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Corrosion in amine units for acid gas treatment : a laboratory study

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Abstract:

Corrosion represents one of the most important operational issues in amine units used for acid gas treatment. Considerable experience is available in the literature both on laboratory and in the field. Based on this experience, proven mitigation strategies are available, using corrosion inhibitors or corrosion resistant alloys at selected locations in the plant. However, the technical causes of the corrosivity of amine solvents are still not well understood. Furthermore, recent field experience showing severe corrosion in sweet units pointed out the difficulty to transpose design solutions from sour to sweet gas. There is obviously a need for more precise data on the impact of different parameters on amine units corrosion.

For this study, experimental work was focused on sweet Diethanolamine (DEA) systems. The impact of acid gas loading and temperature was examined deeply. Electrochemical and weight loss measurements were performed on carbon steel, AISI 410 and AISI 304L. At the same time, thermodynamic calculations were used to determine the composition of the solvent at different temperature and CO₂ loading. For each experimental condition, it was possible to calculate the concentrations of different species, such as carbonate, bicarbonate, residual amine, carbamate, protonated amine and the pH. The comparisons between corrosion data and test solution composition give helpful indications to better understand the causes of the increased corrosivity of highly loaded solvents.

Keywords: Corrosion, alkanolamine, DEA, gas treatment

Introduction

Basics of acid gas absorption by alkanolamines

The primary function of alkanolamine units is to remove acid gases, usually hydrogen sulfide (H₂S) and carbon dioxide (CO₂).

A typical process flow diagram of alkanolamine units is given in Figure 1.

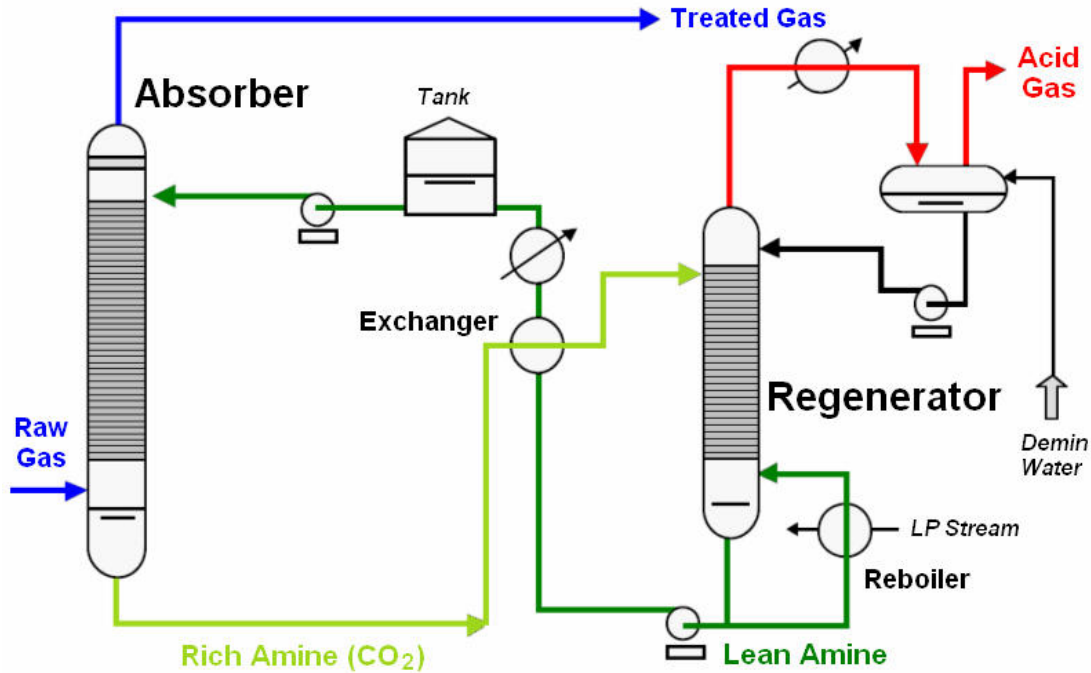
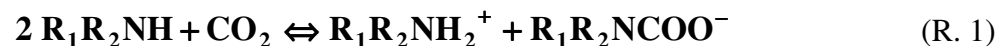


Figure 1: Process flow diagram of gas absorption system [1].

The acid gas absorption process is performed through the following steps. The raw gas enters the unit at the bottom of the absorber column, where acid gases are absorbed by the lean amine solvent that flows countercurrent to the raw gas. The treated gas is the overhead product while the rich amine solution flows from the bottom of the absorber to the lean/rich cross exchanger where it is heated before entering the regenerator column. In the regenerator, acid gases are stripped from the rich amine by heat and steam produced by the reboiler. Acid components leave off at the top of the regenerator and go to the overhead condensers and the reflux accumulator. The hot lean amine from the bottom of the regenerator is cooled via the lean/rich heat exchanger prior to re-entering the absorber.

