# Corrosion in CO 2 Post-Combustion Capture with Alkanolamines – A Review

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**Dossier**

*Post Combustion $CO_2$ Capture*
Captage de $CO_2$ en postcombustion

# Corrosion in $CO_2$ Post-Combustion Capture with Alkanolamines – A Review

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**Résumé — Corrosion dans les procédés utilisant des alcanolamines pour le captage du $CO_2$ en post-combustion** — Les procédés de captage et de stockage du $CO_2$ occupent une place importante dans les stratégies visant à limiter les émissions industrielles de gaz à effet de serre. Les procédés de captage en post-combustion par solvant chimique de type alcanolamine sont bien adaptés au traitement d'émissions ponctuelles massives issues de combustibles fossiles, rencontrées notamment dans les centrales thermiques au charbon et au gaz, ou les industries sidérurgiques ou de production de ciment. La technologie utilisant le principe d'absorption – désorption par les alcanolamines est une des voies les plus matures à ce jour : elle est en effet déjà mise en œuvre, par exemple pour la désacidification du gaz naturel, bien qu'à une échelle sensiblement plus petite. L'opération de telles unités pour le traitement des fumées de combustion présente toutefois de nombreux challenges, parmi lesquels la corrosion des équipements tient une place importante. Le but de cet article est de présenter une revue des connaissances sur cet aspect particulier. Dans une première partie, l'expérience issue de plusieurs décennies d'utilisation de procédés aux alcanolamines dans le domaine de la production d'huile et de gaz est présentée. Dans une seconde partie, les risques spécifiques associés aux particularités des procédés de captage du $CO_2$ en post-combustion sont identifiés et discutés. Différentes stratégies de maîtrise de la corrosion sont décrites, et certains axes prioritaires en matière de recherche et développement sont proposés. Enfin, certaines difficultés en vue du transport du $CO_2$ issu du captage puis de son injection à fin de stockage géologique sont mises en avant, avec des recommandations strictes sur les teneurs maximales en impuretés pour disposer en toute sureté du $CO_2$ issu de ce procédé.

***Abstract* — *Corrosion in $CO_2$ Post-Combustion Capture with Alkanolamines – A Review*** — *$CO_2$ capture and storage plays an important part in industrial strategies for the mitigation of greenhouse gas emissions. $CO_2$ post-combustion capture with alkanolamines is well adapted for the treatment of large industrial point sources using combustion of fossil fuels for power generation, like coal or gas fired power plants, or the steel and cement industries. It is also one of the most mature technologies to date, since similar applications are already found in other types of industries like acid gas separation, although not at the same scale. Operation of alkanolamine units for $CO_2$ capture in combustion fumes presents several challenges, among which corrosion control plays a great part. It is the aim of this paper to present a review of current knowledge on this specific aspect. In a first part, lessons learnt from several decades of use of alkanolamines for natural gas separation in the oil and gas industry are discussed. Then, the specificities of $CO_2$ post-combustion capture are presented, and* *their consequences on corrosion risks are discussed. Corrosion mitigation strategies, and research and development efforts to find new and more efficient solvents are also highlighted. In a last part, concerns about $CO_2$ transport and geological storage are discussed, with recommendations on $CO_2$ quality and concentration of impurities.*

## INTRODUCTION

$CO_2$ capture roughly consists in separating different gases initially mixed in the combustion fumes. The main goal is to extract $CO_2$ before it is released in the atmosphere.

The most widely used process uses alkanolamine-based chemical solvents capable of reacting preferentially with $CO_2$. It is based on reversible chemical reactions between $CO_2$ and the aqueous amine, leading to the formation of bicarbonate and protonated amine (Reaction 1) and/or to the formation of amine carbamate (Reaction 2) [1].

$$CO_2 + H_2O + R_1R_2R_3N \Longleftrightarrow HCO_3^- + R_1R_2R_3NH^+ \quad \text{(Reaction 1)}$$

$$CO_2 + 2R_1R_2NH \Longleftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad \text{(Reaction 2)}$$

In these reactions, $R_1$, $R_2$ and $R_3$ represent alkyl groups or a hydrogen atom.

While the mechanism of Reaction 1 may occur for all types of amine, it proceeds with relatively slow kinetics since it is limited by dissociation of carbonic acid into bicarbonate. It is thus not well adapted to $CO_2$ post-combustion capture which requires fast reactions.

On the contrary, Reaction 2 is much faster. However, since it leads to the formation of amine carbamate, it is only possible with primary or secondary amines which have hydrogen bond to the nitrogen. Therefore, tertiary amines are usually discarded for $CO_2$ capture applications, unless an activator is used to increase the reaction rates.

The industrial process of $CO_2$ capture with alkanolamines is described in Figure 1. It is based on the fact that chemical equilibria of Reaction 1 and Reaction 2 are shifted to the left at high temperature. This property is put into advantage in the industrial process, which consists of successive absorption – desorption in a loop system.

The flue gas which enters in the treatment plant at the bottom of the absorber is typically composed of nitrogen, with 10 to 20% of $CO_2$ and 5 to 10% $O_2$, with contaminants such as $SO_x$ and $NO_x$ at trace levels. The gas pressure is typically between 1 and 2 bar. Lean amine is introduced at the top of the column, and chemical reaction between the amine and $CO_2$ takes place.

