

IFPEN provided to partners who have chosen the DMXTM process solution (*GDF SUEZ*, *Veolia Environnement*, *Lafarge*), the mass and energy balances as well as the sizing of the main equipments:

- *IFPEN* provided balance sheets and equipment sizing devices to *GDF SUEZ* and *Lafarge*;
- *Lafarge* and *GDF SUEZ* made their own economic evaluation based on data provided by *IFPEN* for their respective cases;
- *IFPEN* performed the entire study for the *Veolia* case.

2.3 Study Basis and Economic Assumptions

Emissions flows are described in the basis for studies cited above.

TABLE 1
Flue gas characteristics

Temperature	°C	48 to 360
Pressure	bar abs	1.01
CO ₂ flow rate	t/h	2.5 to 581
Emission flow rate	Nm ³ /h	15 000 to 3 320 000
Emission composition	CO ₂	3 to 15
(vol.%)	H ₂ O	5 to 25
	N ₂	57 to 77
	O ₂	3 to 14
	H ₂	0
	CO	0.1 max
	Ar	0 to 0.9
	CH ₄	0

The economic assumptions are detailed in [Table 2](#).

The cooling water is available on site in sufficient quantities to ensure the capture units needs. Without any previous specification, the temperature of the cooling water was taken equal to 15°C (sea water) and the maximum elevation of the cooling water was set at 10°C to reach a final temperature of 25°C. For the power plant cases (*GDF SUEZ* cases) the Low Pressure (LP) steam needed for the reboilers comes from thermal power, which reduces the production of electricity from the LP turbine. The power consumption of the various equipment is provided by the power plant.

For the other cases, steam comes from a steam generator dedicated to the CO₂ capture plant.

For the calculation of operating costs (OPEX) processes for MEA and DMXTM, the following assumptions were made:

- labor cost (number of operator for CO₂ capture unit) specific for each industrial case ([Tab. 2](#));
- cost of electricity (€/kWh) (*) specific for each industrial case ([Tab. 2](#));
- cost of cooling water (€/m³) specific for each industrial case ([Tab. 2](#));
- cost of TEG: 800 €/t and consumption of 0.094 kgTEG/tCO₂ captured (**) specific for each industrial case ([Tab. 2](#));
- cost of MEA: 1 500 €/t and consumption: 1.6 kgMEA/tCO₂ captured;
- cost of the solvent DMX-1: 5 000 €/t and no consumption (no degradation);

TABLE 2
Economic assumptions for economic study

Parameter\Case	<i>GDF SUEZ</i> Coal-fired power plant*	<i>GDF SUEZ</i> Gas-fired power plant	<i>Veolia</i> <i>Environnement</i>	<i>Rhodia</i>	<i>Arkema</i>	<i>Lafarge</i>
Depreciation (years)	20	20	20	10	10	20
Interest rate (%)	10	10	10	7	7	10
Labor (€/year)	80 000	80 000	65 000	80 000	80 000	80 000
Electricity (€/kWh)	0.06	0.06	0.06	0.07	0.055	0.07
Cooling water (€/m ³)	0.02	0.02	0.05	0.05	0.05	0.05
LP Steam (€/t)	Included in electric production penalty			15	20	15

* For the coal fired power plant and gas fired power plant, economic assumptions were based on past assumptions (from literature review) made for a previous project (CAPCO₂ project funded by the French National Agency for Research, 2006-2008).

- investment depreciation (years) specific for each industrial case (*Tab. 2*);
- interest rate (%) specific for each industrial case (*Tab. 2*).

(*) The power consumption of the capture units/compress CO₂ is considered a loss for the thermal power plant.

(**) TEG unit is devoted to dry CO₂ stream before transportation and injection.

3 COST EVALUATION AND ANALYSIS

The overall CO₂ cost, expressed in €/t CO₂, is obtained by combining CAPEX and OPEX costs in a complete economic analysis. The obtained value corresponds to the minimum price of CO₂ on market for which a CCS project is profitable. That is the minimum price for which it is more interesting to invest in a CCS project rather than buying CO₂ emissions rights on the market. In the present analysis, we split the different costs for the main contribution in the overall CO₂ cost to emphasize the advantages and weaknesses of a given process.

3.1 MEA Evaluation

The techno-economic studies confirmed the very high cost of CO₂ capture for the reference 30 wt% MEA process, whatever the considered case. The cost of capture by amine scrubbing (*Tab. 3*) ranges from 39 €/tCO₂ to 239 €/tCO₂. This is related, in the first analysis, to the scale effect. Indeed, *Arkema* case deals only

2.5 tCO₂/hour of CO₂ while the coal-fired plant emits 582 tCO₂/h. These two extreme costs define the minimum and maximum value for capture costs. A case as small as the *Arkema* case which could correspond to a demonstration case is associated to a very high CAPEX in particular due to building, instrumentation and control costs almost as expensive as a very large case. Otherwise, for comparable emission flow rate, costs range from 63 €/tCO₂ for *Veolia* to 91 €/tCO₂ for *Lafarge*. The explanation here comes from the fact that *Veolia* has lower operating costs related to the integration of the production of steam for regeneration.

