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# **Acid gas removal by amine solvents: bridges between CO<sub>2</sub> capture and natural gas treatment.**

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## **Abstract**

In the oil and gas industry, acid gas removal is required for the treatment of natural gas. New applications were also recently pushed forward for CO<sub>2</sub> capture from the flue gas of power plants. For both applications, the most widespread industrial processes use absorption – desorption by an alkanolamine solvent. In such amine units for acid gas removal, corrosion represents an important operational concern.

The aim of this paper is to review some of the parameters influencing the corrosivity of amine solvents. In the light of literature data and of new experimental results, the influences of temperature and of acid gas loading are discussed. These two parameters appear to have a strong impact on corrosion rates of carbon steel, with extrapolated corrosion rates of several tens of mm/year for the highest temperature and acid gas loading condition.

It is then proposed to discuss about similarities and differences between natural gas processing and CO<sub>2</sub> capture from flue gas. For both applications, alkanolamine processes are used. Still, differences can be found in operating parameters. The most significant gap concerns the lean amine sections. In acid gas treatment, the regeneration of the solvent is often performed down to zero loading. Under these conditions, an extremely low corrosivity of the lean solvent is expected. On the contrary, CO<sub>2</sub> capture from flue gas requires only a partial stripping of the CO<sub>2</sub> in the regeneration section, due to energy efficiency reasons. Then, the lean solvent still contains some acid gas, and subsequently a higher corrosivity.

Finally, the general principles for material selection for the different parts of acid gas removal units are discussed, considering both cases of natural gas processing or CO<sub>2</sub> capture.

# 1 INTRODUCTION

## 1.1 Basics of acid gas removal by alkanolamines

Throughout the petroleum chain, the treatment steps are nearly always designed to purify the fluids, separate various components and eliminate undesirable species, in particular the two acid gases carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S). Treatments to remove CO<sub>2</sub> and H<sub>2</sub>S from natural gas are often implemented as soon as the gas leaves the well. At the other end of the chain, the refinery gases may also need to be stripped of these acid gases. Lastly, these separation treatments are becoming increasingly important in the fight against greenhouse gas emissions and might be used in a near future for the post-combustion capture of CO<sub>2</sub> in combustion fumes from industrial processes [1].

The most widely used process in all these applications uses alkanolamine-based chemical solvents (e.g. MEA, monoethanolamine ; DEA, diethanolamine, MDEA, methyldiethanolamine) capable of reacting preferentially with CO<sub>2</sub> and H<sub>2</sub>S. Figure 1 provides a simplified process flow description of this type of treatment unit. The main components and the operating principles are the same in the three broad domains concerned: natural gas processing, treatment of refinery gases and post-combustion CO<sub>2</sub> capture.

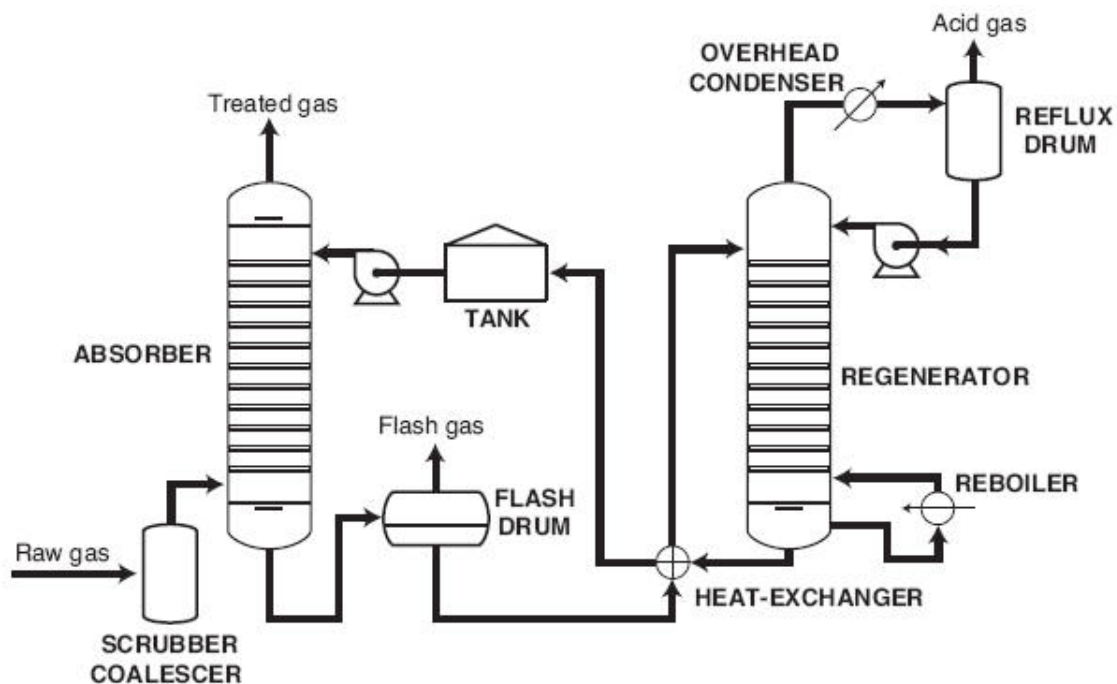


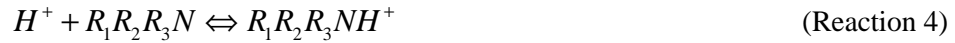
Figure 1: Simplified diagram of an alkanolamine acid gas removal unit

The gas to be treated is introduced in the unit at the bottom of the absorber where it comes into contact with the solvent. The acid gases (CO<sub>2</sub> and/or H<sub>2</sub>S) react and are absorbed by the solvent according to reactions 1 to 6 below.