The main reactions between CO₂ and amines are given below.

Carbon dioxide reacts with amines by the following reactions where R designates an organic group. These reactions can lead to the formation of carbamates (R.1), bicarbonates (R.2) and carbonates (R.3):





Carbonate formation (Reaction R.3) is possible but negligible in amine solutions because of its too high pKa of 10.33 in comparison with the pH observed in these media. Usually, a decrease of the pressure or an increase of temperature displaces the equilibrium from the right to the left side of the reaction. This principle is applied in the regenerator for stripping the CO₂ from the solvent.

Corrosion Issues in Amine Units

Recently, applications for sweet gases (containing only CO₂ without H₂S) have gained interest and an increased number of sweet units were installed. Most often the design criteria based on the experience of sour units were used for sweet units. However, in these sweet conditions, some unusual corrosion problems were experienced on materials which have proven to be satisfactory in sour gas [1,2,3]. Some corrosion failures were even reported for AISI 410 absorber trays (Figure 2) and for AISI 304L internals of a regenerator, with estimated corrosion rates as high as a few mm per year [1]. In both cases, corrosion appeared when temperature and CO₂ loading were high.



Figure 2: Examples of uniform corrosion on AISI 410 internals in sweet service amine unit [4].

Corrosion mechanisms

Several authors have studied the impact of operational parameters on corrosion of carbon steels [5,6] or stainless steels [1,7].

It is well admitted that high temperature is detrimental to corrosion [5,8], through an acceleration of the electrochemical reactions, and also through the thermal degradation of amines into corrosive by-products.

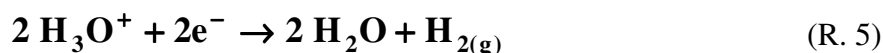
CO₂ loading is also one of the most important parameters controlling the corrosivity of acid gas solvents. It is considered that an increase of CO₂ loading increases the corrosion rate [1,5,6,9].

However, the corrosion mechanisms are not well understood. Some authors proposed a list of hypothetic electrochemical reactions that may occurs in CO₂-DEA solutions [10,11]:

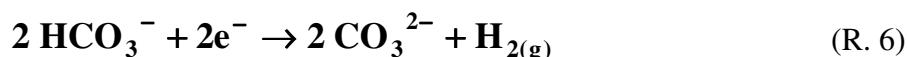
- Oxydation of iron :



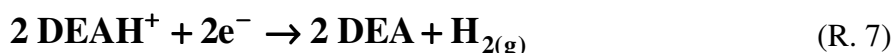
- Reduction of hydronium ion :



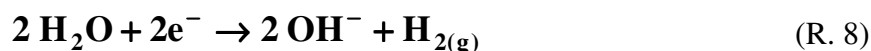
- Reduction of bicarbonate ion :



- Reduction of protonated amine :



- Reduction of undissociated water :



Nevertheless, it is still not clear which reduction reaction(s) is (are) predominant. The objectives of this paper are to investigate relationships between the chemical composition of CO₂-DEA solutions and the corrosion rates of different steel grades. This was performed by corrosion tests under various temperatures and CO₂ loadings. At the same time, thermodynamic calculations of the system composition were made for each experimental condition using home-made programs.

Experiments

Experimental Apparatus

The experiments were carried out in a glass electrochemical corrosion cell as shown in Figure 3.

