

Corrosion experiments for CO₂ solvents

J. Kittel, D. Pasquier, F. Ropital, C. Boudou, A. Bonneau

Institut Français du Pétrole, 1-4 Avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France.

Abstract

The removal of carbon dioxide from industrial gas streams by amine treating units is a well known process, extensively used for many decades. One of the most severe operational difficulties encountered is the corrosion of the process equipment. In practice, corrosion mitigation might be achieved by using appropriate inhibitors, by adequate design and use of corrosion resistant alloys, or by applying process modifications when no other solution is acceptable. Although corrosion problems frequently encountered in amine treatment plants are rather well described in the literature, the corrosion mechanisms are still not well understood. Furthermore, many different forms of corrosion are found, like erosion-corrosion, stress corrosion cracking, or generalized corrosion. The causes of these different types of corrosion might be extremely wide, as well as their consequences.

CO₂ removal being an issue of growing importance, much work is performed to improve the energetic efficiency of current amine treating processes. With that aim, lot of research is done to find new, more efficient solvents. The present study is part of the UE CASTOR project, which aims at developing new, more efficient, solvent. Unfortunately, corrosion risks are extremely dependent on the nature of the amine solution. Other important parameters that might influence the corrosion are the concentration of the amine solution, the charging conditions and the composition of the gas to be treated. It is also well known that amine solvent degradation often increase corrosivity. Degradation of the solvent might be caused by high temperature during regeneration, but also by chemical reactions with some compounds of the gas, like oxygen or sulfur. Appropriate corrosion experiments are therefore required to take into account all such parameters, and to predict the risks of corrosion with new solvents. In the framework of the CASTOR project, our goal is to define a reproducible and selective experimental procedure for corrosivity evaluation of CO₂ solvents, in the specific situation of post combustion, with large volumes of flue gases with low CO₂ content and low pressure.

An experimental procedure is proposed for a rapid assessment of corrosion in amine solutions. The tests are performed in a pressure vessel under controlled loading conditions. Amine degradation occurring during the test leads to an acceleration of corrosion reactions, close to real situation in an amine unit. Corrosion tests were performed by weight loss measurements of specimens exposed in the pressure vessel.

Additionally, corrosion monitoring in a CO₂ capture pilot plant built during the CASTOR program was performed. The first run of the pilot consisted of a 500 hours run with MEA. Corrosion in the pilot plant was compared to laboratory corrosion tests with the same solvent blend.

Keywords: Corrosion, CO₂ absorption, amine solvent, MEA.

1. Experimental methods for laboratory tests

1.1. Corrosion testing apparatus and methods

Corrosion experiments were performed in a dedicated autoclave. The inner diameter of the autoclave is 8 cm, and its height is 20 cm (volume = 1L). The temperature is monitored and controlled up to 200°C. Gas inlet and outlet enable gas composition control and pressure control and monitoring. The autoclave can handle pressure up to 120 bar.

Materials that were tested were usual steel grades used in amine units:

- AISI 1028 (standard carbon steel)

- AISI 304 (stainless steel)
- AISI 316 (stainless steel)

Corrosion samples consisted of flat $30 \times 30 \times 2$ mm³ coupons. Two samples of the same steel grade were used for each experiment. Corrosion rate was evaluated by weight loss measurements after corrosion scale removal, according to ISO 8407 standards [1]. The corrosion rate (CR, in $\mu\text{m}\cdot\text{year}^{-1}$) was calculated from the weight loss (Δg , in g), the material specific weight (d , in $\text{g}\cdot\text{cm}^{-3}$), the test duration (T , in days) and the exposed area (S , in cm^2):

$$\text{CR} = \frac{\Delta g}{S \cdot d} \cdot \frac{365}{T} \cdot 10^4 \quad (1)$$

Corrosion coupon holder also served as magnetic stirrer, enabling a permanent and controlled stirring of the solution.

According to a literature survey on the most severe service conditions in an amine unit [2], the following experimental conditions were chosen for the temperature (120°C) and the initial pressure in the autoclave (2 bar). Other parameters, especially gas composition, were not precisely defined at the start of the program, but had to be defined in the first part of the experimental program.

