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Dossier

Post Combustion CO_2 Capture
Captage de CO_2 en postcombustion

Development of HiCapt+™ Process for CO_2 Capture from Lab to Industrial Pilot Plant

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Résumé — Développement du procédé HiCapt+™ pour le captage du CO_2 : du laboratoire au pilote industriel — Il est aujourd'hui connu que les procédés de captage du CO_2 en postcombustion dits de "première génération" à base de MEA nécessitent une importante énergie de régénération en plus de connaître des problèmes de dégradation du solvant dus à la présence d'oxygène dans les fumées de combustion. Cependant, ce procédé est le seul disponible aujourd'hui à l'échelle industrielle, c'est pourquoi *IFP Energies nouvelles* a développé le procédé HiCpat+, basé sur un solvant conventionnel à la MEA mais mis en œuvre à haute concentration avec des additifs antioxydants. Ces additifs permettent au procédé HiCapt+ de mettre en œuvre un solvant concentré sans connaître de problèmes de corrosion et de dégradation, ce qui engendre des gains notables en terme de consommation énergétique. De plus, la baisse du taux de dégradation du solvant permet de réduire les problèmes opératoires liés à la régénération du solvant ainsi que de limiter les émissions de produits de dégradation légers comme le NH_3 dans le gaz traité.

Abstract* — *Development of HiCapt+™ Process for CO_2 Capture from Lab to Industrial Pilot Plant — *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 oxygen. Nevertheless, it is the only available process for first industrial units. That is why IFP Energies nouvelles, has developed HiCapt+ process, based on a conventional MEA solvent but using high performance oxidative inhibitors and higher amine concentration. These oxidative inhibitors enable HiCapt+'s process to use high solvent concentrations without corrosion or degradation problems and lead to reduction of the regeneration energy demand due to solvent flow rate reduction. Moreover, the huge reduction of solvent degradation rate avoids the difficult management of reclaiming unit, as well as avoiding high concentration of light degradation products in the treated flue gas, like NH_3.*

INTRODUCTION: THE REFERENCE PROCESS MEA AT 30 WT%

It is now well known that "first generation" MEA (MonoEthanolAmine) 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 technology for first industrial units based on an inexpensive and widely available chemical solvent. That is why *IFP Energies nouvelles* and *PROSERNAT*, have developed the HiCapt+™ process, based on a conventional MEA solvent but using high performance oxidative inhibitors and higher amine concentrations.

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 [1] has demonstrated the good operability, security, flexibility, stability and reliability of this process during long run tests (more than 500 h operation without stop). These tests have been done in the pilot plant located at the Dong power plant (Esbjerg, Denmark). This pilot gave realistic data because the flue gas treated came directly from the power plant and the pilot capacity was very large (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 was measured around 3.7 GJ/tCO_2 avoided. It corresponds to a penalty for the power plant around 10.5 points on the net efficiency (for a power plant with a high yield of 40% net).

Moreover another critical point with this reference technology 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 result from this degradation:

- the first one is a high consumption of MEA, approximately 2 batches of solvent per year. The economical impact on the operating costs is really important – more than 7 M€/year for a CO_2 capture unit installed to remove 90% of the CO_2 emissions of a 600 MWe power plant. An other drawback is the management of this huge solvent volume;
- the second one is coming from the degradation products formed during the degradation reactions, which stay in the liquid phase. These products, named HSS (Heat Stable Salt), are mainly organic acids (formic acid, oxalic acid, acetic acid). These acids are very corrosive regarding carbon steel and create a decrease in the solvent reactivity. Thus a reclaiming unit is needed to purify the solvent and remove all the degradation products. 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 were 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.

1 THE HICAPT+™ PROCESS DEVELOPMENT

1.1 From MEA 30 wt% to MEA 40 wt%

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, *IFPEN* and *PROSERNAT* have developed 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 using MEA at higher amine concentration (40 wt%) to lower the energy required at the reboiler. This paragraph focuses on the developments and results achieved with the HiCapt+™ process, in particular the adjustments made to the models (thermodynamics, hydrodynamics and kinetics) to predict the process performances with a high concentrated solvent.

1.1.1 Process Simulation – State of the Art

The performances and design criteria of post-combustion processes using MEA 30 wt% can be evaluated through a process simulation tool like *AspenTech*'s AspenPlus. Based on its knowledge of MEA 30 wt% process, *IFPEN* implemented under this simulation tool all the in-house correlations and models available for MEA 30 wt%.

Starting from these correlations, it is possible to simulate a process running with high MEA concentrations like the HiCapt+ process. Unfortunately, pilot plant data have shown the inaccuracy of the models with MEA 40 wt% tests as shown in Figure 1.

To predict correctly the performances and to perform good designs of the HiCapt+ process, it has been necessary to modify some aspects of the correlations used in the AspenPlus models.

1.1.2 Thermodynamics

The thermodynamic model used in AspenPlus simulation is the Non Random Two Liquids (NRTL)-electrolyte model. Lab scale experiments have been performed in *IFPEN* labs with MEA 40 wt% and the results have been compared to the AspenPlus model (absorption isotherms and enthalpy) as well as to literature data [2-4]. Figure 2 illustrates the comparison between AspenPlus model and literature data at different temperatures.