At the liquid outlet at the bottom of the absorber, the solvent is enriched in acid gas: one speaks of rich amine. At the top of the absorber, the flue gas has been stripped of its $CO_2$.

The rich amine is then pre-heated to 90-110°C by a heat exchanger then fed into the top of a regeneration column (stripper). In this part of the unit, the solvent is raised to higher temperature by steam, typically between 120-130°C, which releases the dissolved $CO_2$. At the liquid outlet of the regenerator, the solvent is hot and contains less acid gas: one speaks 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. Pure $CO_2$ is collected at the top of the regenerator. When $CO_2$ is collected for geological sequestration, it has to be compressed to more than 100 bar for transportation. This compression step also represents an important penalty in terms of energy consumption.

This process using amines for acid gas separation has long been used for natural gas treatment, and it is well known that corrosion represents a major operational issue. A recent evaluation of cost of corrosion in gas sweetening plants concluded that 25% of the maintenance budget was committed to corrosion control [3]. It was also found that approximately half of the maintenance work orders were due to corrosion.

It is thus important to pay great attention to corrosion in the research and development work in progress for $CO_2$ capture with amines.

The present paper aims at presenting the current knowledge on this topic.

In the first section, experience from several decades in natural gas sweetening is presented. The main types of corrosion are described, and the impact of operational parameters on corrosion is discussed. Corrosion risks associated with the main equipments of the gas separation plant are then discussed individually, with a thorough analysis of industrial corrosion failures reported in the literature.

The second section deals with more recent work on amine process for $CO_2$ post-combustion capture. MonoEthanolAmine (MEA) represents the benchmark solvent, and a detailed analysis of laboratory and pilot plant data obtained with this amine is proposed. A short paragraph is also dedicated to work in progress for the development of new solvents, aimed at being more efficient, less costly, and sometimes less corrosive than MEA.

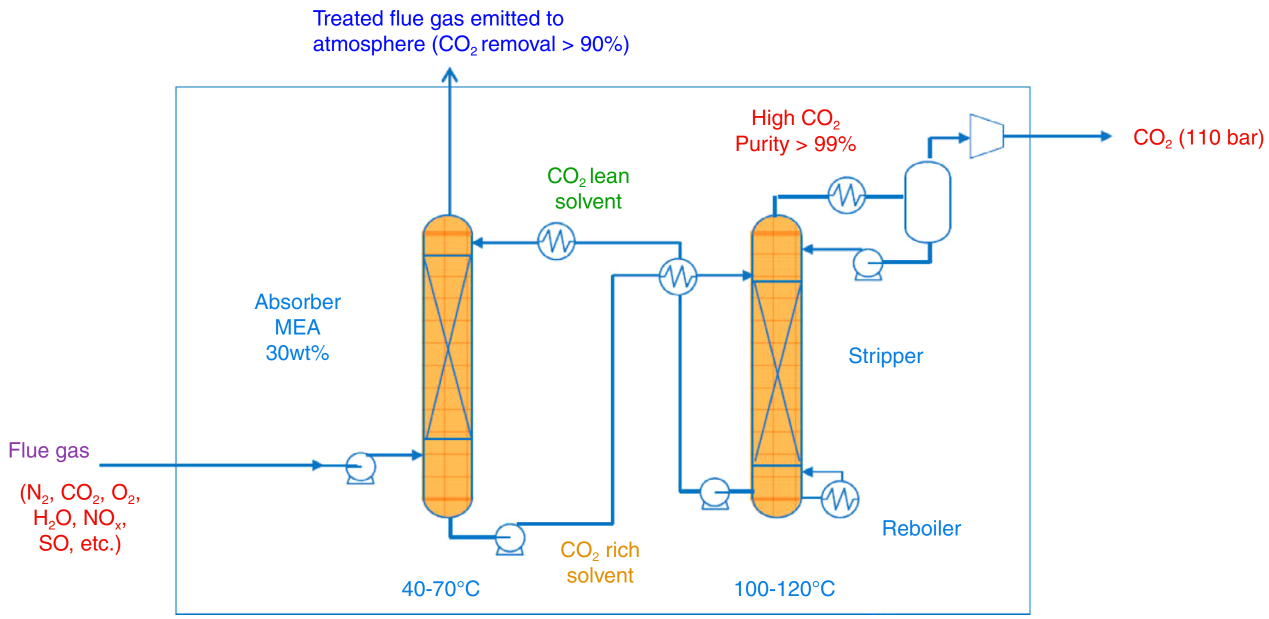


Figure 1

Simplified diagram of a MEA $CO_2$ capture unit [2].

Finally, a brief look at corrosion issues in the $CO_2$ leaving the capture plant for transport and storage concludes the paper.

## 1 EXPERIENCE FROM NATURAL GAS SWEETENING

Using amines for the removal of acid gases is not a new process. It has been used for natural gas treatment or in refineries for several decades, and corrosion has always been considered as one of the major operational problems [4-11]. In the eighties, several industrial failures in gas treating plants were reported, the most important one causing the death of 17 employees [12-14]. Since then, lots of efforts were done to improve the understanding of corrosion processes in amine units. An extensive literature survey is proposed in the next paragraphs.

