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Application of the DMXTM CO₂ Capture Process in Steel Industry

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Abstract

The VALORCO project coordinated by ArcelorMittal and funded by ADEME aims at reducing and valorizing CO₂ emissions from steel industry. This paper presents the main results of task 1.1A of the VALORCO project dedicated to CO₂ capture on blast furnace gases by means of amine scrubbing technologies. Blast furnace gases are characterized by high CO₂ and CO partial pressures and the absence of oxygen. Since few literature data are available on the effect of CO on solvent degradation and CO₂ absorption, experimental work was needed. In this context, three IFP Energies nouvelles (IFPEN) processes initially developed for CO₂ capture on coal power stations were evaluated for blast furnace applications: HicaptTM process (MEA 30 wt.%), Hicapt+TM process (MEA 40 wt.%) and DMXTM process (Demixing solvent).

For the three processes, it was shown that CO absorption is slow and mainly physical even though kinetic studies highlighted a chemical absorption of CO in CO₂-free amine solutions, especially for MEA solvents. This chemical absorption is however largely inhibited in presence of CO₂ which limits this phenomenon to occur in real process conditions. Degradation studies in batch reactors showed a low impact of CO on MEA solutions and no quantitative effect on DMX solvent. Compared to flue gases containing oxygen, amine degradation observed with blast furnace gases is globally negligible for all tested solvents. Above conclusions were confirmed with two long-run tests (~1500 h) on a CO₂ capture mini-pilot at IFPEN. These tests also underlined a high CO₂/CO selectivity with very few CO in CO₂ produced, the possibility of reaching high CO₂ capture rate (>99.5 %) and the good operability for all studied processes. Moreover, DMX solvent allows using carbon steel as process metallurgy and producing CO₂ at 6 bara which turn into subsequent economical savings. Considering an available steam at 21 €/t, it would be possible to produce CO₂ from blast furnace gases at around 40 €/t by using the DMXTM process.

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Keywords: CO₂ capture ;CO; amines based solvents ; MEA ; DMX; two-phase solvents ; process evaluation ; blast furnace, steel industry

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1. Introduction

Steel production is mainly achieved through the use of blast furnaces that convert iron-ore into crude iron at high temperature (1800 – 2200°C) using carbon and air [1]. The combustion of carbon at such high temperatures leads to the production of carbon monoxide (CO) which aims at reducing iron oxides and thus obtaining desired crude iron. However, the oxidation of CO leads to CO₂ and this process is necessarily associated with a CO₂ production. On average, 1.8 tonnes of CO₂ are emitted for every tonne of steel produced. According to the International Energy Agency, the steel industry accounts for approximately 6.7% of total world CO₂ emissions [2].

The VALORCO project coordinated by ArcelorMittal and funded by ADEME aims at reducing and valorizing CO₂ emissions from the steel industry. This paper presents the main results of task 1.1A of the VALORCO project dedicated to CO₂ capture on blast furnace gases by means of amine scrubbing technologies. Blast furnace gases are characterized by high CO₂ and CO partial pressures and the absence of oxygen. Since few literature data are available on the effect of CO on solvent degradation and CO₂ absorption, experimental work was needed. In this context, three IFP Energies nouvelles (IFPEN) processes initially developed for CO₂ capture on coal power stations were evaluated on blast furnace gases : HicaptTM process (MEA 30 wt.%), Hicapt+TM process (MEA 40 wt.%) and DMXTM process (Demixing solvent).

2. CO₂ capture processes

2.1. HiCaptTM and HiCapt+TM processes

HiCaptTM and HiCapt+TM processes developed by IFPEN and licensed by PROSERNAT use, respectively, an aqueous solution of MEA 30 wt.% and 40 wt.%. MEA is the most widely investigated solvent for a carbon dioxide post-combustion capture process. MEA is cheap, largely available, non-toxic; it rapidly reacts with CO₂ and exhibits an interesting cyclic capacity [3]. However, the high energy consumption and the low thermal and chemical stability of MEA are generally the major drawbacks of this type of processes.

2.2. DMXTM process

The DMXTM process is based on the use of specific solvents which are characterized by a critical solubility temperature (LCST) above which two non-miscible liquid phases form [4, 5]. This LCST depends on both CO₂ loading and solvent composition. The solvent used in the DMXTM process is a blend of amines which can be optimized depending on industrial application or targeted performances. The following criteria are generally looked for [6]:

- A LCST slightly higher than the maximum temperature possible in the absorber, so that only one liquid phase exists during CO₂ absorption. This avoids any liquid/liquid mass transfer limitation.
- A CO₂ concentration significantly higher in the heavy liquid phase than in the light phase, so that only the heavy phase is sent to the stripper.
- An optimum between kinetics performances and thermodynamic properties (CO₂ heat of reaction and capacity).

The DMX solvent formulation is therefore a trade-off between above objectives. Besides, DMX solvent is not corrosive, which usually enables the use of low grade, low cost carbon steel. The DMX solvent also offers a very good thermal and chemical stability [6]. This property makes possible the stripper operation under high temperature conditions and by consequence high pressure: so, CO₂ may be produced in pressure up to 6 bara.

Fig. 1 shows the process flow diagram of the DMXTM process. From a MEA based classical scheme, the main difference is the presence of a decanter (V-302) that separates the heavy phase (Stream 21) from the light phase (stream 20). The heavy phase, highly concentrated in CO₂, is sent to the stripper (C-301) in order to be regenerated.

The light phase that contains a low amount of CO₂ is re-combined with regenerated phase (Stream 25) before the overall solvent (Stream 26) is recycled back to solvent tank (T-101) and then sent to the top of absorber (C-201).

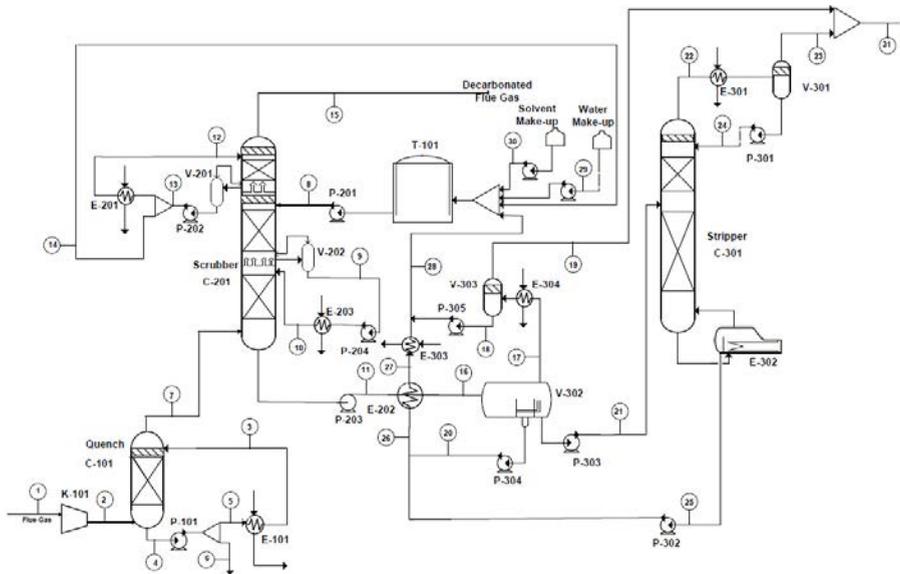


Fig. 1: Typical process flow diagram of the DMXTM process

3. CO₂ capture cases

In task 1.1A of the VALORCO three CO₂ capture cases are considered (see Fig. 2 and Fig. 3):

- Top Gas Recycle (TGR): Blast furnace gases are sent to CO₂ capture unit and purified gases that contain reducing gases (CO and H₂) are re-injected in the blast furnace.
- Blast Furnace (BF): Blast furnace gases are sent to CO₂ capture unit and purified gases are burned in a power station.
- Power Station (PWS): Blast furnace gases are sent to a power station and CO₂ capture is performed on resulting flues gases.

