Influence of Electrolyte Temperature on Corrosion Behaviour of Carbon Steel Pipe API 5L X52 and X70

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***Abstract*— In this study, electrochemical experiments were conducted to select the optimal electrolyte temperature to have excellent corrosion resistance in 0,1M hydrochloric acid using API X52 and X70 carbon steels. The temperature elevation effect was examined in the temperature range from 293- 323 K.**

The experiments showed that the corrosion current density was significantly lower when temperature increases and the aggressive solution effect is more important on X52 steel than X70 steel.

Keywords—corrosion, carbon steel, pipeline steel, temperature effect, acid solution.

I. Introduction

Carbon steel has been widely used in different conditions in every part of the oil and gas industry and as well as other industrial applications [1]. Acid solutions are among the most corrosive environments. Their main applications are the metal stripping baths and the cleaning of industrial plants [2], the stimulation of oil wells, the elimination of localized deposits [3.4], etc. Most of the time, sulphuric and hydrochloric acids are used for such purposes [5]. The main problem with the application of carbon steel is its low corrosion resistance in acidic solutions [6]. The influence of temperature on corrosion processes, particularly in acidic environments, during high-temperature stripping and descaling operations, in order to dissolve corrosion products covering metal installations, has been the subject of several articles [7-9]. In this context, the temperature is considered that is the principal natural environmental factors affecting the deterioration of materials in a given corrosive environment.

In this study, we focus on the effect of increasing temperature in the range of 293 to 323 K on the corrosion behaviour of two carbon steels in 0.1M HCl solution, using electrochemical testes.

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II. Exprememental procedure

A. *Materials and test solution*

The materials tested in this study are an X52 and X70 steel (from *ALFA PIPE ex ALFATUS,* Algerian metal tube company). Chemical compositions of X52 and X70 are shown in Table 1 and Table 2, respectively.

TABLE I. *Minor components concentration in X52 pipeline steel in wt.%.*

% X52	C	Mn	Si	P	S	Ceq	Fe
	0.45	0.5	0.1	0.2	0.1	0.15	sold

TABLE II. Minor components concentration in X70 pipeline steel in wt.% (the rest up to 100 wt% is iron).

% X70	C	Mn	Si	Cr	Ni	Mo	V
	0.123	1.593	0.219	0.2	0.020	0.004	0.06
	S	**Cu**	**Ti**	**Nb**	**Al**	**P**	**Ceq**
	0.03	0.026	0.006	0.063	0.027	0.016	0.953

The 0.1M HCl acid solution was selected as the corrosive environment for this study. The solution was prepared using the 37% concentrated acid (SIGM-ALDRICH) with distilled water. The solution is naturally aerated; It is agitated with the help of a magnetic bar, driven by a magnetic agitator. An average agitation was chosen to homogenize the solution.

B. *Electrochemical test*

Electrochemical measurements were carried out using an electrochemical workstation PGP201 Voltalab potentiostat driven by VoltaMaster 4 software. A three-electrode system was used : the X52 or X70 pipeline steel were the working electrodes, the saturated calomel electrode (ECS) was a reference electrode and the platinum fil was the counter electrode. In addition, the surfaces of the working electrodes were encapsulated in epoxy resin (Goodfellow, purity 99.99%) in the form of a square (1cm x 1.7cm x 1cm), and then abraded to a mirror finish using decreasing grit emery papers (320, 600, 800 and 1200), followed by washing with distilled water.

The open circuit potential (OCP) of the tested samples versus time were recorded during around 30 min in immersion tests. The polarization resistance experiment performed at a scan rate of 0,5 mV/s in an interval of ±250 mV around OCP. The corrosion potentials and current densities were estimated by using Tafel extrapolation .

III. RESULTS AND DISCUSSION

A. Study of corrosion behavior X52 and X70 in 0.1 HCl

Polarization curves of X52 and X70 steel samples in 0.1M HCl at 293 K are shown in Figure 1. Electrochemical parameters obtained from the fitting of the polarization curves are shown in Table 3.

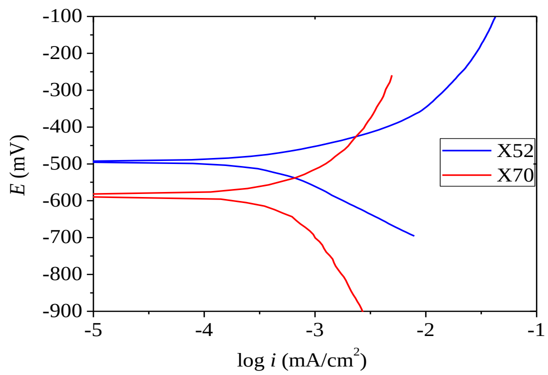

FIGURE 1. POLARIZATION CURVES OF (A) X52 AND (B) X70 STEEL SAMPLES AT VARIOUS TEMPERATURE IN 0.1M HCL SOLUTION AT 293 K.