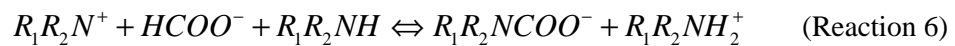
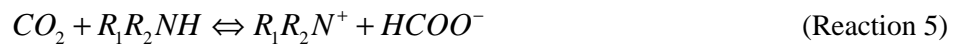
The reaction with H<sub>2</sub>S, which is the same irrespective of the type of amine considered, consists of direct proton transfer (Reaction 1), where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> represent alkyl groups or a hydrogen atom.



The reaction with CO<sub>2</sub> is slightly more complex. Two different mechanisms may be involved. A first reaction may occur, involving the successive formation of carbonic acid and bicarbonate (Reaction 2 and Reaction 3), followed by direct proton transfer identical to that observed for H<sub>2</sub>S (Reaction 4).



This mechanism may occur for all types of amine. The global kinetics is slow, however, since it is limited by dissociation of carbonic acid into bicarbonate (Reaction 3). For the primary and secondary amines, which have hydrogen bond to the nitrogen, a second mechanism is possible.



This second reaction mechanism is generally much faster than the CO<sub>2</sub> hydrolysis reaction (Reactions 2 to 4). For the primary and secondary amines, there is little difference in the reaction kinetics between CO<sub>2</sub> and H<sub>2</sub>S. For the tertiary amines, however, unable to form a carbamate, the reaction kinetics with H<sub>2</sub>S is much faster than with CO<sub>2</sub>. This property is put to good advantage to give some solvents selectivity between CO<sub>2</sub> and H<sub>2</sub>S.

At the liquid output at the bottom of the absorber, the solvent is therefore enriched in acid gas according to one or more of reactions 1 to 6: we speak of rich amine. At the top of the absorber, the gas has been stripped of its undesirable components CO<sub>2</sub> and/or H<sub>2</sub>S.

The rich amine is then pre-heated by a heat exchanger then fed into the top of a regeneration column. In this part of the unit, the solvent is raised to high temperature by steam, which releases the dissolved acid gases. This is due to the fact that the equilibriums of reactions 1 to 6 are shifted to the left at high temperature and low pressure. At the liquid output of the regenerator, the solvent is hot (about 120°C) and contains less acid gas: we speak of lean amine. The solvent is then cooled by the heat exchanger and sent back to the top of the absorber to start a new cycle. The acid gases are collected at the top of the regenerator, where they can be sent for suitable processing.

## 1.2 Corrosion mechanisms and influent parameters

In such complex units, numerous pieces of equipment are exposed to equally numerous types of corrosion. We can nevertheless adopt the classification proposed by Nielsen [2], who identifies:

- wet acid gas corrosion,
- amine solution corrosion.

Wet acid gas corrosion is encountered in all parts of the unit in contact with an aqueous phase with a high concentration of dissolved acid gases CO<sub>2</sub>, H<sub>2</sub>S, as well as NH<sub>3</sub> and HCN for refinery units. This type of corrosion is found primarily in zones where the gaseous phases

have high concentrations of acid gases and where water may condense, mainly at the bottom of the absorber and the top of the regenerator.

For gas containing mostly CO<sub>2</sub>, parts of the installation made from carbon steel may suffer fast uniform corrosion, up to several mm/year. In the presence of H<sub>2</sub>S, this uniform corrosion is generally delayed by the formation of a protective iron sulfide layer. A minimum H<sub>2</sub>S/CO<sub>2</sub> ratio of 1/20 is often considered as sufficient to avoid risks of uniform CO<sub>2</sub> corrosion [3,4]. In the presence of H<sub>2</sub>S however, specific cracking phenomena may also be encountered (hydrogen embrittlement, HIC, SSC, etc.). In the presence of HCN and/or NH<sub>3</sub>, the risks of cracking are also increased.

The second type of corrosive media found in acid gas removal units consists of amine solution. Generally, amines are not intrinsically corrosive, since they associate both high pH and low conductivity. They may nevertheless become corrosive when they absorb CO<sub>2</sub> or H<sub>2</sub>S. Furthermore, since the treatment units operate in semi-closed circuit, the solvent may become enriched with possibly corrosive degradation products.

No consensus has yet been reached concerning the mechanisms of corrosion by amine solutions. The models proposed vary depending on the type of amine (in particular, primary, secondary and tertiary), the H<sub>2</sub>S/CO<sub>2</sub> ratio in the gas to be treated, possible presence of oxygen either as contaminant in the circuit or as component of the input gas (e.g. CO<sub>2</sub> capture in fumes). For more information on specific corrosion models, the reader may refer to the relatively extensive bibliography on this subject [2,5-8].

We may nevertheless identify some systematic trends governing the corrosivity of acid gas chemical solvents. Acid gas loading and temperature are usually considered as the most important factors. The acid gas loading ( $\alpha$ ) is defined as the quantity of acid gas absorbed by a defined quantity of solvent and is often expressed in moles of acid gas per mole of amine. Increasing the acid gas loading increases the corrosivity of amine solutions [7-10]. Temperature generally has an extremely important effect on corrosion phenomena since most electrochemical reactions involved are thermally activated. It is common practice in industry to consider that the corrosion rate is doubled when the operating temperature increases by 10°C to 20°C. For gas treatment units, the effect of temperature is relatively difficult to assess on an individual basis. Temperatures vary widely in the installation, with extreme values ranging from 40°C in the absorber up to 130°C in the reboiler. However, these temperature variations have a significant effect on the chemistry of the solution, in particular the acid gas loading. Taking into account both the loading and the temperature, we may consider that the main corrosion risks are encountered in areas with high loading and high temperatures [8,11]. These conditions are generally found in the rich amine line after the heat exchanger and up to the regenerator input.

The type of amine is also one important factor. Usually, primary amines (e.g. MEA) are the most corrosive, secondary amines (e.g. DEA) slightly less and tertiary amines (e.g. MDEA) exhibit the lowest risks of corrosion [7,8,10,12-15]. Amine concentration also has an influence on corrosion. Excessively high amine concentrations should generally be avoided. Nevertheless, the results obtained from the few laboratory studies conducted on the effect of amine concentration on corrosivity vary widely, between a marked effect [8,10] and a moderate or null effect [16,17].