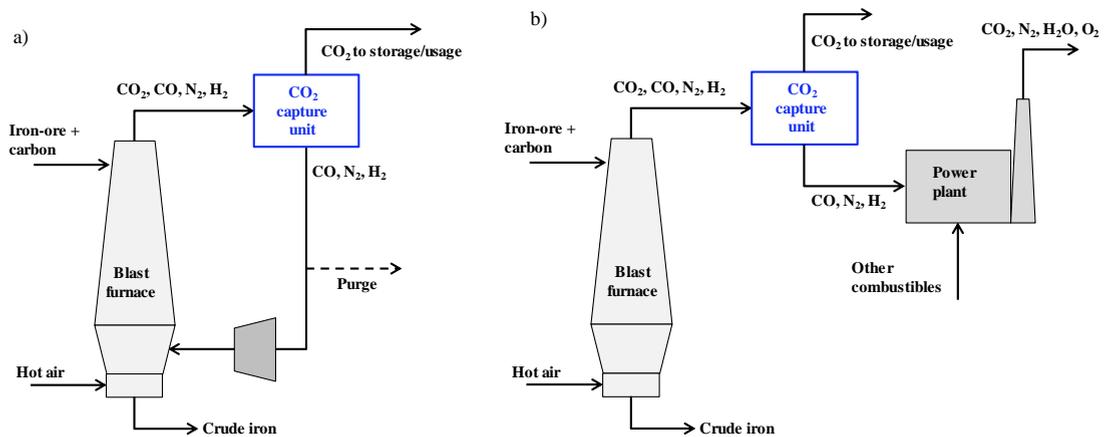
Detailed gas characterizations of above CO₂ capture cases are given in Table 1. Flue gases from the “Power Station” case are very similar to classical exhaust gases from a coal power station [4]: they are delivered slightly below atmospheric pressure, are water saturated and mainly contain N₂ (63.4 vol.%) with CO₂ (27.1 vol.%) and O₂ (2.42 vol.%). As for coal power plant, DeNO_x and DeSO_x processes will be required upstream CO₂ capture unit to avoid excessive solvent degradation. In previous studies [3, 6], HiCaptTM (MEA 30wt.%), HiCapt+TM (MEA 40wt.%) and DMXTM processes were extensively studied by IFPEN on coal power plant flue gases and thus, task 1.1A of the VALORCO project mainly focuses on TGR and BF cases.

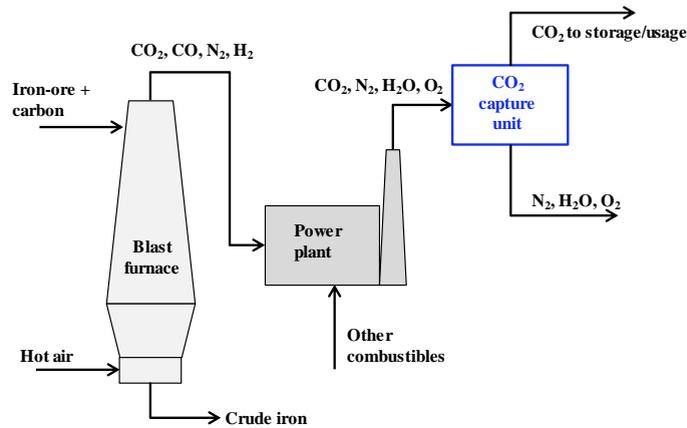
The “Top Gas Recycle” and “Blast Furnace” cases differ in many points from the “Power Station” case: gases are at higher pressure (2.15 – 3 bara), contain high levels of CO (25 – 47 vol.%) whose effect on solvents is not well-known, no oxygen and very low quantities of SO_x and NO_x. Moreover, CO₂ partial pressures are high (0.5 – 1.1 bara) which will lead to a fast absorption. Experimental and simulation work were therefore needed to accurately evaluate IFPEN processes on such cases.

Table 1. Description of CO₂ capture cases

Parameter	Unit	Top Gas Recycle	Blast Furnace	Power Station
Flowrate	Nm ³ /h	245 000	390 000	541 700
Temperature	°C	30	80	126.9
Pressure	bara	3.0	2.15	0.99
CO ₂ capture rate targeted	%	> 99	90	90
H ₂	vol. %	7.04	4.45	-
N ₂	vol. %	9.21	46.7	63.35
O ₂	vol. %	-	-	2.42
CO	vol. %	46.71	25.15	-
CO ₂	vol. %	37.04	23.70	27.10
H ₂ O	vol. %	-	-	7.13
Sum	vol. %	100.00	100.00	100.00
SO _x	vol. ppm	0.9	0.9	57
NO _x	vol. ppm	1.0	1.0	7664
H ₂ S	vol. ppm	76	76	-
BTX	vol. ppm	100	100	-
HCN	vol. ppm	0.2	0.2	-
HCl	vol. ppm	0.1 - 5	0.1 - 5	-
Hg	vol. ppm	9.10 ⁻⁴	9.10 ⁻⁴	-
HAP	vol. ppm	700	700	-
Dust Content	mg/Nm ³	5	5	5

Impurities are present in “Top Gas Recycle” and “Blast furnace” cases. However, they will not be covered in this study as they can be considered either as negligible or easily removable with inexpensive method. For instance, HAP and BTX can be captured on solid adsorbents upstream amine scrubbing process.

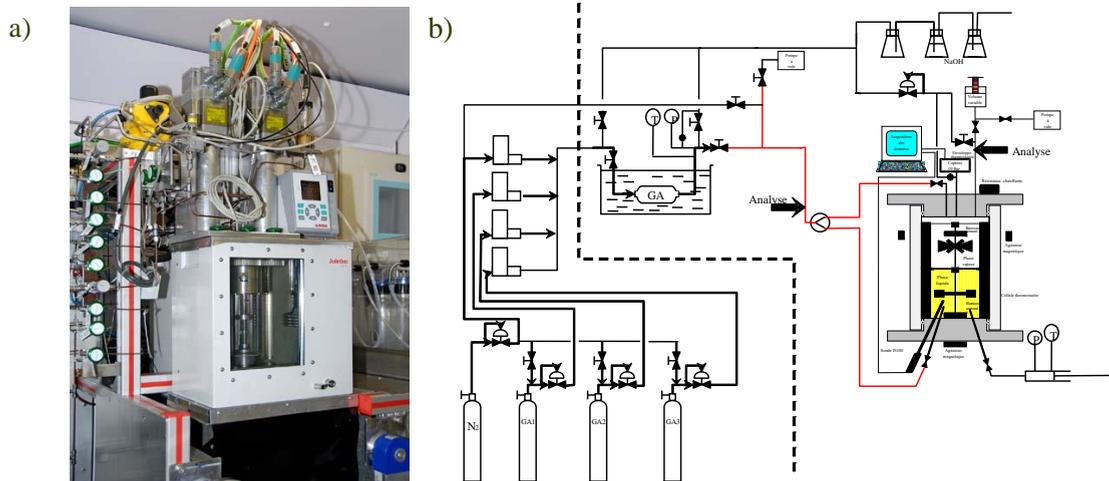
Fig. 2: CO₂ Simplified process scheme of Top Gas Recycle case (a) and Blast Furnace case (b)

Fig. 3: CO₂ Simplified process scheme Power Station case.

