Development of Technologies for CO_2 Capture from Flue Gases

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Abstract

CO_2 capture in natural gas is a very common problematic that has been solved for a very wide range of specifications and applications for many years. The most common processes used to sweeten the natural gas are amine based processes. They have been widely implemented in different gas plants. Thanks to this large industrial experience in natural gas, it could be thought that CO_2 capture in flue gases would be easily deployed at an industrial scale. In fact, in addition to the technical, regulatory and public perception concerns for CO_2 storage, some differences between these two CO_2 capture applications have required some development towards industrial low-energy consumption solutions.

In this paper it is shown that PROSERNAT long industrial experience on amine based processes and large capacity units for major Oil & Gas development projects, combined with significant improvements of MEA based processes and developments of new processes carried out with IFP Energies nouvelles, a world leading R&D centre and more specifically expert of CO_2 capture technologies, have led to two attractive solutions for CO2 capture in flue gases up to now :

- A reliable and attractive solution for CO_2 capture in flue gases : HiCapt+^{TM}. The HiCapt+™ technology uses MEA at 40 % wt with inhibitor against oxidation by O_2. This highly reactive advanced formulated MEA results in 5 main advantages :
    - reduced circulation flow rate of solvent, decreasing total hold-up of solvent
    - reduced heat requirement for solvent regeneration thanks to the use of a highly concentrated solvent
    - Reduced size of some equipments such as pumps and regenerator column as well as size of bulk material & piping
    - drastic reduction of solvent degradation rate, decreasing solvent consumption and thus reclaiming needs.
    - drastic decrease of by-product emission (such as VOC and NH_3) due to the efficiency of the anti-oxidative agents

  A first technico-economic study has led to 15% reduction of the cost of the CO2 captured compared to traditional 30%wt MEA reference process. Tests on an industrial pilot plant will be performed by a joint team between IFP Energies nouvelles and ENEL in 2010-2011.

- An attractive and original DMX™ process based on special solvents which are characterized by the formation of two liquid immiscible phases for given temperature and CO_2 loading conditions. The corresponding process is presented and a technico-economic analysis is given. It is shown that a reboiler duty as low as 2.1 GJ/t CO_2 can be reached, which is significantly lower than the 3.7 GJ/t CO_2 of the 30wt.% MEA reference process. Other performances of the DMX-1™ solvent in terms of degradation and corrosion are shown as well. Further developments including possible tests in a pilot unit are under progress.

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1. Introduction

The global warning effect due to CO_2 and others greenhouse gases is today demonstrated and accepted by the main part of the scientific community. Fossil fuel and coal used to produce energy required by society and also other industries (such as refining, steel, cement and waste industries) are very big emitters of greenhouse gases. Fossil fuel used to produce energy will continue to be used during many decades, with other non fossil sources (such as solar and wind) in an energetical mix that takes some time to be deployed and to be fully efficient. The other industries are also evolving in order to limit their greenhouse gas emissions and to increase their global efficiency. However, some technical solutions must be found and largely deployed at an industrial scale in order to reduce down the emissions of CO_2 of all these industries. CO_2 capture and storage is one of the solution to reduce the CO_2 emissions and avoid the dramatic consequences of global warming. Among the different solutions, the post-combustion CO_2 capture is probably the easiest one to put in place and the most robust technology with the smallest impact on the existing industrial process. CO_2 scrubbing by an aqueous amine solution is a widely proven technology to capture CO_2. However, the high energy consumption is a major drawback of this type of processes. That 's why researches are done to improve this type of process and to find original solutions that induce low energy penalty and that are easy to operate. This topic is clearly a priority for IFP Energies nouvelles and PROSERNAT and a big effort in terms of R&D is done in order to develop and propose more efficient processes to CO_2 emitters. Based on this extensive R&D as well as its large industrial experience on CO_2 removal in natural gas with AdvAmine™ technologies (more than 140 industrial references), PROSERNAT, in charge of licensing natural gas treatment and CO_2 capture processes of the IFP group is now ready to propose the HiCapt+™ process for demonstration. First results on an attractive and original DMX™ process based on special demixing solvents that still is under development are also given.

2. Applying past experience for large scale CO_2 capture from Natural Gases to Flue Gas treatment

Large scale CO_2 capture from natural gases has been experienced for decades and a lot of technology know-how is available to be used for large scale CO_2 capture from flue gas streams. In fact today the oldest large scale experience of CO_2 capture and storage (excluding EOR applications) has been accumulated since 1996 at Sleipner in Norway, where about 1 MT/y CO_2 is extracted through an amine process from a natural gas stream and stored in a deep aquifer. Other similar size projects took place at In Salah in Algeria (1 MT CO_2/y from natural gas since 2004), Weyburn in Canada (3MT/y CO_2 from coal gasifier gas since 2000) and more recently at Snohvit in Norway (0.7 MT/y CO_2 from natural gas since 2008). Prosernat, as licensor of the AdvAmine™ gas sweetening technology portfolio, has an accumulated experience of over 50 years of H_2S and CO_2 removal from natural gases.

Despite many similarities, CO_2 capture from flue gases show some significant differences with natural gas applications which explains why available process technology needs to be specifically adapted and why R&D is still required in this area. The main differences are highlighted in the following points:

Feed gas pressure: whereas natural streams are usually treated under pressure of some tens of bar (typically between 50 and 100 bar); flue gases are available at a pressure close to atmospheric pressure. This has two main consequences in terms of design of the CO_2 capture unit:

- Feed gas partial pressure of CO_2 is typically much lower in a flue gas than in a natural gas stream, accordingly solvents with high reactivity are needed. Some of the amines (e.g. MDEA) which have been proven highly efficient for natural gas treatment, will therefore not be used for flue gas treatment. Unfortunately highly reactive solvents like MEA are also those requiring the highest energy input for regeneration.
- Absorber pressure drop, which is usually not an important concern for natural gas treatment, will become a critical point for flue gas treatment.

Feed gas flow rate and unit size: there is a lot of experience with very large capacity natural gas sweetening unit, with single train flowrates above 600 000 Nm3/h and up to 1 500 000 Nm3/h, which is in the range of what is expected for large scale CO_2 capture from flue gases (about 1 800 000 Nm3/h of flue gas for a 600 MWe coal fired power plant). In terms of equipment size, the solvent flowrate has also to be taken into consideration. Here again natural gas sweetening units with above 1000 m^3/h of solvent flow rate are not uncommon. Past experience for large dimension columns, pumps, heat exchangers, etc… is therefore available for flue gas treatment units. In terms of large diameters contactors, for low pressure flue gases, experience with other technologies than amines can also be referred to. For example with the Claus tail gas treatment technology Clauspol™ or vacuum distillation developed by IFP Energies nouvelles and today licensed by Prosernat, gas liquid contactors having diameters up to 10 m have been built and are under successful operation.