From this work, it has been concluded that the NRTL-electrolyte model used in the AspenPlus simulation is suitable to predict the equilibrium with MEA 40 wt%.

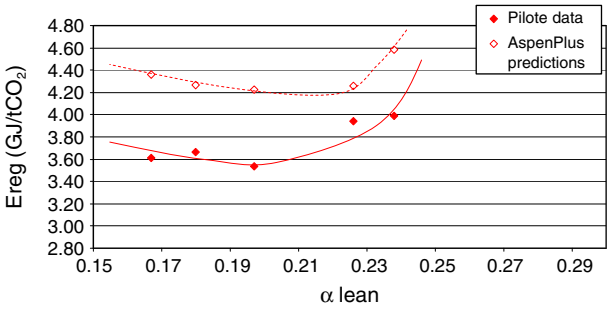


Figure 1

The AspenPlus predictions without models modifications.

1.1.3 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 gas flow rate is really huge (for example approximately 1 700 000 Nm^3/h for a 600 MWe coal power plant). To reduce the size of future post-combustion capture plants and the cost of the columns, high capacity packings are highly needed. Moreover, it is really important to limit the pressure drop generated by the absorber column as it must be compensated by a blower which electric consumption can represent between 5 to 10% of the global utility cost. For the stripper column, as the CO_2 captured must be compressed for the transport before storage, a low pressure drop in the column is also needed.

In order to design properly the columns, absorber and stripper, it is required to have a complete characterization 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:

- k_g (mass transfer coefficient in gas phase),
- k_l (mass transfer coefficient in liquid phase).

To reach this goal, *IFPEN* has done a complete characterization of different commercial structured and ran-

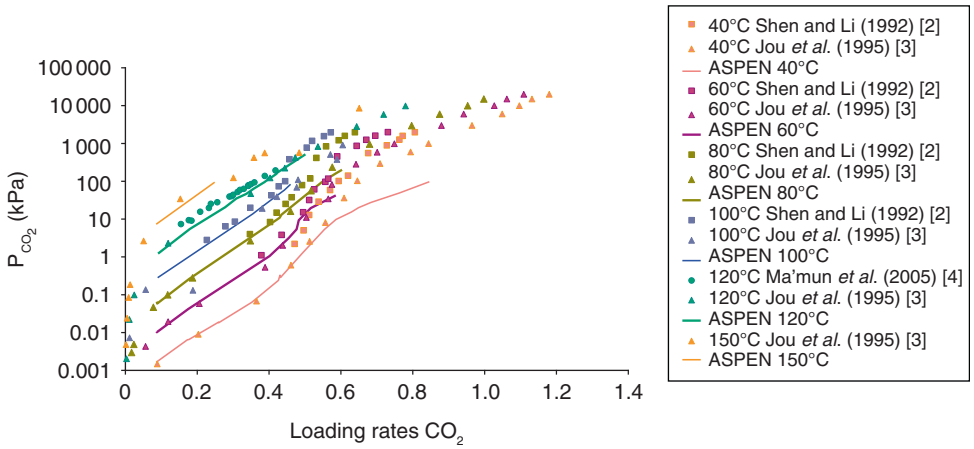


Figure 2

The AspenPlus thermodynamic correlations.