4. Experimental studies

4.1. Kinetic

CO absorption experiments in different alkanolamines were carried out in a Lewis Cell (Fig. 4). Due to its low value of liquid mass transfer coefficient, the Lewis Cell is more suitable for slow kinetic systems. The thermostated glass reactor (Fig. 4) is provided with a Rushton turbine in liquid phase, a propeller in gas phase, and four vertical baffles to avoid vortices formation. A horizontal ring is put at the gas-liquid interface to set both liquid level and interfacial area constant. To control reactor temperature, the whole cell is placed inside a thermostated oil bath. Reactor internal diameter and volume are respectively 6.0 cm and 375 cm³. Stirrer diameter is 3.4 cm and the constant interfacial area is 11.7 cm².

Fig. 4: Lewis Cell CO₂ photography (a) and simplified scheme (b)

Experiments are carried out at 40°C and 80°C. For classical CO₂ absorption experiments in the Lewis Cell, pure CO₂ is injected in the partial pressure range of 100-800 mbar, with stirrer speed of 100 rpm. These conditions allow to satisfy fast kinetic regime assumption [11]. For CO absorption, the mass transfer rate is much lower than for CO₂.

Thus pure CO is injected at a maximum pressure of 5 bara to maximize mass transfer in this device. The stirrer speed in liquid phase is also increased to 200 rpm, without exceeding this value in order to maintain a constant interfacial area. To reach a sufficient amount of CO absorbed in liquid phase, each experiment lasts 18 hours.

Gas-liquid mass transfer rate of CO is measured by the variation of pressure over time after CO injection. The interpretation of the total pressure evolution is based on Whitman's double film theory [12], which takes into account the coupling between mass diffusion of chemical species and reaction into a liquid film near the gas-liquid interface. The global mass transfer coefficient K_G is given by :

$$\frac{\partial \ln(P_{CO} - P_{CO}^*)}{\partial t} = -K_G \cdot \frac{A \cdot RT}{V_G} \quad (1)$$

Where A (m^2) and V_G (m^3) are the interfacial area and the volume of gas phase, respectively. K_G ($mol \cdot Pa^{-1} \cdot m^{-2} \cdot s^{-1}$) is the inverse of the sum of gas and liquid sides mass transfer resistance (k_G and $K_{G,l}$ respectively):

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{K_{G,l}} \quad (2)$$

Due to the injection of pure CO in reactor, there is no mass transfer resistance in gas phase. So the global mass transfer coefficient in the liquid phase $K_{G,l}$ can be written according to equation (3). It has to be noted that CO absorption is so slow that even using a dilute gas, the gas side resistance would have been negligible compared to the liquid side resistance.

$$K_G = K_{G,l} = \frac{E \cdot k_L}{H_{CO}} \quad (3)$$

Where H_{CO} ($Pa \cdot m^3 \cdot mol^{-1}$) is the Henry constant, ratio between the partial pressure of CO and the concentration of molecular CO in the liquid phase, and E is the Enhancement factor. The mass transfer coefficient in the liquid phase k_L ($m \cdot s^{-1}$) was characterised with N_2O absorption experiments in an aqueous solution of MDEA. The values of k_L in the Lewis Cell vary between $0.5 \cdot 10^{-5}$ and $3 \cdot 10^{-5} m \cdot s^{-1}$.

4.2. Degradation

Degradation tests were performed in a Solvent Degradation Rig (SDR) composed of 6 stirred reactors in parallel (Fig. 5). They are working in semi-batch mode which means that liquid remains in the reactor but gases can flow through it. All reactors are totally independent from one to another and can be operated up to 5 bara and 150°C. At the outlet of each reactor, gases are collected in a multi-way valve which distributes them either to vent or to an on-line FTIR analyzer Gasmet DX4000. The selector valve is controlled by a program developed by IFPEN and infrared analyzer is managed by the Calcmet software. Test parameters are programmed, controlled and continuously recorded via a software which manages all temperatures (liquid phase, gas phase condenser head and hot shell), pressures, agitation, and gas flowrates.

MEA 40 wt.% solution and DMX solvent were selected for the degradation studies. Table 2 gives the operating conditions applied on both solvents:

- “ $N_2/CO_2/CO$ ” conditions which aim at simulating TGR case.
- “ N_2/CO_2 ” conditions whose objective is to clearly identify the impact of CO on TGR case by replacing it with inert gas (N_2).
- “ $N_2/CO_2/O_2$ ” conditions which allow comparing the effect of CO ($P_{CO}=1.4$ bara) and O_2 ($P_{O_2} = 0.16$ bara) on amine degradation during absorption step while maintaining the same CO_2 partial pressure.



Fig. 5: Solvent degradation set-up photography

For all experiments, the same temperature, pressure and duration were applied for the absorption step (60°C, 3 bara and 60 min), the regeneration step (150°C, 5.5 bara and 90 min) and pause step (60°C, 5.5 bara and 90 min). The temperature and pressure of regeneration step were set to values close to DMXTM process. For MEA solvent, the same conditions were applied in order to compare both solvent in the same conditions even if they are less representative of HiCapt^{+TM} process. All experiments were performed with 100 g of solvent in each reactor, a stirrer speed of 1000 rpm and a total duration of 340 h (Around 85 cycles).

Table 2. Operating conditions applied during degradation test.

	Step	Duration (min)	Air (NL/h)	N ₂ (NL/h)	CO (NL/h)	CO ₂ (NL/h)	T (°C)	Total pressure (bara)
N ₂ /CO/CO ₂	1 Abs.	60	-	0.8	2.3	1.8	60	3.0
	2 Reg.	90	-	32	-	-	150	5.5
	3 Pause	90	-	5	-	-	60	5.5
N ₂ /CO ₂	1 Abs.	60	-	3.1	-	1.8	60	3.0
	2 Reg.	90	-	32	-	-	150	5.5
	3 Pause	90	-	5	-	-	60	5.5
N ₂ /O ₂ /CO ₂	1 Abs.	60	1.2	1.9	-	1.8	60	3.0
	2 Reg.	90	-	32	-	-	150	5.5
	3 Pause	90	-	5	-	-	60	5.5

Table 3 gives the calculated partial pressures of CO₂, CO and O₂ during absorption steps.

Table 3. Partial pressures of CO, CO₂ and O₂ during absorption steps.

