

Pilot Plant Studies for CO2 Capture from Waste Incinerator Flue Gas Using MEA Based Solvent

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DOSSIER Edited by/Sous la direction de : P.-L. Carrette

PART 2 Post Combustion CO_2 Capture Captage de CO_2 en postcombustion

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Pilot Plant Studies for CO₂ Capture from Waste Incinerator Flue Gas Using MEA Based Solvent

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Résumé — Étude du captage du CO₂ dans des gaz de combustion d'un incinérateur de déchets à l'aide d'un pilote utilisant un solvant à base de MEA — L'étude évalue la faisabilité du captage du dioxyde de carbone (CO₂) dans des gaz de combustion d'un incinérateur de déchets spéciaux. Un pilote à l'échelle laboratoire a été mis en œuvre pour étudier le procédé d'absorption/désorption du CO₂ par un solvant à base de MonoEthanolAmine (MEA). L'étude a été conduite en laboratoire et sur un site industriel. L'installation expérimentale est instrumentée pour obtenir des bilans de matière avec précision. Une étude paramétrique en laboratoire a permis de mesurer le coefficient de transfert global K_Ga_w pour plusieurs régimes de fonctionnement du pilote. Des expériences de longue durée, en laboratoire et sur site industriel, ont analysé la résistance chimique de la MEA au gaz de combustion d'un incinérateur. Ces expériences ont également permis d'étudier l'absorption du dioxyde d'azote NO₂ et du dioxyde de soufre SO₂ dans le solvant de captage. Elles ont abouti à une estimation de la cinétique d'accumulation de sels stables dans un solvant à base de MEA confronté à des gaz de combustion d'un incinérateur.

Abstract — Pilot Plant Studies for CO₂ Capture from Waste Incinerator Flue Gas Using MEA Based Solvent — Experimental study of carbon dioxide (CO_2) capture from waste incinerator flue gas is presented. A specific pilot plant has been achieved based on absorption/desorption process using MonoEthanolAmine (MEA) solvent. Several experiments have been carried out at laboratory and industrial site. The pilot is fully instrumented to establish precise balances. Laboratory experiments allow to measure overall mass transfer coefficient K_Ga_w for several pilot operating conditions. Long laboratory and industrial runs provide an estimation of MEA chemical resistance against waste incinerator flue gas. The experiments also allowed the analysis of NO₂ and SO₂ absorption through the solvent as well as the accumulation of Heat Stable Salts (HSS) for a full scale CO₂ capture unit fed by a waste incinerator flue gas.

NOMENCLATURE

$K_G a_W$	Overall mass transfer coefficient (mol/Pa.s.m ³)
$P^*_{\mathrm{CO}_2}$	CO_2 partial pressure in equilibrium with the
	solvent (Pa)
$P_{\rm CO_2}$	CO_2 partial pressure (Pa)
V_{pck}	Absorption packing volume (m ³)
Φ_{CO_2}	Absorption rate (mol/s)
M_{ln}	Logarithmic average
MEA	MonoEthanolAmine

- DEA DiEthanolAmine
- MDEA MethylDiEthanolAmine
- CO₂ Carbon Dioxide

INTRODUCTION

The amine process is one of the most mature technologies on account of the industrial use for natural gas treatment in the oil industry (solvent are based on MonoEthanolAmine (MEA) and MethylDiEthanol-Amine (MDEA)). The most used amine is MEA developed by *Fluor Daniel*, *MHI (Mitsubishi Heavy Industries*). Other actors also develop this process in order to adjust it to CO_2 capture from flue gases (*e.g. Alstom* (with *Dow Chemical*), *Prosernat* process (IFPEN)).

Veolia Environnement has a variety of CO_2 emissions with coal combustion plants and waste incinerators. Waste incinerators flue gases have specific composition compared to those from fossil fuel-based. Those specificities are composition and instabilities of flue gas in time related to the large variety of waste (*Tab. 1* for gas specifications and interval of values). Industrial waste incinerator are often close to waste productors. These industrial areas lead to the creation of circular economy. Indeed, CO_2 captured by waste incinerator can be easily reused by other industrial. This is a particular illustration of the concept of industrial symbiosis.

Therefore, the aim of the research program was to validate the technical feasibility of CO_2 capture using MEA on hazardous waste incineration flue gas. Assuming this feasibility, the conventional methods of CO_2 capture with amines could be transposed to all combustion plants of the group without major modification of the combustion unit.

As a first step, a laboratory pilot scale was created with a synthetic combustion gas supply. Then, the pilot laboratory was moved to an industrial plant to validate the operation with real flue gas. In order to observe the behavior of the process related to the use of waste incinerator flue gas, methods have been developed for absorbing pollutants (SO_x , NO_x) and production of stable salts, in terms of mass transfer and degradation of the solvent.

First, the MEA process and the incinerator flue gas characteristics are presented. Second, a description of the pilot laboratory is given and finally the results of the main experimental trials are discussed.

1 CO₂ CAPTURE BY MEA BASED TECHNOLOGY FROM INDUSTRIAL INCINERATOR FLUE GAS

1.1 Industrial Incinerator Flue Gas Characteristics

The MonoEthanolAmine (MEA) based technology is widely used for commercial CO₂ production in small scale (< 30 tonCO₂/h) (Chapel *et al.*, 1999). Nevertheless, several technology gaps were clearly identified (Rochelle *et al.*, 2001; Steeneveldt *et al.*, 2006; Johnsen *et al.*, 2009) to use this technology in carbon

TABLE	1	
	•	

	Coal fired power plan	t (Artanto <i>et al.</i> , 2012)	Target industrial incinerator unit
Temperature	160-1	70°C	
Pressure	1 atm		1 atm
H ₂ O	20-23 (vol.% wet)		30 (vol.% wet)
CO ₂	10-11 (vol.% wet)	12.5-14.5 (vol.% dry)*	5-11 (vol.% dry)
O ₂	4-5 (vol.% wet)	5.0-6.5 (vol.% dry)*	8-12 (vol.% dry)
SO ₂	120-200 (wet ppm volume)	260-457 (dry mg/m ³)*	6.2 (dry mg/m ³)
NO _x	150-250 (wet ppm volume) (≈ 99% NO, balance NO ₂ and N ₂ O)	237-410 (dry mg/m ³)*	91 (dry mg/m ³) ($\approx 80\%$ NO, balance NO ₂)

* Converted data from literature.