Treated gas partial pressure: Due to low feed gas pressure, the residual partial pressure of CO_2 in the treated flue gas will be very low (about 10 mbar residual CO_2 partial pressure after 90 % CO_2 removal on a flue gas containing 10 % CO_2). But in fact these figures are still above the figures that are achieved with natural gases, for instance upstream natural gas liquefaction units where specifications of 50 ppmv are typically required, which results in 3.5 mbar partial pressure for a gas @70 bar. Therefore meeting the treated gas specification is not expected to be an issue.

Presence of oxygen: Oxygen is normally not present in natural gas streams. Furthermore oxygen ingress, for instance through make-up water of in storage tanks, must be avoided in order to limit amine degradation and subsequent enhanced corrosivity of the degraded amine solvent. With flue gases, obviously oxygen presence cannot be avoided and therefore solutions need to be developed in order to cope with this issue.

Regeneration heat requirement: Heat input is always necessary to regenerate amine based solvents, but for the sweetening of natural streams, although an important point to consider, it is usually not the main deciding factor for selecting a technology, compared with other factors such as treated gas specifications and capital costs. For the CO_2 capture in electricity production the energy penalty related to the capture process itself becomes in fact the main technology selection factor and the development of highly energy efficient CO_2 capture technologies is today the central challenge of technology development in this area.

After a quick description of the basic 30 %wt MEA reference process, it will be shown in the following sections that HiCapt+ and now DMX-1^{TM} has been developed or are under development keeping all the above points in mind.

3. The reference process MEA at 30 % wt

Aqueous solution of MEA is the most widely investigated solvent for a carbon dioxide post-combustion capture process. MEA is cheap, largely available, non toxic and highly effective because of its high capacity for CO_2 capture and its fast reaction kinetic. CO_2 scrubbing by an aqueous amine solution of MEA 30 %wt is a widely proven technology to capture CO_2. The European project Castor (4) has demonstrated the good operability, flexibility, stability and reliability of this process during long run tests (more than 500 h of continuous operation). These tests have been done in the pilot plant located in the Dong power plant (Esbjerg – Denmark). This pilot gives very reliable data because the flue gas treated is coming directly from the power plant and the pilot capacity is large enough (approximately 1 t/h of CO_2 captured).

However, the high energy consumption is a major drawback of this type of processes. The energy used for the stripping of rich amine in the reboiler is measured around 3.7 GJ/tCO_2 avoided. It corresponds to a penalty for the power plant around 10.5 points on the yield (for a power plant with a high yield of 40 %).

Moreover another critical point with this reference process concerns the amine degradation by oxidation with the O_2 contained in the flue gas. This degradation has been evaluated in the Castor pilot around 1.4 kg MEA degraded / t CO_2 captured. Different troubles results from this degradation:

- the first one is a high consumption of MEA, approximately 2 batches of solvent per year. The economical impact on OPEX is really important (more than 7 M€/year for a CO_2 capture unit in a 600 MWe power plant)
- the second one is coming from the degradation products which stay in the liquid phase. These products named HSS (Heat Stable Salt) are mainly organic acids and they are very corrosives. Thus a reclaiming unit is needed to remove them. This adds some complexity to the operation of the plant and of course increases the CAPEX and the OPEX.
- the third one is the emission of "light" degradation products in the treated flue gas and in the CO_2 produced because MEA oxidation by O_2 generates products such as NH_3. For example in the Castor pilot plant approximately 25 mg/Nm^3 of NH_3 are measured in the treated flue gas.

So MEA 30 % wt is a proven process and could be operated for CO_2 capture but has some important drawbacks.

4. A new solution for CO_2 Capture : the HiCapt+™ process

It is now well known that "first generation" MEA based post-combustion carbon capture processes require high energy consumption and have problems with solvent degradation due to the presence of oxygen in the inlet flue gas. Nevertheless, it is the only available and proven process for first industrial units based on inexpensive and widely available chemical. That is why IFP Energies nouvelles and PROSERNAT, have first developed **HiCapt+™ process**, based on a conventional MEA but using high performance oxidative inhibitors and higher amine concentration.

4.1 The HiCapt+™ development

Based on all the knowledge acquired during pilot tests of the 30% MEA reference process and in order to improve it and to develop a realistic industrial technology, IFP Energies nouvelles and PROSERNAT have developed the **HiCapt+™ process**. It is based on a conventional MEA solvent but using high performance oxidative inhibitors to limit as much as possible oxidative degradation of the solvent and by-products formation and higher amine concentration (40 % wt) to lower energy required at the reboiler. This paragraph focuses on the developments and results achieved with the HiCapt+™ process.

4.1.1 Corrosion

One of the most critical operational issues encountered with amine based processes is the corrosion of the process equipment. Based on extensive R&D and operational industrial feed back, PROSERNAT, TOTAL and IFP Energies nouvelles have already developed a large expertise for the design and operation of natural gas Amine units (8, 9). Of course, corrosion risks are extremely dependent on the nature of the amine solution, MEA, DEA, MDEA, formulated MDEA (respectively from the most corrosive to the lowest corrosive). Other important parameters that influences the corrosion are the temperature, the solvent loading conditions, the liquid velocity and the composition of the gas to be treated. It is also well known that amine solvent degradation often increases corrosivity. Except for the use of oxidative inhibitors which decrease drastically solvent degradation (see below) in the case of HiCapt+™ process, all these parameters are unfavourable for post-combustion CO_2 capture of the flue gas: MEA is a primary amine which is very corrosive; the high amine concentration as well as the high content of oxygen in the inlet flue gas promote degradation and increase corrosion; the CO_2 loading which is never lowered down to zero increases corrosion. That is why appropriate corrosion experiments and particular design and operational attention are therefore required to take into account such parameters, to predict the risks of corrosion and to select the optimized material for unit.
To solve this question IFP Energies nouvelles has made various test of corrosion in his lab for all the conditions that could be found in the process and with different types of carbon steel and stainless steel. Moreover, IFP Energies nouvelles was responsible of the corrosion monitoring during the Castor project and has developed a strong expertise in that field. The corrosion evaluation for the CASTOR project consisted in implementing corrosion monitoring tools to the Castor pilot plant (1). Weight loss corrosion coupons were chosen as the most convenient method, and 6 insertion points were selected. For each insertion point, one carbon steel and one stainless steel (AISI 316) corrosion coupons were installed. After the first 500 hours run of the pilot plant with 30wt% MEA, the coupons were removed for visual observation and corrosion rate evaluation.