In such complex units, numerous pieces of equipment are exposed to equally numerous types of corrosion.

An interesting classification of the types of corrosion occurring in gas treatment plants was proposed by Nielsen [15], who identifies:
– wet acid gas corrosion,
– amine solution corrosion.

### 1.1 Acid Gas 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 $CO_2$, $H_2S$, as well as $NH_3$ 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 [15, 16].

For gas containing mostly $CO_2$, parts of the installation made from carbon steel may suffer fast uniform corrosion, up to several mm/year. In the presence of $H_2S$, this uniform corrosion is generally delayed by the formation of a protective iron sulfide layer. A minimum $H_2S/CO_2$ ratio of 1/20 is often considered as sufficient to avoid risks of uniform $CO_2$ corrosion [17-19]. In the presence of $H_2S$ however, specific cracking phenomena may also be encountered (hydrogen embrittlement, hydrogen induced cracking HIC, sulfide stress cracking SSC, etc.). In the presence of HCN and/or $NH_3$, the risks of cracking are also increased [16].

### 1.2 Corrosion by Amine Solution

#### 1.2.1 Mechanisms and Influent Parameters

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 $CO_2$ or $H_2S$. Furthermore, since the treatment units operate in semi-closed circuit, the solvent may become enriched with possibly corrosive degradation products [15, 18, 19].

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 $H_2S/CO_2$ ratio in the gas to be treated, the possible presence of oxygen either as contaminant in the circuit or as component of the input gas (*e.g.* $CO_2$ capture in fumes) [8, 10, 18, 20-23].

One may nevertheless identify some systematic trends governing the corrosivity of acid gas chemical solvents.

Acid gas loading ($\alpha$) and temperature are usually considered as the most important factors. The acid gas loading 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 [18, 19, 24, 25].

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 K to 20 K. For gas treatment units, the effect of temperature is relatively difficult to asses 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, it is usually considered that the main corrosion risks are encountered in areas with high loading and high temperatures [26]. 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 an important factor. Usually, primary amines (*e.g.* MEA) are the most corrosive, secondary amines (*e.g.* DiEthanolAmine, DEA) slightly less and tertiary amines (*e.g.* Methyl DiEthanolAmine, MDEA) exhibit the lowest risks of corrosion [18, 19, 25, 27-30]. 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 [18, 25] and a moderate or null effect [31, 32].

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 $CO_2$, 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 corrosion by these degradation products date back a number of years, the general conclusion being an absence of specific corrosivity [27, 28]. 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 [33-35].

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: 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 [16, 17, 24, 36].

### 1.3 Equipments Concerned by Corrosion

This section describes the specific corrosion risks for the main equipment in gas treatment units. A summary is proposed in Table 1.

#### 1.3.1 Absorber

The absorber may suffer several types of corrosion.

Among the parameters which affect corrosion, temperature and acid gas loading may vary on a wide range in the absorber. Temperature might typically evolve between ambient and 80°C, due to the exothermicity of absorption reactions. Acid gas loading may vary from lean (*i.e.* typically below 0.1 $mol_{CO_2}/mol_{amine}$) at the top of the absorber to rich (*i.e.* typically above 0.4 $mol_{CO_2}/mol_{amine}$) at the bottom. Therefore, the highest risks of corrosion by amine solution are found in the hot rich section at the bottom of the absorber. Erosion – corrosion represents an aggravating factor. In particular, the high flow rate at gas inlet may lead to turbulence and impingement of solution against the walls, creating conditions favourable to this type of corrosion. The same phenomenon is observed on the plates and in case of excessive flow rates.

TABLE 1
Summary of feedback on corrosion in amine units (CS = Carbon Steel)

