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J. Kittel, R. Idem, D. Gelowitz, P. Tontiwachwuthikul, G. Parrain, et al.. Corrosion in MEA units for CO<sub>2</sub> capture: pilot plant studies. Energy Procedia, 2009, 1 (1), pp.791 - 797. 10.1016/j.egypro.2009.01.105 . hal-02419487

**HAL Id: hal-02419487**

**<https://ifp.hal.science/hal-02419487>**

Submitted on 19 Dec 2019

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GHGT-9

## Corrosion in MEA units for CO<sub>2</sub> capture: pilot plant studies

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### Abstract

Among the technologies that are under study for CO<sub>2</sub> capture from flue gas, the separation process using monoethanolamine (MEA) could be the first to be available for immediate industrial applications in the next few years. The principles of CO<sub>2</sub> separation using alkanolamines were discovered nearly a century ago. The process has been applied successfully for several decades in areas such as natural gas processing or coal gasification. The application to flue gas treatment was introduced in the early 1980s, but was not widespread.

In such industrial processes, corrosion represents one of the major operational problems. For the capture of CO<sub>2</sub> from flue gas using MEA, the problem is even more critical since (i) MEA is one of the most corrosive amine when compared to secondary or tertiary amines that are also used for gas sweetening, and (ii) flue gas contains a certain amount of oxygen, which can react with the amine to form corrosive degradation products.

In the framework of the CAPRICE project, which is an International cooperation and exchange project supported by the EU, The International Test centre for CO<sub>2</sub> Capture from the University of Regina (CA) and IFP (F) have shared their experience on corrosion monitoring from CO<sub>2</sub> capture pilot plants. The first pilot plant facility is owned by ITC. It has a capacity to capture 1 ton CO<sub>2</sub>/day from a natural gas burner. It is equipped with corrosion control instruments and other monitoring systems. The second pilot plant is located in a coal fired power station in Esbjerg (DK). It was built with the financial support of the UE through the CASTOR project under the lead of IFP. It has been in operation since early 2006, and has a capacity of 1.0 ton CO<sub>2</sub>/hour. It is equipped with weight loss coupons for corrosion evaluation at different locations in the process.

This paper presents the major results of corrosion testing from both pilot plants under MEA operation. It appeared from both pilot plants that the areas most susceptible to corrosion were the stripper inlet and outlet, with corrosion rates around 1 mm. year<sup>-1</sup> for carbon steel.

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Keywords: CO<sub>2</sub> capture, MEA, corrosion

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## 1. Introduction

The objectives of this paper are to present ITC and IFP experience on corrosion monitoring in CO<sub>2</sub> capture pilot plants using MEA. Experience gained from two pilot plants is reported:

- The Castor pilot plant, recently built in Denmark with a capacity to capture 1 ton CO<sub>2</sub>/hour from a coal fired power station.
  - The ITC's pilot plant, built in Canada with a capacity to capture 1 ton CO<sub>2</sub>/day from a natural gas burner.
- Corrosion was monitored on both pilot plants at different locations, during CO<sub>2</sub> capture by MEA. Two different monitoring methods were used: weight loss coupons for the Castor pilot plant and corrosometer probes in the ITC system.

## 2. Castor pilot plant

### 2.1. Corrosion monitoring system

The castor CO<sub>2</sub> capture pilot plant was built in the framework of a EU funded project, which started in 2004 and lasted 4 years. A pilot plant was built close to a coal fired power station operated by Dong in Denmark. The pilot plant capacity is approximately 1 ton CO<sub>2</sub> per hour. It has been in operation since 2006, and was used for testing different solvent among which MEA was used as reference.

During the MEA campaigns, corrosion monitoring was performed using weight loss coupons installed at 6 different locations in the plant (Figure 1). Coupon holders are made of AISI 316 stainless steel. Corrosion coupons are flat rectangular samples,  $3 \times \frac{1}{2} \times \frac{1}{16}$  in<sup>3</sup> (76×13×1.6 mm<sup>3</sup>). Two steel grades were used for each campaign: AISI 1018 (carbon steel) and AISI 316 (stainless steel) or AISI 304 (stainless steel).