With all these experiments (internally at IFP Energies nouvelles or during Castor project) we have now a clear view of corrosion in the HiCapt+™ process and more generally in MEA based processes. For carbon steel, results are sammurized in figure 1. This figure shows the estimated speed of corrosion for carbon steel versus temperature for different loadings of the solvent (i.e. mol of CO_2 / mol of MEA in the liquid phase). The green part represents an area with corrosion speed lower than 0.1 mm/year which could be considered as acceptable. The blue dashed circles represent the conditions of temperature and loading existing in the absorber and stripper. From this figure, it clearly appears that the use of carbon steel is not possible for MEA based process.

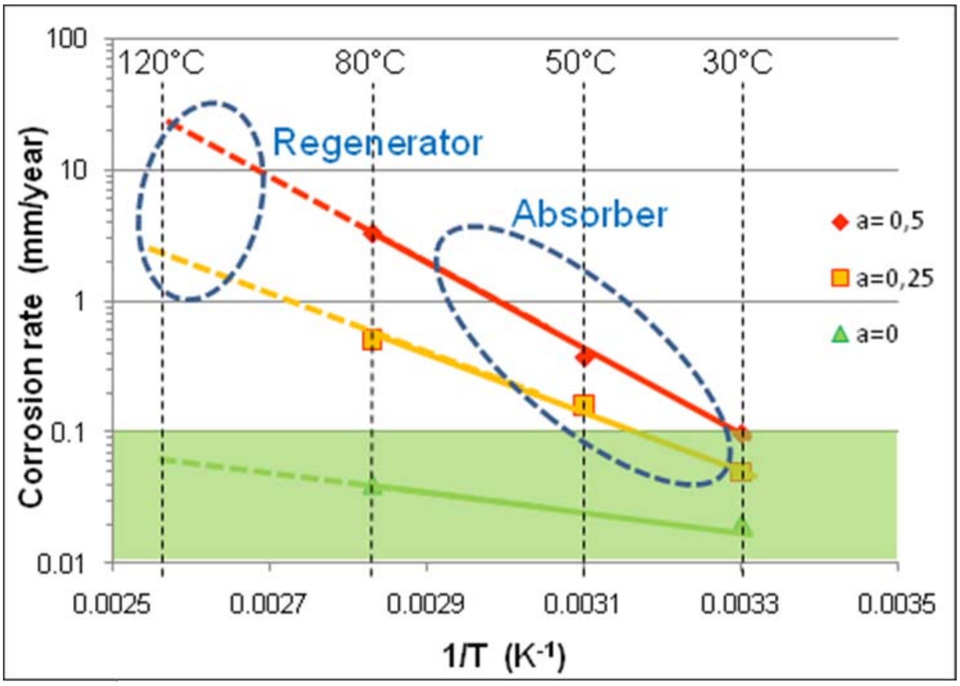


Figure 1 : Corrosion speed for carbon steel in aqueous 30% weight MEA solvent versus process parameters (temperature and loading (a))

Identical tests performed with stainless steel show corrosion speed lower than 10 µm/year for all process conditions. Consequently HiCapt+™ process is designed with equipment made of stainless steel.

4.1.2 Hydrodynamic and mass transfer

An other critical point for the optimization of the process concerns the design of the absorber and stripper columns which may represent 30 to 50 % of the CAPEX of the unit and the packing of the absorber, up to 50% of the absorber itself. As a matter of fact, in post combustion technologies, because of dilution by nitrogen, the flow rate is really huge (for example approximately 1 800 000 Nm3/h for a 600 MWe coal power plant). To reduce the size of future post-combustion capture plants and the cost of columns, high capacity packings are highly needed. Moreover, it is really important to limit the pressure drop. For the absorber, it must be compensated by a blower (electric consumption could represent between 5 to 10 % of the global utility cost) and for the stripper, the CO_2 captured must be compressed for the transport before storage.

So, in order to design properly the columns, absorber and stripper, it is required to have a complete characterisation of each packing in term of :

- liquid hold-up
- liquid distribution
- effective area (this is the area available for the mass transfer, different from the geometric area of the packing)
- pressure drop

More over the mass transfer coefficients must be known :

- kg (mass transfer coefficient in the gas phase)
- kl (mass transfer coefficient in the liquid phase)

To reach this goal, IFP Energies nouvelles has done a complete characterization of different commercial structured and random packings, like IMTP50 developed by Koch Glitsch or Mellapak 252Y (2) and Mellapak 250X developed by Sulzer. This work is done using different units available at IFP Energies nouvelles, for example in the figure 2 is presented a 400 mm diameter column equipped with a high resolution gamma tomographic system.