| Material and type of corrosion | Causes | References |
|---|---|---|
| Absorber | | |
| CS – Cracking and mechanical failure | Hydrogen embrittlement or ASCC arising from non PWHT welds | [12, 14, 40, 42, 43] |
| CS – Uniform corrosion at bottom of absorber | Galvanic coupling with copper deposits from the corrosion inhibitor | [44] |
| CS – Erosion-corrosion at bottom of absorber | Turbulence at the raw gas inlet | [19, 45] |
| AISI 410 – Uniform corrosion of the plates | Higher corrosivity of sweet services units in high temperature and high loading zones | [26, 46] |
| Rich amine lines | | |
| CS – Stress corrosion (ASCC) | No PWHT | [12, 14, 40, 42, 43] |
| CS – Erosion-corrosion | Excessive flow rates and acid gas flash | [19, 26, 45, 46] |
| CS – Localised corrosion with perforation | Large quantities of oxygen in the raw gas | [47] |
| Exchanger | | |
| CS – Amine Stress Corrosion Cracking (ASCC) | No PWHT | [12, 14, 40, 42, 43] |
| CS – Erosion-corrosion | High temperatures and turbulence | [26, 46] |
| CS – Erosion-corrosion and pitting | Turbulence and acid gas flash from too high lean loading | [19, 40, 45] |
| 316L and 254SMO – Failure of the exchanger trays | Possible case of stress corrosion | [26, 46] |
| Regenerator | | |
| CS – Amine Stress Corrosion Cracking (ASCC) | No PWHT | [40] |
| CS – Erosion-corrosion of the internal parts | High corrosivity of the rich amine | [19, 26, 45, 46] |
| CS – Serious uniform corrosion | High HSS contents – Acid water condensation zones | [44, 48] |
| AISI 410 – Uniform corrosion of the trays | Corrosive conditions specific to sweet units, due to high loading and high temperatures | [26, 46] |
| AISI 304L – Uniform corrosion of internal parts and shells | Specific case of a DiGlycolAmine (DGA) unit | [49] |
| Reboiler | | |
| CS – Uniform corrosion and erosion-corrosion | Turbulence, high concentration of degradation products | [26, 46, 50] |
| Lean amine lines | | |
| CS – Amine Stress Corrosion Cracking (ASCC) | No PWHT | [12-14, 42] |
| CS – Erosion-corrosion | Too high lean loading | [40] |
| CS – Erosion-corrosion | Significant amine degradation due to the presence of oxygen in the raw gas | [41] |

Wet acid gas corrosion may also develop at the bottom of the absorber and on the first plates, if the walls are not wetted sufficiently by the solvent: in this case, water may condense and become loaded with acid gases. Sour service units are prone to risks of hydrogen embrittlement.

For $H_2S$ treatment units, specific risks of Amine Stress Corrosion Cracking (ASCC) are also possible, especially in the lower part of the absorber where the loading is highest. Post Weld Heat Treatment (PWHT) is then essential to reduce these risks [17].

#### 1.3.2 Rich Amine Lines

Corrosion risks are especially high in this section where the amine is loaded with acid gas. Depending on the location before or after the heath exchanger, the temperature varies between 60°C to 110°C. Corrosion-erosion is the most frequent risk encountered with carbon steel lines subjected to high flow rate or flow disturbance. In particular, up to the flash drum, the solvent is pressurised and highly loaded with acid gas, and there is a high risk of degassing, which may aggravate the turbulence effects. Similarly, between the rich/lean amine exchanger and the regenerator, the risks of degassing remain high and are combined with a higher solvent temperature.

In the rich amine lines, it is commonly admitted that the solvent flow rate should not exceed 1.8 m/s [17].

#### 1.3.3 Rich/Lean Amine Exchanger

This equipment is exposed to a wide range of highly specific corrosion risks.

On the rich amine side, the risks of erosion-corrosion mentioned in the previous paragraph still remain, especially if the rich amine inlet has been badly designed [4, 15].

When stainless steel plate exchangers are used, the main risks are stress corrosion cracking (especially at welds or in case of repairs) and crevice corrosion.

Sour service units are prone to risks of hydrogen embrittlement on the rich amine side of the exchanger, if it is made of carbon steel.

#### 1.3.4 Regenerator and Acid Gas Outlet (Condenser, Reflux Drum)

The solvent at the top of the regenerator is still rich and already at high temperature. The intrinsic corrosivity is therefore very high and there is a serious risk of erosion-corrosion in case of turbulence. If there is no significant turbulence in the medium, extensive uniform corrosion of carbon steel is frequently observed. For this type of corrosion, it would also appear that the risks are greater in sweet service units (only $CO_2$), where fast uniform corrosion has been observed [26, 37, 38].

Wet acid gas corrosion is another major risk, especially at the top of the regenerator and in the acid gas outlet lines. The condenser is also highly sensitive. Experience has shown that keeping the gas flow rates above 8 m/s limits these risks considerably by preventing accumulation of condensates [26].

For sour service units, hydrogen embrittlement may occur at the top of the regenerator and in the acid gas outlet lines, in case of inappropriate choice of metal (non sour service carbon steel) or heat treatment (failure to carry out PWHT) [17].

#### 1.3.5 Reboiler

Due to the high temperatures, the reboiler is relatively sensitive to corrosion and fouling [39]. The risks are elevated by solutions containing high concentrations of degradation products. If the regenerator fails to operate correctly (insufficient stripping), solvent still loaded with acid gas may be brought up to the reboiler, significantly increasing the risk of corrosion. Excessive temperatures also represent a recognised risk factor.

#### 1.3.6 Lean Amine Lines

An extensive survey launched following the explosion of an absorber in 1984 detected cases of amine stress corrosion cracking in the lean amine lines, due mainly to failure to carry out PWHT [13, 14].

A case of erosion-corrosion has been reported for a MDEA unit in Indonesia [40], possibly due to an excessive lean loading ($\alpha > 0.02\ mol_{CO_2}/mol_{amine}$).

Another case is reported for a MDEA unit, where very severe corrosion of the lean amine parts developed just a few months after starting the unit [41]. This case would seem to have been caused by very fast degradation of MDEA to form bicine, due to the presence of oxygen in the gas to be treated, at a concentration of 90-100 ppmv.