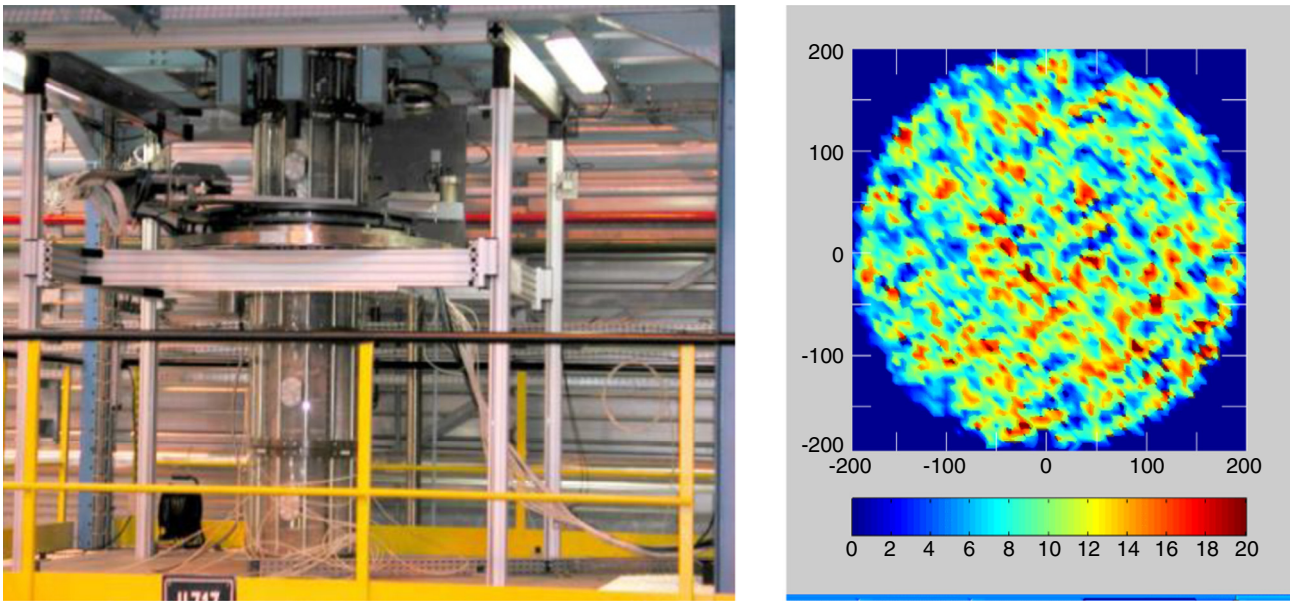


Figure 3

400 mm diameter column and liquid distribution map obtained with gamma tomograph.

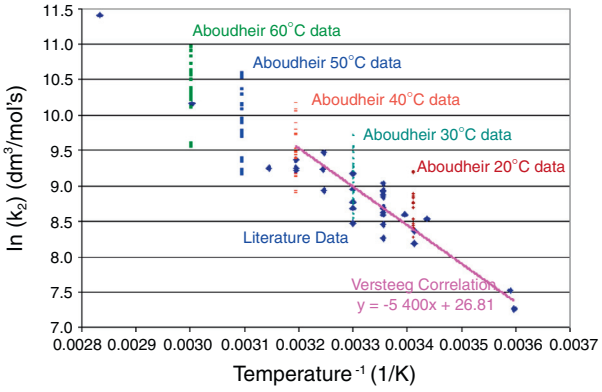


Figure 4

Aboudheir data [6] and Versteeg *et al.* [7] correlations.

dom packings, like IMTP50 developed by *Koch Glitsch* or Mellapack 250X developed by *Sulzer* [5]. This work was done using different pilot units available at *IFPEN*, for example in Figure 3 is presented a 400 mm diameter column equipped with a gamma tomography and the liquid map obtained.

From this work, correlations were obtained for effective area of packing (*ae*), mass transfer coefficient in gas phase (k_g) and mass transfer coefficient in liquid phase (k_l). These correlations were obtained as function of the solvent parameters such as viscosity and surface tension to take into account the increase in solvent concentration in the HiCapt+ process.

All the obtained correlations were implemented in the *AspenTech*'s AspenPlus simulation tool.

1.1.4 Kinetics

To increase the accuracy of the AspenPlus model, it has been decided to use Aboudheir data [6], which are validated from 20 to 40 wt% MEA, loading between 0.1 and 0.5, temperature between 20 to 60°C. It has been found out that the Aboudheir data were not in agreement with the Versteeg *et al.* [7] correlation, which was obtained in diluted unloaded solutions, as shown in Figure 4.

It has been chosen to refine the raw Aboudheir data to make them compatible with the AspenPlus thermodynamics (NRTL-electrolyte) and formalism. Moreover, correction factors had been used to take into account:

– the activity coefficient in highly concentrated solutions,
– the viscosity of the solution in highly loaded solutions.

The new kinetic correlation has been implemented in the AspenPlus RateSep model. The extrapolation of this in-house model to unloaded solutions is consistent with the Versteeg correlation for different MEA concentrations, which demonstrates the validity of the methodology used in this work.



Figure 5

Picture and location of the 2.25 t/h post-combustion CO_2 capture pilot plant in *ENEL* power plant of Brindisi.

1.1.5 Models Validation at Industrial Pilot Scale

1.1.5.1 Pilot Plant Description

In 2009, an agreement between *ENEL* and *IFPEN* was signed in order to collaborate in the field of CO_2 capture processes. This collaboration was mainly focused around the future operation of the industrial pilot plant built by *ENEL* (*Fig. 5*). This pilot which started up during summer 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 CO_2 captured for 12 000 Nm^3/h of flue gas.

Different tests have been done with MEA at 20, 30 wt% and also with MEA 40 wt% which is the basis of the HiCapt+^{TM} process (but no additive was tested). These tests performed on this semi industrial unit allowed *IFPEN* to optimize and validate the process performances at high MEA concentration (40 wt%) in real and continuous operation. Moreover, long run tests gave the reference figures for MEA 40 wt%.

The pilot plant engineering phase started in 2008, construction was done from March 2009 to June 2010 and finally start up phase and validation of the unit were done from June to September 2010 using a solvent at 20 wt% MEA.

Detailed description of the pilot plant is given here below. First, a fan compresses the flue gas just after the DeSOx unit of the power plant. Flue gas flow rate could vary from 3 000 up to 15 000 Nm^3/h and the fan could compensate the pressure losses resulting from the pilot units.