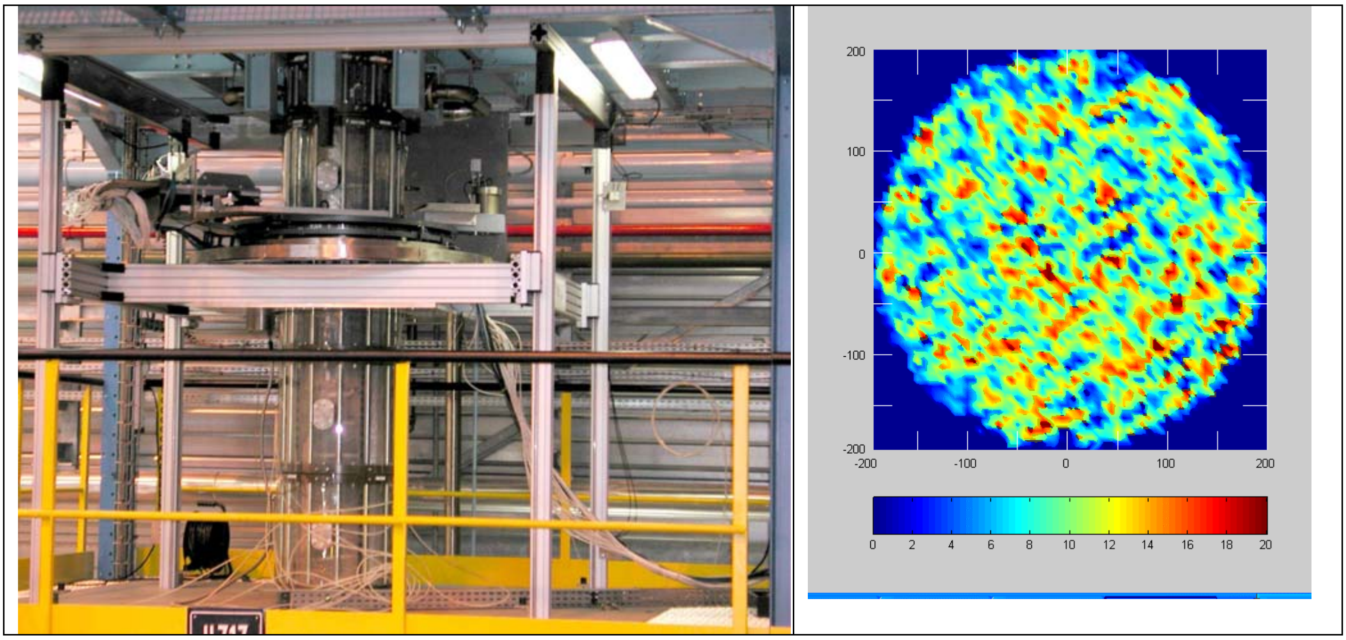


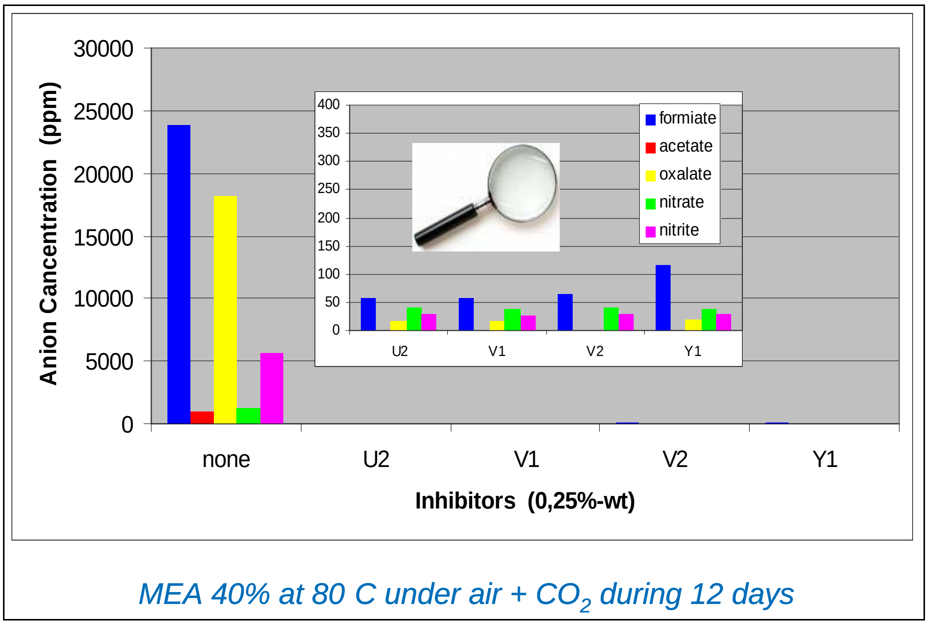
Figure 2 : 400 mm diameter column and liquid distribution map obtained with gamma tomographic system.

4.1.3 Degradation of MEA by oxidation with O_2

It is well known that when MEA is exposed to oxygen, oxidative degradation occurs in a significant amount. When water wash section is used on top of the contactor and temperature is well controlled at the reboiler and the stripper, this oxidative degradation for a MEA represents almost all the process loss of MEA which would be of about 2 batches of solvent per year. Oxidation of MEA is not only a source of solvent consumption but moreover leads to formation of volatile compounds and ammonia which need to be removed from the treated gas and also of many carboxylic acids trapped as salts in the solvent. These acids can also promote corrosion phenomena.
For these reasons, the control of degradation is a major challenge. Solving the problem allows for the design of processes using solvents with an increased MEA concentration, enhancing the performance in CO_2 capture. Oxidative degradation, which is a critical point for the development of an industrial process, can be minimized by the use of antioxidant additives in the HiCapt+™ process.

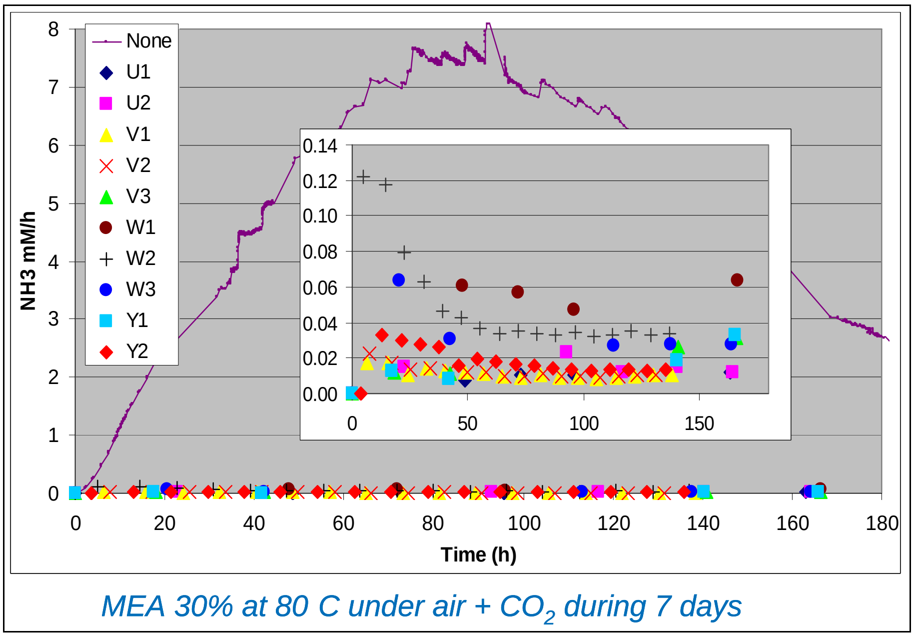
A lab scale evaluation test of MEA degradation associated with analysis of degradation products and then an evaluation of different antioxidant additives have been done at IFP Energies nouvelles (6) (7). More than 150 products have been tested and compared in regard to their oxidation inhibition capacity. Conventional antioxidant additives were found to be poorly active or inactive. But new classes of additives have been found to be effective and considerably reduce the degradation.

Some results of this investigation could be shown in figure 3 and figure 4. The figure 3 represents the concentration of the main HSS resulting from degradation in the sample collected after 12 days of degradation test in IFP Energies nouvelles lab. It clearly appears that with 0.25 % wt of inhibitor (U2 or V1 or V2 or Y1) the level of HSS stays at a negligible concentration, near the detection limit of the analytical method. In figure 4, we could see ammonia analysis of gas exiting the lab reactor used for degradation test. The results are in line with those obtained for HSS detection and it is shown that some inhibitors are really efficient. The use of these additives has been patented by IFP Energies nouvelles.