### 1.4 From Natural Gas Sweetening to $CO_2$ Capture

If both natural gas sweetening and $CO_2$ capture can be described by amine absorption – desorption process of Figure 1, three major differences have to be mentioned as concerns corrosion risks evaluation, as illustrated in Table 2:

- gas composition and partial pressures,
- nature of the amine used,
- lean loading level.

In natural gas processing, the gas to be treated usually has high pressure up to 100 bar, and might contain a significant proportion of $CO_2$ and/or $H_2S$, up to several tens of percent. Oxygen contamination is not supposed

TABLE 2

Main differences between amine processes for natural gas treatment and $CO_2$ post-combustion capture

| Parameter | Natural gas treatment | $CO_2$ post-combustion capture |
|---|---|---|
| Gas composition | High $P_{CO_2}$ (1-100 bar) No $O_2$ | Low $P_{CO_2}$ (< 0.5 bar) 5-10% $O_2$ |
| Type of amine | Secondary or tertiary | Primary (MEA) |
| Lean loading level | < 0.1 $mol_{CO_2}/mol_{amine}$ | 0.25 $mol_{CO_2}/mol_{amine}$ |

to be present. The main goal of the process is to recover natural gas with a minimum amount of acid gas contaminants. Concerning $H_2S$, complete removal is usually expected, while $CO_2$ removal efficiency depends on the application (between 2-3% for conventional applications, but down to less than 50-100 ppmv for Liquefied Natural Gas, LNG). Optimisation of the process then allows using secondary or tertiary amines, and requires complete regeneration of the solvent, *i.e.* hardly no acid gas is present in the solvent at the outlet of the regenerator column, with a lean loading typically below 0.1 $mol_{CO_2}/mol_{amine}$ [16].

On the other hand, $CO_2$ capture from combustion fumes responds 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 10-15% $CO_2$, for a total pressure close to 1 bar. The $CO_2$ 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 $CO_2$, 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 $CO_2$ removal, without penalising too much the power plant efficiency. For this reason, $CO_2$ regeneration is not complete in $CO_2$ capture processes: then, the lean amine loading is generally not zero, but preferably around 0.25 $mol_{CO_2}/mol_{amine}$ in the case of MEA.

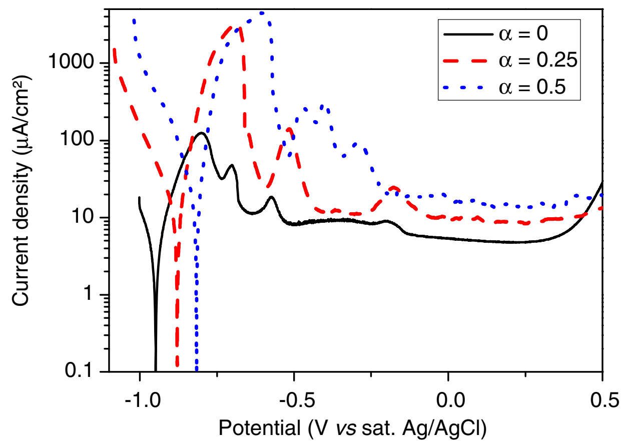


Figure 2

Typical polarization curves of carbon steel in MEA at different $CO_2$ loading (results taken in reference [52]).

## 2 RECENT INVESTIGATIONS ON CORROSION IN $CO_2$ POST-COMBUSTION CAPTURE PROCESSES

### 2.1 Laboratory Studies on MEA

Several papers presenting laboratory corrosion measurements in MEA solutions have been published in the last years [21, 23, 25, 51, 52]. Most of these studies were performed in glass cells at moderate temperature (max. 80°C) and at ambient pressure, and used electrochemical measurements to examine the impact of several parameters on corrosion. Most of the time, corrosion rate was evaluated by extrapolating the cathodic region to the corrosion potential in order to determine the corrosion current density.

The electrochemical behaviour of carbon steel in 30% MEA solution at 80°C for different levels of $CO_2$ loading is illustrated in Figure 2. These results were taken in [52], where a detailed description of experimental conditions can be found. These curves are typical of an active corrosion behaviour. Both the cathodic and the anodic reaction rates are increased with an increase of $CO_2$ loading. A passive region is also observed at high overpotential, with a plateau current value increasing with $CO_2$ loading.

The impact of amine concentration was studied in [21, 25, 52]. At constant $CO_2$ loading, a weak increase of corrosion rate is observed when the MEA concentration is raised from 6 to 30% [25]. At higher concentration, between 30% and 55% MEA, polarisation curves show very similar corrosion rates [21, 52].

This weak impact of MEA concentration on corrosion might sound contradictory with past experience of natural gas treatment, where a classical rule-of-thumb indicates that MEA should not exceed 20-30% [15, 53]. However, it is also well admitted that concentrated amine solutions are more prone to degradation, forming corrosive by-products [53, 54]. Therefore, the increased corrosivity with amine concentration is more a consequence of increased degradation than an intrinsic property of concentrated solutions.

The impact of temperature on corrosion in MEA was mainly evaluated between ambient temperature and 80°C in laboratory conditions. As expected, the rate of electrochemical reactions increases with temperature. Both the cathodic and anodic reactions are affected [21, 25, 52, 54]. This result is a typical consequence of thermally activated electrochemical reactions.