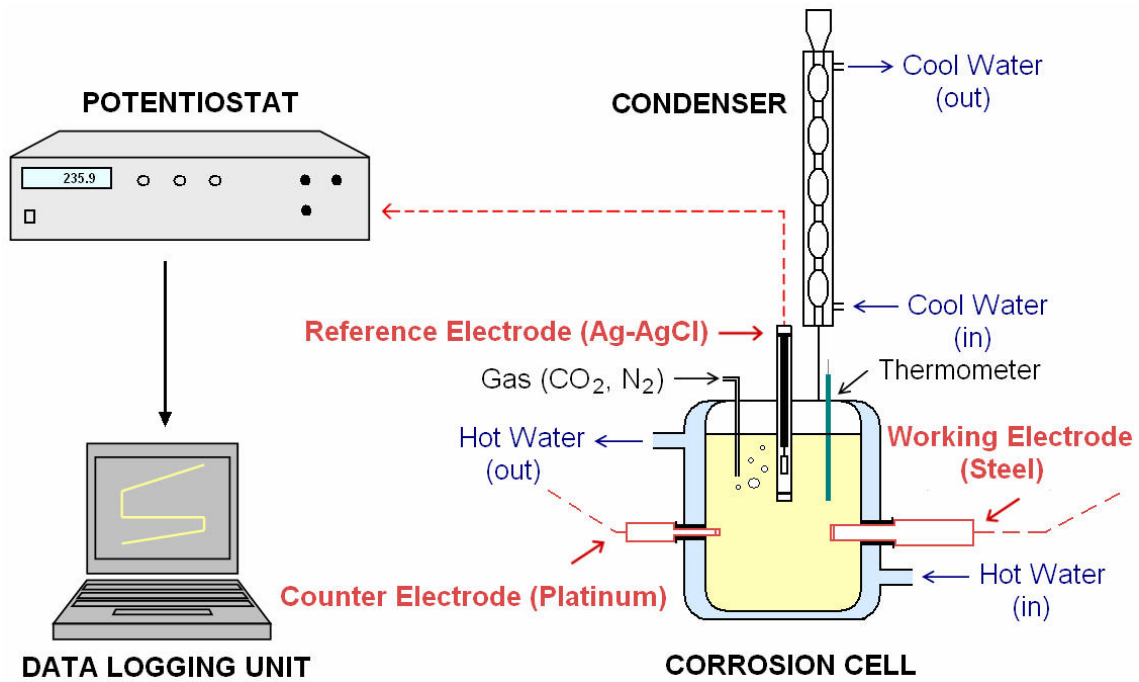


Figure 3: Experimental setup for the electrochemical corrosion tests.

The experimental setup consisted of:

- A three-electrode setup was used, with a working electrode consisting of a disc coupon (surface area = 1 cm²) inserted in a PEEK electrode holder, an Ag/AgCl reference electrode and a circular Platinum-counter electrode.
- Two thermostated baths, for heating the double-wall electrochemical cell, and for a condenser used to prevent water evaporation from the cell.
- A thermometer controlling the inner cell temperature.
- A gas preparation system for feeding the test cell with carbon dioxide (CO₂) or nitrogen (N₂).
- A potentiostat Bio-Logic VMP2 with its data acquisition system.

Preparation of corrosion specimens and of test solutions

Three different steel grades were used for the electrochemical tests : AISI 1018 carbon steel, AISI 304L austenitic stainless steel, and AISI 410 martensitic stainless steel. The composition of each steel grades is given in Table 1. Before experiments, the working electrode was wet-polished to 1200-grit silicon carbide (SiC) papers, rinsed with ethanol and distilled water. Then, it was dried with compressed air and immediately immersed in the test solution.

Table 1: Composition of alloys used for corrosion experiments.

ALLOY GRADES	COMPOSITION OF ALLOY ELEMENTS (%)							
	C	Mn	Si	Cr	Mo	Ni	S	P
AISI 1018	0.16 - 0.22	0.4 - 0.7	0.15 - 0.35	0.40	0.1	0.4	<0.035	< 0.035
AISI 304L	0.03	2	1	18-20	0	8-11	0.03	0.045
AISI 410	0.15	1	1	11-13	-	0	-	-

The corrosion experiments were carried out in 4.0 mol/L aqueous solution of DEA at various CO₂ loadings and temperatures.

At the beginning of each experiment, 300 mL of fresh solvent was introduced in the corrosion cell.

For the experiments in rich amine, the solution was saturated by bubbling CO₂ for 2 hours.

Until saturation, the CO₂ loading obtained at 80°C is about 0.45 mol CO₂ / mol DEA and 0.65 mol CO₂ / mol DEA at 30°C. For the experiments in lean conditions, nitrogen (N₂) was used to deaerate the solvent and avoid any CO₂ charging during the tests. For intermediate CO₂ loadings of 0.25 mol CO₂ / mol DEA (or 0.45 mol CO₂ / mol DEA at 30°C), saturated and deaerated solutions were mixed. N₂ bubbling was kept in the cell to maintain the CO₂ loading during the experiment.

For all test solutions, CO₂ loading was determined by chemical analysis: a small amount of test solution was sampled and an excess of strong acid was added. The volume of degassed CO₂ could then easily be measured [12]. Such measurements were systematically made before and after each corrosion test.

Range of test solution loading and temperature are given in Table 2.

Table 2 : Range of temperature and CO₂ loading of experimental tests.

		CO ₂ Loading, α (mol CO ₂ / mol DEA)			
		0.0	0.25	0.45	0.65
Temperature (°C)	30	X	X	X	X
	50	-	-	X	
	80	-	-	X	

Experimental Procedure

Before polarization, the potential of the working electrode was measured until steady state. Then, potentiodynamic polarization experiments were carried out with a scan rate of 1 mV/s. The scan began from cathodic (-1.1 V vs Ag-AgCl) to anodic (1V vs Ag-AgCl) potentials.