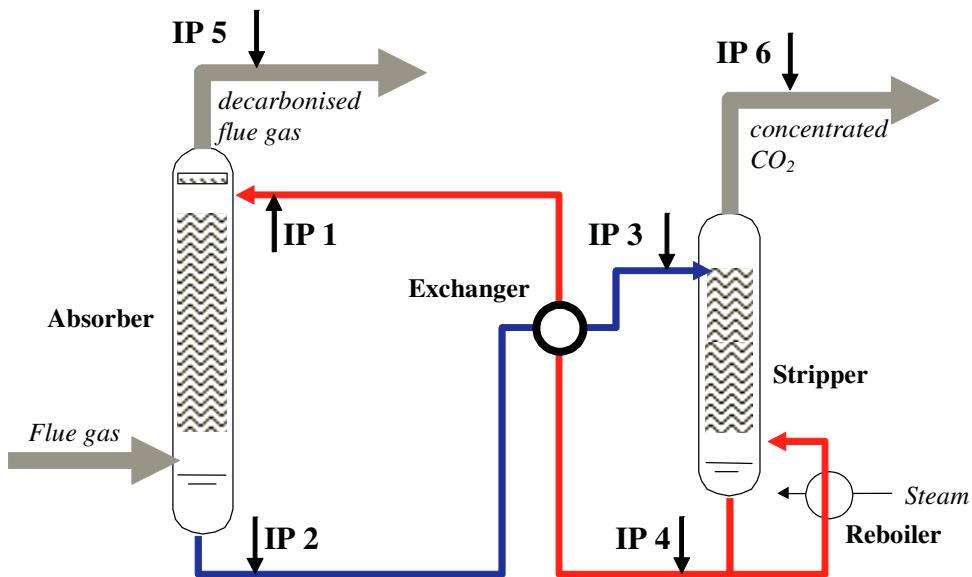


Figure 1: Schematic CO<sub>2</sub> absorber pilot plant and corrosion monitoring insertion points (IP).

## 2.2. Summary of corrosion rates in MEA operation in the Castor pilot plant

Two successive campaigns were performed using MEA 30%. The first one was realised in early 2006 and the second one was realised from December 2006 to February 2007. For each campaign, corrosion monitoring was performed through a 500 hours exposure period.

Table 1 compares for each campaign the oxygen content in the flue gas and the temperature of the solvent at different locations. The other difference between both campaigns is the use of a corrosion inhibitor for the first one, while the second one was performed with pure MEA.

Table 1: Operating conditions during MEA campaigns

	first campaign	second campaign
O <sub>2</sub> in flue gas	6% (min. 4.7% – max 9%)	5.6% (min. 0% - max 15%)
Temperature inlet absorber		39°C (min 13°C – max 40°C)
Temperature outlet absorber		49°C (min 24°C – max 53°C)
Temperature inlet stripper		107°C (min 19°C – max 110°C)
Temperature outlet stripper	106°C (min 47°C – max 111°C)	116°C (min 19°C – max 120°C)

Table 2 summarizes the corrosion rates that were measured for AISI 1018 carbon steel and AISI 304L or AISI 316L stainless steel.

Table 2: Corrosion rates during MEA 30% campaigns.

Monitoring point	Corrosion rates ( $\mu\text{m}.\text{year}^{-1}$ )			
	AISI 1018* 1 <sup>st</sup> campaign	AISI 316L 1 <sup>st</sup> campaign	AISI 1018 2 <sup>nd</sup> campaign	AISI 304L 2 <sup>nd</sup> campaign
Lean solvent inlet absorber ( $\approx 40^\circ\text{C}$ )	286	< 1	< 1	< 1
Rich solvent outlet absorber ( $\approx 50^\circ\text{C}$ )	< 1	< 1	< 1	< 1
Rich solvent inlet stripper ( $\approx 105^\circ\text{C}$ )	Lost coupon	Lost coupon	4	4
Lean solvent outlet stripper ( $\approx 115^\circ\text{C}$ )	4500	2	8500	< 1
Flue gas outlet absorber	< 1	< 1	< 1	< 1
CO <sub>2</sub> gas outlet stripper	6	1	3	< 1

These results confirm the extremely high corrosion of carbon steel in the hot lean solvent at the outlet of the stripper. During the first campaign, the corrosion rate of carbon steel at the outlet of the stripper was  $4.5 \text{ mm}.\text{year}^{-1}$ . During the second campaign, it was even higher, around  $8.5 \text{ mm}.\text{year}^{-1}$ . After three weeks of exposure, the carbon steel corrosion coupon of campaign n°2 had lost 80% of its initial weight, as illustrated in Figure 2.