Next, the flue gas is sent to a dedicated DeSOx unit that enables to operate at very low value for SO_2 content in flue gas. The unit uses a spray tower with a limestone slurry. Efficiency of SOx removal is higher than 95%. Right after the DeSOx unit, two WESP (Wet Electro-Static Precipitator) remove the entrained particles. They can be used in series, only one at a time or bypassed totally. After this pre-treatment, flue gas arrives in the CO_2 removal loop composed of the absorber and the stripper columns.

The different materials composing the CO_2 capture section are the following:

- absorber column:
  - diameter = 1 500 mm/height = 45 m,
  - absorption zone (structured packing): 3 beds × 7.35 m, washing section packing: 1 bed × 4 m, others: 2 demisters in the top,
  - 3 possible feeds for liquid (operation with 1 or 2 or 3 beds of packing);
- stripping column:
  - diameter = 1 300 mm/height = 31 m,
  - packing below feed (random packing): 3 beds × 3.7 m, washing section packing (up to the feed): 1 bed × 3 m, 2 possible feeds for liquid (operation with 2 or 3 beds of packing);
- rich solvent/lean solvent heat exchanger:
  - plate fine type;
- filtration section:

- 2 mechanical filters;
- 1 carbon filter;

– others:
- solvent storage 2 × 100 m^3 tanks;
- cooling water section: external loop sea water;
- industrial cooling water loop: sea water/cooling water heat exchanger.

The pilot is also fully instrumented with more than 400 acquisition points. All the regulation and control loop are exactly the same than for industrial unit.

The pilot is equipped with 5 corrosion monitoring points, each containing 6 corrosion probes. Analysis are done on line for CO_2 content in the gas (on line regulation of plant efficiency) and daily analysis are done for all the values regarding liquid phase (loadings, solvent concentration, etc.).

1.1.5.2 AspenTech *AspenPlus* Model Validation

In order to collect and use all the data obtained during the development (thermodynamic, kinetic, mass transfer, hydrodynamic, etc.) a dedicated predictive model was created. This model was created inside the *AspenTech* AspenPlus environment, using the special Aspen RateSep model. As discussed previously:

– physical properties such as density and viscosity were adjusted in Aspen's properties to match data correlations produced by Weiland et al. [8] and also produced at *IFPEN* lab. Heat of formation and heat capacity data were adjusted;
– highly concentrated and highly loaded MEA reaction 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. The effect of ionic strength on the kinetics was quantified and implemented into the model;
– specific hydrodynamic and mass transfer properties were also implemented into the model for the packings characterized at *IFPEN*. Correlations developed by *IFPEN* 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 the Castor pilot plant experiments and appeared to represent correctly all the cases tested. In Figure 6, 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 show the model predictions. It is clearly shown in this figure that the model representation is really good.

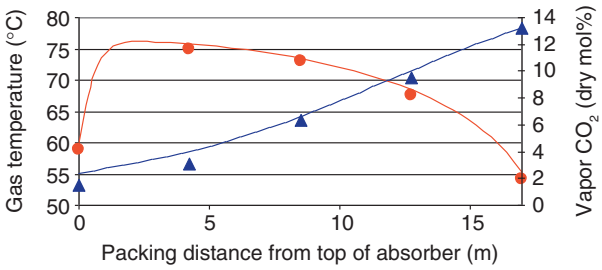


Figure 6

Comparison of HiCapt+™ model results with data of Castor pilot plant.

During the MEA 40 wt% pilot plant campaign, the AspenPlus model had been extended with additional lab experiments to cover the new operating conditions (mean temperature, densities, viscosities, etc.). Pilot plant data were directly compared to the model prediction with success. All the parametric studies made on the pilot plant with MEA 40 wt% as well as the long run test were pretty well predicted by the model. Figure 7 illustrates the model prediction for all the parametric tests (more than 50 operating conditions with MEA 40 wt%), before and after model modifications made for MEA 40 wt%.

All the results of the new AspenPlus model are in the range of ±5% with respect to industrial pilot plant data. The developed simulation tool as well as results from *ENEL* pilot plants can be used for design of industrial scale CO_2 capture plant.

1.2 Corrosion

The removal of carbon dioxide from industrial gas streams by amine treating units is a well known process, extensively used for many decades in natural gas treatment. One of the most severe operational difficulties encountered is the corrosion of the process equipments. Based on extensive R&D and operational industrial feed back, *PROSERNAT* and *IFPEN* have already developed a large expertise for the design and operation of natural gas Amine units [9, 10]. 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

