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New IFP optimized first generation process for post-combustion carbon capture : HiCapt+ TM

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Abstract

It is now well known that "first generation" MEA based post-combustion carbon capture process requires 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, has developed HiCapt+ process, based on a conventional MEA but using high performance oxidative inhibitors and higher amine concentration. This inhibition enable to increase the solvent concentration without corrosion or degradation problems and lead to reduction of the regeneration energy demand due to flow rate reduction. Moreover, the huge reduction of solvent degradation avoids the difficult management of reclaiming unit, as well as avoiding high concentration of degradation product in the treated flue gas, like NH3.

Moreover this process will be tested next year in 2010 in the ENEL pilot plant of Brindisi.

Keywords : CO2, post combustion, MEA, additive, HiCapt+ TM, first generation, post-combustion, IFP, Prosernat

1. A new solution for CO2 Capture : 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 and PROSERNAT, have developed **HiCapt+™ process**, based on a conventional MEA but using high performance oxidative inhibitors and higher amine concentration.

1.1. 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

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European project Castor (3) has demonstrated the good operability, 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 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 very large (approximately 1 t/h of CO_2 captured).

However, the high energy consumption is a major drawback of this type of processes. This 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.

1.2. 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 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 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.

1.2.1. 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 equipment. Based on extensive R&D and operational industrial feed back, PROSERNAT and IFP 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 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

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 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 is 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 (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 5M MEA, the coupons were removed for visual observation and corrosion rate evaluation.

With all these experiments (internally at IFP or during Castor project) we have now a clear view of corrosion in the HiCapt+™ process and more generally MEA based processes. For carbon steel, results are resumed in the 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 HiCapt+™ process.

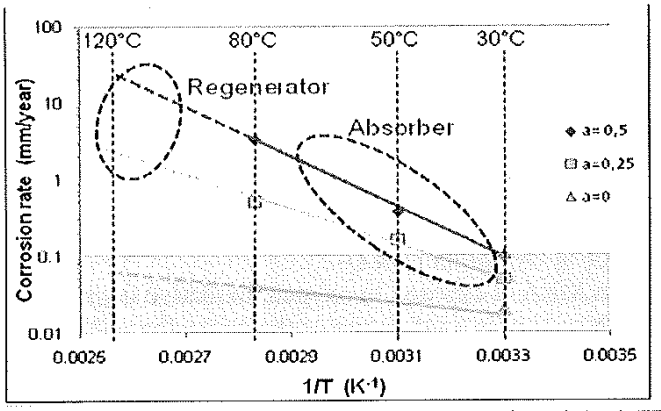

Figure 1 : Corrosion speed for carbon steel in aqueous 30% weight MEA solvent versus process parameters (temperature and loading (a))

Identical tests done with stainless steel show corrosion speed lower than 10 µm/year in all the process conditions. So that 's why the HiCapt+™ process is designed with equipment made of stainless steel.

1.2.2. 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 900 000 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

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

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

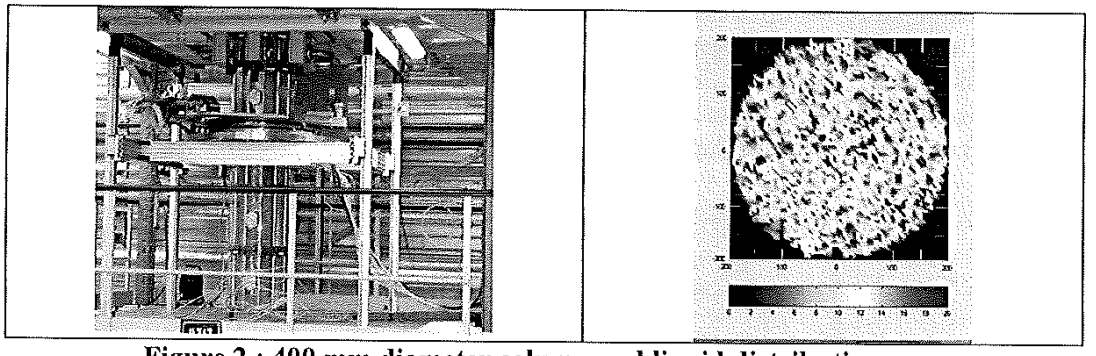

Figure 2 : 400 mm diameter column and liquid distribution map obtained with gamma tomograph

1.2.3. 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 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 are done in IFP (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.

the concentration of the main HSS resulting from degradation in the sample collected after 12 days of degradation test in IFP lab. Il 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 the 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.