Results and discussion

Influence of the CO₂ loading

Figure 4 presents the polarization curves of different steel grades in 4 mol/L DEA solutions at 30°C and with different levels of CO₂ loading.

Figure 5 reports the value of the free corrosion potential measured for each condition (steel grade and test solution) before the polarisation experiment.

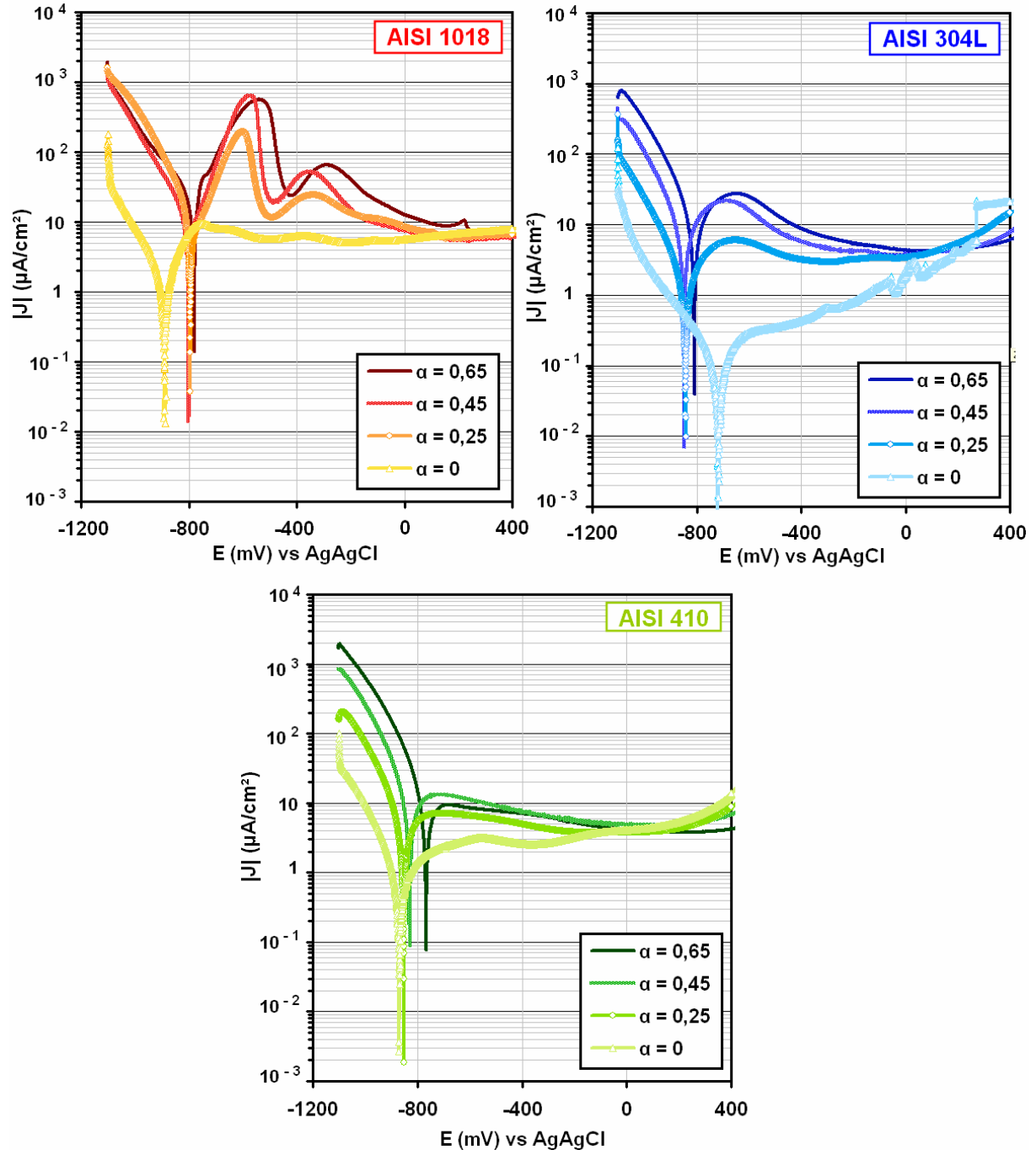


Figure 4: : Influence of CO₂ loading on polarization curves measured in 4 mol/L DEA at 30°C for different steel grades.