Tested solvents were prepared from chemical grade reagents and ultrapure water.

1.2. Definition of gas composition and loading conditions

The definition of an adequate set of gas composition and gas loading conditions constituted the first step of the experimental work within the CASTOR project. Several preliminary experiments were therefore conducted with varying gas composition and loading conditions. For these tests, the solution was always a 30 wgt.% MEA solution, which served as reference solvent. The objective was to obtain a fast, accurate, and reproducible experimental protocol for testing and ranking the corrosivity of amine solvents and comparing the corrosion resistance of different steel grades. Typical time scale of one corrosion test had to be in the order of 1 month.

For all tested conditions, it was decided to fix the temperature in the autoclave to 120°C. The gas loading was performed the following way :

- 1) saturation of the solvent by gas bubbling at ambient temperature and atmospheric pressure;
- 2) filling of the autoclave with the saturated solvent ;
- 3) at ambient temperature and after closing of the autoclave, purging the gas sky and filling with test gas to 1 bar (repeated 5 times) ;
- 4) start of heating and stirring (400 rpm) ;
- 5) when temperature of 120°C is reached, adjusting the pressure to 2 bar with the testing gas.
- 6) closing all valves of the autoclave, monitoring of pressure and control of temperature.

2. Experimental results of laboratory tests

2.1. Preliminary results with MEA: choice of gas loading composition

Three sets of gas composition and loading conditions were compared:

- 1) SO₂ 10 ppm ; NO 20 ppm ; CO₂ 15% ; N₂ (balance)
This gas composition is representative of real loading condition in an amine unit.
- 2) CO₂ (pure)
This composition was selected to increase the severity of CO₂ loading.
- 3) CO₂ 75% ; O₂ 5% ; N₂ 20%
This composition is supposed to favour the degradation of the solvent, by reaction (oxidation) with O₂, amine degradation products being more corrosive.

For all these tests, corrosion rates were evaluated after 1 month. Table 1 summarises the corrosion rates that were obtained for the three selected gas compositions. For each test, corrosion rate is the mean value of two identical samples. Gas composition n°1 and n°2 were tested once, while gas composition n°3 was tested three times.

After one month testing in MEA 30% loaded with gas n°1 and n°2, the amine solution had turned to light yellow, indicating a low degradation of the solvent. The corrosion rates measured in these conditions are extremely low. These values are definitely not representative of severe service conditions. Furthermore, ranking different solvents or materials with such experimental conditions would require extremely long testing time. Therefore, those two gas compositions were discarded. Three tests were then performed with gas composition n°3, two of them lasted 1 month, while the last one was stopped after 15 days. All three tests exhibited a high amine degradation, as illustrated by the dark colour of the solution after the test. Corrosion rates measured under these conditions were also far higher than in solutions loaded with non oxygen containing gas blends: 420 $\mu\text{m}\cdot\text{year}^{-1}$ for AISI 1028, 55 $\mu\text{m}\cdot\text{year}^{-1}$ for AISI 304, and 14 $\mu\text{m}\cdot\text{year}^{-1}$ for AISI 316. This is also a strong indication that amine degradation leads to an important increase of corrosivity. This problem is often encountered in real amine units, where corrosion problems are often attributed to unexpected oxygen entry in the system.

Table 1: Corrosion rates (in $\mu\text{m}\cdot\text{year}^{-1}$) of AISI 1028, AISI 304 and AISI 316 in MEA 30% loaded with different gas compositions

	AISI 1028	AISI 304	AISI 316
1) SO ₂ 10ppm ; NO 20ppm ; CO ₂ 15% ; N ₂	~ 0	0.4	1
2) pure CO ₂	48	38	12
3) CO ₂ 75% ; O ₂ 5% ; N ₂ 20%	420 ± 180	55 ± 20	14 ± 10

According to these results, the experimental protocol including loading with gas composition n°3 (75% CO₂ and 25% air) was selected for the next step of the CASTOR program. Following this experimental protocol, we thus expect to be able to rank the corrosivity of different solvent compositions, compare the corrosion resistance of different materials, while being representative of severe service conditions.