The extremely high corrosivity of the solvent at that location in the pilot plant could be a result of high temperature. The higher temperature reached during the second campaign could explain the higher corrosion rate. CO<sub>2</sub> loading could also play an important role in the high corrosivity. The comparison with gas treatment is interesting: usually, for gas treatment, it is considered that lean amine lines do not suffer from corrosion problems at

all. But in that case, lean loadings are always close to zero. For CO<sub>2</sub> capture, the same "lean loading" terminology is used but the CO<sub>2</sub> content is closed to approximately 0.25 mol/mol. At such levels, the solvent probably still exhibits an extremely high corrosivity, close to that of a rich solvent.

Surprisingly, the corrosion rates of carbon steel in the rich solvent at the inlet of the stripper remained extremely low. The hypothesis of two-phase flow condition at the location where the corrosion coupons are installed has to be checked. Possible exposure of the coupons in the gas phase could explain the low corrosion rates observed before the stripper.

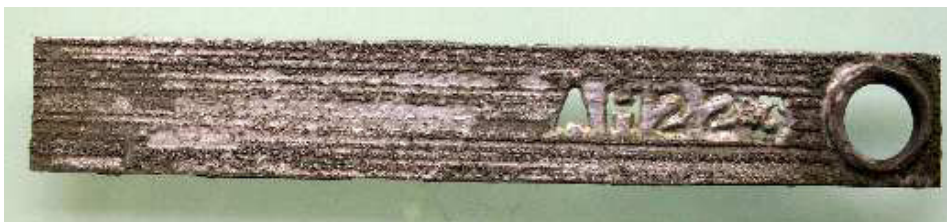


Figure 2: AISI 1018 carbon steel coupon after 3 weeks exposure in the lean solvent outlet of the stripper.

### 2.3. Lessons learnt from the Castor pilot plant

The main learning of the Castor pilot plant corrosion tests is as follows:

- The highest corrosivity is found at locations with the higher temperature and fluid velocity, i.e. the outlet of the stripper.
- Surprisingly, carbon steel exhibited good performances in the hot rich solvent at the inlet of the stripper.
- Stainless steel grades exhibited excellent resistance for all locations in the pilot plant, with a fully passive behaviour and corrosion rates below 5  $\mu\text{m}.\text{year}^{-1}$ .

## 3. ITC pilot plant

### 3.1. Corrosion monitoring system

Corrosometer probes were used to test the corrosion rate in the pilot plant. This probe can be operated at a temperature of up to 260°C and a pressure of up to 27.6 MPa. This covers the operating range in a conventional CO<sub>2</sub> capture unit.

These probes were inserted into various positions within the CO<sub>2</sub> capture process. Nine probes were inserted into the system (Figure 3), including the stripper overhead (IP1), rich amine to stripper (IP2), reflux and vapour (IP3), CO<sub>2</sub> product (IP4), stripper bottom (IP5), absorber bottom (IP6), lean amine to storage (IP7), absorber overhead (IP8), and absorber off-gas (IP9).

In each location, the tail of the probe holder was connected to the remote data collectors to measure a current density, which subsequently was converted into a thickness reduction.