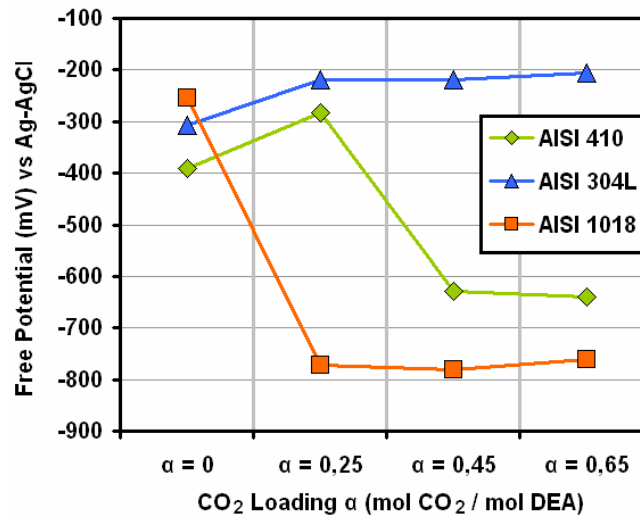


Figure 5: Free potentials of carbon steel AISI 1018 and stainless steels AISI 304L and AISI 410 depending on CO₂ loading of DEA solutions.

From the polarization curves, we can observe that carbon steel exhibits an important anodic peak, followed by a passive region at higher potentials. The anodic peak is also seen for the AISI 304L steel grade, but with lower current levels. Surprisingly, AISI 410 exhibits a fully passive behaviour, suggesting that it has a higher corrosion resistance than AISI 304L. However, these results have to be analysed in the light of free corrosion potential measurements. Indeed, we can observe in Figure 5 that the free corrosion potential of AISI 304L remains in the passive region for all CO₂ loadings at 30°C.

On the other hand, AISI 1018 is passive only in the lean condition ($\alpha = 0$), and becomes active as soon as CO₂ is present in the system. AISI 410 presents intermediate evolution of free corrosion potentials, with a passive to active transition between 0.25 and 0.45 CO₂ loading.

Even though the temperature of these tests was not representative of real operating conditions, these results point out extremely interesting facts:

- some stainless steel grades might present an active anodic dissolution region
- passive to active transitions might occur when the corrosivity of the test solution increases

This could probably explain the extremely rapid uniform corrosion observed on industrial units for AISI 410 and AISI 304L under high temperature and high loading conditions [1].

The results reported in Figure 4 also indicate that both cathodic and anodic reaction rates are increased for high CO₂ loading. This increase is most effective for the cathodic reactions measured on AISI 304L and AISI 410. When the CO₂ loading is increased from 0 to 0.65, the cathodic current density is increased by nearly two orders of magnitude. In order to better understand the origin of this increase, thermodynamic calculations were performed to determine more accurately the solution compositions at the different CO₂ loadings. A home-made program developed at IFP were used for this purpose. The results are summarised in Table 3.

Table 3: Concentrations of major species contained in DEA solutions as a function of CO₂ loading (DEA at 4 mol/L - 30°C).

Expérimental Conditions: 4M DEA		Concentrations (mol/L)							
		[CO ₂]	[HCO ₃ ⁻]	[CO ₃ ²⁻]	[H ⁺]	[OH ⁻]	[DEA]	[DEAH ⁺]	[DEACOO ⁻]
30°C	α = 0	0	0	0	0,013.10 ⁻¹⁰	470.10 ⁻⁵	4,0	0,005	0
	α = 0.25	0,28.10 ⁻⁴	0,054	0,062	5,7.10 ⁻¹⁰	3,9.10 ⁻⁵	2,0	1,1	0,87
	α = 0.45	6,4.10 ⁻⁴	0,27	0,084	31.10 ⁻¹⁰	0,9.10 ⁻⁵	0,66	1,9	1,4
	α = 0.65	220.10 ⁻⁴	1,3	0,062	240.10 ⁻¹⁰	0,1.10 ⁻⁵	0,12	2,6	1,2

Among these species, the candidate oxidising elements are:

- hydronium ion
- bicarbonate ion
- protonated amine

For each experimental condition, the concentrations of these species were compared to current density measured in the cathodic region, corresponding to the reduction reactions. In Figure 6 are presented in a same graph the cathodic currents measured at E= -1V/Ag-AgCl on AISI 410 and the concentration of each oxidising species as a function of CO₂ loading.