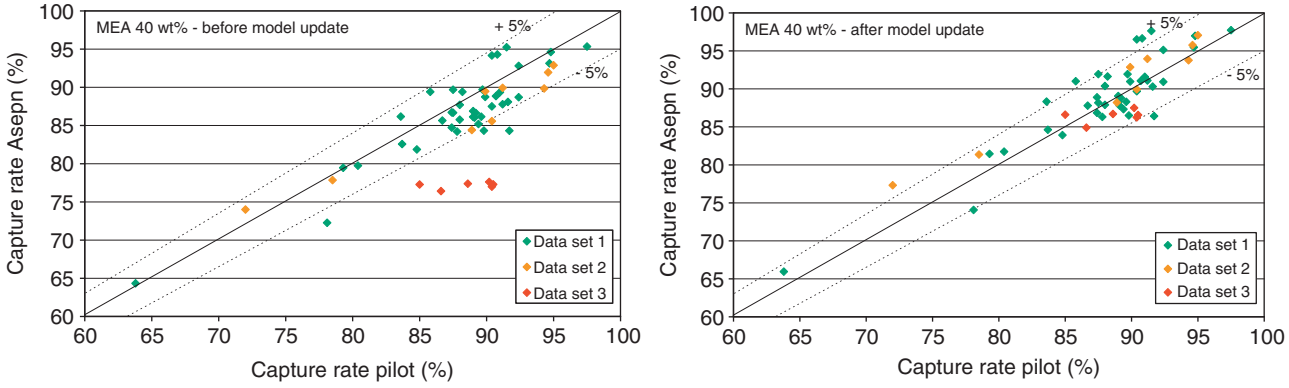


Figure 7

Comparison of HiCapt+™ model with data of MEA 40 wt% pilot plant.

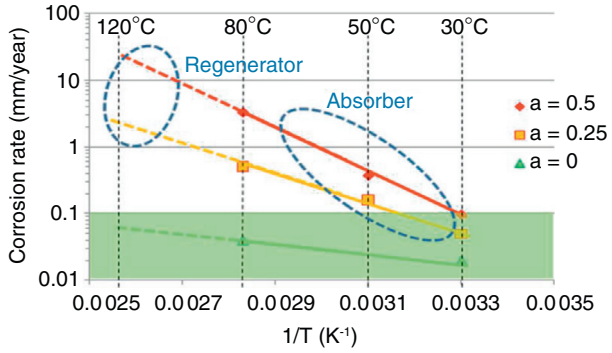


Figure 8

Corrosion speed for carbon steel in aqueous 30 wt% MEA solvent *versus* process parameters (temperature and loading (*a*)).

corrosive). Other important parameters that influence the corrosion are the temperature, the concentration of the amine solution, 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 and post-combustion CO_2 capture of the flue gas, all these parameters are unfavourable: 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 also the 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 these questions *IFPEN* has made various tests of corrosion in its lab for all the conditions that could be found in the process and with different types of carbon steel and stainless steel. Moreover, *IFPEN* was responsible of the corrosion monitoring during the Castor project. The corrosion evaluation for the Castor project consisted in implementing corrosion monitoring tools to the Castor pilot plant. 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 5M MEA, the coupons were removed for visual observation and corrosion rate evaluation.

With all these experiments (internally at *IFPEN* or during Castor project) we have now a clear view of corrosion in the HiCapt+™ process and more generally in MEA based processes. For corrosion of carbon steel in MEA at 30 wt%, results are shown in Figure 8. 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 bottom green part of the figure represents an area in which corrosion speed is lower than 0.1 mm/year, which could be considered as an acceptable corrosion rate for an industrial unit. The blue dashed circles represent the conditions of temperature and loading existing in the absorber and stripper of a MEA 30 wt% standard process. From this figure, it clearly appears that the use of carbon steel is not possible for a MEA 30 wt% process, and by extension for all MEA based processes.

Identical tests done with stainless steel showed corrosion speed lower than 10 µm/year in all the process conditions.

But the combination of MEA and anti-oxydative agent changes the corrosivity of raw MEA solvent. Considering there may be a risk of corrosion in hot parts of the *ENEL* industrial pilot plant during long test runs, it was thus decided not to use HiCapt+^{TM} solvent containing inhibitor in the *ENEL* pilot plant. Nevertheless, others materials like duplex steels are identified and have been tested with really good results, less than 5 or 10 µm/an of corrosion speed with the full HiCapt+ solvent composition.

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 the water wash section is used on top of the contactor and the temperature is well controlled at the reboiler and the stripper, this oxidative degradation of the MEA molecule represents almost all the solvent losses of the unit, which would be about 2 batches of solvent per year for a typical 30 wt% MEA. Oxidation of MEA is not only a source of solvent consumption but also leads to formation of volatile compounds and ammonia which need to be removed from the treated gas. Moreover many carboxylic acids are formed and trapped as salts in the solvent. These acids can also promote corrosion phenomena.

For these reasons, the control of degradation is a major challenge in MEA based technologies. As the increase in the solvent concentration will end with an increase of the degradation issues, solving this problem will allow to design 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+^{TM} process.

A lab scale evaluation test of MEA degradation associated with a dedicated analysis of degradation products and then an evaluation of different antioxidant additives were done by *IFPEN* [11, 12]. 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 issues in MEA processes.

Some results of this investigation could be shown in Figures 9 and 10. Figure 9 represents the concentration of the main HSS resulting from degradation in the sample collected after 12 days of degradation in lab test performed at *IFPEN*. 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 10, we could see the ammonia analysis of the gas exiting the lab reactor used for degradation tests. The results are in line with those obtained for HSS detection and it is shown that some inhibitors are really efficient.