It can be seen that the corrosion rate of X52 steel is higher than that of X70 steel at the same temperature (293 K), which means the most important rate of dissolution is attributed to X52 steel compared to X70 Steel. The comparative study of the corrosive acid medium effect on the nuance of the two tested steels shows that X52 steel is more susceptible to corrosion and its resistance is lower than that of X70 steel. In addition, X52 steel has the highest corrosion potential (E_{corr}) and paradoxically the highest corrosion current density (I_{corr}) (354.20 mA/cm^2).

TABLE III. POLARIZATION PARAMETERS FOR X52 AND X70 IN 0.1M HCL SOLUTIONIN AT 293 K.

	T (°K)	E_{corr} (mV/ECS)	i_{corr} (µA/cm^2)	b_a (mV/dec)	b_c (mV/dec)
X52	293	-492.90	354.20	69.80	-114.10
X70	293	-586.30	231.40	90.40	-132.20

The microscopic corrosion morphology of the samples was observed by optical microscope to assess the surface condition of the two steels before and after polarization, in the chosen acid medium. Micrographic observations (figure 2: C-D) show significant differences compared to references (2. A-B) which represent the optical micrographs of the surface state of the both X52 and X70 steels, respectively, before their immersion in tested solution.

The micrographs obtained confirm the electrochemical results, which revealed that the X52 steel shows a low corrosion resistance in the HCl environment compared to the X70 steel at the concentration of 0.1 M. Indeed, the surface of the X52 steel has several cavities and the attack is more localized, it appears in the form of cavities of different dimensions and geometries, whereas the X70 steel, its surface has fewer cavities which it is about corrosion by stings, characteristic of the medium HCl [13].

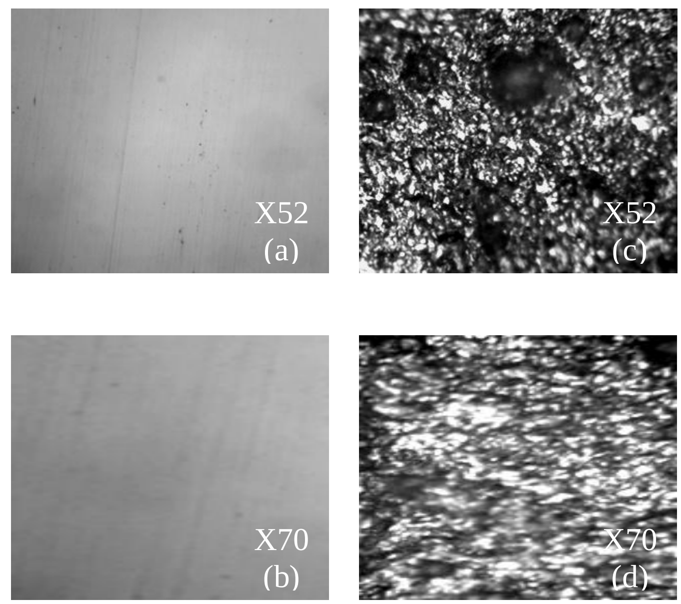

FIGURE 2. OPTICAL MICROGRAPHS OF X52 AND X70 STEEL SAMPLES BEFORE AND AFTER IMMERSED IN 0.1 M HCL SOLUTION.

B. Study of Effect of temperature

The influence of temperature on corrosion processes, particularly in acidic environments, during high-temperature stripping and descaling operations, in order to dissolve corrosion products covering metal installations, has been the subject of several articles [14-24]. Because temperature is one of the factors likely to alter the electrochemical behaviour of materials in a given corrosive environment, we have proposed to conduct a potentiodynamic study on the resistance of X52 Steel and X70 steel. In the middle HCl at 10-1n at different temperatures between 293 and 323 K (Fig. 3).

Figure (3) represents the effect of temperature on the cathodic and anodic polarization curves of X52 and X70 steel in the acidic medium in question.

The temperature increase did not alter the overall appearance of the global polarization curves in the studied environment, indicating that the corrosion mechanism remains unchanged throughout the temperature range explored. However, a translation of the global polarization curves is observed at the highest current densities in both cases. unavoidable.