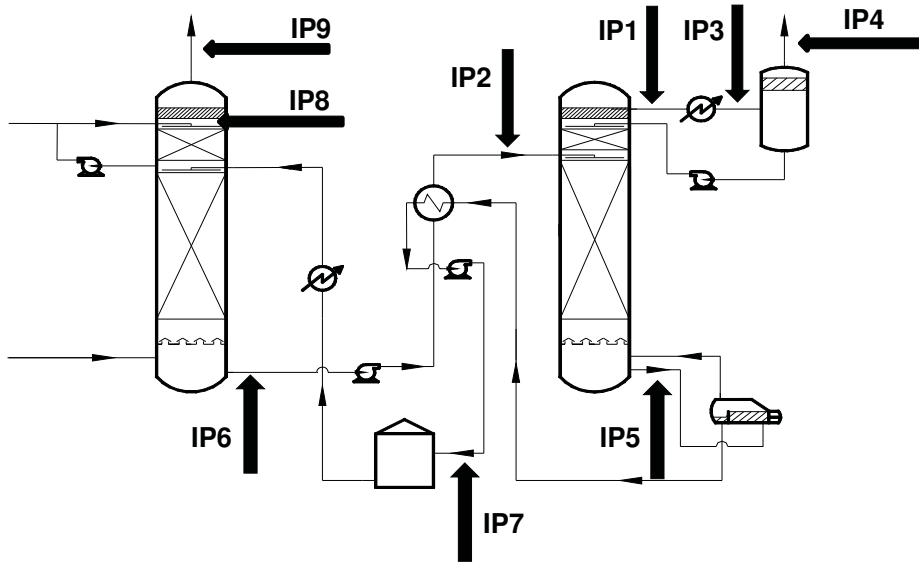


Figure 3: Schematic ITC's CO<sub>2</sub> capture unit and corrosion monitoring insertion points (IP).

The empirical equation used to convert a corrosion current density into a thickness reduction per time unit (ds/dt) is demonstrated by Equation 1 and 2:

$$\frac{ds}{dt} = \frac{i \cdot M}{z \cdot F \cdot \rho}, \text{cm/s} \quad (1)$$

$$\frac{\Delta s}{\Delta t} = 128661 \cdot \frac{i \cdot M}{z \cdot \rho}, \text{mpy} \quad (2)$$

where  $i$ ,  $M$ ,  $z$ ,  $F$  and  $\rho$  denote a current per area (A/cm<sup>2</sup>), mass of a metal (g/mol atoms), a number of electrons for an anodic reaction, Faraday's constant (96,485 coulombs/mole of electrons) and a density of metal (g/cm<sup>3</sup>), respectively.

### 3.2. Summary of corrosion rates in MEA operation in the ITC pilot plant

Table 3 summarizes the corrosion rate results. It is noted that this study focused on 4% and 8% CO<sub>2</sub> by volume in the flue gas with 30% by weight MEA solution. The rate is calculated to correlate with the power law rate equation as shown in Eq. (3). The equation can be linearized as simplified by Eq.(4). This is done to determine rate parameters, which include a frequency factor ( $k_o$ ), activation energy ( $\Delta H$ ) and reaction orders ( $a, b$  and  $c$ ).

$$r_A = k_o e^{-\frac{\Delta H}{T}} \cdot [\text{MEA}]^a \cdot [\text{CO}_2]^b \cdot [\text{O}_2]^c \quad (3)$$

$$\ln(r_A) = \ln(k_o) - \Delta H \cdot \frac{1}{T} + a \cdot \ln[MEA] + b \cdot \ln[CO_2] + c \cdot \ln[O_2] \quad (4)$$

where, T represents temperature (K), and [MEA], [CO<sub>2</sub>] and [O<sub>2</sub>] represent a liquid concentration (kmol/m<sup>3</sup>) of MEA, CO<sub>2</sub> and O<sub>2</sub>, respectively.

Table 3: Corrosion rate on each position in ITC's pilot plant

	4% CO <sub>2</sub>		8% CO <sub>2</sub>	
	Corrosion Rate (μm.year <sup>-1</sup> )	Temperature (°C)	Corrosion Rate (μm.year <sup>-1</sup> )	Temperature (°C)
LP1: Stripper Overhead	535	103.91	538	100.44
LP2: Rich to Stripper	533	111.58	1075	110.99
LP3: Reflux and Vapour	83	26.23	233	28.42
LP4: CO <sub>2</sub> Product	22	26.32	23.6	35.54
LP5: Stripper Bottom	47	118.97	28	117.94
LP6: Absorber Bottom	4	49.16	5	46.08
LP7: Lean to Storage	2	54.18	2	54.95
LP8: Absorber Overhead	0	NA	164	NA
LP9: Absorber Offgas	49	50.16	698	53.44