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

– the consumption of MEA would be reduced by more than a factor 10;

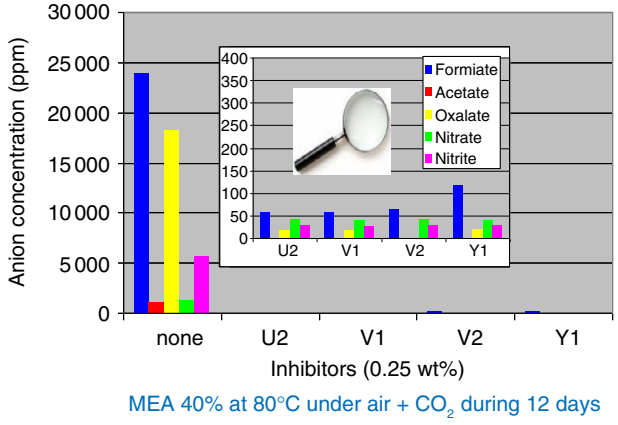


Figure 9

Concentration of HSS in solvent using different inhibitors.

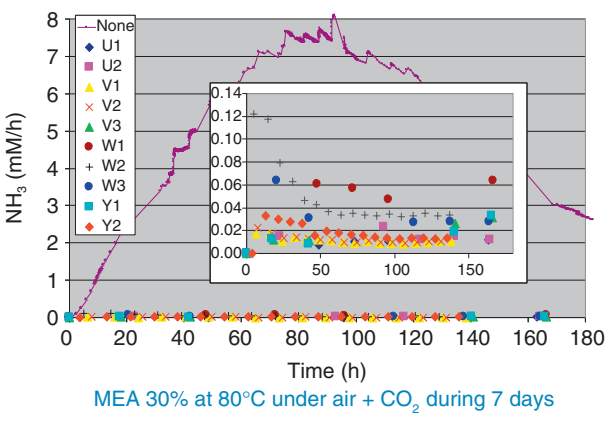


Figure 10

Concentration of NH_3 in the outlet gas for different inhibitors.

– the reclaiming unit will be smaller than in conventional units,
– the ammonia concentration in the treated flue gas would meet the environmental specifications 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 and piping.

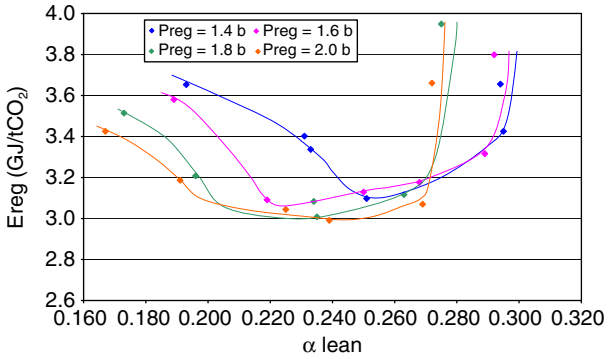


Figure 11

Lean loading and stripper pressure optimization for MEA 40 wt% at 90% capture rate.

2 THE HICAPT+^{TM} PROCESS OPTIMIZATION

2.1 Results of Pilot Plant Tests – Optimization of MEA at 40 wt% Process

A first campaign on the *ENEL*'s pilot plant was done from June to September 2010 with MEA at 20 wt%. This campaign enables to start up the unit, validate all the methods and procedures and to perform the guarantee tests. Following this start-up phase, the tests campaigns with MEA 30 wt% and 40 wt% started. This paper will only focus on MEA 40 wt% campaign. But we could say that results obtained with MEA 30 wt%, which is considered as a reference, are totally coherent with literature. This is an other proof of the pilot plant representativity.

The campaign with MEA at 40 wt%, performed without anti oxidation additives, took place from February 2011 to June 2011. This campaign represented a challenge because MEA 30 wt% is considered as the reference process and a process using MEA at 40 wt% has not been operated at such a big scale by any competitors in the field of CO_2 post-combustion capture technologies.

A first part of the test campaign corresponded to a parametric optimization for the key process parameters such as:
– stripper pressure – 1.6/1.8 and 2.0 bar (a),
– lean loading variation,
– capture rate 80%, 90% and 95%,
– flue gas flow rate variation – from 3 000 to 12 000 Nm^3/h,
– packing height variation in absorber and stripper columns.

For all these parametric studies, the process has been optimized with respect to energy consumption and techno-economic analysis including Capex evaluation, specially for packing height experiments. Some of the results obtained are illustrated in Figures 11, 12 and 13.

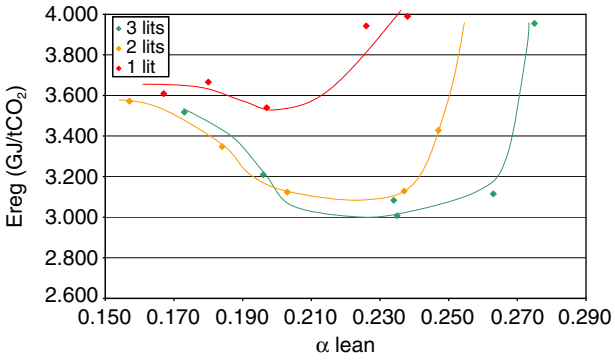


Figure 12

Packing height optimization in the absorber column for MEA 40 wt% at 90% capture rate.