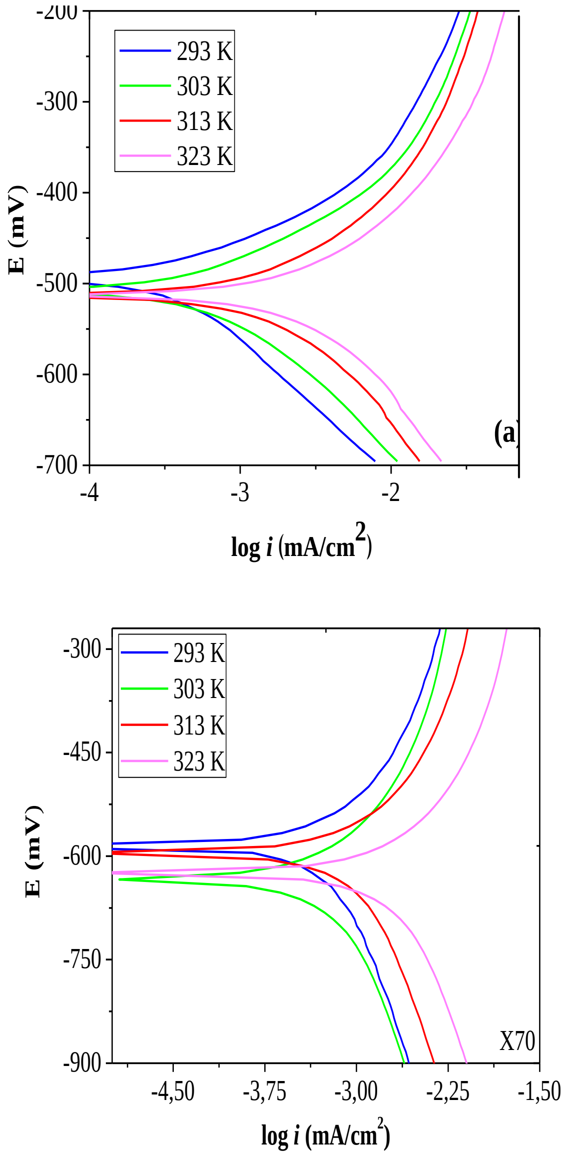

FIGURE 3. EFFECT OF TEMPERATURE ON THE CATHODIC AND ANODIC RESPONSES FOR (A) X52 AND (B) X70STEEL IN 0.1 M HCL.

Table (4) consolidates the electrochemical parameters, resulting from the exploitation of the Tafel's right method. We note that the temperature rise has almost no effect on the corrosion potential of the both steels (E_{corr}) in HCl acid.

For corrosion current densities (I_{corr}), they record an increase in their values, thus revealing an increase in the proton discharge velocity of the cathodic side and the dissolution of the two X52 and X70 steels on the anodic side.

TABLE IV. *MINOR COMPONENTS CONCENTRATION IN X52 PIPELINE STEEL IN WT.% (THE REST UP TO 100 WT% IS IRON).*

material	T (°C)	E_{corr} (mV/ECS)	i_{corr} (µA/cm²)	b_a (mV/dec)	b_c (mV/dec)
X52	293	-492.90	354.20	69.80	-114.10
	303	-510.70	493.50	78.20	-145.30
	313	-512.80	635.20	86.50	-164.70
	323	-511.20	909.70	91.10	-181.00
X70	293	-586.30	231.40	90.40	-132.20
	303	-615.50	493.50	78.20	-143.70
	313	-597.70	635.20	86.50	-161.30
	323	-609.20	909.70	91.10	-173.40

C. *Determination of Thermodynamic activation parameters*

Arrhenius-type dependence is observed between the corrosion rate and temperature. This relationship was used to calculate the values of apparent activation energy (Ea) of the corrosion process in the acid solution (equation. 1). The Icorr corrosion current densities used are those obtained by the Tafel method [12].

$$i_{corr} = k \exp(-Ea / R T) \qquad (1)$$

Where T: is the absolute temperature, K is the preexponential constant of Arrhenius, R the universal constant of the perfect gases and (Ea) the energy of activation of the corrosion process.

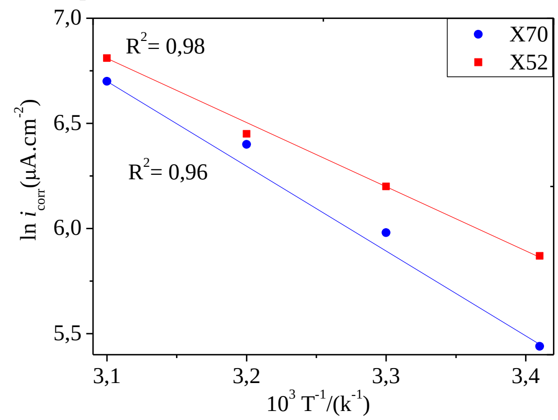

FIGURE 4. ARRHENIUS PLOTS FOR THE CORROSION OF X52 AND X70 IN 0.1 M HCL SOLUTION.