	PCO ₂ (bara)	PCO (bara)	PO ₂ (bara)
N ₂ /CO ₂ /CO	1.12	1.40	-
N ₂ /CO ₂	1.12	-	-
N ₂ /CO ₂ /O ₂	1.12	-	0.16

4.3. Long run tests on mini-pilot

In order to confirm degradation conclusions and acquire additional data on a more representative system, two long-run tests (~1500 h) were performed on a CO₂ capture mini-pilot at IFPEN. This mini-pilot is operated on a 24/7 basis to enable long duration tests and thus make quantitative degradation, emissions and corrosion measurements. Fig. 6.b shows a simplified scheme of the mini-pilot in DMX solvent configuration. This unit can be seen as the succession of 3 sections:

- Section 1, not shown on Fig. 6.b, corresponding to the preparation of the synthetic gas where N₂, CO₂, air and three other gases can be injected and mixed in different proportions.
- Section 2, corresponding to the absorption section equipped with a column (C-10) and a condensing system (V-10). The absorption column dimensions are 5.0 cm diameter and 1.0 meter height of structured packing (Sulzer EX).
- Section 3, corresponding to the regeneration step, including heat exchangers, heaters, the decanter in DMX configuration (T-30, V-30) and the stripper (C-20, V-20). The decanter (T-30) is vertical and equipped with a glass window which makes possible the visualization of decantation process. Stripper dimensions are similar to those of absorber. Thermal heat required for solvent regeneration is generated by an electrical device inside the stripper.

Concerning analytical measurements, gases from C-10, V-10, V-20 and V-30 can be analyzed on-line by a Fourier Transform InfraRed Spectrometer (FTIR) in order to quantify major gases (CO₂, H₂O...) and several impurities (NH₃, VOC, other degradation products...). Punctual gas samplings can be performed to cross-check FTIR results with other analytical methods (mainly Gas Chromatography). All gas flowrates are measured with a dedicated counter. Liquid can be sampled and analyzed off-line thanks to 5 Sampling Points ("SP" symbols on Fig. 6b). It has to be noted that due to significant heat losses on the mini-pilot, the accurate determination of thermal energy requirement is not possible.

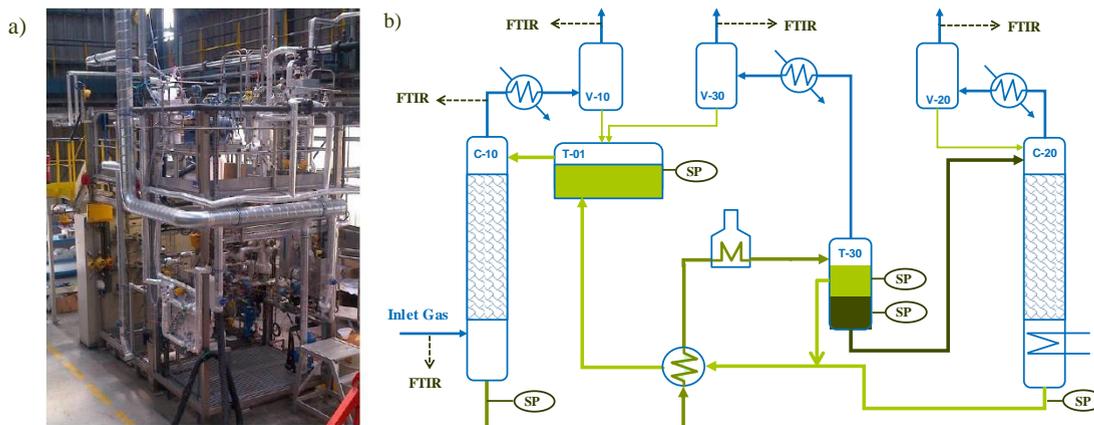


Fig. 6: CO₂ capture mini-pilot photography (a) and simplified scheme in DMX solvent configuration (b)

The two long-run tests were performed on TGR case as it significantly differs from a classical coal power station case (high partial pressure of CO₂ and CO, no oxygen). The first test was operated in Hicapt⁺ process conditions (MEA 40 wt.%) and DMXTM process was tested during the second test. Table 4 shows the characteristics of synthetic gas mixture used to simulate TGR gases. One can see that, H₂ was substituted by N₂ as it behaves as an inert gas and no gas impurities were considered as they can be considered either as negligible or easily removable with inexpensive method upstream absorber. Gas flowrate was limited to 171.3 NL/h due to carbon monoxide security reasons. Since inlet gases are dry, punctual water make-ups were made based on H₂O FTIR measurements

to compensate for water losses at condensers top.

Table 4. Synthetic gas mixture used for mini-pilot experimentations

Parameter	Unit	Value
Flowrate	NL/h	171.3
Temperature	°C	30
Pressure	bara	3.0
N ₂	vol. %	16.25
CO ₂	vol. %	46.71
CO	vol. %	37.04

5. Main experimental results

5.1. Kinetic

Fig. 7 shows the pressure decrease observed during CO and CO₂ absorption cases after injection into DMX solvent in Lewis Cell. Injection of CO was carried out at a pressure of 5 bara in this study to increase the absorbed quantity of CO in the solvent, while CO₂ injection was carried out at 300 mbar. Despite this, one can see that 95% of CO₂ is absorbed in almost 1 hour, while only 5% of CO is absorbed after 20 hours of experiment.

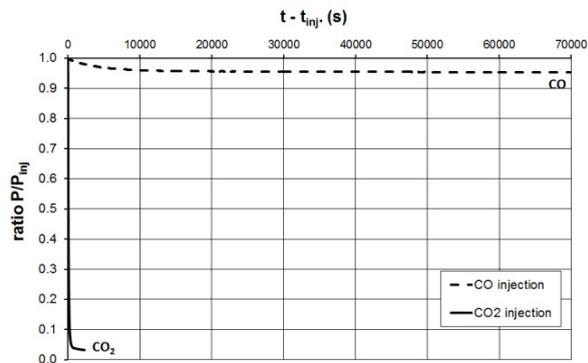


Fig. 7 : Comparison of the pressure decrease observed during CO and CO₂ cases - Lewis Cell conditions: DMX solvent, T = 40°C, 100 rpm, P_{inj}(CO₂) = 300 mbar, P_{inj}(CO) = 5 bara

Mass transfer of CO in Lewis Cell was so low that it was not possible to obtain sufficiently high values of enhancement factor to reach the fast kinetic regime. All the experiments were carried out close to the physical regime. Indeed, the calculated Hatta number for these experiments varies between 0.02 and 0.04, and thus enhancement factors were close to 1. This means that CO reaction occurs not only in the liquid film but also in the liquid bulk [13]. This kind of behaviour is difficult to analyze with an analytical approach. The enhancement factor value depends on both diffusion and chemical reaction of CO in the solvent. Therefore, it is needed to have a rigorous model with a "diffusion – reaction" approach to determine rate constants of the different reactions.

Nevertheless, it is possible to compare and analyze the shape of the experimental curves. Thus, Fig. 8a and 8b show a set of CO absorption experiments into 30 wt.% aqueous solutions of MEA, DEA and MDEA (CO₂-free) at 40°C and 80°C.