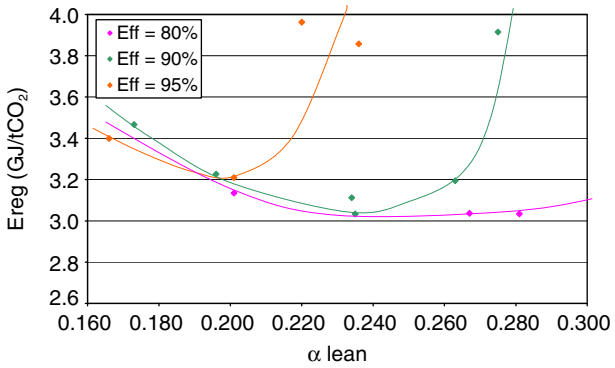


Figure 13

Lean loading optimization for different process efficiencies for MEA 40 wt%.

Figure 11 shows a series of tests performed at 90% capture rate to optimize the lean loading of the solvent for different stripper conditions (pressure). These tests allowed to determine an optimum lean loading around 0.22 and 0.24 depending of the stripper pressure. Moreover it can be seen on the graph that the higher the pressure is in stripper, the larger will be the stable operation range for the process. The drawback of operation at high stripper pressure will be an increase in the degradation rate of the solvent as temperature will be higher (over 125°C the thermal degradation for MEA 40 wt% starts to be not negligible).

Figure 12 shows another series of experiments performed still at 90% capture rate as the reference efficiency for the process. These tests aimed at optimizing the packing height in the absorber column, meaning optimizing the investment costs of the technology. For 3 different packing heights, the lean loading was optimized to minimize the energy consumption of the unit.

As expected, it is observed that for a high packing height, the lean loading is still optimum around 0.22-0.24. When the height of packing were decreased to an intermediate value, no variation of the lean loading optimum was observed and no significant increase on the energy requirement at the optimum was observed. When the height of packing was decreased to the smallest value, we observed first an increase of the energy requirement, meaning that such a gain in investment costs starts to increase operating costs. Then we observed a slight move of the lean loading around 0.20, meaning that it is possible to compensate slightly the decrease of effective area by increasing the reactivity of the solvent by a better regeneration.

In Figure 13, the lean loading was again optimized but for different capture rates. We can observe that for efficiency, the optimum lean loading increased to 0.26 (80% capture rate) whereas for high capture rates (95%) the optimum lean loading decreased around 0.2. One can also notice on this graph that the optimized energy consumption is higher for high capture rates.

2.2 Results of Pilot Plant Tests – Process Performances Validation

After the parametric campaign, the optimized operating conditions were fixed and validated during a long run test. The test conditions and results are the following (see also *Fig. 14* and *15* for main parameters trend):

Parameters:

- flue gas flowrate: 12 033 Nm^3/h,
- solvent flowrate: 32.3 m^3/h,
- stripper pressure: 1.8 bar(a),
- test duration: 380 h.

Results:

- CO_2 production: 2 327 kg/h,
- efficiency (capture rate): 89.7%,
- energy consumption: ~3.02 GJ/tCO_2,
- solvent loadings: α lean = 0.23, α rich = 0.48.

These results proved the interest of this MEA 40 wt% process, with a reduced energy penalty at the reboiler down to around 3 GJ/tCO_2. It can be considered today as one of the best proven and simple solution in terms of energy consumption per tons of CO_2 avoided (proven during 380 h with a total CO_2 captured around 900 tons). Moreover, this MEA 40 wt% process is reliable, well known (same operation than standard MEA 30 wt% process), easy to operate. However, the major drawback of this process is

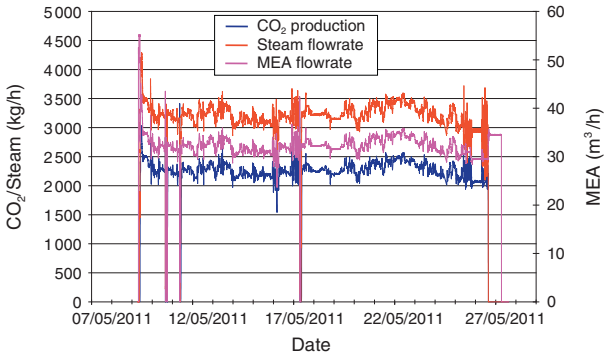


Figure 14

Parameters trend for MEA 40 wt% – long run test.

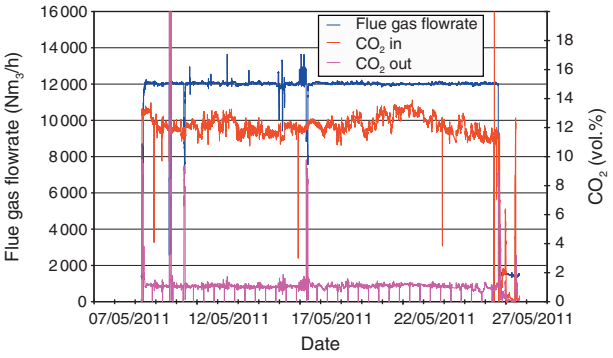


Figure 15

Parameters trend for MEA 40 wt% – long run test.