The concentration in degradation products and contaminants can significantly influence corrosion reactions. A distinction must be made between basic and acidic degradation products. Basic amine degradation products mainly result from chain reactions between amine and CO<sub>2</sub>, for example the following compounds: HEOD (3-(2-hydroxyethyl)-2-oxazolidone),

BHEP (N,N'-bis(2-hydroxyethyl)piperazine), THEED (N,N,N'-tris(2-hydroxyethyl)ethylenediamine). The studies on corrosivity by these degradation products date back a number of years, the general conclusion being an absence of specific corrosivity [13,14]. Most acidic degradation products result from reactions with oxygen. The main products include salts of oxalic, glycolic, formic and acetic acids, which are stronger than carbonic acid. As a result these salts are not thermally regenerated in the process, hence their name: Heat Stable Salts (HSS). The effect of these products on corrosion has been well documented through laboratory tests; they increase corrosion of carbon steel [18-20]. Finally, the solvent flow rate and conditions favourable to turbulence (gas flash, gas injection zones, etc.) may cause risks of erosion-corrosion. This type of corrosion is specific to carbon steels, since stainless steel grades are far more resistant. This type of corrosion is probably aggravated when the content of degradation products becomes too high: as indicated above, some of these products have a chelating effect on iron and may favour more efficient and faster dissolution of the protective deposits exposed to erosion [2,3,9,21].

### 1.3 Objectives of the experimental study

The first objective of this paper is to offer a comparison of corrosive conditions between CO<sub>2</sub> capture and acid gas treatment. If both applications can be described by amine absorption – desorption process of Figure 1, three major differences have to be mentioned, on the gas composition, the nature of the amine used, and the lean loading level.

In natural gas processing, the gas to be treated usually has high pressure up to 70 bars, and might contain a significant proportion of CO<sub>2</sub> and/or H<sub>2</sub>S, up to several tens of percent. Oxygen contamination is not supposed to be present. The main goal of the process is to recover natural gas with a minimum amount of acid gas contaminants. Concerning H<sub>2</sub>S, complete removal is usually expected, while CO<sub>2</sub> removal efficiency depends on the application (between 2-3 % for conventional applications, but down to less than 50-100 ppmv for LNG). Optimisation of the process then allows using secondary or tertiary amines, and requires regenerating the solvent down to zero loading, i.e. no acid gas is present in the solvent at the outlet of the regenerator column.

On the other hand, CO<sub>2</sub> capture from combustion fumes respond to different constraints, and has slightly different objectives. The first important factor is in the composition and pressure of the gas to be treated. Usually, it contains up to 10-15% CO<sub>2</sub>, for a total pressure close to 1 bar. The CO<sub>2</sub> partial pressure is then extremely low, while the emitted fumes flow-rate is extremely high. It is therefore required to have a solvent capable of a very fast absorption reaction with CO<sub>2</sub>, which is generally the case of primary amines, but not secondary or tertiary amines. Additionally, the presence of up to 5% oxygen in the flue gas is also an important factor, since it might react with the amine to form corrosive degradation products. Lastly, operating conditions are aimed at finding a compromise between a good CO<sub>2</sub> removal, without penalising too much the power plant efficiency. For this reason, CO<sub>2</sub> regeneration is not complete in CO<sub>2</sub> capture processes: then, the lean amine loading is generally not zero, but preferably around 0.25 mol<sub>CO<sub>2</sub></sub>/mol<sub>amine</sub> in the case of MEA.

In the light of these aspects, the experimental program is aimed at studying how these differences in operating conditions might influence the risks of corrosion. MEA was chosen as reference solvent, since it represents the choice amine for CO<sub>2</sub> capture applications. The impact of temperature and of acid gas loading will be studied, in order to cover as much as

possible all operating conditions of both applications. The impact of other factors, such as oxygen contamination in the amine, will also be investigated.

## 2 EXPERIMENTAL

### 2.1 Test solutions and steel specimens

Test solutions were prepared with analytical grade MEA and deionised water. Most of the experiments used 30% mass. MEA solutions (corresponding approximately to 5M). Some specific tests used 20% and 40% MEA concentrations.

Acid gas loading was achieved by purging CO<sub>2</sub> gas for approximately 12 hours, at the temperature of the test. For some specific tests aimed at checking the impact of dissolved oxygen, initial loading was performed by purging a gas mix composed of CO<sub>2</sub> (75%) and air (25%). The quantity of absorbed CO<sub>2</sub> was then measured by a volumetric method after adding an excess amount of hydrochloric acid to a sample of the solution [22]. Acid gas loading was then expressed as the ratio between the number of moles of CO<sub>2</sub> and the number of moles of amine. When intermediate CO<sub>2</sub> loadings were required, CO<sub>2</sub> saturated solution was mixed with a fresh lean solution. CO<sub>2</sub> titration was checked after mixing, to ensure that the target loading was reached.

During all tests, a gas stream was maintained in the gas phase of the test cell. For the tests under saturated solutions, the gas stream was pure CO<sub>2</sub> or CO<sub>2</sub> + air mix. When solutions with intermediate loading were used, N<sub>2</sub> was used, mainly to avoid oxygen entry in the test cell.

After all corrosion tests, CO<sub>2</sub> titration was systematically performed to ensure that the loading did not significantly evolve.

Carbon steel specimens were used for the corrosion evaluation. The composition is given in Table 1. The specimens were cut into cylindrical shape, 30 mm long and 10 mm diameter, with a 6 mm thread for electrical connection and support. Before each experiment, the specimen was grinded with 600 grid SiC paper, degreased with ethanol and rinsed with deionised water.

*Table 1: Chemical composition of carbon steel used as working electrode in electrochemical corrosion tests.*

C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Ag	Al	Ti	V	Nb	Fe
0.39	0.64	0.23	0.012	0.028	0.16	0.14	0.02	0.25	0.008	0.024	0.018	0.003	0.003	bal.