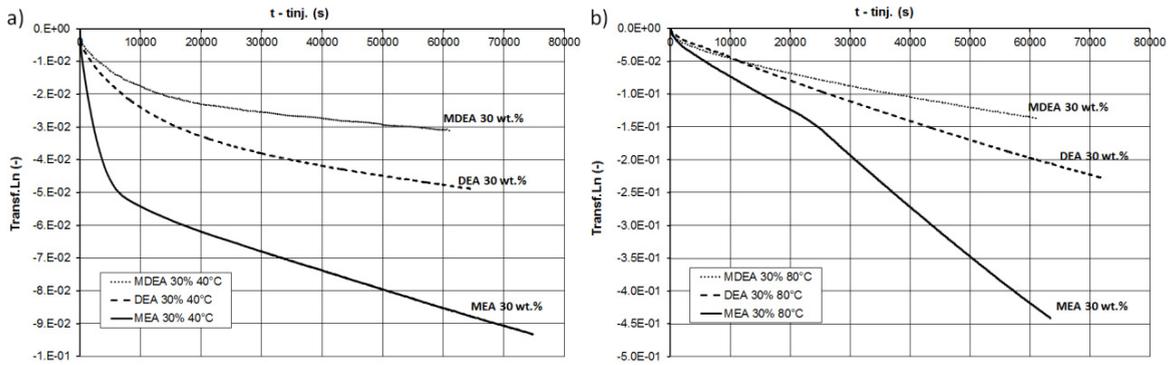


Fig. 8 : Absorption of CO in 30 wt.% aqueous alkanolamines solutions at 40°C (a) and 80°C (b). Effect of the type of amine

As expected, it can be seen that the absorption rate is higher for a primary amine than for a secondary and a tertiary amine. This is consistent with the conclusions of the Jamal's work [7]. According to Jamal, the two main chemical reactions that can occur are:

- Formate formation : $CO + OH^- \rightarrow HCOO^-$
- Direct insertion : $CO + Am \rightarrow AmCO$ (only for MEA and DEA)

Although these reactions are extremely slow, they are irreversible. The AmCO compound could be obtained from the direct insertion of CO into DEA (formyl-diethanolamine) and MEA (formyl-monoethanolamine). MDEA, as a tertiary amine is not expected to react with CO.

For the purpose of the VALORCO project, the two evaluated solvents are MEA 40 wt.% and DMX solvent. A comparison between these two solvents is presented in Fig. 9a and 9b. At the beginning of injection, the decrease of pressure is higher for DMX solvent than for MEA which means that the solubility of CO is higher in the DMX solvent. But during the test, the absorption rate of CO is significantly reduced in DMX solvent compared to MEA. This can be explained by a higher reaction rate of CO with MEA solution than with DMX solvent.

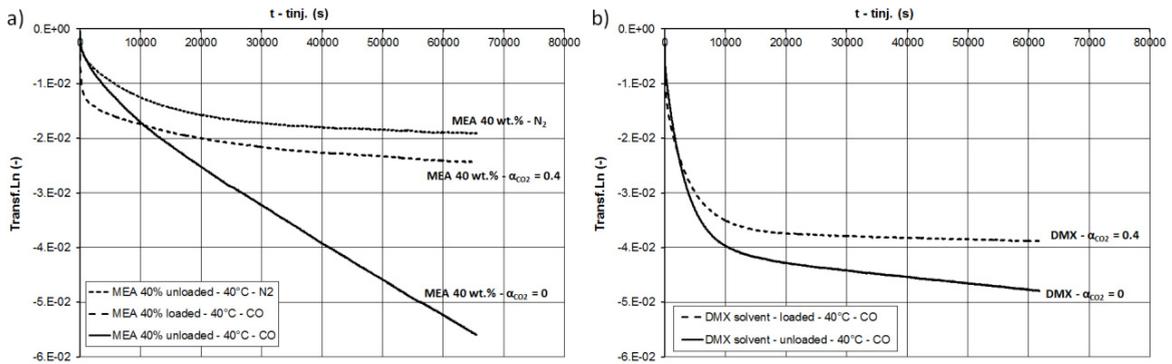


Fig. 9 : Experimental curves of CO absorption at 40°C into unloaded and CO₂ loaded solutions. (a) 40 wt.% MEA ; (b) DMX solvent

This assumption seems to be confirmed with the injection of CO into CO₂ loaded solutions of MEA and DMX. This experiment is interesting since solvents used in an industrial process should be CO₂ loaded. The loading used in this experiment is $\alpha_{CO_2} = 0.4 \text{ mol}_{CO_2}/\text{mol}_{alk}$ corresponding to an average loading for the two solvents in an absorber. It can be seen that the presence of CO₂ in the solvent drastically inhibits the chemical reaction of CO with the amine.

This is probably due to the fact that, at this loading, molar concentrations of free amine and hydroxyl ions in solutions are greatly reduced.

For the DMX loaded solvent (Fig. 9b), the decrease of pressure reaches an asymptotic value and almost no more CO absorption occurs after 10 hours. But the loading effect is not so important since the influence of reaction is not preponderant compared to the physical absorption. For the MEA loaded solution (Fig. 9a), the loading effect is much more visible because chemical reaction is an important part of the CO absorption process with respect to solubility. Moreover, it can be seen in Fig. 9a that the CO absorption curve in the MEA loaded solution has a similar behavior to the one with N₂, for which only physical absorption occurs. From these observations, it can be concluded that absorption of CO should be negligible at industrial scale.

5.2. Degradation

Table 5 gives the amine concentrations measured by gas chromatography in all solutions recovered at the end of ageing experiments. For both “N₂/CO₂/CO” and “N₂/CO₂” conditions, amine concentrations can be considered as constant within analytical uncertainties for MEA and DMX solvents. However, MEA solution appears very sensitive to the presence of O₂ since MEA concentration falls to 27 wt.% after 340 h. These results indicate that the effects of temperature (regeneration step at 150°C) and carbon monoxide on MEA degradation are negligible compared to oxygen impact. The good behavior of DMX solvent under the same oxidant conditions (DMX concentration remains constant) is consistent with previous IFPEN studies [6].

Table 5 : Quantitative GC analyzes of solutions after ageing experiments

	Duration	MEA (wt.%)	DMX (wt.%)
	t = 0	41.3	39.1
N ₂ /CO ₂ /CO	340 h	39.6	41.2
N ₂ /CO ₂	340 h	40.3	38.6
N ₂ /CO ₂ /O ₂	340 h	27.7	38.2

Table 6 gives the Heat Stable Salts (HSS) analyses performed by ionic chromatography. HSS analyses confirm that, under oxidant conditions, MEA is strongly degraded. Indeed, several HSS highly increase, especially formate concentration which rises up to 3700 mg/kg. Important NH₃ emissions were also detected by IR analysis for MEA 40 wt.% under “N₂/CO₂/O₂” conditions. In the absence of oxygen, MEA degradation is much less pronounced.

Table 6: HSS analyzes of solutions after ageing experiments (relative uncertainty = 15%)

		Duration (h)	Glycolate (mg/kg)	Acetate (mg/kg)	Formate (mg/kg)	Propionate (mg/kg)	Nitrite (mg/kg)	Oxalate (mg/kg)	Nitrate (mg/kg)
MEA 40 wt. %	-	t=0	< 50	< 50	28	< 9	< 5	< 9	< 5
	N ₂ /CO ₂ /CO	340	< 50	< 50	280	< 9	< 5	< 9	< 5
	N ₂ /CO ₂	340	< 50	< 50	83	< 9	< 5	< 9	< 5
	N ₂ /CO ₂ /O ₂	340	548	591	3676	< 9	< 5	506	270
DMX	-	t=0	< 50	< 50	54	< 9	< 5	< 9	8
	N ₂ /CO ₂ /CO	340	< 50	< 50	144	< 9	< 5	< 9	10
	N ₂ /CO ₂	340	< 50	< 50	109	< 9	< 5	< 9	< 5
	N ₂ /CO ₂ /O ₂	340	57	< 50	524	< 9	9	< 9	< 5

The presence of carbon monoxide seems to increase the production of formate ions for MEA 40 wt.% : 280 mg/kg are detected at the end of “N₂/CO₂/CO” conditions compared to 83 mg/kg without CO. This increase in

formate ions (HCOO^-) concentration could be due to direct addition of carbon monoxide on hydroxide ion (OH^-) present in solution as described by Jamal [7]. As expected, this reaction seems however more limited with DMX solvent since formate ions slightly increase from 109 mg/kg under “ N_2/CO_2 ” conditions to 144 mg/kg under “ $\text{N}_2/\text{CO}_2/\text{CO}$ ” conditions. All these elements clearly indicate a very low impact of CO on both solvents. In addition, HSS analyzes performed at the end of “ $\text{N}_2/\text{CO}_2/\text{O}_2$ ” test with DMX solvent confirm its good behavior towards oxidant conditions.