3.2 DMXTM Evaluation

The *GDF SUEZ* coal-fired plant case, the *Veolia* and *Lafarge* cases were considered for the DMXTM process.

It appears that the DMXTM process could be a very interesting technology. The evaluation of this process showed significant gains on the cost of CO₂ capture as one can observed in *Table 4*. Indeed when compared to the MEA process, it appears that the DMXTM process can offer reduction of –20% and up to –50% in CO₂ capture cost. So, with this breakthrough technology, it is possible to meet part of the initial goal of the ACACIA project: 50% of the cost of CO₂ capture.

Some comments can be made on these results:

- About *Lafarge* case (cement plant):
The cost of CO₂ capture is halved with DMXTM compared to the reference MEA process, which was the objective of the project.

TABLE 3
MEA economic evaluation results

Parameter\Case	<i>GDF SUEZ</i> Coal-fired power plant	<i>GDF SUEZ</i> Gas-fired power plant	<i>Veolia</i> <i>Environnement</i>	<i>Rhodia</i>	<i>Arkema</i>	<i>Lafarge</i>
Emission flow rate (Nm ³ /h)	2 244 000	3 320 000	245 000	231 000	17 480	250 000
vol.% of CO ₂	13.2	3.4	9	9.6	7.2	14.9
CO ₂ inlet (t/h)	582	236	43.3	43.5	2.5	73.2
CO ₂ captured (t/h)	524	212	39	39	2.2	64
Depreciation (years)	20	20	20	10	10	20
Interest rate (%)	10	10	10	7	7	10
Labor (€/year)	80 000	80 000	65 000	80 000	80 000	80 000
Electricity (€/kWh)	0.06	0.06	0.06	0.07	0.055	0.07
Cooling water (€/m ³)	0.02	0.02	0.05	0.05	0.05	0.05
LP Steam (€/t)	Included in electric production penalty			15	20	15
TEG (€/t)	800	800	800	800	800	800
MEA (€/t)	1 500	1 500	1 500	1 500	1 500	1 500
CO ₂ capture cost (€/tCO ₂)	39	70	63	71	239	91

TABLE 4
Economic comparison between DMXTM and MEA process

Parameter\Case	<i>GDF SUEZ</i> Coal-fired power plant			<i>Veolia</i>			<i>Lafarge</i>		
	MEA	DMX TM	Gain	MEA	DMX TM	Gain	MEA	DMX TM	Gain
CO ₂ captured (t/h)	524	524		39	39		64	64	
Plant efficiency	34.3	35.6	+3.8%	N/A	N/A		N/A	N/A	
CO ₂ capture cost (€/tCO ₂)	37.1	31.4	-15.4%	63	52	-17.4%	93	44.9	-51.7%

It is interesting to discuss how such a gain can be explained. Three main reasons can explain this result:

- a small part is due to the investment, a little lower for DMXTM: -4%. (for the *Lafarge* case, it is necessary to build a boiler in order to generate the steam necessary for the solvent regeneration/size of this boiler is reduced for the DMXTM process);
- the most important part corresponds to variable costs and especially steam: -20%;
- the low possibility of heat integration between the cement plant and the DMXTM process explains the better performance of the process DMXTM, by a significant reduction of steam consumption from utility device;

- About *GDF SUEZ* case (coal power plant):

The gain for the plant performance related to the use of DMXTM process is 1.3% for the thermal overall efficiency (see *Tab. 4* above). *IFPEN* expects to have more than 2 points performance gain with an innovative heat integration with the power plant steam cycle.

The cost of captured CO₂ is estimated at 37.1 €/tCO₂ for the reference MEA, and 31.4 €/tCO₂ for DMXTM process, that implies a decrease of 15.4% of the capture cost.

- About *Veolia Environnement* case (central waste incineration):

The emissions flow rates are comparable to the cement plant and the cost of treatment with DMXTM is the same order of magnitude (52 €/tCO₂ captured).

However, the cost reduction compared to MEA is not as important, from 63 €/tCO₂ to 52 €/tCO₂.

The thermal integration is here already done for MEA case by steam extraction available on the incineration plant, the transition to DMXTM is less profitable even if it allows a significant reduction in cost.

CONCLUSIONS

With the DMXTM process patented and developed by IFPEN, it is possible to have significant energy savings compared to the reference MEA. This gain was 1.3% on energy penalty for the coal power plant but studies show that it is even possible to achieve a gain of 2%. Gains on operating costs (OPEX) enable cost reduction CO₂ capture 15 to 50% depending on the cases.

In order to go one step further in terms of process development, it is now necessary to perform industrial demonstration of the DMXTM process. This is one of the goal of the European FP7 OCTAVIUS project, which started on March 1st 2012. Tests at large scale are scheduled to be performed in 2015-2016 on the ENEL pilot plant in Brindisi which treats 10 000 Nm³/h of flue gases issued from a coal fired power plant (2.5 t/h CO₂ captured equivalent), and for which a important revamp is planned.

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