MEA 40% at 80 C under air + CO_2 during 12 days

Figure 3 : Concentration of HSS in solvent using different inhibitors



MEA 30% at 80 C under air + CO_2 during 7 days

Figure 4 : Concentration of NH_3 in the outlet gas for different inhibitors

In consequence, with the very efficient inhibitors found, HiCapt+™ process can operate at high MEA concentration (40 % wt) without any trouble linked to oxidative degradation. Compared to the reference 30 %wt MEA process, use of our efficient oxidative inhibitors results in three direct advantages :

- the consumption of MEA would be reduced by more than a factor of 10,
- the reclaiming unit will be really small,
- the ammonia concentration in the treated flue gas would be on specification without additional treatment.

The use of a high concentration MEA solvent (40 %wt) results in three main advantages :

- reduced circulation flow rate of solvent, decreasing total hold-up of solvent,
- reduced heat requirement for solvent regeneration,
- reduced size of some equipments such as pumps and regenerator column as well as size of bulk material & piping.

4.2 The HiCapt+™ simulation Model

In order to collect all the data obtained during the development (thermodynamic, kinetic, mass transfer, hydrodynamic, etc.) a dedicated model was created. This model was implemented in the Aspen+ software, using the special Aspen RateSep model.

Physical properties such as density and viscosity were adjusted in Aspen's properties to match data correlations produced by Weiland (5) and also produced at IFP Energies nouvelles lab. . Highly concentrated and highly loaded MEA rate data were shown to match unloaded, dilute literature data when activity coefficient corrections were properly considered. The temperature dependence of the Versteeg rate constant correlation was shown to be valid up to 60°C with an acceptable extrapolation to 80°C (4). Specific hydrodynamic and mass transfer properties were also implemented into the model for the packings characterized at IFP. Correlations developed by IFP Energies nouvelles were used to calculate the liquid holdup, interfacial area and the liquid film mass transfer coefficients.

It is important to state that there are no fitting parameters in the model which force it to match experimental data. The thermodynamic, kinetic, hydrodynamic and other aspects of the model were defined independently .

The model was tested with data coming from Castor pilot plant experiment and represent correctly all the twelve cases tested. In the figure 5, dots are temperature measurements and triangles are CO_2 concentrations in gas phase, all measured in the absorber of Castor pilot plant during a test using MEA at 30 % wt. The lines are model prediction. It is clearly shown on this figure that the model representation is really good.

Since the model does not use any fitting parameters to match results to the Castor pilot plant, the model can be used as a reliable and efficient tool to predict MEA-CO_2 capture performance for HiCapt+™ process. Moreover, the design of the Castor pilot plant is large enough to allow good representation of all hydrodynamic phenomena and consequently to avoid all scale effect or select the most appropriate packing for HiCapt+ mass flow rate conditions. Thus the developed simulation tool as well as results from the Castor Pilot plant can be used for design of industrial scale CO_2 capture plant.

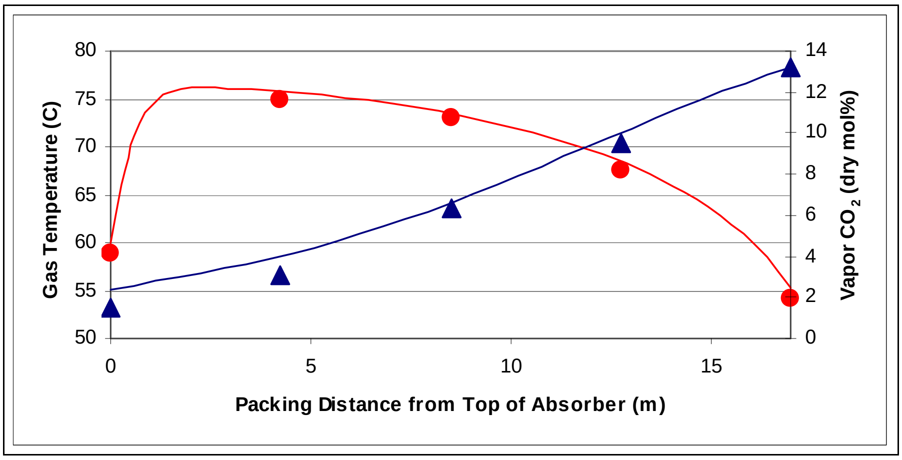


Figure 5 : Comparison of HiCapt+™ model results with data of Castor pilot plant

4.3 Process and techno-economical evaluation of the HiCapt+™ Process

Simulations with the HiCapt+™ model have been done with a flue gas coming from a 630 MWe coal power plant and with a full integration with the electricity production unit. They show an energetic penalty around 9 points (compared to 10.5 for reference process) and an energetic consumption between 3.1 to 3.3 GJ/ t CO_2 avoided which places HiCapt+^{TM} among the most energy effective current process technologies for CO_2 removal from flue gases. A technico-economic evaluation of HiCapt+™ compared to classical MEA 30 % wt process shows an improvement around 15 % in the cost of CO_2 captured A part of the results could be seen in Figure 6. It has to be noted that prices indicated is function of many parameters like coal price, reference year for investment estimation (2008), limit of the process (included CO_2 compression), ... all this has to be taken into account when comparing one process to others.

Please note as well that HiCapt+™ technology is based on cheap and widely available chemicals (including the additives).

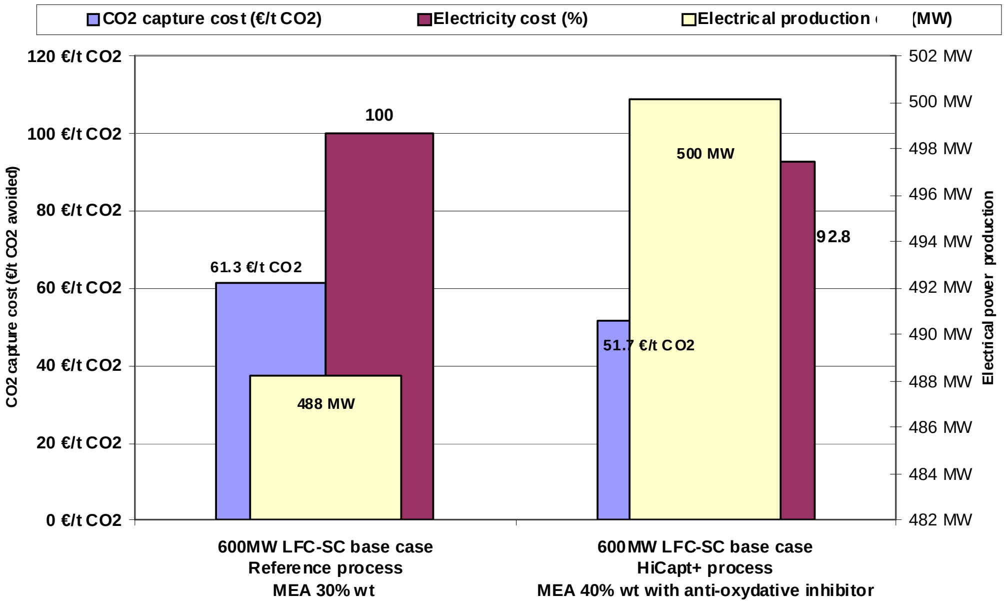


Figure 6 : technico-economic comparison between standard MEA 30 % wt process and HiCapt+™ process

5. Demonstration of HiCapt+™ process in the ENEL pilot plant

In 2009, an agreement between ENEL and IFP Energies nouvelles was signed in order to collaborate in the field of CO2 capture process. This collaboration is mainly focused around the future operation of the industrial pilot plant built by ENEL (see figure 7). This pilot which start up has been done in June 2010, is located in Brindisi, in the south of Italy, on the site of a 4*660 MWe coal power plant. It has a capacity of 2.25 t/h of CO2 captured for 12 000 Nm3/h of flue gas.