2.2. Comparative corrosivity of different solvents

After the preliminary tests with 30% MEA, the testing protocol was applied to measure the corrosion rates of carbon steel and stainless steels in diethylenetriamine (DETA), diethylethanolamine (DEEA) and in a specific solvent formulated within the CASTOR project (referred to as CASTOR 1 solvent). Finally, real solvent (MEA) sampled in the CASTOR pilot plant (see §3.2.) was also tested. Corrosion rates are summarised in Table 2.

Table 2: comparative corrosion rates of laboratory tests in different solvent compositions.

	AISI 1018	AISI 304	AISI 316
MEA 5M (30%)	420 $\mu\text{m}\cdot\text{year}^{-1}$	55 $\mu\text{m}\cdot\text{year}^{-1}$	14 $\mu\text{m}\cdot\text{year}^{-1}$
MEA 5M + inhibitor*	215 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$
DETA 5M (60%)**	615 $\mu\text{m}\cdot\text{year}^{-1}$	9 $\mu\text{m}\cdot\text{year}^{-1}$	7 $\mu\text{m}\cdot\text{year}^{-1}$
DEEA 2.5M	23 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$
CASTOR 1 solvent	< 5 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$	< 1 $\mu\text{m}\cdot\text{year}^{-1}$

* real solvent that was sampled in the pilot plant before use, see § 3.2.

**The DETA concentration of the test was erroneously 5M (which corresponds to 60 wgt.%), when a concentration of 2.5M (30 %) should have been tested.

Among the tested solvent, MEA exhibited the highest corrosivity. It is to be noted that the corrosion inhibitor that was present in the MEA sampled from the Castor pilot plant did not seem to perform well for carbon steel, as its efficiency was less than 50%. This inhibitor seemed more efficient for stainless steel, but this result does not have much sense, as corrosion inhibitors are usually used to avoid high grade steels. DETA 5M also exhibited a high corrosivity, but this test was done on an extremely highly concentrated solvent (5 M instead of 2.5 M).

DEEA 2.5M seemed to be far less corrosive than MEA. CASTOR 1 solvent offered the best performance in terms of corrosivity.

For all the tests, AISI 316 gave an excellent corrosion resistance. AISI 304 was also satisfactory, except in the MEA 30% without inhibitor, where the corrosion rate was too high for a stainless steel grade.

3. Pilot plant experiments

3.1. Corrosion monitoring tools

Within the CASTOR project, a CO₂ absorption pilot plant was built and is operated by ELSAM (DK). Corrosion monitoring was implemented to the pilot. Six monitoring points were selected for that purpose, considering the locations most susceptible to corrosion damages [2] (Figure 1):

- lean solution at the inlet of the absorber,
- rich solution at the outlet of the absorber,
- rich solution at the inlet of the stripper,
- lean solution at the outlet of the stripper,
- absorber gas outlet,
- stripper gas outlet.

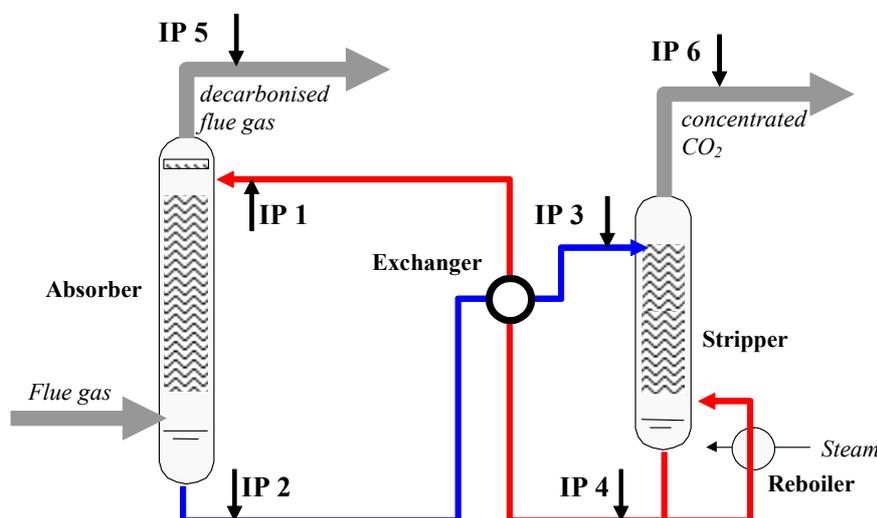


Figure 1: Schematic CO₂ absorber pilot plant and corrosion monitoring insertion points (IP).