Fig. 10 shows CPG qualitative analysis results for the fresh MEA solvent ($t=0$) and the three aged solutions. One can see that degraded compounds are much more abundant under oxidant conditions (“ $\text{N}_2/\text{CO}_2/\text{O}_2$ ” case). Well-known MEA degraded compounds can be identified in Fig. 10.b: HEF, HEA, HEGly, OZD, HEI, HEPO and $M = 176$ which two structural formula are suggested by Gouedard [8]. One interesting observation is that no significant differences can be identified between chromatograms obtained under “ N_2/CO_2 ” or “ $\text{N}_2/\text{CO}_2/\text{CO}$ ” conditions. This clearly means that CO has a negligible impact on MEA degradation. Globally, in absence of O_2 (Fig. 10.c and 6.d), few degraded compounds were detected. The main peak is attributed to an unknown compound (“1?”) which is not present under oxidant conditions (Fig. 10.b). One can suggest that latter compound is consumed in the presence of O_2 . OZD is also detected in Fig. 10.c and 6.d and could be explained by the intramolecular cyclization reaction of MEA carbamate [9].

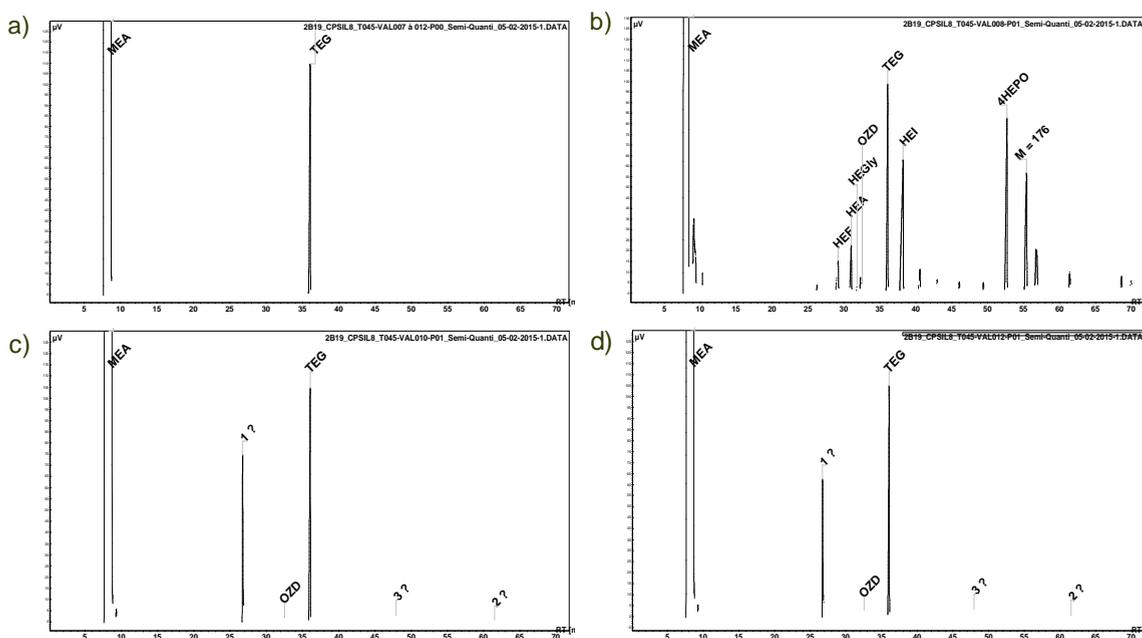


Fig. 10 : CPG Semi-quantitative analysis of fresh MEA solvent (a) and degraded MEA solutions under $\text{N}_2/\text{CO}_2/\text{O}_2$ conditions (b), N_2/CO_2 conditions (c) and $\text{N}_2/\text{CO}_2/\text{CO}$ conditions (d) - TEG is internal standard.

5.3. Long run tests on mini-pilot

Mini-pilot test campaign showed a good operability of both HiCaptTM and DMXTM processes on TGR case. In particular, no issues related to phase decantation or high pressure regeneration were encountered all along DMX long run test. The possibility of reaching high CO_2 capture rate (>99.9%) with both solvents were also proven. From Fig. 11, one can appreciate the stability of amine concentration during the two long-run tests (~37.0 wt.% of MEA and ~ 33 wt.% of total amines in DMX solvent) which is an indication of the good stability of both solvents when treating TGR gases. During MEA test, CO_2 lean loading was maintained to the energetically optimized value of 0.24

molCO₂/molMEA [3] by acting on stripper electric power while varying liquid flowrate to obtain a CO₂ capture rate > 99% and a rich loading close to 0.55 molCO₂/molMEA (thermodynamic conditions). When stabilized, an average liquid flowrate of 1.6 kg/h at absorber top is obtained for MEA solution. During DMX long-run test, liquid flowrate at absorber top was progressively decreased from 2.4 to 1.4 kg/h while maintaining a lean loading of around 0.2 molCO₂/molAmine. One can see that rich loadings up to 1.3 molCO₂/molAmine can be achieved with DMX solvent under these conditions.

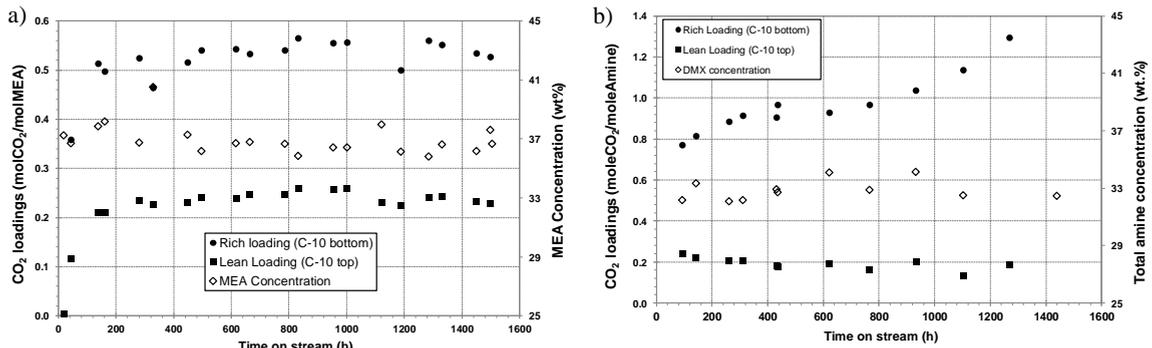


Fig. 11 : Experimental CO₂ loadings and amine concentrations obtained during the two long-run tests on TGR case with MEA 40 wt.% solution (a) and DMX solvent (b)