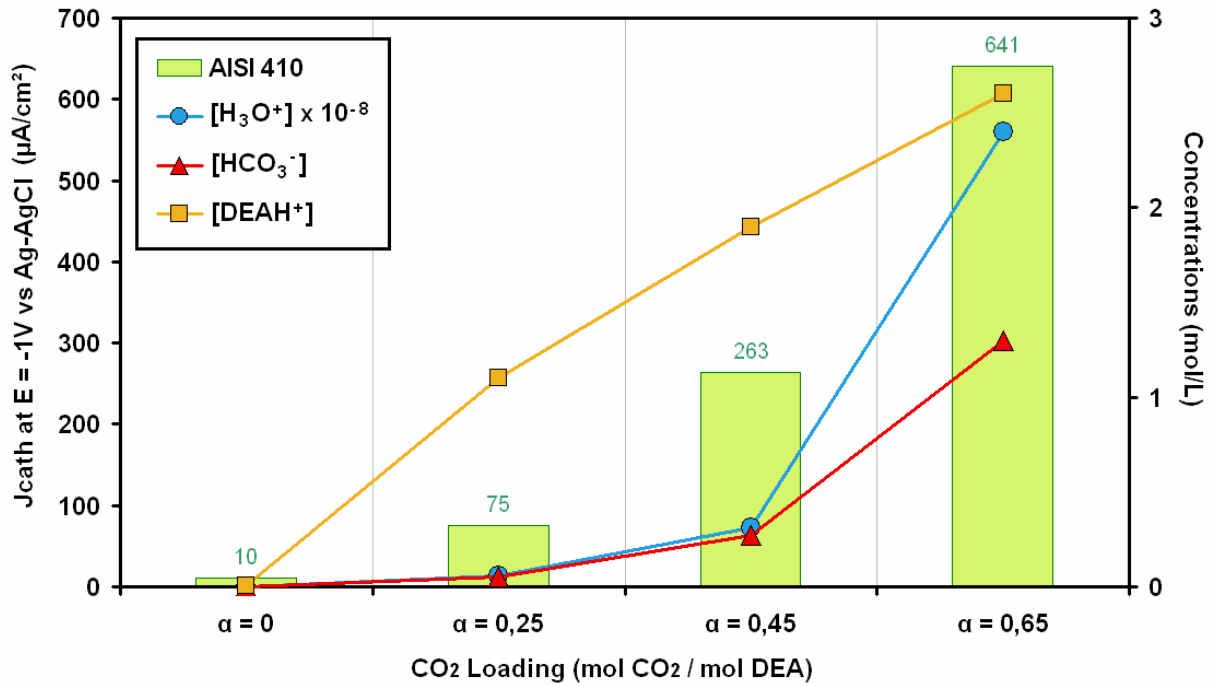


Figure 6: Evolution of cathodic currents at -1V/Ag-AgCl and concentrations of candidate oxidising species as a function of CO₂ loading.

The following trends are observed when the CO₂ loading increases:

- the cathodic current density increases
- the concentrations of hydronium, bicarbonate and protonated amine increase

The concentrations of all oxidising species follow the same trend than the cathodic current, i.e. an increase with CO₂ loading. Nevertheless, we can notice that the concentration of hydronium is extremely low compared to that of bicarbonate or protonated amine. The hypothesis of a significant contribution of hydronium reaction to the cathodic current is therefore very unlikely considering the pH of the solutions (around 8.5).

Then, bicarbonate and protonated amine are the most serious oxidising candidates. However, at this stage, it is not possible to conclude for one or another species and additional experiments with synthetic solutions with controlled levels of each element need to be performed in a next step of this experimental program.

Furthermore, we can also notice from the thermodynamic calculations that the concentration of amine carbamates (DEACOO⁻) is also rising when CO₂ loading increases. Carbamates are often presented as good chelating agents that easily complex with metals, and might then increase the corrosivity of the solution.

Even if this is far beyond the scope of this paper, this might be one of the causes of the passivity breakdown which was observed for some conditions in this study.

Influence of the temperature

Figure 7 presents the influence of the temperature on the current versus potential curves for different steel grades in 4 mol/L DEA solutions and with a constant CO₂ loading ($\alpha = 0.45$).