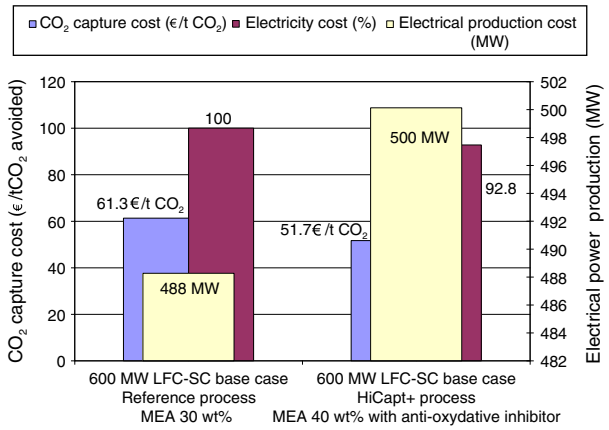


Figure 16

Technico-economic comparison between standard MEA 30 wt% process and HiCapt+TM process.

the high solvent degradation, significantly more than for MEA 30 wt%. That is why *IFPEN* and *PROSERNAT* have developed degradation inhibitors with the HiCapt+TM process.

2.3 Process and Techno-Economical Evaluation of the HiCapt+TM Process

Computed simulations with the HiCapt+TM 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. The simulations showed an energetic penalty around 9 points (compare to 10.5 for the reference process) and an energetic consumption between 3.1 to 3.3 GJ/tCO_2 avoided which places HiCapt+TM among the most energy effective process technologies for CO_2 removal from flue gases. A technico-economic evaluation of HiCapt+TM 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 16. It has to be noted that prices indicated are functions of many parameters like coal price, reference year for investment estimation (2008), limit of the process (included CO_2 compression), so the absolute value is difficult to compare with others studies. It should be noted as well that HiCapt+TM technology is based on cheap and widely available chemicals as solvent. And even with duplex steel (a family of stainless steel) the CAPEX is still competitive because mechanical properties are better than for austenitic stainless steel and enable the reduction of total weight of material.

3 A NEW AND EFFICIENT SOLUTION FOR CO_2 CAPTURE: HICAPT+TM PROCESS

As explained previously, the Brindisi pilot plant tests confirmed the interest of the process in terms of energy penalty and operability. However solvent degradation must be controlled in order to operate this process at full scale and decrease degradation and by products emissions. After an extensive research and tests of a large number and types of chemicals, *IFPEN* has developed and selected the most efficient inhibitors. Among all tests, corrosion tests have shown that most inhibitors are quite corrosive in hot conditions for some steels such as carbon steels or stainless steels but they have also demonstrated what specific material to be used in some specific hot parts of the process with the HiCapt+TM solvent. Nevertheless, specific materials are identified and have been tested with really good results, that is to say less than 5 or 10 μm/an of corrosion speed.

The degradation inhibitors used by the HiCapt+TM process being not fully compatible with the material of hot parts of the Brindisi industrial pilot plant which is built in austenitic 316L stainless steel, only the "process" part corresponding to the increase of concentration to 40 wt% MEA has been tested in Brindisi. Complete test of HiCapt+TM process in the Brindisi pilot plant would require some modifications in some specific hot parts of the unit, which is not yet planed.

Regarding the experiments done in the *IFPEN* lab, we are totally confident concerning the degradation limitation, and for the performance of the future HiCapt+ process. Moreover we could add that the HiCapt+TM solvent will be tested shortly in a mini pilot at *IFPEN* including a complete absorber/stripper loop and with correct material.

CONCLUSION

Robustness, stability, reliability and process performance of HiCapt+TM process (using MEA at 40 wt%) have been proven during the pilot tests with *ENEL*. Among other performance, it was demonstrated that an energy at the reboiler as low as 3 GJ/tCO_2 avoided can be steadily achieved with 90% CO_2 capture. A simulation tool including in-house models has been successively cross checked and validated by the huge number and large range of experimentations obtained on the industrial pilot unit.

Regarding degradation, anti-oxidative additive efficiency is clearly proven by lab tests done at *IFP Energies nouvelles*. Reliability of corrosion lab tests is confirmed

by good agreement between lab results and pilots results (Castor or Brindisi). Corrosion *IFP Energies nouvelles* lab tests have identified materials in order to operate HiCapt+™ process safely.

HiCapt+™ process could offer an efficient solution for CO_2 capture:

- low energy consumption, around 3 GJ/tCO_2,
- low solvent degradation with efficient inhibitor (*IFP Energies nouvelles* and *PROSERNAT* tests only),
- safe material design,
- very large flexibility,
- reliable and easy to operate.

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 proposed for demonstration unit.

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