Figure 1

Schematic flow sheet of absorption/desorption process for CO₂ capture process.

capture and storage from power plant flue gas. Therefore, high amounts of R&D were launched including several pilot plant studies (Wang *et al.*, 2011) and mainly applied to carbon capture from coal fired power plant.

Results and conclusions of these studies are useful to check the sustainability of carbon dioxide capture from incinerator flue gas without providing an exhaustive answer. Table 1 shows typical compositions of an actual coal-fired power plant flue involved in pilot experiments and the associate flue gas composition of the target incinerator.

Table 1 shows that coal fired flue gas has a higher partial pressure of CO_2 and a lower partial pressure of O_2 compared to the incinerator flue gas. Moreover, coal fired flue gas has a low composition fluctuation. At the opposite, the incinerator inlet raw material composition varies depending on the waste to be treated and induces a constant fluctuation on outlet flue gas composition.

Coal power plant raw flue gas contains a high fraction of pollutants (SO₂, NO_x) and needs a gas pretreatment prior to its introduction in MEA capture unit. Incinerator already includes efficient gas purification units and provides flue gas with low level of pollutants (SO₂, NO_x).

To sum up, CO_2 capture from incinerator flue gas is in the commercial scale of MEA based technology but no industrial references could confirm the sustainability of this new application.

1.2 CO₂ Capture by MEA Based Technology

A schematic view of the CO₂ capture process is shown in Figure 1. The bottom of the absorption column is connected to the inlet flue gas. CO2 transfer from gas to solvent along this column which is facilitated by a packing and a counter current flow. The lean carbon flue gas (3) leaves the top of the column to the atmosphere. The CO_2 rich solvent is then pumped from the bottom of the absorption column to the stripper (4). As the solvent progresses towards the stripping column, its temperature increases thanks to the heat provided by the reboiler at the bottom. CO2 and steam are released and flow up to the condenser. Decreasing flue gas temperature leads to water condensation. The purified CO_2 leaves the condenser (5). The lean solvent is then conducted from the boiler to the absorption column for a new capture cycle. The crossover heat exchanger allows an energy saving by warming up the rich solvent and cooling the lean solvent.

1.3 Potential Interactions with the Solvent and the Incinerator Flue Gas

In the case of coal or gas power plant flue gas, comprehensive studies around the stability of 30 wt% MEA solvent have been published (Wang *et al.*, 2011). Although differences over the composition of these flue gases, the following degradation mechanisms of MEA can be transposed in our study.

First, thermal degradation of the solvent can occur through carbamate polymerization. This reaction takes place mainly in the stripper section of the process because a high level of temperature is needed. Several studies conclude that thermal degradation kinetics could be limited if temperature does not exceed 110°C (Bello and Idem, 2005; Davis and Rochelle, 2009; Davis, 2009; Lepaumier *et al.*, 2009a; Rochelle, 2012).

Oxygen fraction of the flue gas creates a second way of degradation: oxidative degradation. Indeed, MEA has strong interaction with oxygen (Supap et al., 2001, 2006; Bello and Idem, 2005; Chi and Rochelle, 2002; Goff and Rochelle, 2004, 2006; Sexton and Rochelle, 2009; Bedell, 2009, 2011; Bedell et al., 2011; Lepaumier et al., 2009b, c). Working closer to the absorption conditions, Sexton and Rochelle (2009) have shown that ammonia is the major by-product in the gas phase and is a good indicator of MEA oxidative degradation. They found that organic acids are strongly present in the liquid phase. Moreover, Bello and Idem (2005) have identified from 10 to 30 oxidative mechanisms and products. Several suggested pathways exhibit the sensitivity of the chemistry system. It has been demonstrated that metal present in setup serves as catalyst for oxidize the reaction. Bedell (2009) proposed a pathway using radical mechanisms for the oxidative degradation. As summarized in Figure 2, the metal cation reacts with oxygen to generate radicals which attack the MEA molecules. The metal cation is then regenerated by the water for a new cycle of reaction.

The most active metallic ions in this kind of degradation are iron, chrome and nickel. Based on the strong interaction between metal and solvent degradation, the major source of metal comes from the corrosion of the facilities. The corrosion is a very significant problem in alkanolamines processes (Veawab and Aroonwilas, 2002) and can impact strongly process facilities



Catalytic way of oxidative degradation of MEA.

(Dupart *et al.*, 1993a, b). The ability of the solvent in corrosion activity depends strongly on the gas stream composition. For incinerator flue gas, it is expected that, in presence of oxygen, MEA degradation generates acid molecules. Veawab and Aroonwilas (2002) proved that acids increase the corrosiveness of alkanolamine solvents, which increases the metal concentration in the solvent. Furthermore, some pollutants like chloride are well known as corrosion agents. Therefore, corrosion and degradation runaway is expected if an appropriate solution is not implemented. Several additives can be used to limit oxidation. For example, Sexton and Rochelle (2009) propose vanadium and copper based additives.

The incinerator flue gas contains acidic pollutants traces from waste. After dissolution and hydrolysis these pollutants will lead to strong acids which shall be added to the quantity of strong acids produce by MEA oxidative degradation. When the acid is weak like the CO_2 , the equilibrium is reversed with a temperature increase. Conversely the reaction with strong acids is not reversible and leads to Heat Stable Salts (HSS). Accordingly, the process effectiveness decreases each time that strong acids are added to the solvent. For the incinerator flue gas, no experimental data quantify this phenomenon:

A H + HO
$$^{NH_2} = HO ^{NH_3} + A^{-}$$

 SO_2 is the main acidic pollutants in incinerator flue gas. Kohl and Nielsen (1997) show clearly that the sulfur dioxide has a high reactivity with alkaline solution. Starting from $DeSO_x$ alkaline processes feedback, we assume the following mechanisms for SO_2 absorption in MEA solvent:

$$SO_2 + H_2O + HO \rightarrow NH_2 \implies HSO_3 + HO \rightarrow NH_3 + HSO_3 + 1/2 O_2 + HO \rightarrow NH_2 \implies SO_4^2 + HO \rightarrow NH_3 + HSO_3 + HSO$$