Different tests will be done with MEA at 20, 30 wt % and also with the HiCapt+™ process. This operation will validate the HiCapt+™ process performances in real and continuous operation.

Figure 7 : Picture of the ENEL pilot for CO_2 capture in Brindisi (ITALY)

6. The DMX process

Although HiCapt+™ process decreases significantly captured CO2 cost, by product emissions and energy penalty, further research and development have been decided and carried out in order to set-up breakthrough solutions, called "second generation" processes for mid term and long term deployment. One of them is the DMX-1™ technology.

6.1 Concept

The DMX-1™ process under development at IFP Energies nouvelles and PROSERNAT is based on special solvents which are characterized by the formation of two immiscible phases for given temperature and CO2 loading conditions.

Composition of the two liquid phases depends of various parameters like amine concentration in the solvent, carbon dioxide partial pressure or temperature. In the present DMX-1™ process, after the heat cross exchanger, between the absorber and the stripper, we can obtain a water rich phase, with a very high carbon dioxide loading and an amine rich phase, with a very low carbon dioxide loading. Actually, this last phase does not need to go through the stripper, as its loading is very low. Then, separation of the phases allows us to reduce the liquid flow rate in the stripper, and thus the energy requirement for the regeneration of the solvent. Several solvents have been studied at IFP Energies nouvelles, in the present paper we focus on the so-called DMX-1 solvent which shows impressive capacity of absorption of carbon dioxide, very good stability towards potential degradation, low corrosion, and fast separation of the two phases. These latter characteristics are discussed in the following section.

6.2 Results

6.2.1 Thermodynamic data

In this paper, we focus only on two of the fluid properties necessary to fully simulate a process : phase equilibrium and heat of absorption. The main data are the liquid – vapor between CO2 and the DMX-1 solvent which has been performed in equilibrium cell using the static method [10-11]. Precisely known quantities of solvent and carbon dioxide have been introduced inside an equilibrium cell and its temperature and pressure in equilibrium conditions have been recorded. The partial pressure of carbon dioxide and the overall composition of the liquid phase have been deduced from mass and volume balances. These measurements give also access to the bubble pressure of the solvent. Figure 8 shows such results with the partial pressure of CO2 as a function of the liquid composition expressed in mol of CO2 by mass of solvent for a temperature of 313.15 K. We have also added some results of the literature about the water + MEA + CO2 system at the same temperature [12-13]. The DMX-1 solvent shows a significantly different behaviour from the MEA solvent. It can be seen that the DMX-1 solvent shows a much better cyclic capacity than the aqueous solution of MEA for pressure varying from 0.001 close to 0.01 MPa which are the pressure range of the flue gas at outlet and inlet of the absorption section respectively. The difference in shape for both isotherms has also a strong impact on the stripping of CO2. With DMX-1 solvent, a lower stripping is required for solvent regeneration compared to MEA solutions. This result has a direct impact on the heat of regeneration of the solvent.

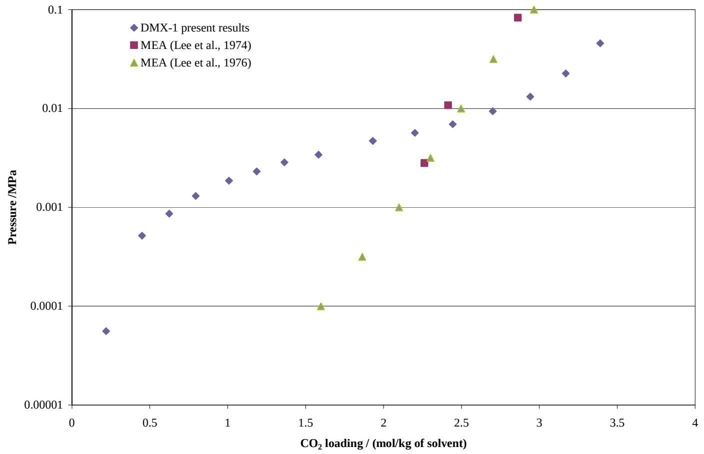


Figure 8 : Isotherms of absorption of CO_2 in DMX-1 and MEA solvent at 313.15 K.

The data have been modeled with a semi-empirical approach coupling i) the mass action law of the chemical reactions, ii) the mass balances of the compounds, iii) the electro-neutrality of the solution and iv) the Henry law for the phase equilibrium. The heat of absorption of CO2 into the solvent is directly deduced from this model using the van't Hoff law [14]. The calculated heat of absorption is close to -60 $kJ.mol^{-1}$ for the considered temperature range as compared to -85 $kJ.mol^{-1}$ obtained for CO2 - MEA system. For the liquid – liquid equilibrium, measurements have been performed in a transparent cell where both liquid phases are sampled [15]. Each of them has then been analyzed by acid and volumetric titrations in order to access to the amine and CO2 contents. This information has been directly used in the simulator to calculate the liquid phases split and to further determine the flow that will be sent at regeneration step. From these four pieces of information, high cyclic capacity, low stripping energy, low heat of absorption, only a proportion of the fluid towards the regeneration step, one can expect important energy savings. Volumetric properties such as density and viscosity have also been determined for different CO2 loadings and temperatures; these properties are used for the design of equipments. All these data are compiled in in-house thermodynamic routines that are further used for process evaluations as discussed in section 6.3.

6.2.2 Operational issues

From previous thermodynamic data, one can easily deduce that energy penalty will be significantly lowered with DMX-1™ solvent compared to MEA. However, to go from the very attractive solvent properties to a realistic industrial process, one has to make sure that such good performances can actually be reached without any operational issues.