### 2.2 Corrosion testing methods

All tests were carried out in a 0.5L glass cell. Temperature was adjusted by circulating hot water in the double-wall of the test cell.

Most of the tests were carried out using electrochemical method, with a three-electrode assembly. Ag/AgCl reference electrode was introduced in a bridge tube filled with water saturated with KCl. A platinum plate with a 1 cm<sup>2</sup> section was introduced directly in the test solution and used as counter-electrode. Carbon steel cylinder was used as working-electrode. Electrochemical testing was performed in successive steps. Once the test solution had reached the expected temperature, the working electrode was immersed and the open current potential

( $E_{oc}$ ) was measured. Once a stable value was reached, or after 24 hours immersion, potentiodynamic polarization measurement was started, in the range  $E_{oc} - 250\text{mV}$  to  $E_{oc} + 1\text{V}$ . The scanning rate was 10 mV/min. Measurement apparatus was a VMP2 Biologic potentiostat.

Analysis of the polarization plots was done according to ASTM G3 and ASTM G102 [23,24]. Tafel extrapolation was used to evaluate the corrosion current density ( $J_{corr}$ ). The corrosion ( $CR$ , in  $\mu\text{m}\cdot\text{year}^{-1}$ ) rate was then calculated from the corrosion current density (in  $\mu\text{A}\cdot\text{cm}^{-2}$ ) using the following equation, derived from the Faraday's law:

$$CR = 11.7 \times J_{corr} \quad (\text{Equation 1})$$

For some specific conditions, weight loss measurements were performed for comparison with electrochemical results. Weight loss coupon was strictly similar in shape and surface preparation than the coupon used as working electrode. The coupon was immersed in the test solution for three weeks. Before final weighing, it was rinsed with distilled water and dried. When needed, corrosion scales were removed using a plastic brush and/or by a chemical cleaning method, as proposed in ASTM G1 standard [25].

### 3 RESULTS

#### 3.1 Impact of oxygen

The first series of experiments was aimed at evaluating the impact of dissolved oxygen. Experiments were carried out in  $\text{CO}_2$  saturated MEA 30% at  $80^\circ\text{C}$ , with or without dissolved oxygen.

The first test was then realized after saturation of the solution by purging pure  $\text{CO}_2$ . Then, during all the experiment,  $\text{CO}_2$  stream was maintained in the test cell.  $\text{CO}_2$  loading was measured to  $0.5 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$ .

The same protocol was applied for the second test, except that a gas mix composed of 75%  $\text{CO}_2$  and 25% air was used instead of pure  $\text{CO}_2$ . The same level of  $\text{CO}_2$  loading was measured, and oxygen content was close to 5%, which is the typical content in fumes from coal-fired power stations.

Polarization curves of carbon steel in MEA solution with or without dissolved oxygen are compared in Figure 2.



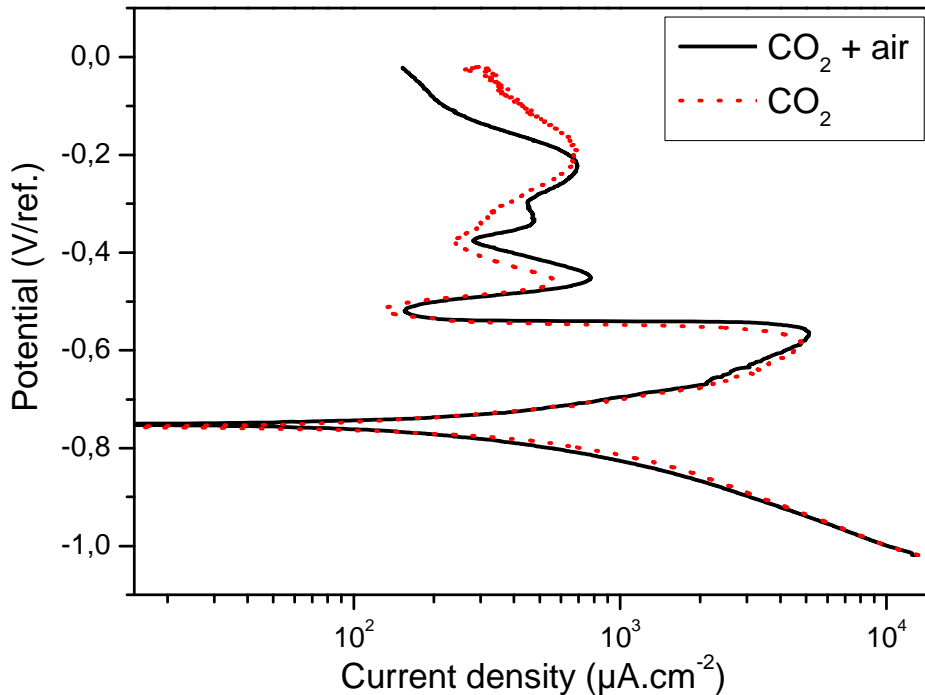


Figure 2 : Polarization curves of carbon steel in 30% MEA at 80°C and saturated with CO<sub>2</sub> (loading = 0.5), with or without dissolved oxygen.

Both polarization curves present very similar trends.

The corrosion potential ( $E_{corr}$ ) is -750 mV/ref., very close to the open current potential ( $E_{oc}$ ) measured before polarization (-770 to -775 mV/ref.). The cathodic branches present a linear evolution of the logarithm of the current density with the potential, with a Tafel slope close to 200 mV/decade. The anodic region presents an active dissolution peak followed by a passive region with several secondary oxidation peaks. The critical current density is close to 5 mA.cm<sup>-2</sup>, and the primary passivation potential is close to -570 mV/ref.