In the case of NO_x compounds absorption in alkaline solution is complex. First several gas phase reactions occur like described by Carta (1984):

		NO	+	1/2 O ₂	>	NO ₂		
				2 NO ₂	\rightleftharpoons	N ₂ O ₄		
		NO	+	NO_2	$ \longrightarrow$	N_2O_3		
NO	+	NO ₂	+	H ₂ O	$ \longrightarrow$	2 HNO ₂		
	3	NO_2	+	H ₂ O	\rightleftharpoons	$2 HNO_3$	+	NO

Once the NO_x species (NO, NO₂, N₂O₄, HNO₂, HNO₃) have been absorbed in the liquid phase, the following mechanisms for the reaction with MEA are assumed (Decanini *et al.*, 2000; Hüpen and Kenig, 2005):

1.4 Study Goals

The study objective is to validate the sustainability of CO_2 capture from incinerator flue gas with a laboratory pilot. A target unit was chosen and a specific pilot was designed and built to analyze:

- the MEA solvent chemical stability in front of high oxygen fraction and incinerator flue gas pollutants,
- the process performance stability for CO₂ capture and the energy consumption relative to the flue gas fluctuations and the solvent degradation.

First, laboratory experiments allowed checking pilot performance for CO_2 capture and energy consumption. At the same time, we perform measurements on solvent stability against flue gas without the variation on inlet flue gas compositions.

Second, the pilot was installed in the target incinerator unit to validate the sustainability of the process.

2 EXPERIMENTAL SETUP

2.1 Previous Studies

During the last decade, numerous research and development projects have studied the CO₂ capture with a MEA technology using pilots (Wang *et al.*, 2011). Table 2 presents the experimental units described on literature and on which our pilot design was based. Although the setups have a wide range of CO₂ production, from 1 kgCO₂/h to 100 tonCO₂/day, they share the following characteristics:

- dense instrumentation for the temperature, flow and composition measurements with high number of gas and liquid sampling points;
- multipurpose absorption and stripper equipment to perform parametric studies with a wide range of operating conditions.

All published results mainly focus on the process performances for CO₂ capture energy consumption by varying L/G ratio and strippers operations conditions for different solvent formulation (Mimura *et al.*, 1995; Gabrielsen, 2007; Chen, 2007; Idem *et al.*, 2009; Knudsen *et al.*, 2009; Tatsumi *et al.*, 2011; Artanto *et al.*, 2012; Notz *et al.*, 2012). Notz *et al.* (2012) have provided the most complete published data for the MEA based solvent with detailed measurements of 47 pilot runs in various operating conditions.

Nevertheless, pilot results on the MEA chemical stability are rare (Mimura *et al.*, 1995; Kittel *et al.*, 2009; Knudsen *et al.*, 2009) and a lack of pilot data is observed for the MEA degradation, the material corrosion and the foaming phenomena. To fill this gap, the pilot was built with the following specifications:

- setup specifications equivalent to the industrial processes for the temperature, the pressure, the column hydrodynamic and the mass transfer coefficients;
- temperature measurement of liquid and gas input and output streams and temperature profile for each column;
- flow rate measurement of liquid and gas input and output streams for each column;
- composition measurement of liquid and gas input and output streams and composition profile for each column;
- energy balance measurement tool for each heat exchanger and stripping column;
- gas generator section which controls temperature, flow rate and gas stream composition;
- no metal as raw material;
- gas analysis tools for concentration measurements of CO₂, O₂, pollutants, ammonia and MEA volatility;
- liquid analysis tools for MEA concentration, dissolved pollutants and organic acids;
- water balance measurement tool for the overall process;
- automatic control of pilot setup for long term experiments and thorough data system acquisition.

2.2 Pilot description

A classic flow diagram of alkanolamine process underlies the development of our unit (*Fig. 1*) (Aouini *et al.*, 2011). The temperature and the pressure are identical to industrial process specifications as well as the column hydrodynamic and mass transfer conditions.

Absorption column gas feeding is operated by a mixing unit starting from pure gas cylinders. The controlled parameters are flow rates, temperatures and compositions. The chosen gas composition is achieved by using mass flow meters. First, the nitrogen and

Research group		Flue gas source	CO ₂ production	Columns dimensions	References
Institute of Thermodynamics and Thermal Process Engineering	University of Stuttgart, Germany	Natural gas burner	10 kgCO ₂ /h	Absorption: $H = 4.2 \text{ m}; \emptyset = 0.125 \text{ m}$ Stripper: $H = 2.55 \text{ m}; \emptyset = 0.125 \text{ m}$	Mangalapally and Hasse (2010), Notz <i>et al.</i> (2012)
SINTEF-NTNU	NTNU, Trondheim, Norway	Gas reconstituted	10 kgCO ₂ /h	Absorption: $H = 4.3 \text{ m}; \emptyset = 0.15 \text{ m}$ Stripper: $H = 3.9 \text{ m}; \emptyset = 0.1 \text{ m}$	Tobiesen <i>et al.</i> (2007), Gabrielsen (2007)
International Test Centre for CO ₂ Capture (ITC)	University of Regina, Canada	Natural gas burner	1 tonCO ₂ /day	Absorption: $H = 10 \text{ m}; \emptyset = 0.33 \text{ m}$ Stripper: $H = 10 \text{ m}; \emptyset = 0.33 \text{ m}$	Idem <i>et al.</i> (2006), Idem <i>et al.</i> (2009), Kittel <i>et al.</i> (2009)
Projet SOLVit (SINTEF, NTNU, Aker clean carbon)	SINTEF, Trondheim, Norway	Not mentioned	l tonCO ₂ /day	Absorption: $H: 19 \text{ m}; \emptyset = 0.2 \text{ m}$ Stripper: $H = 13.6 \text{ m}; \emptyset = 0.162 \text{ m}$	Mejdell et al. (2011)
Luminant Carbon Management Program	University of Texas at Austin, USA	Gas reconstituted	4 tonCO ₂ /day	Absorption: $H = 13.3 \text{ m}; \emptyset = 0.43 \text{ m}$ Stripper: $H = 13.3 \text{ m}; \emptyset = 0.43 \text{ m}$	Dugas (2006), Chen (2007)
Nanko pilot KEPCO and MHI	Osaka, Japan	Natural gas turbine	2 tonCO ₂ /day	Not mentioned	Mimura <i>et al.</i> (1995), Tatsumi <i>et al.</i> (2011)
International Test Centre for CO ₂ Captage (ITC)	Boundary Dam, Canada	Coal fired power plant	4 tonCO ₂ /day	Absorption: $\emptyset = 0.46 \text{ m}$ Stripper: $\emptyset = 0.40 \text{ m}$	Idem et al. (2006)
Projet CASTOR and projet CESAR	Esbjervaerket, Danemark	Coal fired power plant	24 tonCO ₂ /day	Absorption: $H = 17 \text{ m}; \emptyset = 1.1 \text{ m}$ Stripper: $H = 10 \text{ m}; \emptyset = 1.1 \text{ m}$	Knudsen <i>et al.</i> (2009), Kittel <i>et al.</i> (2009)
IFPEN and ENEL	Brindisi, Italy	Not mentioned	54 tonCO ₂ /day	Not mentioned	Lemaire et al. (2011)