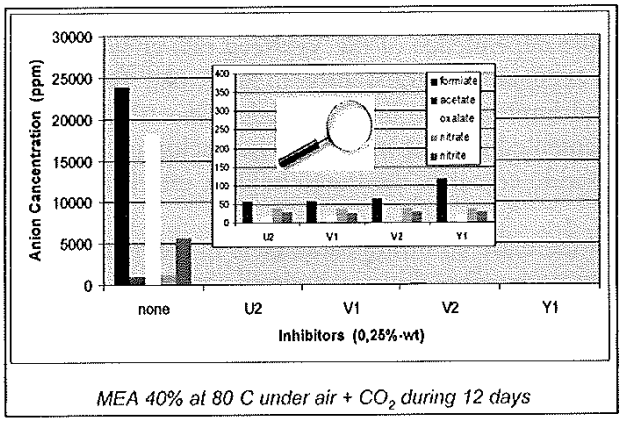

Figure 3 : Concentration of HSS in solvent using different inhibitors

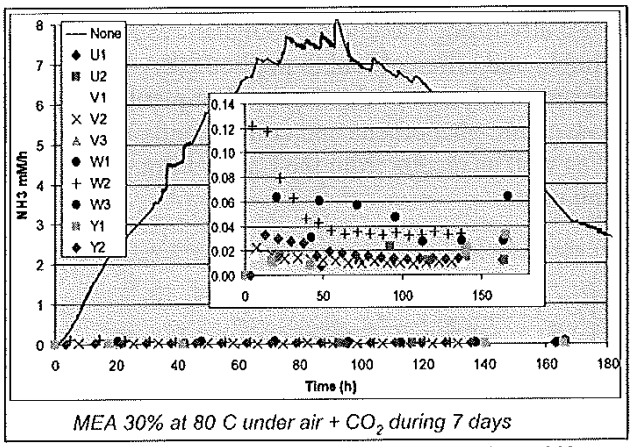

Figure 4 : Concentration of NH_3 in the outlet gas for different inhibitors

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 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.

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 created 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 lab. Heat of formation and heat capacity data were adjusted. 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). 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 IFP. Correlations developed by IFP were used to calculate the liquid holdup, interfacial area and the liquid film mass transfer coefficient.
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 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. 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.

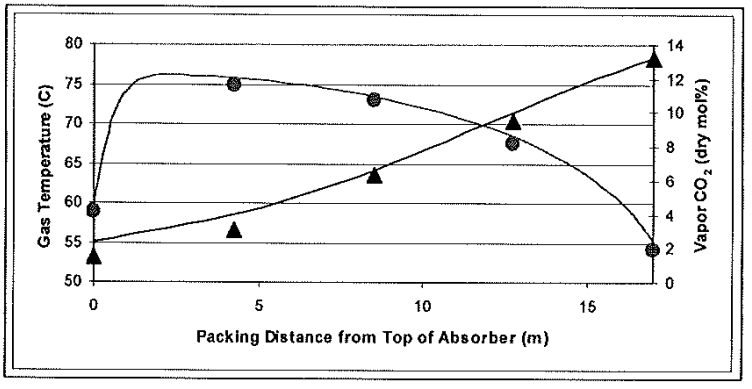

Figure 5 : Comparison of HiCapt+™ model results with data of Castor pilot plant

1.4. 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 (compare to 10.5 for reference process) and an energetic consumption between 3.1 to 3.3 GJ/ t CO_2 avoided which places HiCapt+™ 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

investment estimation (2008), limit of the process (included CO_2 compression), so the absolute value is difficult to compare with others processes.
Please note as well that HiCapt+™ technology is based on cheap and widely available chemicals.

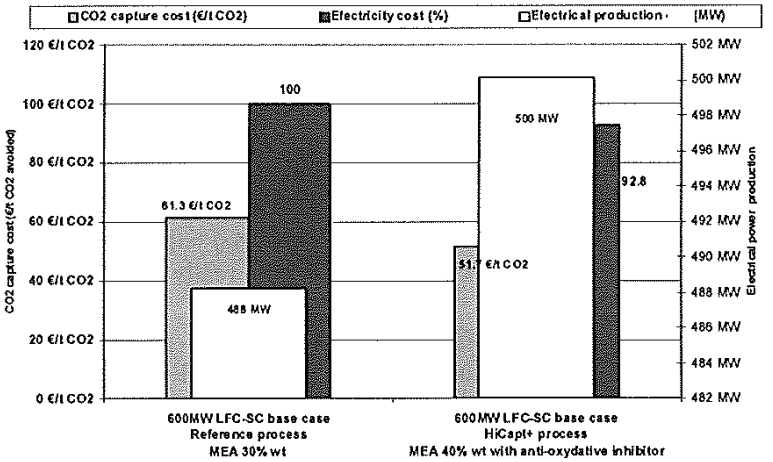

Figure 6 : technico-economic comparison between standard MEA 30 % wt process and HiCapt+™ process

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

In 2009, an agreement between ENEL and IFP was signed in order to collaborate in the field of CO_2 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 is planned 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 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.

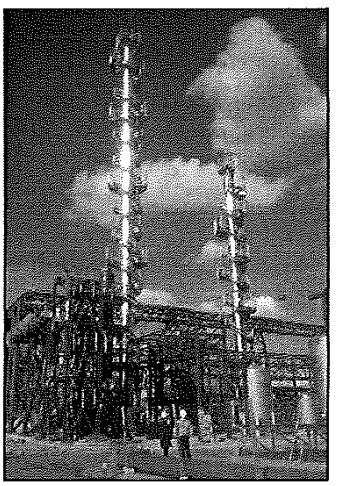

Figure 7 : Picture of the ENEL pilot for CO_2 capture in Brindisi (ITALY)

IFP and PROSERNAT have developed an optimized CO_2 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 O_2. 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 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 CO_2 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+™ CO_2 capture process technology, its further relevant experience in CO_2 dehydration (Prosernat provided TEG CO_2 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.

Thanks

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