From these polarization curves, extrapolation of the cathodic region to  $E_{corr}$  allows estimating the corrosion current density to 500  $\mu\text{A}/\text{cm}^2$ , corresponding to a corrosion rate close to 5 mm/year. For comparison, weight loss tests were performed on carbon steel coupon exposed for three weeks in the same solution (with oxygen). At the end of the test, the coupons were covered with a thin black deposit. XRD analysis revealed that it consisted mainly of siderite (FeCO<sub>3</sub>). The corrosion rate, measured after removal of the iron carbonate scale, was approximately 2 mm/year, which is somewhat lower than the 5 mm/year estimation from electrochemical experiments. This difference could be explained by the fact that electrochemical evaluation is made only a few hours after immersion, on a clean specimen without significant corrosion scale. On the other hand, iron carbonate deposit was formed during long term immersion. This deposit probably had a protective action against corrosion. Nevertheless, both weight loss measurements and electrochemical evaluation give corrosion levels in the same order of magnitude.

From these experiments, two main results should be emphasized:

- dissolved oxygen does not have a significant impact on the corrosivity of rich MEA,
- in CO<sub>2</sub> saturated MEA at 80°C, the corrosion rate of carbon steel reaches several mm/year.

### 3.2 Impact of MEA concentration

Another parameter often presented in the literature to have an important impact on corrosion is the concentration of amine. For MEA, 20-30% is often considered the maximum range, above which corrosion risk dramatically increases [26,27].

However, contradictory laboratory data can be found in the literature [8,10,16,17]. In order to make our own opinion, three tests were launched in 20 / 30 / 40% MEA, saturated in CO<sub>2</sub> and at 80°C. The corresponding polarization plots are presented in Figure 3.

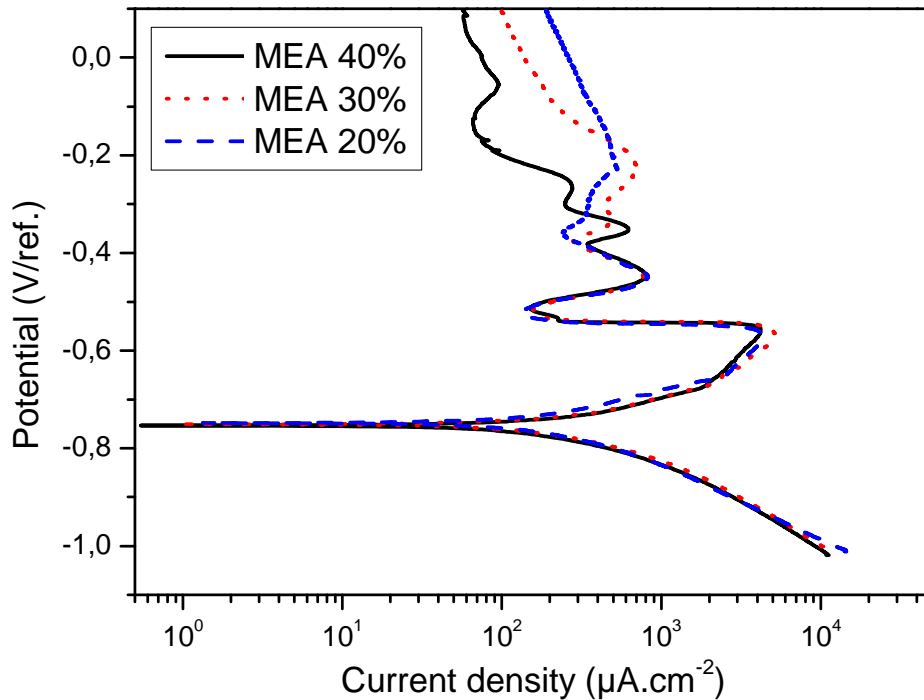


Figure 3: Polarization curves of carbon steel in CO<sub>2</sub> saturated 20%, 30% and 40% MEA at 80°C.

For all these experiments, the open circuit potential measured at the beginning of the test was extremely close to the corrosion potential, determined from the polarization curves.

Some differences on the polarization curves can be observed in the passive region. In this potential domain, above  $-0.5$  V/ref., the measured current is produced by secondary oxidation reactions, some of them corresponding to the build-up of a protective or passive layer. Unfortunately, this part of the polarization curves is extremely complex, with several successive oxidation peaks. Furthermore, the reproducibility was poor, especially regarding the level of current density plateau above  $-0.4$  V/ref. It was therefore impossible to rank the impact of MEA concentration from this part of the polarization plots.

However, in the active region, reproducibility was far better, with less than 10% differences in the current density measured at a given potential for duplicate tests. Then, it can easily be concluded from Figure 3 that MEA concentration does not have a significant impact on the active part of the polarization curves. The critical current density is close to  $5 \text{ mA/cm}^2$ , and the primary passivation potential is close to  $-570 \text{ mV/ref.}$  Corrosion current density is close to  $500 \text{ } \mu\text{A.cm}^{-2}$  for all MEA concentrations.

This result could seem in contradiction with literature recommendations, mentioning that corrosion rate increase dramatically above 20 to 30% MEA [27]. Our results suggest that at a given temperature and CO<sub>2</sub> loading, the first order impact of MEA concentration on corrosion is moderate to null. However, it is also well admitted that concentrated amine solutions are

more prone to degradation [27]. It is also known that some degradation products enhance the corrosivity of the solvent, either by decreasing the pH and increasing the conductivity, or by forming complexes with iron, thus decreasing the protectivity of corrosion scales. The 30% limit for MEA could be linked with this kind of second order factors.

### 3.3 Impact of temperature and CO<sub>2</sub> loading

The two last parameters that were tested in this study were temperature and acid gas loading. Experiments were carried out at 30, 50 and 80°C, and at 0, 0.25 and 0.5 mol<sub>CO<sub>2</sub></sub>/mol<sub>MEA</sub>. The impact of temperature is illustrated in Figure 4 for the series of experiments at  $\alpha = 0.5$ , while Figure 5 presents the results obtained at 50°C and at various CO<sub>2</sub> loadings.