TABLE 2 Pilot for CO_2 capture from flue gas and using MEA based technology

oxygen mixture goes through a humidifier column where the gas flow is saturated with water. The desired temperature is reached by controlling the hot water flow. Due to their high solubility in water, the CO_2 and the pollutants are added afterwards. Electric tracing holds the temperature of the gas flow and avoids condensation between the humidifier and the absorption columns.

The absorption column is made of glass. It is about 1.5 m high and 0.06 m in diameter and is filled with ceramic packing (*Tab. 3* for packing specifications). The packing section is divided in three parts including a temperature measurement, one liquid and two gas samplings. The gas flows from the bottom to the top and is mixed counter-currently with the MEA solvent. Temperature, pressure, flow rate and composition of gas and solvent are measured at the bottom and at the top of the

TABLE 3

Packing specifications	Packing	specifications
------------------------	---------	----------------

	Unit	Beads
Size	mm	6.4
Number of elements per volume unit	Nb elements/m ³	3 715 000
porosity ε	% vol.	36.8
density ρ	kg/m ³	1 500
Specific area	m^2/m^3	480

column. To increase its temperature, the rich solvent goes through a heat exchanger controlled by a thermo-static bath.

Name	Number of runs	Experimental duration	Gas inlet composition	L/G	Temperature & pressure	Results
1	15	\approx 5 hours	CO ₂ : 5, 7, 9, 11, 13% vol. dry; H ₂ O (saturation); N ₂ (complementary)	From 6 to 9.5	50°C; 1 atm	Mass balance, $K_g a_w$
2	1	\approx 4 days	CO ₂ : 8 vol. dry; H ₂ O (saturation); N ₂ (complementary)	6	50°C; 1 atm	Mass balance; $K_g a_w$, MEA degradation, HSS
3	2	pprox 4 days	$\begin{array}{c} CO_2: \ 8 \ vol. \ dry; \\ O_2: \ 12 \ vol. \ dry; \\ SO_2: \ 40 \ mg/m^3 \ dry; \\ NO_2: \ 25 \ mg/m^3 \ dry; \\ H_2O \ (saturation); \\ N_2 \ (complementary) \end{array}$	6	50°C; 1 atm	Mass balance, K _g a _w , MEA degradation, HSS
4	5	From 12 to 90 days	Real incinerator flue gas	From 2.5 to 9.5	50°C; 1 atm	MEA degradation, HSS

TABLE 4 Experimental protocol

The stripping column is featuring the absorption column except geometric dimensions (2 m high and 0.12 m in diameter). Heat is provided to the reboiler through the glass wall by an electrical resistance. Energy balance is done. Two liquid samplings give the solvent composition at the inlet and the outlet of the reboiler. An energy balance is done on the condenser upper the column and a gas sampling gives the purity of the outlet flow. The overall desorption pressure is controlled by proportional relief valve. On the reboiler outlet, the lean solvent goes through a second heat exchanger also controlled by a thermostatic bath. An energy balance is done by using temperature and flow rate measurements. For each column, a liquid distributor is placed at the top of the packing. Hydrodynamic validations have been conducted (Aouini et al., 2011).

The pilot is controlled by a *National Instrument* controller using an in-house LabviewTM program. It allows getting a real-time acquisition of temperatures, pressures, flow rates, energy balances and gas compositions. Those profiles are reported on the screen and stored in a data acquisition system.

2.3 Analytical Protocols

The pilot gas samples are sent to an IR-analyser which gives the concentrations of:

- CO₂ (0 to 20 \pm 0.5% vol. dry);

- O_2 (0 to 25 \pm 0.5% vol. dry);

- SO₂ (0 to 250 \pm 2 mg/m³ dry);

- NO_x (0 to 250 \pm 2 mg/m³ dry).

For liquid samples, a *Dionex* CS-11 cationic column allows the analysis of MEA concentration.

The CO_2 load of the solvent is quantified by gas chromatography by using the protocol of Jou *et al.* (1995). Finally, a *Dionex* AS-23 anionic column allows the analysis of the concentration of organic acids and pollutant dissolution products.

2.4 Experimental Protocol

Four experiments were performed as detailed in Table 4. Experiments 1, 2 and 3 have been carried out in the laboratory using the gas generator while experiment 4 was performed when the pilot was plugged on the industrial incinerator. For all runs, stripper column conditions are the same (100°C and 1 atm).

First, we carried out for experiment 1 a parametric study of CO₂ absorption without O₂ and pollutants in absorption gas inlet with short runs. The main variable was the CO₂ gas concentration on absorption inlet (5, 7, 9, 11, 13 vol. dry). Those experiments have yielded to a data set for mass balances and overall mass transfer coefficient $K_{g}a_W$ calculations. Second, we have studied in experiment 2 and 3 the MEA degradation and pollutants absorption on the solvent using long laboratory runs. Experiment 2 studied MEA degradation without O₂ and pollutants in absorption gas inlet while experiment 3 has included them in average range of waste incinerator flue gas compositions. Finally, experiment 4 has yielded data on the process performance in real industrial conditions.