The impact of $CO_2$ loading is usually considered as the most influencing parameter. As illustrated in Figure 2, the evolution of acid gas loading from 0 to 0.5 induces a tenfold increase of the corrosion current density. $CO_2$ loading affects both electrochemical reactions, but the impact is more pronounced on the cathodic side [21, 23, 25, 51, 52].

A few other studies focussed on the impact of impurities, *i.e.* oxygen [21, 25, 51, 52], HSS [35, 51, 55], $SO_2$ and $NO_2$ [56, 57]. All these impurities were found to be detrimental to corrosion, by an increase of the rates of electrochemical reactions. HSS is also known to decrease the protectivity of corrosion scale by a chelating effect. Concerning $SO_2$ and $NO_2$, the main impact is probably on amine degradation rather than on corrosion.

For all these impurities, it can be concluded that the amplitude of corrosion rate increase remains of second order in comparison with the impact of $CO_2$ loading and temperature.

A synthetic view of the evolution of carbon steel corrosion rate with $CO_2$ loading and temperature is presented in Figure 3 [52]. At a given $CO_2$ loading, it appears quite clearly that the corrosion rate follows a linear evolution with the reciprocal of temperature, confirming thermal activation. From this diagram, corrosion rates can be estimated at any temperature and $CO_2$ loading encountered in the unit. It appears that even in the presumably least severe conditions, *i.e.* moderate temperature (50°C) and lean loading (0.25 $mol_{CO_2}/mol_{amine}$), carbon steel corrosion still exceeds 100 μm/year. On the other hand, in the hot rich amine, corrosion rate above several mm/year is predicted, and this level was confirmed by pilot plant experiments [58].

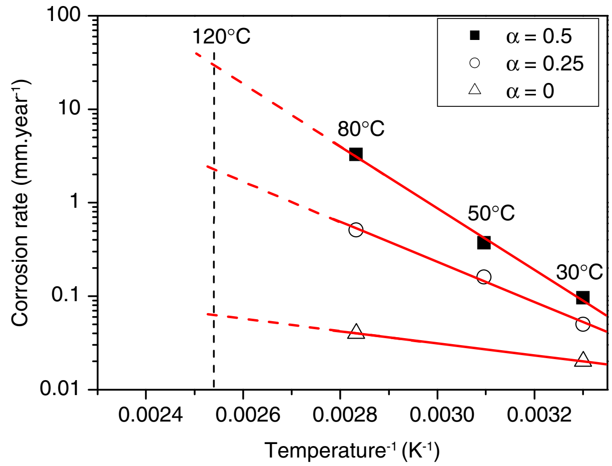


Figure 3

Impact of temperature and $CO_2$ loading on the corrosion rate of carbon steel in 30% MEA [52].

From all laboratory studies, it appears that carbon steel grades cannot be used safely in all operating conditions encountered in a MEA capture unit.

It also appears from most laboratory studies that austenitic stainless steel grade 316L seems to perform well [35, 52].

## 2.2 Corrosion Prevention Strategies

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. The second alternative consists in using stainless steel grades in those parts of the plant exposed to extremely corrosive conditions. Although investment costs are usually increased, it allows reducing operational costs, and permits more versatility. advantages and drawbacks of these two options for $CO_2$ capture units are discussed below.

Corrosion inhibition is commonly used in acid gas treatment plants, where it often allows using carbon steel grades rather than more expensive alloys. Two types of inhibitors are found.

Oxidizing passivators react electrochemically with the steel surface to promote the formation of a stable protective passive layer. Most of the time, these inhibitors consist of inorganic molecules. For gas sweetening applications, they are usually presented as the most efficient [20, 59]. Sodium metavanadate is probably the most cited molecule, and the first patents for gas treatment applications date 1936, in US patent No. 2.031.632. Positive feedback from field experience was reported in [11], about a MEA unit in a hydrogen refining plant. Other salts of heavy metals can be used, like antimony, cobalt, bismuth or nickel. However, these types of inhibitors are largely becoming obsolete, mainly because of high toxicity and the cost of waste disposal. As a more environmental friendly alternative, copper salts are also known to inhibit corrosion in amine units. The first reference to this property was found in US patent No. 2.377.966 issued in 1945. However, inhibiting corrosion with copper salts presents some difficulty for application in $CO_2$ capture plants due to the high concentration of oxygen in the gas. Indeed, a catalysis of amine oxidative degradation can be caused by such salts of heavy metals [60, 61]. Furthermore, in the stripper section where dissolved oxygen vanishes, precipitation of metallic copper might happen, causing severe bimetallic corrosion and consumption of the inhibitor [62]. In spite of these problems, copper carbonate and sodium metavanadate are often used as reference inhibitors in recent studies for $CO_2$ capture with MEA. The excellent performance of both products was confirmed in [62-65]. It was confirmed, however, that in the absence of oxygen, copper carbonate was less efficient and a pitting tendency could be observed, associated with the precipitation of metallic copper on steel surfaces [62].