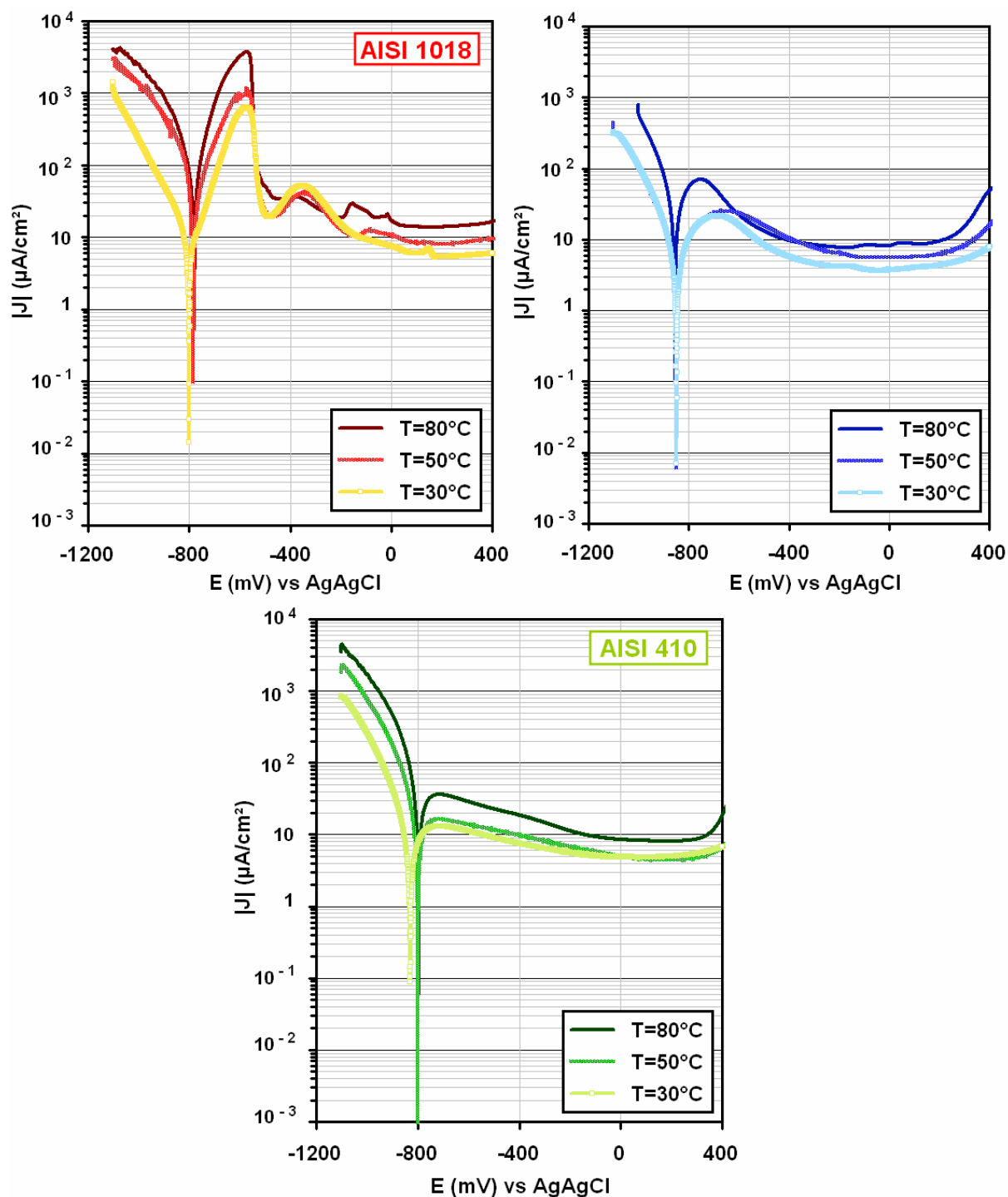


Figure 7: Effect of temperature on carbon steel AISI 1018 and on stainless steels AISI 304L and AISI 410 (4M DEA – 0.45 mol CO₂ / mol DEA)

In the anodic region, the same trends are observed at higher temperature than previously at 30°C. The anodic peak for carbon steel is more pronounced than for AISI 304L stainless steel, while AISI 410 exhibits a fully passive behaviour.

When the temperature is increased, an increase of the cathodic and anodic currents are also observed, in agreement with the literature [3].

The same thermodynamic calculations were performed for these experimental conditions, and are reported in Table 4.

Table 4: Concentrations of principal species contained in DEA solutions depending on temperature (4M DEA – 0.45 mol CO₂ / mol DEA).

Expérimental Conditions: 4M DEA		Concentrations (mol/L)							
		[CO ₂]	[HCO ₃ ⁻]	[CO ₃ ²⁻]	[H ⁺]	[OH ⁻]	[DEA]	[DEAH ⁺]	[DEACOO ⁻]
$\alpha = 0.45$	30°C	0,64.10 ⁻³	0,27	0,08	3,1.10 ⁻⁹	8,6.10 ⁻⁶	0,66	1,87	1,43
	50°C	1,8.10 ⁻³	0,35	0,06	7,8.10 ⁻⁹	1,3.10 ⁻⁶	0,74	1,84	1,37
	80°C	8,3.10 ⁻³	0,46	0,03	28.10 ⁻⁹	19,7.10 ⁻⁶	0,86	1,82	1,29

According to these data, the following trends are observed when the temperature increases:

- the concentrations of bicarbonate and hydronium slightly increase
- the concentration of water is constant
- the concentration of protonated amine slightly decreases

However, the temperature influences the kinetics of reaction and particularly accelerates the rates of reduction reactions. This influence of the temperature is illustrated in Figure 8, where it is shown that the cathodic current measured at -1V/Ag-AgCl obeys an Arrhenius law.