This paper proposes the results about the mass balances and overall mass transfer coefficient $K_g a_W$ measurements obtained from the laboratory experiments. Moreover, MEA degradation and pollutants absorption will be discussed from laboratory and industrial experiments.

3 EXPERIMENTAL RESULTS

3.1 Mass Balances

The mass balances were calculated using CO₂ molar flow measurements in several points presented at Figure 1. The CO_2 absorption inlet is calculated with the measurements on flue gas (1) and solvent flow (2). The CO_2 gas inlet flow for the absorption column (1) is provided by a mass flow meter while the liquid inlet flow (2) is calculated with the solvent circulation flow and the CO₂ concentration at the reboiler liquid outlet. The CO₂ absorption outlet is figured out with the measurements at (3) and (4). The CO_2 gas inlet flow (3) is calculated from the total gas outlet flow and the CO₂ concentration measurement. At point (2), the liquid CO_2 inlet flow is calculated by multiplying the solvent circulation flow and the CO₂ concentration at the absorption liquid outlet. The CO₂ stripper outlet is the sum of the measurement of the mass flow meter at (5) and the flow at (2). The CO₂ stripper inlet is provided by the measurement at (4). Finally, the process mass balance is performed with the measurement at point (1) for the inlet and the sum of point (3) and (5) for the outlet. Influence of CO_2 loading on density can be neglected (< 0.3%) as shown in Aouini et al. (2011).

Figures 3, 4 and 5 present the 37 mass balances provided by experiments 1, 2 and 3. Figure 3 focuses on the overall process mass balance while Figure 4 checks data for the absorption section and Figure 5 deals with the stripper section.

The results of mass balances show an uncertainty below 10% which demonstrate the accuracy of the pilot instrumentation and the analytical methods for the solvent composition.

3.2 Overall Mass Transfer Coefficient Measurements K_Ga_W

The overall mass transfer coefficient ($K_G a_W$) is the most useful tool for comparing the hydrodynamic efficiency for CO₂ absorption of different equipments in various operating conditions. DeMontigny *et al.* (2001) proposed a comprehensive pilot study of CO₂ absorption in MEA solvents with several packing structures, CO₂ gas inlet concentrations, MEA solvent concentrations, and operating conditions. Dugas (2006) carried out a





Overall process mass balances.





Absorption mass balances.



Figure 5 Stripper mass balances.

study on the CO_2 absorption in 30 wt% MEA solvent in a full pilot plant. The author varied the CO_2 gas inlet concentration, the fluid flow rates, and the desorption conditions.

The overall mass transfer coefficient $(K_G a_W)$ measurement method is based on the transfer unit theory by applying the following expression:

$$K_G a_W = \frac{\Phi_{\rm CO_2}}{V_{pck} \times \left(P_{\rm CO_2} - P^*_{\rm CO_2}\right)_{M_{10}}}$$

Starting from experimental CO₂ concentration measurements in the flue gas and the solvent flow, the absorption rate Φ_{CO_2} is obtained by mass balances and the logarithm mean average driving force $(P_{CO_2} - P^*_{CO_2})_{M_m}$ is calculated using the operating and equilibrium CO₂ partial pressure at the top and bottom of the absorber (Aouini *et al.*, 2012).

Nevertheless, the heat of absorption of CO₂ in amine solvent induces a temperature gradient along the absorption column called bulge (Kohl and Nielsen, 1997). Kvamsdal and Rochelle (2008) show that bulge has strong effect on mass transfer performance, and therefore on the overall mass transfer coefficient ($K_G a_W$) measurements.

The runs of experiment 1, 2 and 3 (*Tab. 3*) were performed with a high solvent-to-gas ratio (L/G) (higher than 6). Heat of absorption is then dissipated in a higher liquid flow limiting temperature increase of the liquid phase. Minimizing heat accumulation in liquid phase to homogenise temperature allows to consider a uniform mass transfer along the packing. For all the experiments, the temperature gradient was less than 10°C.

Figure 6 presents the overall mass transfer coefficient $(K_G a_W)$, for experiment 1 runs, plotted as a function of CO₂ concentration gas inlet and the solvent-to-gas ratio (L/G).

The overall mass transfer coefficients ($K_G a_W$) are similar with the DeMontigny *et al.* (2001), and Dugas (2006) measurements. As expected by DeMontigny *et al.* (2001), $K_G a_W$ value decreases as CO₂ concentration increases, reflecting that hydrodynamic contribution in mass transfer is disadvantaged by the CO₂ partial pressure increase. Indeed, increase of CO₂ content in the gas phase leads to a higher α (loading ratio) which impact k_G through the enhancement factor. Our L/G range doesn't seem to have any influence on the overall mass transfer coefficients.

Nevertheless, as shown in Figure 7, the mass balances show that the absorption rate Φ_{CO_2} increases with high CO₂ partial pressure inlet which induce a higher thermodynamic driving force $(P_{CO_2} - P_{CO_2}^*)_{M_{lo}}$ over the



Figure 6

Overall mass transfer coefficient ($K_G a_W$) in function of CO₂ gas inlet for runs of experiment 1.





absorption packing. Figure 8 presents overall higher thermodynamic driving force $(P_{CO_2} - P^*_{CO_2})_{M_{ln}}$, for experiment 1 runs, plotted as a function of CO₂ concentration gas inlet and the solvent-to-gas ratio (L/G). In both case, the ratio L/G doesn't show a great influence on the absorption rate on the driving force. The hydrodynamic behavior of the column isn't modified other the range of L/G values.

Therefore, the thermodynamic driving force is predominant in CO_2 absorption compared with hydrodynamic, and higher the CO_2 partial pressure inlet is, lower the needed absorption height is.



Figure 8

Absorption thermodynamic driving force $(P_{CO_2} - P^*_{CO_2})_{M_{b_i}}$ in function of CO₂ gas inlet for runs of experiment 1.

Finally, the overall mass transfer coefficient $(K_G a_W)$ coefficient remained stable during long runs of experiments 2 and 3 which show that the accumulation of MEA degradation product was not sufficient to affect CO₂ mass transfer.