Film forming inhibitors represent the other family of molecules commonly used for gas treatment applications. This type of molecules adsorbs on the steel surface to form a thin layer which impedes access of the corrosive solution to the surface. However, for this specific application, they are considered to be less efficient than inorganic compounds [20, 59]. For $CO_2$ capture application, investigation on low-toxic organic inhibitors with promising results was proposed in [65]. However, it was concluded that none of the tested molecules was as efficient as sodium metavanadate.

Although a few companies propose processes including corrosion inhibitors [66], the most followed strategy is to use corrosion resistant alloys in those parts of the plant exposed to extremely corrosive conditions. For acid gas treatment units, it is 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 [26, 46, 67-69], in order to operate at higher flow-rates, and also to provide versatility to the unit for easier solvent swapping.

In the case of $CO_2$ capture with MEA, carbon steel presents high levels of corrosion in the entire parts of the plant, either rich or lean solvent sections as illustrated in Figure 3. Therefore, stainless steel represents an interesting alternative when one wants to avoid using proprietary and often ecotoxic inhibitors. Furthermore, most industrial applications to date consist in demonstration pilot plants, for which versatility is a premium requirement. To serve this demand, using corrosion resistant grades allows easier solvent swap for benchmark studies with new solvents.

### 2.3 Corrosion Aspects in the Development of New Solvents

$CO_2$ capture by 30% MEA represents the reference technology for post-combustion applications. However, it is well admitted that the cost of $CO_2$ removal with this process is too high, and needs to be reduced.

Thus, a lot of research programs aims at developing new solvents, with a particular focus on the energy consumption needed at regeneration step. Minimizing solvent degradation is also often considered as the second immediate priority. Even if this research is usually not driven by corrosion aspects, testing the corrosivity of new molecules is often considered at the early stages of research and development efforts, and a few papers were found in the recent literature.

An extensive study on more than 20 amines including degradation and corrosion evaluations was proposed by Martin *et al.* [70]. Molecules with a greater stability and less corrosivity than MEA were identified, and a Quantitative Structure Property Relationship (QSPR) model was built that can be applied to predict degradation.

Solutions composed of MEA and piperazine were tested in [71]. Such solutions showed more corrosion than in pure MEA.

A great deal of attention is also given to activated solutions of tertiary amines. MDEA using piperazine as activator is one of the favourite subject of investigation in the recent years [72-74]. Corrosion in this type of solution was studied in [75], showing the same detrimental impact of $CO_2$ loading and temperature as already observed in MEA or in other amine solutions.

Sterically hindered amines have also received a great deal of attention due to good performances in terms of absorption and desorption capacity. It is also thought that sterical-hindrance might limit the interactions between the amine and the steel surface, thus reducing the corrosivity. Investigation of AMP (2-Amino-2-Methyl-1-Propanol) was proposed in [65]. In comparison with MEA, AMP shows less corrosivity at elevated temperature and in lean loading conditions.

Other good corrosion performances were mentioned in several papers presenting new proprietary solvents, without a precise description of the amine nature.

This is the case of the DMX[tm] amine developed by IFP Energies nouvelles, showing carbon steel corrosion below 10 μm/year at temperature up to 160°C in $CO_2$ loaded conditions [76].

### 2.4 Corrosion Monitoring at Pilot Plant Scale

Corrosion evaluation at the pilot scale was performed at several locations worldwide. MEA 30% is usually used as benchmark solvent, to which newly developed solvents with promising features are compared.

The CASTOR pilot plant, located in Denmark at a coal-fired power station was used for process evaluations with MEA and other proprietary solvents [77]. Corrosion monitoring was performed with weight loss coupons at different locations in the pilot plant. Carbon steel corrosion at a rate exceeding millimeters' per years was found at the outlet of the stripper with 30% MEA. During the same study, stainless steel grades (304L and 316L) performed extremely well, without significant weight loss corrosion [58]. In the same paper, results obtained on the ITC pilot plant from the University of Regina (Canada) were also presented, confirming that corrosion in 30% MEA was the highest in the rich section from the heat exchanger to the stripper. This pilot plant also revealed corrosion in the stripper overhead, where $CO_2$ saturated water is subject to condensation.

Other corrosion results in pilot plants operated with 30% MEA were recently published. Different types of stainless steels and polymeric materials as well as concrete were tested in the lignite-fired Niederaussem power station (Germany) [78, 79]. Carbon steel corrosion was evaluated in the Tarong coal-fired power station (Australia), confirming once more the high corrosivity of the rich MEA [80]. Similar results were also obtained in the Brindisi pilot plant (Italy) [81].

Another study presented pilot plant experiments on a proprietary solvent specified by *Toshiba*. It was found that the corrosion rate in this solvent was the highest in the rich amine section, similarly as in MEA or other amines [82]. It was shown also that corrosion and amine degradation was increased when $SO_2$ was present in the flue gas [83].