Table 7 shows mini-pilot emissions measured on TGR case with MEA 40 wt.% and DMX solvent. Results from a previous test campaign performed on coal power station flue gases with MEA 30 wt.% is also given for comparison. All results are given at condensers outlets (V-10, V-20 and V-30, see Fig. 6.b) where temperatures are controlled to around 20-25°C. One can see that NH₃ and solvent emissions at absorber top are relatively low with DMX solvent (around 1-2 vol. ppm, close to FTIR detection limit). In similar conditions, MEA 40 wt.% shows higher emissions than DMX solvent but still much less than MEA 30 wt.% treating coal power station flue gases. In latter case, degradation is largely intensified by oxygen presence (see section 5.2) which explains the high NH₃ emissions. The higher MEA emissions in coal PWS case at absorber top (20 – 40 vol. ppm) is attributed to the presence of SO_x and NO_x in flue gases that promotes aerosol formation [10]. Regarding solvent emissions at stripper or decanter top (after condensers), they are relatively low due to high CO₂ partial pressures that acidify condensed water enabling the chemical absorption of basic compounds like amines. From above consideration, one can conclude that solvent losses through degradation and emissions phenomena seem very limited for both solvents when treating blast furnace gases.

Table 7: Emissions results after 1400 h of mini-pilot operation on TGR case with MEA 40 wt.% and DMX solvent – Comparison with a coal power station case performed with MEA 30 wt.% on the same mini-pilot

	Absorber top (V-10)		Decanter top (V-30)		Stripper top (V-20)	
	NH ₃ (vol. ppm)	Solvent (vol. ppm)	CO (vol. ppm)	Solvent (vol. ppm)	CO (vol. ppm)	Solvent (vol. ppm)
MEA 40 wt.% (TGR)	8 - 12	2 - 5	-	-	375	< 1
DMX solvent (TGR)	1 - 2	1 - 2	560	< 1	< 10	< 1
MEA 30 wt.% (Coal PWS)	50 - 70	20 - 40	-	-	-	3 - 5

Concerning the presence of CO in produced CO₂ (Table 7), an average concentration of 375 vol. ppm (measured by gas chromatography on gas samples) is obtained for MEA 40 wt.% and values of 560 vol. ppm and < 10 vol. ppm are respectively obtained with DMX solvent at decanter and stripper tops. The absence of CO at stripper top with DMX solvent indicates that CO is entirely and easily released in decanter (physical absorption). In DMXTM process, CO₂ from decanter and stripper are re-combined and CO concentration is to be considered in the overall

CO₂ stream. This latter concentration is calculated to be around 360 vol. ppm which is very similar to the value of 375 vol. ppm measured for MEA 40 wt.%. CO capture rate is therefore calculated to be around 0.03% on mini-pilot for both solvents which is far below the CO₂ capture rate of 99.9% obtained all along tests. In addition, thermodynamic calculations based on CO Henry constants showed that the physical absorption of CO is probably not at equilibrium at absorber bottom of the mini-pilot. Indeed, if equilibrium was reached, CO concentration in CO₂ stream would be 2 and 4 times more important for respectively MEA 40 wt.% and DMX solvent. This is consistent with kinetic studies that show a slow physical absorption of CO in CO₂ loaded solutions of amines (section 5.1). Since the absorber of the mini-pilot is over-designed compared to a large scale column, one could expect a decrease of CO concentration in CO₂ produced by an industrial unit. In conclusion, amine scrubbing technologies show high CO₂/CO selectivity which is very interesting since CO₂ produced exhibits a relatively good purity and 99.97% of CO can be recovered and thus valorized.



Fig. 12 : Stripper inlet carbon steel coupons recovered at the end of DMX long-run test (~1500h)

At the beginning of DMX long-run test, two carbon steel coupons were located at stripper inlet where corrosion conditions are the most severe (high temperature, high CO₂ loadings). Fig. 12 shows the good condition of these coupons after 1500 h of operation. Analytical measurements confirmed that corrosion rate is very low and around 5 μm/year. Therefore, this confirms previous IFPN studies [6] on the possibility to use carbon steel for several pieces of equipment in DMXTM process.

6. Process techno-economic evaluation

6.1. Bases of study

Based on experimental results and IFPEN knowledge, HiCaptTM, HiCapt+TM and DMXTM processes were techno-economically evaluated on TGR, BF and PWS cases described in section 3. Below are the main study bases considered for the techno-economic evaluation:

- Steam required to regenerate solvent is produced by a dedicated boiler at 8 bara and 170°C. Steam price (without heat integration with steel facility) was evaluated at 21€/t.
- For all cases, CO₂ is delivered at 6 bara at process battery limits.
- Intercooling absorber systems are implemented on all cases in order to improve process performances.
- Washing columns are considered for BF and PWS cases to decrease inlet gas temperature and reduce some pollutants (dust particles...).
- For PWS cases, blowers are installed upstream washing columns to overcome pressure drops in absorber.
- For TGR cases, recycle compressor required to send gases back to blast furnace is not part of CO₂ capture process battery limits.
- For DMXTM process, carbon steel is considered for several equipment whereas stainless steel 316L is the only metallurgy applied to MEA 30 wt.% and 40 wt.% processes.
- Amine degradation is neglected in all TGR and BF cases. However, this aspect is taken into account for PWS cases based on IFPEN knowledge.
- For all cases, following equipment sizing rules were applied :
 - Temperature approaches for coolers, amine/amine heat exchangers and reboilers are respectively

fixed at 4, 10 and 12°C.

- Maximum reboiler duty is set to 32 MWth
- Due to operational reasons, a maximum of 4 reboilers per regenerator is considered and each regenerator has a dedicated absorber.

6.2. Main results

Table 8 gives the main equipment sizing and total erected costs for all studied CO₂ capture processes. For PWS case, one can see that similar total erected costs are obtained for the three processes (from 65.6 M€ with DMXTM process to 68.9 M€ with HiCaptTM process). This result is consistent with previous process comparison performed by IFPEN on coal power station flue gases [6]. However, for CO₂ capture application on blast furnace gases (TGR and BF cases), total erected cost of DMXTM process is however much lower. Indeed, in comparison to HiCaptTM process, significant reductions of 38% and 23% are obtained with DMXTM process on respectively TGR and BF cases (Table 3). Latter result can be explained by different factors that largely compensate for additional equipment and absorber height increase with DMXTM process:

- The low thermal energy requirement of DMXTM process, the possibility to perform regeneration at high pressure and the reduction of flowrates thanks to demixtion phenomenon lead to have only one regenerator versus two regenerators with MEA processes.
- The high stability of DMX solvent offers the possibility to perform the regeneration directly at 6.0 bara which turns into important investment savings since CO₂ compression is not required contrary to MEA processes where a compressor is needed to raise CO₂ pressure from 1.9 to 6.0 bara.
- Due to their operating pressure (respectively 3 and 2.15 bara for TGR and BF cases) absorbers have a lower contribution to total erected cost in TGR and BF cases compared to PWS case. Therefore, an increase of absorber height with DMXTM process has a moderate impact on final cost result.
- The use of carbon steel for several pieces of equipment with DMXTM process.