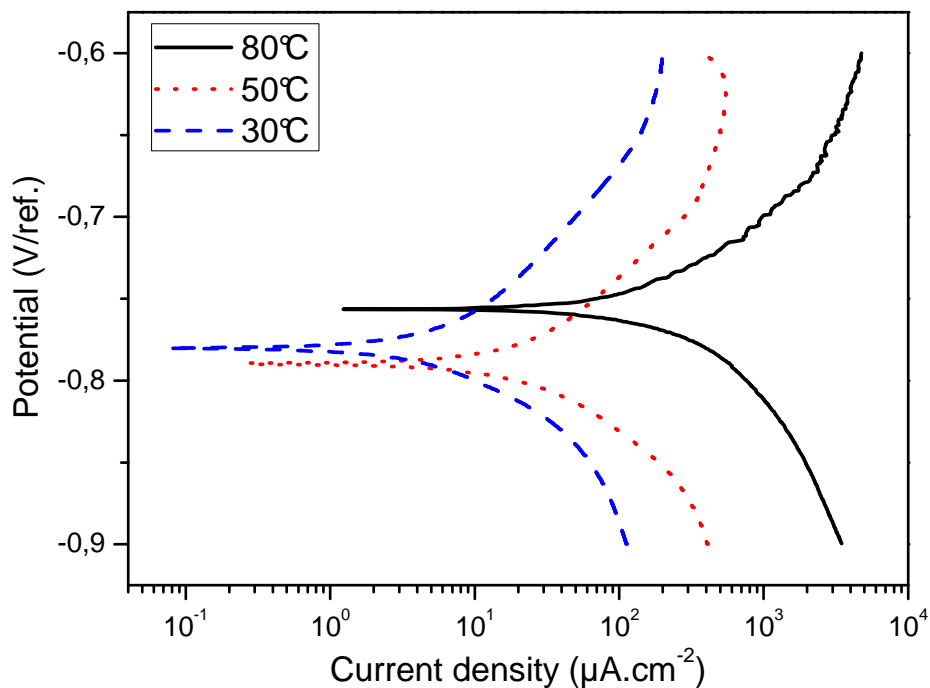


Figure 4: Polarization curves of carbon steel in 30% MEA, with  $\alpha = 0.5 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$ , and at different temperatures.

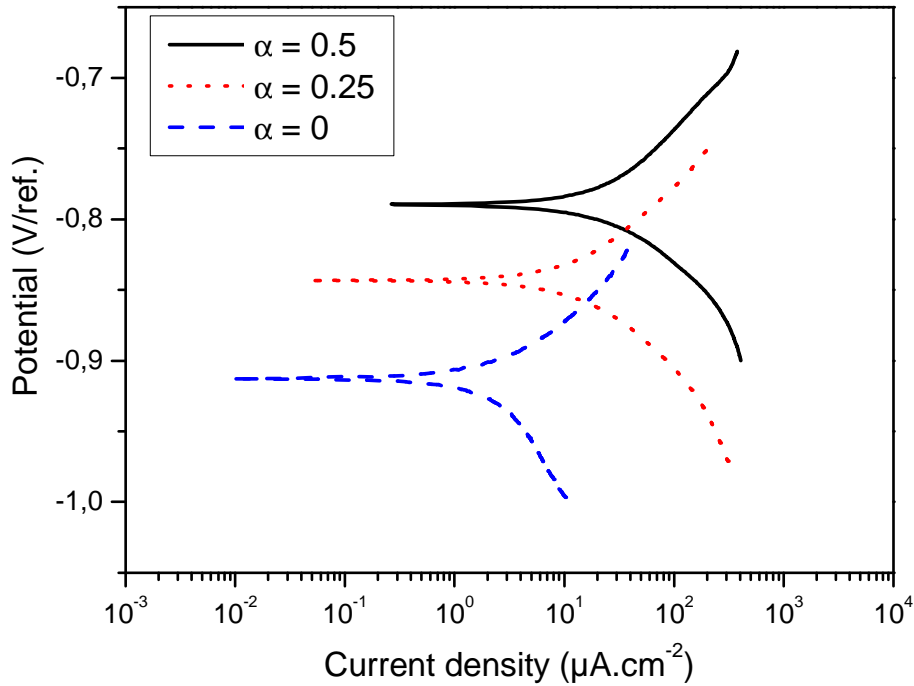


Figure 5: Polarization curves of carbon steel in 30% MEA at 50°C, at different CO<sub>2</sub> loadings.

The increase of temperature has an impact on both the cathodic and anodic reactions, with an increase of current densities at higher temperature. This result is a typical consequence of thermally activated electrochemical reactions.

The impact of CO<sub>2</sub> loading is quite different. It affects principally the cathodic current density, which undergoes an important increase with the acid gas content.

Both results are in good agreement with literature data [8,10,28].

A more detailed analysis of temperature and CO<sub>2</sub> loading influence is proposed in the next part of this paper.

## 4 DISCUSSION

From the experimental results of this study, temperature and acid gas loading appear as first order parameters on the corrosion rate of carbon steel in MEA. On the other hand, MEA concentration appeared to have no direct impact on the corrosivity of loaded amine to carbon steel.

Detailed analysis of experimental results was then focused on the series of experiments in 30% MEA at different temperatures and CO<sub>2</sub> loadings. All polarization plots were analysed using Tafel extrapolation to evaluate the corrosion current density, and the corrosion rate was then calculated using the Faraday's law [23,24]. Since the results of experiments at different temperature (Figure 4) shown thermal activation, the corrosion rates were plotted with the reciprocal of temperature ( $T^{-1}$ , expressed in  $K^{-1}$ ), for all tests at different temperatures and CO<sub>2</sub> loadings (Figure 6). For each CO<sub>2</sub> loading, linear evolution of the corrosion rate with  $T^{-1}$  is observed. Thus, it is possible to extrapolate to 120°C to cover all temperatures and CO<sub>2</sub> loadings encountered in natural gas treatment or CO<sub>2</sub> capture units.