## 3 CONSEQUENCES FOR $CO_2$ TRANSPORT AND STORAGE

Another important aspect of the $CO_2$ Capture and Storage (CCS) chain is the transport of $CO_2$ from the post-combustion capture unit to the storage site. Most of the time, dense phase $CO_2$ at pressure above 100 bar will circulate in a pipeline network. Transportation of high pressure dry $CO_2$ through carbon steel pipelines is commonly used for enhanced oil recovery for more than several decades, with extremely positive feedback. As long as the water content is maintained below saturation, corrosion will be insignificant. On the other hand, as soon as free water can condensate, it is highly concentrated in $CO_2$ and extremely rapid and localised corrosion can occur in range above 10 mm/year. Based on the good experience of Enhanced Oil Recovery (EOR), it has long been considered that transportation of post-combustion $CO_2$ was not a major issue, and this area received much less attention and funding for R&D programs. However, recent publications showed that it was not as straightforward, and that corrosion risks had to be examined carefully [84-97]. Indeed, it appears that water solubility in dense phase $CO_2$ is strongly modified in presence of impurities like $SO_x$ and $NO_x$, or $O_2$. Furthermore, when $SO_2$ is present with water and oxygen, extremely corrosive sulphuric acid might form.

Understanding the impact of all impurities present in the $CO_2$ after post-combustion capture on water solubility is therefore a major task in order to develop CCS safely. At the present time, there are no commonly accepted specifications for the maximum levels of impurities required for pipeline transport. Some recommendations were proposed after two European projects within the sixth framework programme (FP6), Dynamis[1] and Encap[2], and often referred as Dynamis $CO_2$ quality recommendations (*Tab. 3*) [98, 99]. These recommendations were established from a set of criteria, including health and safety, operation and design, but it was acknowledged that "the mechanisms of the water related corrosion for $CO_2$ pipelines of carbon steel are not fully understood". As an illustration, several experimental studies have been carried out below or close to the the Dynamis recommendations, and showed some risks of corrosion.

According to Dugstad *et al.* [91] water solubility in pure $CO_2$ at 100 bar and in the temperature range 4-25°C exceeds 1 900 ppmv. This was confirmed by corrosion experiments in pure $CO_2$ with 500 ppm to 1 200 ppm $H_2O$, giving no corrosion of carbon steel coupons. However, when 500 ppmv $H_2O$ and 100 ppmv $NO_2$ is present, the corrosion rate was high ($>$ 0.1 mm/year). Considering several impurities at the same time, these authors also showed that corrosion could take place with as low as 200 ppmv $H_2O$ when $SO_2$ and $O_2$ were present [94].

[1] Project website www.dynamis-hypogen.com.

[2] Project website www.encapCO2.org.

TABLE 3
Dynamis $CO_2$ quality recommendations (concentrations in ppmv) [98, 99]

| Component | Concentration | Limitation |
|---|---|---|
| $H_2O$ | 500 ppm | Design and operational considerations |
| $H_2S$ | 200 ppm | Health and safety considerations |
| CO | 2 000 ppm | Health and safety considerations |
| $CH_4$ | Storage in aquifer: 4%EOR: 100-1 000 ppm | As proposed in ENCAP project |
| $N_2$ | 4% | As proposed in ENCAP project |
| Ar | 4% | As proposed in ENCAP project |
| $H_2$ | 4% | Further reduction of $H_2$ is recommended because of its energy content |
| $SO_x$ | 100 ppm | Health and safety considerations |
| $NO_x$ | 100 ppm | Health and safety considerations |
| $CO_2$ | > 95.5% | |

It seems therefore essential to continue to work on the impact of impurities on high pressure $CO_2$ corrosion, to gain more confidence in $CO_2$ quality recommendations.

Lastly, after $CO_2$ transport through a pipeline network, underground injection might inevitably put free water in contact with high pressure $CO_2$ and impurities. In this situation, corrosion rate of carbon steel easily reaches several tens of mm/year, and even some corrosion resistant alloys might suffer corrosion above hundreds of μm/year [84, 96].

## CONCLUSIONS

Corrosion issues are encountered in the whole CCS chain.

In the $CO_2$ post-combustion capture process, the corrosive environment mainly consists of aqueous amine. Identification of corrosion risks and mitigation strategies benefit from several decades experience of natural gas treatment with amines. Nevertheless, important differences have to be kept in mind. Currently, the most widespread process uses primary amines which are the more prone to degradation and corrosion, in comparison with secondary or tertiary amines. For this process using MEA, current challenges consist in limiting the degradation by oxygen, and to mitigate corrosion of the installation.

It was shown also that corrosion is often taken into account at the early stages of research programmes dedicated to new molecules. Laboratory tools and pilot plants equipped with corrosion monitoring devices are helpful for this purpose.

Impact on corrosion of impurities in the post-combustion $CO_2$ was also emphasized. Commonly accepted recommendations for the composition of $CO_2$ might not provide complete assurance of the absence of corrosion of steel pipelines used for transport. More work has to be done to predict the impact of impurities on water solubility.

At the very end of the chain, it was shown also that formation water and supercritical $CO_2$ might combine to form a very corrosive environment for the injection facilities.

For both transport and storage steps, experience from EOR and oil and gas production should be put to good advantage to find appropriate mitigation strategies. Nevertheless, it seems important also to address the specificities of high pressure $CO_2$ coming from the capture process, and especially the impact of impurities.

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