3.3 MEA Chemical Stability

The degradation of MEA in the solvent was followed by measuring its concentration variations during long runs experiments. Nevertheless, CO_2 capture by amine solvents is sensitive to the water evaporation or accumulation at the absorption section linked to the variation of the process operating conditions.

Therefore, the actual MEA concentration ([MEA]) is corrected with a Lithium concentration ([Li]). Lithium carbonate was added to the solvent as a non-reactive and a non-volatile compound. The lithium concentration follows the water balance of the solvent. For example an increase of Li concentration occurs when water is lost in the liquid loop. Then the corrected MEA concentration ([MEA]*) is calculated as following:

$$[\text{MEA}]_t^* = [\text{MEA}]_t \times \frac{[\text{Li}]_t}{[\text{Li}]_0}$$

Figures 9, 10 and 11 present the evolution of MEA and lithium concentrations during long runs performed in experiments 2, 3 and 4 (*Tab. 3*).



Figure 9

Evolution of MEA and Lithium concentration during experiment 2.



Figure 10





Figure 11

Evolution of MEA and Lithium concentration during a run of experiment 4.

Runs	SO ₂ inlet	SO ₂ outlet	SO ₂ capture ratio	NO ₂ inlet	NO ₂ outlet	NO ₂ capture ratio
1	40 ppm	0 ppm	100%	25.6 ppm	14.1 ppm	45%
2	40 ppm	0 ppm	100%	26.2 ppm	13.9 ppm	47%

 $\label{eq:TABLE5} TABLE\ 5$ SO_2 and NO_2 concentration in the gas inlet and outlet of the absorption column in experiment 3

Figure 9 shows that MEA did not undergo degradation in the experiment 2 conditions. In the same manner, Figure 10 shows that O_2 and pollutants did not affect MEA concentration for 100 hours in the experiment 3. A minimum of concentration is clearly observed between 20 and 40 hours which could be explained by experimental error like uncertainty of analytical method. Figure 11 confirms the results for a longer run in industrial conditions.

The 30 wt% MEA solvent shows a good resistance during 300 hours against the incinerator flue gas. Nevertheless, it is important to remember that metallic materials are avoided in the pilot to minimize the oxidative degradation of MEA. Thus, this result could be projected in industrial scale in the case of a narrow control of the corrosion.

3.4 Absorption of SO₂ et NO₂

We carried out two runs in the experiment 3 where gas inlet composition includes sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) in average range of actual waste incinerator flue gas concentrations. The inlet gas composition did not vary during those runs allowing accurate calculation for the capture ratio of the pollutants.

Table 5 gives the absorption results of SO_2 and NO_2 in experiment 3.

As Table 5 shows, the SO₂ was completely absorbed in less than 10 cm of packing which may correspond to an instantaneous regime for the gas-liquid transfer. NO₂ was partially absorbed in the solvent with an average of 46%. It corresponds to a fast regime for the gas-liquid transfer and it agrees with Hüpen and Kenig (2005) results.

3.5 Heat Stable Salts Accumulation

Previously, MEA reactivity review shows that it reacts into HSS with strong acid anions. Organic strong acid anions (formiate, acetate, and oxalate) are produced by the oxidative degradation of MEA. All of the SO_2 of the absorption inlet gas leads to sulfate anions and the absorption fraction of NO_2 produces nitrite and nitrate anions. Those observations were confirmed by experiment 2 where the gas inlet has excluded oxygen (O_2) , SO_2 , and NO_2 leading to the absence of accumulation of HSS.

The purpose of this section is to evaluate induced MEA losses for an industrial scale. The high reactivity of SO_2 makes the calculation obvious while organic and NO_2 HSS were evaluated starting from measurements obtained during runs of experiment 3. The two runs gas inlet composition includes O_2 , SO_2 , and NO_2 in average range of waste incinerator flue gas concentrations.

Figure 12 presents the accumulation of organic during a run of experiment 3. It shows that organic HSS concentration increases regularly which leads to calculate an average kinetic of production.

In the same way, Figure 13 shows the accumulation of nitrite and nitrate HSS during experiment 3 and leads to calculate an average kinetic of production.

The average kinetic of production of organic and NO_2 Heat Stable Salts was obtained by the slopes of the linear regressions of experimental measurements presented in Table 6.

The results of experiment 3 agree with industrial measurements obtained during experiment 4. Figure 14 presents an example of organic Heat Stable Salts





Organic Heat Stable Salts accumulation during experiment 3 (laboratory).



Figure 13

NO₂ Heat Stable Salts accumulation during a run of experiment 3 (laboratory).



Figure 15

NO₂ Heat Stable Salts accumulation during experiment 4 (industrial measurements) (L/G = 4).

 TABLE 6

 Average kinetic of production of organic and NO₂ Heat Stable Salts during the runs of experiment 3

Runs	Organic HSS mol/(h.L)	R^2	NO ₂ HSS mol/(h.L)	R^2
1	2.08×10^{-05}	0.969	3.33×10^{-05}	0.933
2	2.77×10^{-05}	0.977	2.86×10^{-05}	0.979
Average	2.42×10^{-05}		3.10×10^{-05}	

accumulation while Figure 15 illustrates the accumulation of NO_2 salts.

For an industrial scale, MEA losses due to Heat Stable Salts formation are estimated from previous results and with the following assumption:



Figure 14

Organic Heat Stable Salts accumulation during experiment 4 (industrial measurements) (L/G = 4).

 TABLE 7

 MEA blocked on Heat Stable Salts during 0.7 year running using 30 wt

 % MEA solvent

	Organic HSS	NO ₂ HSS	SO ₂ HSS	Sum
% MEA blocked	2.97%	3.80%	5.75%	12.52%

- the inlet gas composition corresponds to the composition of experiment 3 (except $SO_2 = 6 \text{ mg/m}^3 \text{ dry}$),
- the capture unit works with L/G ration close to 4,
- the corrosion is negligible and avoids catalysis of MEA oxidation.

Table 7 presents the proportion of MEA blocked on Heat Stable Salts for an industrial unit which has been running for 0.7 year (6 132 hours) using a 30 wt% solvent.