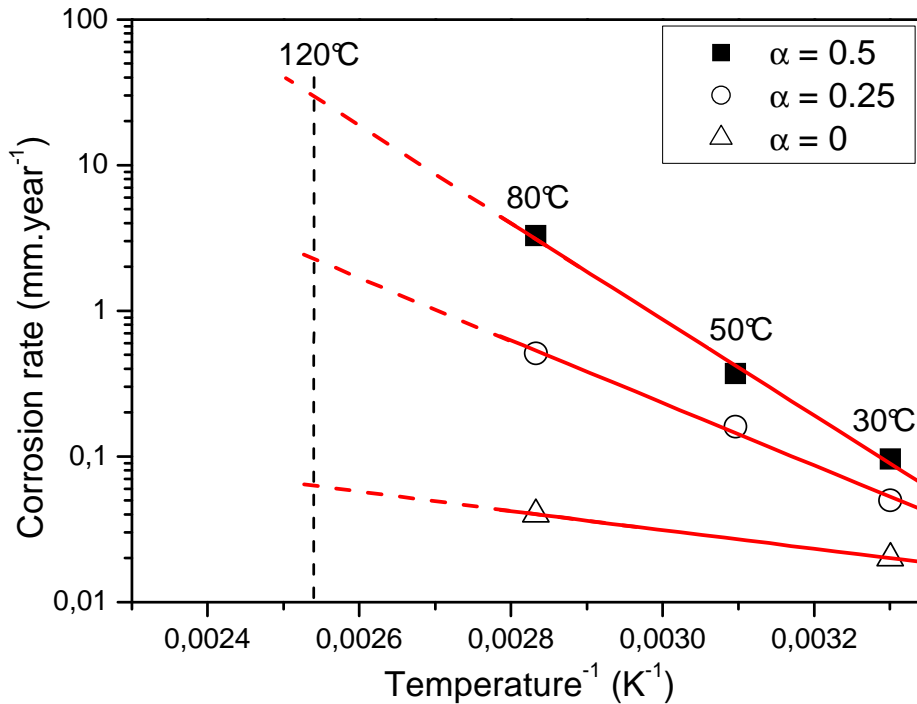


Figure 6: Synthetic view of the impact of temperature and of CO<sub>2</sub> loading on the corrosion rates of carbon steel in 30% MEA, determined from electrochemical measurements. Extrapolation at the maximum temperature of the process (120°C) using Arrhenius law.

This figure is a perfect illustration of differences between acid gas treatment and CO<sub>2</sub> capture. Indeed, the main difference between both applications concerns the lean loading level. In acid gas treatment, the regeneration of the solvent is often performed down to zero loading. On the contrary, CO<sub>2</sub> capture from flue gas requires only a partial stripping of the CO<sub>2</sub> in the regeneration section, due to energy efficiency reasons. The practical consequence is a huge difference with regards to corrosion risks between both types of applications. For acid gas treatment, where the lean solvent contains no CO<sub>2</sub> ( $\alpha = 0$ ), carbon steel corrosion does not exceed 60  $\mu\text{m}\cdot\text{year}^{-1}$  even at 120°C. On the other hand, for CO<sub>2</sub> capture, the lean loading is typically 0.25 mol<sub>CO<sub>2</sub></sub>/mol<sub>MEA</sub>. As a consequence, the corrosion rate might reach several mm $\cdot\text{year}^{-1}$  at the outlet of the stripper, where the temperature is close to 120°C.

The comparison of typical operating conditions and corresponding corrosion levels are presented in Table 2 for both applications.

Table 2: Comparison of typical operating conditions in a CO<sub>2</sub> capture unit and in a natural gas treatment unit.

	CO <sub>2</sub> capture			Gas treatment		
	$\alpha$	T (°C)	CR (mm $\cdot\text{year}^{-1}$ )	$\alpha$	T (°C)	CR (mm $\cdot\text{year}^{-1}$ )
<b>Absorber inlet</b>	0.25	40-45	0.1-0.2	< 0.05	40-75	< 0.05
<b>Absorber outlet</b>	0.5	60-65	1-1.5	0.4-0.6	60-80	0.5-5
<b>Regenerator inlet</b>	0.5	105-110	10-20	0.4-0.6	105-110	5-30
<b>Regenerator outlet</b>	0.25	120-125	2-3	< 0.05	120-125	0.06

These predicted corrosion rates could be used to comment on the use of carbon steel as construction material for acid gas treatment of CO<sub>2</sub> capture units. A traditional rule of thumb consists in a 3 mm corrosion allowance associated with an acceptable corrosion rate of less than 0.1 mm/year, for a lifetime of 30 years. As can be seen from Table 2, the compatibility of carbon steel with this upper limit of 0.1 mm.year<sup>-1</sup> is only reached in the lean solvent sections of acid gas treatment applications. In the rich section of gas treatment units, and in the entire part of CO<sub>2</sub> capture units, the estimated corrosion rate of carbon steel exceeds 0.1 mm.year<sup>-1</sup>.

This analysis is clearly a shortcut, as many other parameters might affect corrosion risks, thus the associated corrosion mitigation strategy. Although a detailed analysis is out of the scope of this paper, it is still possible to examine qualitatively some of the most important ones.

The first one refers to the nature of the amine: in CO<sub>2</sub> capture, MEA is still the preferred choice. In acid gas treatment, MEA was progressively replaced by secondary or tertiary amines, like DEA or MDEA, which are known to be less corrosive [7,8,10,12-15,29]. Unfortunately, this solvent swap to secondary or tertiary amines is not possible in CO<sub>2</sub> capture: the extremely high gas flow rate requires a solvent exhibiting a fast reaction with CO<sub>2</sub>. Using less rapid solvent than MEA is still possible, but it would then require increasing the height of the absorber column, which is extremely penalising in terms of investment cost.