Corrosion weight-loss coupons and coupon holders were purchased to Rohrback Cosasco Systems. Insertion in the pilot plant was realised through $\frac{3}{4}$ " NPT nozzles, located at the selected insertion points. Corrosion coupons were flat rectangular samples, $3 \times \frac{1}{2} \times \frac{1}{16}$ in³ ($76 \times 13 \times 1.6$ mm³), made of AISI 1018 (carbon steel) and AISI 316 (stainless steel). After each pilot operation, coupons are removed cleaned and weighed for corrosion evaluation.

3.2. Corrosion after 500 h running under 30% MEA + inhibitor

After conditioning of the pilot plant, the first CO₂ absorption tests were realised for 500 hours with the reference solvent (30% MEA) to which a commercial corrosion inhibitor was added. Corrosion coupons were installed January 10th (2006) just before starting this operating period. Coupons were removed from the pilot plant February 2nd.

During this period, the oxygen content in the flue gas varied from 4.7 % vol. to 9 % vol., with an average concentration of 5.95 % vol. (wet basis composition). This high oxygen content (values between 3 – 4 % vol. were expected) might have induced an acceleration of the degradation of the solvent, leading to an increased corrosivity. The solvent temperature at the bottom of the stripper varied from 47 to 111 °C, with an average of 106 °C. During the 500 hours run, no reclaiming of the solvent was carried out. Therefore, heavy degradation products were not eliminated.

Table 3 summarises the corrosion rates that were measured at the different locations in the pilot plant. Unfortunately, coupons that were installed at the inlet of the stripper were lost, probably due to insufficient clamping of the screw with the coupon holder.

Table 3: Corrosion rates and pictures of weight loss coupons recovered from the pilot plant.

	AISI 1018	AISI 316
1- Lean solvent, inlet of the absorber	$3.6 \cdot 10^3 \mu\text{m} \cdot \text{year}^{-1}$	$8 \mu\text{m} \cdot \text{year}^{-1}$
2- Rich solvent, outlet of the absorber	$4 \mu\text{m} \cdot \text{year}^{-1}$	$5 \mu\text{m} \cdot \text{year}^{-1}$
3- Rich solvent, inlet of the stripper	Coupons were lost in the pilot plant	
4- Lean solvent, outlet of the stripper	$56 \cdot 10^3 \mu\text{m} \cdot \text{year}^{-1}$	$23 \mu\text{m} \cdot \text{year}^{-1}$
5- Flue gas, outlet of the absorber	$4 \mu\text{m} \cdot \text{year}^{-1}$	$5 \mu\text{m} \cdot \text{year}^{-1}$
6- CO ₂ gas, outlet of the stripper	$80 \mu\text{m} \cdot \text{year}^{-1}$	$14 \mu\text{m} \cdot \text{year}^{-1}$

From these results, it is obvious that the most severe conditions are encountered with the lean solvent, at the outlet of the stripper (Figure 2), where the temperature is the highest (average of 106°C during the operating period) and at the inlet of the absorber. Corrosion rates of carbon steel (AISI 1018) at these locations are extremely high, respectively 56 and 3.6 mm.year⁻¹. It is obvious that this material is definitely forbidden for use in such conditions, even though a corrosion inhibitor was added to the MEA 30% solvent !

The rich solvent seems to be far less corrosive: corrosion rates measured at the outlet of the absorber are extremely low.