6.2.2.1 Liquid/liquid decantation

First of all, it was needed to check that liquid/liquid separation would not make any problem. To do so, experiments have been performed in a stirred cell and in a lab-scale decanter. The first set of tests was used for adjusting different parameters depending on solvent properties including breakup/coalescence properties, while the second set of tests was used to validate the liquid/liquid decantation simulation approach. In parallel to these tests, Euler/Euler CFD calculations have been performed for both types of tests for scaling-up purposes.

Concerning the first set of tests performed in a stirred cell, with control of the temperature, it could be seen that after stop of the Ultra-Turrax, decantation of the DMX-1 solvent (loaded with CO2) has occurred in less than one minute (figure 9). At 40s for those specific conditions, one observes that the light phase (containing the lean solvent) is very limpid indicating that this phase is not mixed with heavier rich phase and can be directly sent back to the absorber without being regenerated, as expected. The heavy phase, which contains the CO2, is opaque due to the presence of micro-droplets of the light phase. Although this phase can be sent to the regenerator as it is, it is seen here that some improvement of the decantation conditions may be reached.

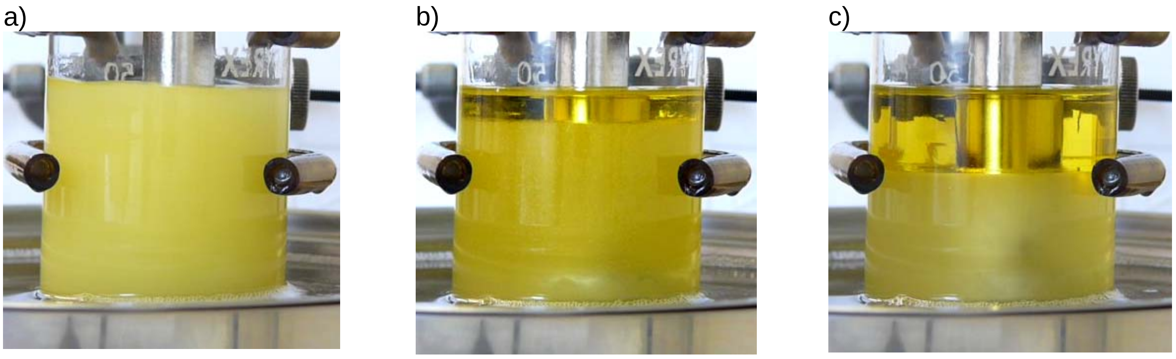


Figure 9 : Stirred-cell tests for the DMX-1 solvent : system at a) t = 0 s, b) t = 15 s and c) t = 40 s.

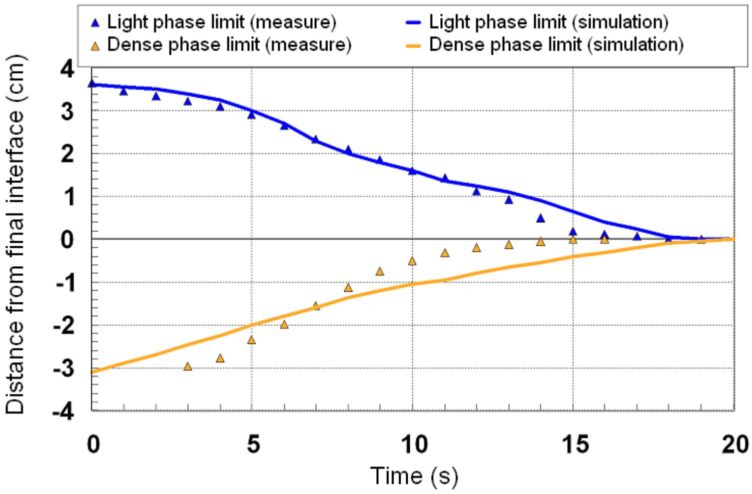


Figure 10 : CFD simulation of stirred cell tests, comparison between experimental and simulated profiles.

With such tests, decantation times and decantation fronts have been determined for several operating conditions. CFD calculations have been performed to reproduce such evolutions. The measured parameter is the distance between the front of the superior and inferior interfaces and the final interface. Figure 10 shows the interfaces evolutions with time for operating conditions different from those corresponding to Figure 9, here two fronts can easily be determined. The light phase front is represented in blue, and the dense phase front in yellow. One observes from Figure 10 that, via the use of adapted in-house user-defined functions taking into account physical properties of the fluids and breakup/coalescence phenomena, CFD is able to reproduce experimental tests with a good accuracy even if a slight discrepancy is noticeable for the dense phase limit profile.

6.2.2.2 Degradation

The stability of the solvent is an important property. Indeed, degradation of the solvent results in corrosion, foaming, unwanted emissions... In order to handle these problems, a reclaiming of the solvent can be done, or the inventory of solvent can be replaced, but these solutions have a huge impact on the operational costs. Definitively, the more stable a solvent is, the less operating problems are encountered. First laboratory scale degradation tests have been performed in more drastic conditions in terms of temperature and CO2 and O2 partial pressures than in in an industrial plant : comparative tests of different solvents were performed over a period of 15 days, in closed reactors maintained at 140°C with a high pressure of carbon dioxide (up to 20 bar) and/or oxygen (up to 4.2 bar) (compared to usual plant operation conditions, up to 120°C, and up to 2 bar of total pressure). In these conditions, a very low degradation of DMX-1 has been observed and DMX-1 has less degradation than most molecules tested in these conditions [16-17].

In addition, as regeneration of the solvent at a higher temperature and pressure could be a way to reduce the cost of Post combustion capture (a higher temperature at reboiler corresponds to a higher pressure which further induce a lower compression energy required for delivering high pressure carbon dioxide), we increased the duration of our tests and we increased the temperature of the reactors up to 180°C.

Results in terms of percentage of degradation of the solvent over time are shown in Figure 11 where DMX-1 is compared to 40 wt.% MDEA. MDEA has been taken as a reference since it is already widely used in natural gas treatment without any known problem of degradation and because in similar tests it has been shown that it is the most stable amines among commercial ones [16-17]. Without CO2 (open symbols), degradation rate of DMX-1 appeared to be seven times lower than the one of MDEA. The same trend is observed with an additional pressure of 20 bar of CO2 (closed symbols). All these results make us confident to have a low degradation of DMX-1, even in the case of a regeneration at high temperature.

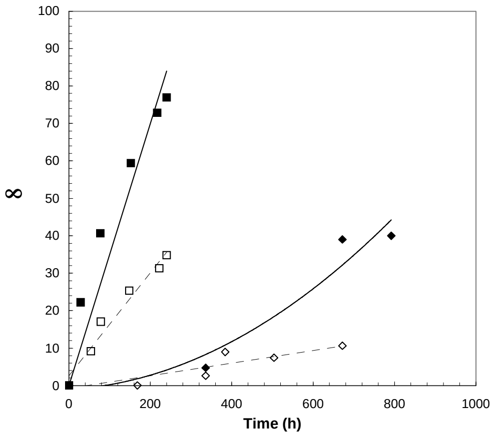


Figure 11 : Percentage of degradation of solvents in time at 180°C (square : MDEA; lozenge : DMX-1), with or without 20 bar CO_2 (respectively closed and open symbols).