Table 6 shows that Heat Stable Salts accumulation is not negligible for CO_2 capture from industrial incinerator flue gas and could lead to loss of performance and corrosion problems. Thus for the future industrial units, it is important to implement a reclaiming unit to draw back these salts.

CONCLUSIONS

The pilot plant presented in this paper allows studying process performances of absorption/desorption CO_2 capture unit using MonoEthanolAmine (MEA) solvent and feed by waste incinerator flue gas.

The pilot is fully instrumented to establish balances with an uncertainty below 10%. A laboratory parametric study allows analyzing CO_2 mass transfer in the absorption pilot column for various operating conditions. Experiments show that it is important to use a high

gas-to-liquid ratio (L/G) to avoid heat accumulation in the liquid phase and to obtain a uniform mass transfer through the packing. The CO₂ absorption rate decreases with the reduction of CO₂ partial pressure gas inlet while the overall mass transfer coefficient $(K_G a_W)$ increases. Therefore, the thermodynamic driving force is predominant compared with hydrodynamics in CO₂ absorption using MEA solvent.

Laboratory and industrial long runs were carried out to evaluate MEA chemical stability against waste incinerator flue gas. The experiments show that the 30 wt% MEA solvent has a good resistance during 300 hours against the incinerator flue gas. They also provide useful information on behavior of incinerator flue gas pollutants (SO₂, NO₂) with the 30 wt% MEA solvent. Sulfur dioxide (SO₂) has a high reactivity with the solvent. It is fully absorbed and leads to sulfate salts formation with MEA. Nitrogen dioxide has less reactivity with an absorption ratio close to 46% and also leads to nitrite and nitrate salts formation.

Finally, long runs permit to evaluate the Heat Stable Salts (HSS) accumulation through a MEA solvent with the waste incinerator treated flue gas. According to SO_2 reactivity, sulfate salt accumulation is calculated by mass balance. Organic, nitrite and nitrate salts accumulation rates were obtained by experimental data regressions. Calculations show that the proportion of MEA blocked on HSS is about 10 to 15% for an industrial unit which has been running for 0.7 year (6 132 hours) using a 30 wt% solvent. Therefore, it is important to implement a reclaiming unit to draw back these salts.

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REFERENCES

Aouini I., Ledoux A., Estel L., Mary S., Grimaud J., Valognes B. (2011) Study of carbon dioxide capture from industrial incinerator flue gas on a laboratory scale pilot, *Energy Procedia* **4**, 1729-1736.

Aouini I., Ledoux A., Estel L., Mary S., Evrard P., Valognes B. (2012) Experimental study of carbon dioxide capture from synthetic industrial incinerator flue gas with a pilot and laboratory measurements, *Procedia Engineering* **42**, 704-720.

Artanto Y., Jansen J., Pearson P., Do T., Cottrell A., Meuleman E., Feron P. (2012) Performance of MEA and amine-blends in the CSIRO PCC pilot plant at Loy Yang Power in Australia, *Fuel* **101**, 264-275. Bedell S.A. (2009) Oxidative degradation mechanisms for amines in flue gas capture, *Energy Procedia* 1, 771-778.

Bedell S.A. (2011) Amine autoxidation in flue gas CO₂ capture – Mechanistic lessons learned from other gas treating processes, *International Journal of Greenhouse Gas Control* **5**, 1, 1-6. doi: 10.1016/j.ijggc.2010.01.007.

Bedell S.A., Worley C.M., Darst K., Simmons K. (2011) Thermal and oxidative disproportionation in amine degradation -O₂ stoichiometry and mechanistic implications, *International Journal of Greenhouse Gas Control* **5**, 3, 401-404. doi: 10.1016/j.ijggc.2010.03.005.

Bello A., Idem R. (2005) Pathway for the formation of products of oxidative degradation of CO_2 -loaded concentrated aqueous MonoEthanolAmine solutions during CO_2 absorption from flue gases, *Industrial and Engineering Chemistry Research* **44**, 945-969.

Carta G. (1984) Role of HNO₂ in the absorption of nitrogen oxides in alkaline solutions, *Industrial and Engineering Chemistry Research* **23**, 260-264.

Chapel D.G., Mariz C.L., Ernest J. (1999) Recovery of CO₂ from flue gases: Commercial trends, *The Canadian Society of Chemical Engineers Annual Meeting*, Saskatoon, Saskatchewan, Canada, 4-6 Oct.

Chen E. (2007) Carbon dioxide absorption into piperazine promoted potassium carbonate using structured packing, *PhD Thesis*, University of Texas at Austin.

Chi S., Rochelle G.T. (2002) Oxidative degradation of Mono-EthanolAmine, *Industrial and Engineering Chemistry Research* **41**, 4178-4186.

Davis D.J. (2009) Thermal degradation of aqueous amines used for carbon dioxide capture, *PhD Thesis*, University of Texas at Austin.

Davis D.J., Rochelle G.T. (2009) Thermal degradation of Mono-EthanolAmine at stripper conditions, *Energy Procedia* 1, 327-333.

Decanini E., Nardini G., Paglianti A. (2000) Absorption of nitrogen oxides in columns equipped with low pressure drops structured packing, *Industrial and Engineering Chemistry Research* **3**, 5003-5011.

DeMontigny D., Tontiwachwuthikul P., Chakma A. (2001) Parametric Studies of Carbon Dioxide Absorption into Highly Concentrated MonoEthanolAmine Solutions, *The Canadian Journal of Chemical Engineering* **79**, 137-142.

Dugas R.E. (2006) Pilot plant study of carbon dioxide capture by aqueous MonoEthanolAmine, *M.S.E Thesis*, University of Texas at Austin.

Dupart M.S., Bacon T.R., Edwards D.J. (1993a) Understanding corrosion in Alkanolamine gas treating plants Part I, *Hydrocarbon Processing* April, 75-80.

Dupart M.S., Bacon T.R., Edwards D.J. (1993b) Understanding corrosion in Alkanolamine gas treating plants Part II, *Hydrocarbon Processing* May, 89-94.

Gabrielsen J. (2007) CO₂ Capture from Coal Fired Power Plants, *PhD Thesis*, Technical University of Denmark.

Goff G., Rochelle G.T. (2004) MonoEthanolAmine degradation: O_2 mass transfer Effects under CO_2 capture conditions, *Industrial and Engineering Chemistry Research* **43**, 6400-6408.