Corrosion in the gas phases were also monitored, outlet of the absorber (decarbonised flue gas) and outlet of the stripper (rich CO₂). In both cases, traces of condensation were observed on the coupons freshly removed from the pilot. It seems that CO₂ at the outlet of the stripper is more corrosive than the decarbonised flue gas. This could result from condensation on the materials surface and CO₂ dissolution, leading to acid water corrosive environment, and ferrous carbonate scale precipitates, as indicated by the visual aspect of the carbon steel coupon (Figure 2). Nevertheless, the corrosion rates of AISI 1018 carbon steel remain quite low, below the limit of 100 μm.year⁻¹, which is often considered to be the upper acceptable corrosion rate.

For all the locations monitored in the pilot plant, and as expected from the literature [2, 3], AISI 316L was fully satisfactory.



Figure 2: Corrosion coupons removed from the lean amine section at the outlet of the stripper (left) and removed from the CO₂ gas outlet of the stripper.

Comparisons with the laboratory tests are not obvious at this stage. It is reminded that a corrosion rate of 215 μm.year⁻¹ was measured for carbon steel in the solvent sampled from the pilot plant at the very beginning of the operation. This laboratory corrosion rate is far less than the corrosion rate in the lean amine parts of the pilot plant, but also far more than that in the rich amine in the pilot plant. Nevertheless, the laboratory study did not aim to simulate accurately some specific areas of the pilot plant: its goal was only to have a good method for the ranking of different solvent compositions. In order to compare more accurately laboratory and pilot plant corrosion results, other laboratory tests will be performed throughout the project with other solvents sampled from the pilot plant :

- 30% MEA degraded by a 500 hours flue gas treatment period,

- Castor 1 solvent at the start and at different ageing periods of flue gas treatment in the pilot plant.

The corrosion experiments and gas treatment in the pilot plant will also be coupled with chemical analysis of the solvents. Identification of the degradation by-products should give more information on the real causes of the corrosivity of amine solvents, and will be helpful to find new and more accurate means to mitigate corrosion in gas treatment plants.

Conclusion

Definition of a fast, accurate, and reproducible experimental protocol for testing and ranking the corrosivity of amine solvents and comparing the corrosion resistance of different steel grades was the primary objective of the laboratory testing program. The following testing conditions were selected for the autoclave laboratory tests:

- temperature: 120°C ;
- initial pressure: 2 bars (then free to evolve during the test) ;
- gas composition: CO₂ 75% ; O₂ 5% ; N₂ 20% ;
- loading procedure: saturation at ambient temperature ;
- stirring: 400 rpm ;
- steel grades: AISI 1028, AISI 304, AISI 316 ;

Using this protocol, the following ranking could be proposed for the corrosivity of different solvents : MEA 30% \approx DETA 5M \geq MEA 30% + inhibitor \gg DEEA 2.5M \geq CASTOR 1.

For all tested solvents, AISI 316 was fully resistant. It was interesting to note that the corrosion inhibitor added to MEA 30% offered an efficiency of only 50%, far less than the values usually expected when using inhibitors ($> 90\%$ efficiency).

Corrosion rates in the CASTOR gas treatment pilot plant were easily monitored by weight loss coupons inserted in the pilot plant. A period of 15 days immersion was sufficient to detect with a good accuracy the sections with high risks of corrosion.

In the pilot plant, and with the reference solvent (30% MEA + inhibitor), the corrosion rate of carbon steel was considerable in the "lean amine areas", at the outlet of the stripper and at the inlet of the absorber, greater than several mm.year⁻¹. The areas with the "rich solvent" exhibited far less corrosion of carbon steel: less than 10 $\mu\text{m}\cdot\text{year}^{-1}$. In the gas phases, the highest risk seemed to be for the CO₂ outlet: in the case of condensation, CO₂ saturation of the liquid phase could lead to extremely acid and corrosive situation. Some traces of condensation were observed when removing the coupons. Although the corrosion rates measured in this test remained reasonable, it is not impossible that a more severe condensation could occur at a specific area (a specific height) in the gas pipe, creating risks of local corrosion.

For all monitoring points, AISI 316 stainless steel always exhibited corrosion rates lower than 50 $\mu\text{m}\cdot\text{year}^{-1}$, with no evidence of pitting or localised attack.

Pilot plant and laboratory tests will be continued with new solvents. Solvent analysis will also be performed at different ageing times, in order to identify degradation by-products, and try to find correlations with the corrosivity.

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