6.2.2.3 Corrosion

As it was discussed above, with conventional MEA technologies corrosion represents a major operational issue [18-22]. It was shown that corrosivity of MEA is enhanced by high temperature and CO2 loadings and pilot plant experiments showed corrosion rates of carbon steel to reach more than 1 mm/year in the hot amine sections at the inlet or outlet of the stripper [17]. Although HiCapt+™ technology addresses this operational issue by selecting corrosion resistant alloys a low corrosivity solvent would be of great interest. For comparison, some corrosion tests were performed in the DMX-1™ solvent. On the IFP Energies nouvelles pilot plant, corrosion rates of carbon steel coupons were found to be negligible (< 2 µm/year) at stripper inlet and at outlet (temperature ≈ 105°C). Other tests were performed in more severe conditions in autoclave, at 180°C and under 20bar CO2. Even under these conditions, carbon steel gave excellent performance, with approximately 10 µm/year corrosion rate. Even if additional tests in more representative conditions are required (e.g. hydrodynamic and phase separation), all the corrosion results available to date indicate that the DMX-1™ solvent is far less corrosive than MEA. Therefore, less costly construction materials should be employed, and the use of costly proprietary corrosion inhibitors should also be avoided.

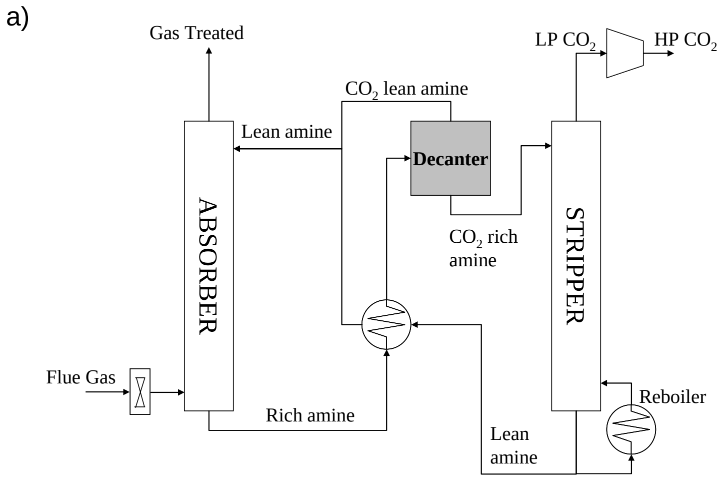
6.3 Process evaluation

6.3.1 Process description

The DMX™ process is based on the particular property of demixing solvents to form two immiscible liquid phases for specific CO2 loadings or temperature conditions, one having a particular high CO2 loading. The possibility of easy separation of the two phases by decantation allows us to consider an important decrease of solvent mass flow at regeneration. Figure 12 shows a corresponding possible configuration for the process flow diagram. The DMX™ process mainly differs from the MEA process by having an additional operation unit of decantation. The decanter is preferably positioned after the amine/amine heat exchanger and before the regenerator. This unit operation exploits the liquid/liquid separation property of the solvent with the simultaneous effect of CO2 charge and heat. Only the dense phase having a high CO2 concentration is injected in the regenerator. The light phase is mixed with the regenerated solvent coming from the stripper and injected to the absorber.

6.3.2 Cost analysis of the DMX-1 process

Process simulations have been performed with SimSci PRO/II using IFP Energies nouvelles’s proprietary thermodynamic model via user added subroutines, the design of the columns being made with an in-house simulator. Figure 12b presents the main characteristics of the DMX-1™ process used for the simulations. The main result, is the significant decrease of the energy consumption of the process : 2.3 GJ/ton CO2 compared to 3.7 GJ/ton CO2 with 30 wt.% MEA. With a particular process scheme, not shown here, this energy consumption can be as low as 2.1 GJ/ton CO2.



b)

Solvent	DMX-1
Energy consumption	2.3 GJ/t CO_2
CO_2 output	110 bar (a)
Absorber packing	Mellapak 250X
Stripper packing	IMTP 50
Reboiler type	Kettle
Heat exchanger type	Gasketed Plates

Figure 12 : a) Simplified process flow diagram of the IFP Energies nouvelles DMX™ process and b) corresponding main process characteristics.

The first technico-economic process evaluation of the DMX-1™ process finally results in a reduction of CO2 cost of 25% compared to the 30%wt MEA reference process case with same boundary conditions. Further optimization are undergoing via intensive research considering all aspects, thermodynamic properties, kinetics, mass transfer properties, process optimization.

7. Conclusion

IFP Energies nouvelles and PROSERNAT have developed an optimized CO2 capture process based on the robust and proven MEA 30 % wt process. The HiCapt+™ technology uses MEA at 40 % wt with inhibitor against oxidation by O2. Among other advantages, this advanced technology results in a reduced heat requirement for solvent regeneration, a drastic decrease of solvent degradation rate, decreasing solvent consumption and thus reclaiming needs and drastic decrease of by-product emission in the treated flue gas (such as VOC and NH3) due to the efficiency of the anti-oxidative agents. A first technico-economic study has led to 15% reduction of the cost of the CO2 captured.

A complete simulation model has been developed for the HiCapt+™process which performances will be demonstrated this year in the ENEL industrial pilot plant.

Based on all this R&D as well as PROSERNAT's industrial experience on similar technologies for natural gas sweetening, HiCapt+™ technology is now ready to be demonstrated at industrial scale.

Furthermore, Prosernat with the HiCapt+™ CO2 capture process technology, its further relevant experience in CO2 dehydration (Prosernat provided TEG CO2 dehydration units for the In Salah project) and in association with relevant partners when appropriate, is in a position to address globally the CCS chain for whatever type of applications.

Other second generation technologies are under development, such as DMX-1™ process. From thermodynamic studies and associated process simulations, it is shown that DMX-1™ enables important savings in terms of energy consumption, the energy at reboiler being decreased from 3.7 GJ/ton CO2 (30wt.% MEA) down to 2.3GJ/ton CO2 and even down to 2.1GJ/ton CO2. It is also shown that common operational issues that could stop a development before industrial application have been studied and are in favor of this process. A first technico-economic study has led to 25% reduction of the cost of the CO_2 captured compared to the 30%wt MEA reference process case. Next step consists in going from laboratory tests to pilot plant currently under design and to then large scale pilot validation.

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