Goff G., Rochelle G.T. (2006) Oxidation inhibitors for copper and iron catalyzed degradation of MonoEthanolAmine, *Industrial and Engineering Chemistry Research* **45**, 2513-2521. Hüpen B., Kenig E.Y. (2005) Rigorous modelling of NO_x absorption in tray and packed columns, *Chemical Engineering Science* **60**, 22, 6462-6471.

Idem R., Wilson M., Tontiwachwuthikul P., Chakma A., Veawab A., Aroonwilas A., Gelowitz D. (2006) Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the university of Regina CO₂ capture technology development plant and the Boundary Dam CO₂ capture demonstration plant, *Industrial and Engineering Chemistry Research* **45**, 2414-2420.

Idem R., Gelowitz D., Tontiwachwuthikul P. (2009) Evaluation of the performance of various amine based solvents in an optimized multipurpose technology development pilot plant, *Energy Procedia* **1**, 1543-1548.

Johnsen K., Helle K., Myhrvold T. (2009) Scale-up of CO₂ capture processes: The role of technology qualification, *Energy Procedia* **1**, 163-170.

Jou F.Y., Mather A.E., Otto F.D. (1995) The Solubility of CO₂ in a 30 Mass Percent MonoEthanolAmine Solution, *The Canadian Journal of Chemical Engineering* **73**, 140-147.

Kittel J., Idem R., Gelowitz D., Tontiwachwuthikul P., Parrain G., Bonneau A. (2009) Corrosion in MEA units for CO₂ capture: Pilot plant studies, *Energy Procedia* **1**, 791-797.

Knudsen J.N., Jensen J.N., Vilhelmsen P.J., Biede O. (2009) Experience with CO₂ capture from coal flue gas in pilot-scale: Testing of different amine solvents, *Energy Procedia* **1**, 783-790.

Kohl A., Nielsen R. (1997) Gas purification, 5th ed., Gulf Professional Publishing.

Kvamsdal H.M., Rochelle G.T. (2008) Effects of the temperature bulge in CO₂ absorption from flue gas by aqueous Mono-EthanolAmine, *Industrial and Engineering Chemistry Research* **47**, 867-875.

Lemaire E., Bouillion P.A., Gomez A., Kittel J., Gonzalez S., Carrette P.L., Delfort B., Mongin P., Alix P., Normand L. (2011) New IFP optimized first generation process for postcombustion carbon capture: HiCapt + TM, *Energy procedia* **4**, 1361-1368.

Lepaumier H., Picq D., Carette P.L. (2009a) New amines for CO₂ capture. I. Mechanisms of amine degradation in the presence of CO₂, *Industrial and Engineering Chemistry Research* **48**, 9061-9067.

Lepaumier H., Picq D., Carette P.L. (2009b) Degradation study of new solvents for CO_2 capture in post-combustion, *Energy Procedia* **1**, 893-900.

Lepaumier H., Picq D., Carette P.L. (2009c) New amines for CO₂ capture. II. Oxidative degradation mechanisms, *Industrial* and Engineering Chemistry Research **48**, 9068-9075.

Mangalapally H.P., Hasse H. (2010) Pilot plant experiments with MEA and new solvents for post combustion CO_2 capture by reactive absorption, *Distillation Absorption*, Eindhoven, The Netherlands.

Mejdell T., Knuutila H., Hoff K.A., Hallvard V.A., Svendsen F., Vassbotn T., Juliussen O., Tobiesen A., Einbu A. (2011) Novel full height pilot plant for solvent development and model validation, *Energy Procedia* **4**, 1753-1760.

Mimura T., Shimojo S., Suda T., Iijima M., Mitsuoka S. (1995) Research and development on energy saving technology for flue gas carbon dioxide recovery and steam dioxide recovery in power plant, *Energy Conversion Management* **36**, 6-9.

Notz R., Mangalapally H.P., Hasse H. (2012) Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA, *International Journal of Greenhouse Gas Control* **6**, 84-112.

Rochelle G.T., Bishnoi S., Chi S., Dang H., Santos J. (2001) Research needs for CO_2 capture from flue gas by aqueous absorption/stripping, Final report for DOE contract DE-AF26-99FT01029.

Rochelle G.T. (2012) Thermal degradation of amines for CO_2 capture, *Current Opinion in Chemical Engineering* **1**, 183-190.

Sexton A., Rochelle G.T. (2009) Catalysts and inhibitors for MEA oxidation, *Energy Procedia* 1, 1179-1185.

Steeneveldt R., Berger B., Torp T.A. (2006) CO₂ capture and storage closing the knowing–doing gap, *Trans. IChemE, Part A, Chemical Engineering Research and Design* **84**, 739-763.

Supap T., Idem R., Veawab A., Aroonwilas A., Tontiwachwuthikul P., Chakma A., Kybett B.D. (2001) Kinetics of the oxidantive degradation of aqueous MonoEthanolAmine in flue gas treating unit, *Industrial and Engineering Chemistry Research* **40**, 3445-3450.

Supap T., Idem R., Tontiwachwuthikul P., Saiwan C. (2006) Analysis of MonoEthanolAmine and its oxidative degradation products during CO₂ absorption from flue gases: A comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations, *Industrial and Engineering Chemistry Research* **45**, 2437-2451.

Tatsumi M., Yagi Y., Kadono K., Kaibara K., Iijima M., Ohishi T., Tanaka H., Hirita T., Mitchell R. (2011) New energy efficient processes and improvements for flue gas CO₂ capture, *Energy Procedia* **4**, 1347-1352.

Tobiesen F.A., Svendsen H.F., Juliussen O. (2007) Experimental validation of a rigorous absorber model for CO₂ postcombustion capture, *AIChE Journal* **53**, 846-864.

Veawab A., Aroonwilas A. (2002) Identification of oxidizing agents in aqueous amine-CO₂ systems using mechanistic corrosion model, *Corrosion Science* **44**, 5, 967-987.

Wang M., Lawal A., Stephenson P., Sidders J., Ramshaw C. (2011) Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review, *Chemical Engineering Research and Design* **89**, 1609-1624.

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