The second important difference between acid gas treatment and CO<sub>2</sub> capture is linked with the oxygen content in the gas to be treated. Indeed, the combustion fumes of power plants contain up to 5% oxygen, whereas it is usually completely absent in natural gas. As already mentioned, reaction of MEA with oxygen leads to the formation of salts of carboxylic acids (formic, acetic, oxalic, and glycolic acids) [13,14,30-32]. These products can increase the corrosivity by two distinct ways: either by decreasing the pH and increasing the conductivity of the solvent, or by increasing the solubility of metals (formation of complexes), thus decreasing the precipitation tendency. Therefore, the risks of amine degradation into corrosive by-products are much higher in CO<sub>2</sub> capture from flue gas as compared to natural gas processing.

Another important parameter that was not accounted for in this study is the ability of carbon steel to form iron carbonate by reaction with either forms of dissolved CO<sub>2</sub>. Under certain circumstances, iron carbonate can precipitate at the steel surface, and provide some protective action. It is however difficult to predict if such scale is able to form spontaneously, and if it is able to provide efficient protection. Furthermore, spontaneous precipitation is not sufficient, as external factors might also contribute to weaken or eliminate a protective scale. This could be the case with too high flow rates with solid particles, giving erosive conditions.

Two alternatives are usually considered as corrosion protection measures.

The first one consists in the addition of corrosion inhibitors. Use of corrosion inhibitors is often recommended when the operator wants to minimise investment costs and make most components from carbon steel. In acid gas treatment, the family of film-forming amines is often cited. These inhibitors bind to the metal, creating a protective barrier layer. They are therefore extremely sensitive to turbulence and are generally inefficient in pipes subject to high flow rate, for example. The other family of inhibitors used in gas treatment consists of heavy metal salts, e.g. chromium and vanadium. They have a highly oxidising effect, favouring the formation of a protective layer of Fe<sub>2</sub>O<sub>3</sub>. These inhibitors are inefficient in the presence of H<sub>2</sub>S, when other non protective species are formed. Moreover, most of these metals are ecotoxic, which tends to limit their use. In CO<sub>2</sub> capture copper carbonate represents

an interesting alternative to heavy metals [33]. However, this inhibitor requires residual oxygen content; otherwise it might spontaneously react at the carbon steel surface to precipitate as metal copper. Additionally, when carbon steel is used, it is usually also required to observe strict recommendations in terms of amine concentration, rich loading levels, degradation product concentration, etc. Continuous monitoring of inhibitor content is also mandatory.

The second alternative consists in using stainless steel grades in those parts of the plant exposed to extremely corrosive conditions. For acid gas treatment units, the therefore recommended to use stainless steel at least in the rich amine parts of the unit. However, some authors recommend stainless steel even in lean solvent sections [11,34], in order to operate at higher flow-rates, and also to provide versatility to the unit for easier solvent swapping.

In the case of CO<sub>2</sub> capture, and as illustrated in the experimental section of this report, carbon steel presents high levels of corrosion in the entire parts of the plant, either rich or lean solvent sections. Therefore, stainless steel represents an interesting alternative when one wants to avoid using proprietary and often ecotoxic inhibitors. The other advantage is also to allow easy solvent swap, if a new solvent more efficient than MEA comes to market in the near future.

## 5 CONCLUSION

This paper provided a discussion on the common points and differences of the corrosive factors in acid gas treatment and CO<sub>2</sub> capture units. Both processes rely on similar concept of CO<sub>2</sub> absorption - desorption by amines.

Bibliographic study shown that temperature and acid gas loading were the most significant factors controlling corrosion in such systems. Experimental study was then launched, consisting of electrochemical evaluation of carbon steel corrosion in MEA at different temperature and CO<sub>2</sub> loading. For a constant CO<sub>2</sub> loading, the corrosion rate showed Arrhenius evolution with the reciprocal of temperature. It was therefore possible to extrapolate corrosion rates in all temperature and CO<sub>2</sub> loading of either CO<sub>2</sub> capture or acid gas treatment operating conditions. The higher risks of corrosion in the former case are then clearly illustrated. The most important difference stands in the lean solvent level: in acid gas treatment, regeneration is usually performed down to zero loading. Under these conditions, the corrosivity to carbon steel is reasonable. On the contrary, CO<sub>2</sub> capture from flue gas requires only a partial stripping of the CO<sub>2</sub> in the regeneration section, due to energy efficiency reasons. Then, the lean solvent still contains some acid gas, and subsequently a higher corrosivity.

Two other factors leading to increased risks of corrosion in CO<sub>2</sub> capture were identified. The first one is the nature of the amine used. If MEA is the preferred choice for CO<sub>2</sub> capture, acid gas processing has moved to secondary or tertiary amines, which are known to be less corrosive. The second factor is linked with the oxygen content in the gas to be treated. While hardly any oxygen is present in natural gas, combustion fumes might contain up to 10% oxygen, leading to oxidative degradation in corrosive by-products.

Corrosion mitigation strategies were then discussed. When carbon steel is used as construction material, corrosion inhibitors have to be used, in conjunction with some limitations in operating conditions.

The other alternative consists in using stainless steel in the parts of the units presenting the higher risks of corrosion. This option often represents an effort in the investment costs, but offers more versatility in the operating conditions. In particular, debottlenecking and solvent swapping is made easier.

Finally, all these aspects can be regarded in the light of current research activities. In the field of acid gas treatment, the types of solvent are well established and accepted by the operators, leaving limited room for new solvents to reach the market. However, the need for improved CO<sub>2</sub> removal is increasing, for example for LNG applications. The capability of the unit to be pushed-up to increase its performance is therefore important.

For CO<sub>2</sub> capture, the market is still far from maturity. The increasing demand of such processes is extremely recent, and linked with the need to reduce green-house gases emissions. Much research efforts are undertaken worldwide, with a global objective to reduce the costs. Several solutions are under study, among which: new solvents with reduced energy needs, reduced corrosivity, and with a higher stability with oxygen, new inhibitors to reduce the oxidative degradation and corrosion... If MEA still represents the reference solvent for CO<sub>2</sub> capture, a rapid evolution to other formulations might be forecasted. In that sense, the versatility of the unit would represent an important advantage.

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