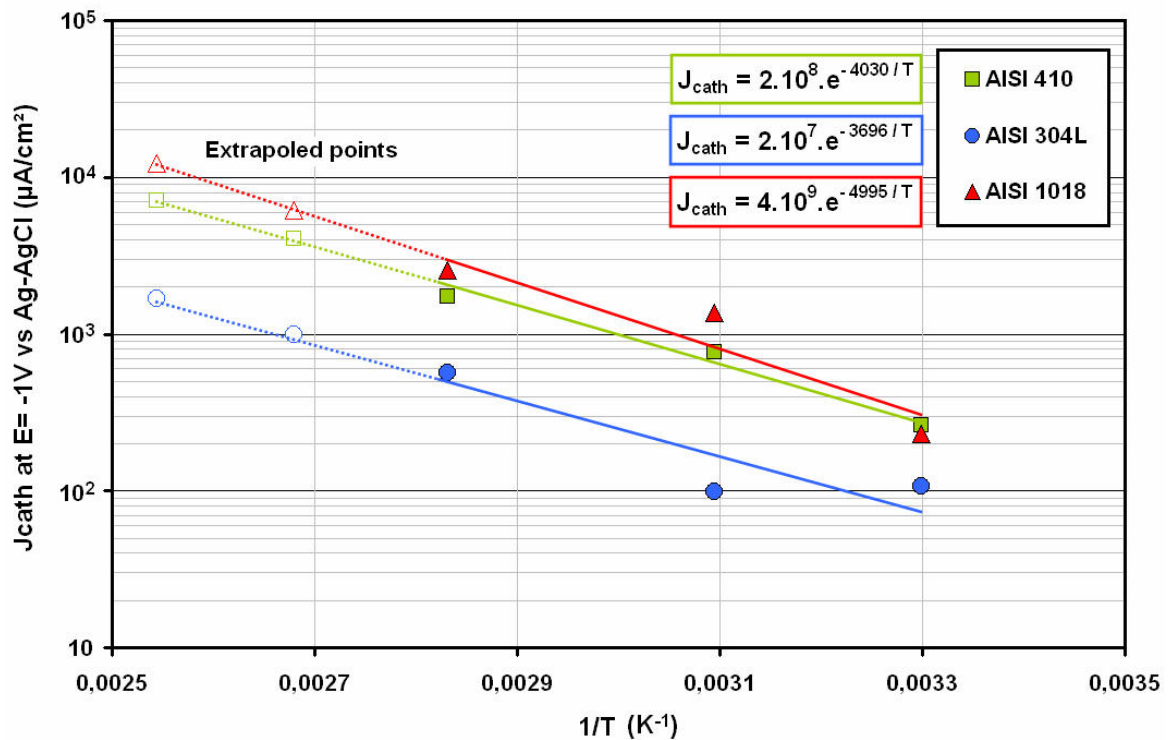


Figure 8: Evolution of cathodic currents at $E = -1V/Ag-AgCl$ as a function of $1/T$ for each steel grades.

These results confirm that the thermic activation of the amine-CO₂ system increases the cathodic currents of nearly one or two magnitude when the temperature is increased from 30°C to 80°C. An extrapolation for higher temperatures of 100°C and 120°C has been done, allowing to predict the cathodic currents in more extreme conditions and also the corrosivity of DEA solvents towards the various steel grades that are tested.

Conclusion

The objectives of this study were to illustrate the influence of temperature and CO₂ loading on the corrosivity of CO₂-amine systems and to correlate the chemical compositions of solvents with the shape of the polarization curves.

It appeared that CO₂ loading was the most influent parameter, with a difference of one or two orders of magnitude between the cathodic currents of a lean amine than that of a rich. The temperature is also a relevant parameter to take into account, especially since the temperature used in this study are lower than that of industrial gas treatment units. In that way, highest temperature can imply much corrosion damages even on stainless steel grades as it was shown by extrapolation curves till 120°C.

These results also underline a better corrosion resistance of stainless steels (AISI 304L and AISI 410) than that of carbon steel (AISI 1018). Indeed, free potentials of carbon steel indicate an active behaviour in CO₂-amine solutions whereas stainless steels are passive but deactivation might occur in these experimental conditions.

Especially, martensitic steel AISI 410 seems to loose his passivity as soon as CO₂ loading is too high. The tests have not yet been performed for highest temperatures but it is expected that both higher CO₂ loading and temperature lead to higher corrosion rates.

The chemical compositions of the solutions were calculated in order to highlight the influence of oxidising species like bicarbonate, hydronium ions, undissociated water and/or protonated amine. These results are not sufficient to conclude on the influence of one or another species, but can allow us to focus on some mechanisms and especially on the influence of bicarbonate.

In our future investigations, it will be important to consider more aggressive experimental conditions, such as highest temperatures, in order to reproduce industrial conditions. Furthermore, it appears also necessary to take into account some others species of CO₂-DEA solutions such as carbamates and other degradation by-products of amine which can act as chelating agents.

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