It is noted that the rate parameters in the power law rate equation consider only the liquid phase, not the gas phase. This results in a corrosion rate equation that is summarized in Eq.(5). Table 4 demonstrates the comparison results between the experiment and the model. Both experiment and model are in a good agreement as can be seen in Figure 4. The R<sup>2</sup> of this correlation is equal to 0.99.

$$\ln(r_A) = 19.0760 - 8963.2741 \cdot \frac{1}{T} + 3.3238 \cdot \ln[MEA] + 2.4087 \cdot \ln[CO_2] + 0.00314 \cdot \ln[O_2] \quad (5)$$

Table 4: Corrosion rate comparisons between the experiment and the model.

		Rate, μm.year <sup>-1</sup> (experiment)	Rate, μm.year <sup>-1</sup> (model)
4% CO <sub>2</sub>	Rich to Stripper	533	426
	Stripper Bottom	47	34
	Absorber Bottom	4	6
	Lean to Storage	2	1
8% CO <sub>2</sub>	Rich to Stripper	1075	919
	Stripper Bottom	28	104
	Absorber Bottom	5	5
	Lean to Storage	2	2

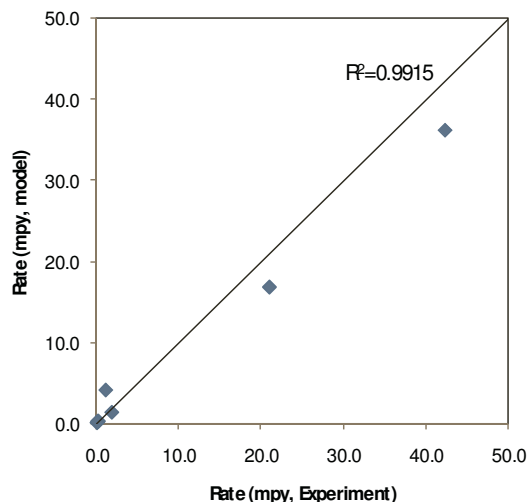


Figure 4: Parity plot of corrosion rates between experiment and model

### 3.3. Lessons learnt from the ITC pilot plant

The corrosion rate in the rich to stripper (IP2) and stripper overhead positions (IP1) is significantly high, as can be seen in Table 1. This implies that temperature plays an important role in increasing the rate of corrosion. However, there is also a high temperature at the stripper bottom (IP5), but the solution in this position is lean. In this location the solution has a high MEA concentration and a low  $\text{CO}_2$  concentration. This indicates that the concentration of MEA also contributes to an increase in the corrosion rate. By the power law rate equation expressed in Eq.(5), the power orders of MEA and  $\text{CO}_2$  are 3.324 and 2.409, respectively. Therefore, a low MEA and  $\text{CO}_2$  concentration in IP5 can result in a low corrosion rate, when compared to the rates seen in IP1 (high MEA) and IP2 (rich  $\text{CO}_2$ ).

Regardless of the temperature, MEA has more of an impact on the corrosion rate than  $\text{CO}_2$  and  $\text{O}_2$ . According to the power order, the effect of the corrosion rate by concentration can be ranked by MEA ( $a=3.324$ ) >  $\text{CO}_2$  ( $b=2.409$ ) >  $\text{O}_2$  ( $c=0.003$ ).

## 4. Conclusions

The main common trend from both pilot plants corrosion monitoring is the relatively low corrosion in the cool parts of the unit, i.e. absorber inlet and outlet.

On the other hand, the highest corrosion rates were always measured in the hottest parts of the unit, at the inlet and outlet of the stripper. However, for these locations, Castor and ITC results do not exhibit exactly similar trends. In the Castor pilot plant, the highest corrosion was observed at the bottom of the stripper, with more than 1 mm.year<sup>-1</sup> thickness reduction. Comparable corrosion rates were observed in the ITC pilot plant, but at the inlet of the stripper, in the hot rich MEA. This is a clear illustration that the combination of a high temperature and  $\text{CO}_2$  loading give rise to a corrosive situation.