Table 8: Main equipment sizing and total erected costs of studied cases

Case	Process	Absorber(s)			Regenerator(s)			Unit
		Number (-)	Diameter (m)	Packing height (m)	Number (-)	Diameter (m)	Packing height (m)	
Top Gas Recycle (TGR)	HiCapt TM	2	3.6	10.5	2	4.8	14.7	41.9
	HiCapt ⁺ TM	2	3.4	10.5	2	4.4	14.5	37.3
	DMX TM	1	5.0	13.0	1	4.5	14.3	25.8
Blast Furnace (BF)	HiCapt TM	2	4.7	10.5	2	4.7	15.0	49.6
	HiCapt ⁺ TM	2	4.6	10.5	2	4.3	15.0	45.9
	DMX TM	1	7.0	24.0	1	4.7	13.7	38.0
Power Station (PWS)	HiCapt TM	2	7.0	10.5	2	6.2	15.0	68.9
	HiCapt ⁺ TM	2	7.0	10.5	2	5.5	15.0	64.7
	DMX TM	2	7.0	25.3	2	4.1	13.8	65.6

Fig. 13 shows that steam energy consumption and CO₂ production cost (steam price set at 21€/t) of a given amine scrubbing process increase when decreasing inlet gas CO₂ partial pressure. This was expected as CO₂ absorption is thermodynamically and kinetically favored by an increase of CO₂ partial pressure. One can notice that CO₂ partial pressure effect is more pronounced on DMX solvent: reductions of 14% and 30% are respectively observed for energy consumption and CO₂ production cost when CO₂ partial pressure is increased from 0.27 to 1.1 bara compared to 8% and 17% decrease for HiCaptTM process in similar conditions. Fig. 13 also highlights the good performances of DMXTM process since thermal energy requirement is reduced by 20-25% compared to HiCaptTM

process and by 13-18% compared to HiCapt+™. This low energy demand combined with an attractive total erected cost (Table 3), make DMX™ process possible to diminish CO₂ production cost by 11 to 15 €/t compared to MEA 30 wt% based process. Considering TGR case and a steam price of 21 €/t, it is therefore possible to produce CO₂ at 6 bara for a price of around 40 €/t with DMX™ process.

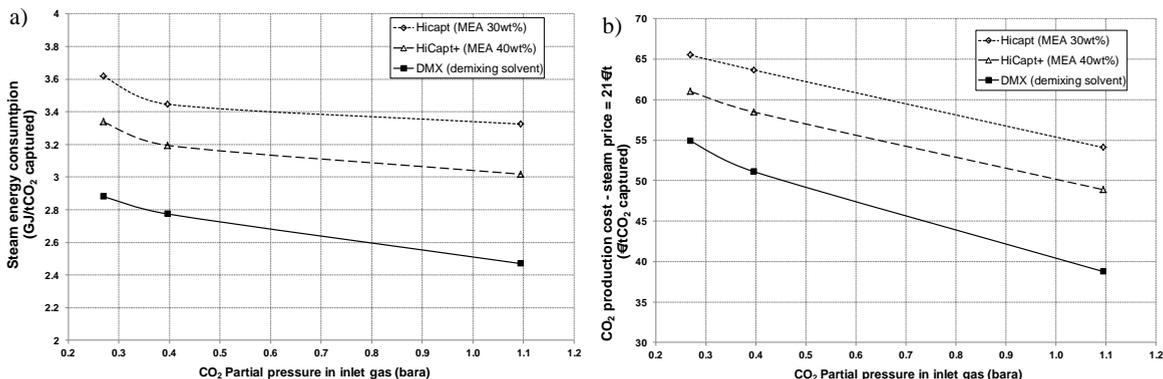


Fig. 13 : Effect of inlet gas CO₂ partial pressure on steam energy consumption (a) and on CO₂ production cost at a steam price of 21 €/t (b) – PP_{CO₂} (TGR) = 1.1 bara / PP_{CO₂} (BF) = 0.4 bara / PP_{CO₂} (PWS) = 0.27 bara

Fig. 14 shows that steam price has a large impact on CO₂ production cost. For instance, a steam price reduction from 21 to 15€/t makes the cost of CO₂ produced by DMX™ process decrease by 17% for studied cases. Based on this observation, heat integration work was performed with ArcelorMittal company in order to reduce steam price. By recovering some heat losses in different locations of steel facility, steam price could be reduced to around 12 €/t allowing the production of CO₂ (@6 bara) at 27 €/per ton with DMX™ process on TGR case.

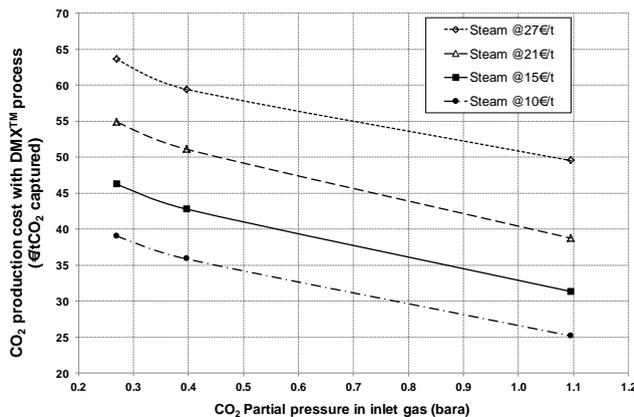


Fig. 14 : Effect of steam price and inlet gas CO₂ partial pressure on CO₂ production Cost (@6 bara) with DMX™ process – PP_{CO₂} (TGR) = 1.1 bara / PP_{CO₂} (BF) = 0.4 bara / PP_{CO₂} (PWS) = 0.27 bara

7. Conclusion

The VALORCO project coordinated by ArcelorMittal and funded by ADEME aims at reducing and valorizing CO₂ emissions from steel industry. This paper presents the main results of task 1.1A of the VALORCO project dedicated to CO₂ capture on blast furnace gases by means of amine scrubbing technologies. Three IFP Energies nouvelles (IFPEN) processes initially developed for CO₂ capture on coal power stations were evaluated for blast furnace application : HiCapt™ process (MEA 30 wt.%), HiCapt+™ process (MEA 40 wt.%) and DMX™ process

(Demixing solvent).

For the three processes it was shown that CO absorption is slow and mainly physical even though kinetic studies highlighted a chemical absorption of CO in CO₂-free amine solutions, especially for MEA solvents. This chemical absorption is however largely inhibited in presence of CO₂ which limits this phenomenon to occur in real process conditions. Degradation studies in batch reactors showed a low impact of CO on MEA solutions and no quantitative effect on DMX solvent. Compared to flue gases containing oxygen, amine degradation observed with blast furnace gases is globally negligible for all tested solvents. Above conclusions were confirmed with two long-run tests (~1500 h) on a CO₂ capture mini-pilot at IFPEN. These tests also underlined a high CO₂/CO selectivity with very few CO in CO₂ produced, the possibility of reaching high CO₂ capture rate (>99.5 %) and the good operability for all studied processes. Moreover, DMX solvent allows using carbon steel as process metallurgy and producing CO₂ at 6 bara which turn into subsequent economical savings. Considering an available steam at 21 €/t, it would be possible to produce CO₂ at around 40 €/t by using the DMXTM process in steel industry. By recovering some heat losses in different locations of steel facility, steam price could be reduced to around 12 €/t allowing the production of CO₂ at 6 bara at 27€/t with DMXTM process.

So DMXTM process is very promising for CO₂ capture on blast furnace gases but it needs now to be demonstrated in an industrial scale pilot plant.

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