Figure (4) shows the logarithm variation of the corrosion current density as a function of the inverse of the absolute temperature. The plots of Ln I_{corr} = f (1/T), relative to the two steels in acidic medium studied at different temperatures, are represented by straights. The values found from (E_a) are grouped in table (5).

In general, the temperature infule predominantly on the corrosion phenomena. Indeed, the rate of corrosion increases when the test temperature rises, this phenomenon induces changes in the process of dissolutio.

An alternative formulation of Arrhenius equation allows the determination of the enthalpy and entropy of activation according to the following equation [26]:

$$i_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^{\circ}}{R}\right) \exp\left(-\frac{\Delta H_a^{\circ}}{RT}\right) \quad (2)$$

where h is Planck's constant, N is Avagadro's number, ΔS a is the entropy of activation and ΔH a is the enthalpy of activation.

Figure 5 shows a plot of *Ln* (I_{corr}/T) vs. 1/*T*. Straight lines are obtained with a slope of ΔH a /R and an intercept of *Ln R*/*Nh* + *ΔS* a /R from which the values of *ΔS* a and *ΔH* a are calculated and are given in Table 6.

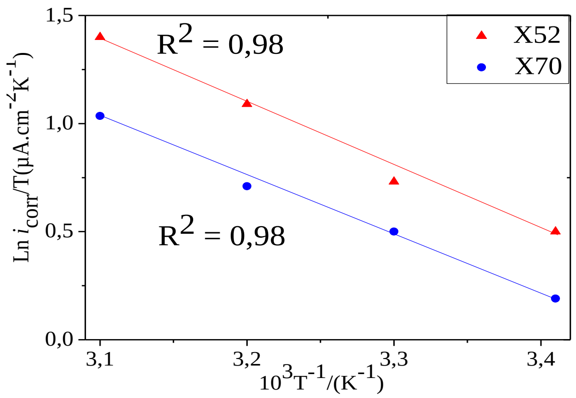

FIGURE 5. ARRHENIUS PLOTS FOR THE CORROSION OF X52 AND X70 IN 0.1 M HCL SOLUTION.

TABLE V. *THE VALUES OF ACTIVATION PARAMETERS FOR STEEL IN 0.1M HCL.*

material	E_a (kJ.mol^{-1})	ΔH_a (kJ.mol^{-1})	ΔS_a (J.mol^{-1})
X52	24,79	22,17	-120,5
X70	23.08	20.35	-136.56

The positive sign of enthalpies (ΔHa °) reflects the endothermic nature of the process of dissolving steel.

Nevertheless, all the values of the activation energies (Ea) are higher than those of ΔHa ° indicating that the mechanism of dissolution implies a gaseous reaction, that of the formation of H_2 [27-28]. We can thus infer that the corrosion process is governed by a one-molecular reaction, characterized by the following equation [27,29-31]:

$$Ea - \Delta Ha^{\circ} = RT \quad (3)$$

IV. CONCLUSION

At the end of this study, the following conclusions may be stated:

- the X52 steel is the most affected steel by the phenomenon of corrosion compared to X70 steel, in 0.1M HCl Solution, with a rate corrosion in the following order: I_{corr} (X52) > I_{corr} (X70).
- Increased electrolyte temperature will increase the corrosion current densities of tested samples in the chosen acid solution, irrespective of the temperature.
- The optical micrographs reveal surface attacks, the morphology of which differs as well as the geometry and the size of the stings according to the surface state and the chemical composition of our steel.
- The calculation of enthalpies of activation ΔHa° confirmed an endothermic nature of the dissolution reaction. Moreover, the activation energy of corrosion process for the steel does not remarkably influenced by the nature and concentration of the aggressive solution.

REFERENCES

[1] M.A. Deyab, "Effect of cationic surfactant and inorganic anions on the electrochemicalbehavior of carbon steel in formation water", Corrosion Science, Vol.49. pp 2315–2328, 2007.

[2] R.M. Latanision, "Thermodynamique des réactions de corrosion", Matériels Performance, Vol.26.pp.9,1987.

[3] S.A. Abd El-Maksoud, A.S. Fouda, "Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium", Materials Chemistry and Physics, Vol.93.pp.84-90, 2005.

[4] M.A. Migahed, I.F. Nassar, " Corrosion inhibition of tubing steel during acidization of oil and gas wells", Electrochimcal Acta, Vol.53.pp.2877-2882, 2008.

[5] K.F. Khaled, "Application of electrochemical frequency modulation for monitoring corrosion and corrosion inhibition of iron by some indole derivatives in molar hydrochloric acid", Materials Chemistry and Physics, Vol.112. pp.290-300, 2008.

[6] J. Aljourani, M.A. Golozar, K. Raeissi, "The inhibition of carbon steel corrosion in hydrochloric and sulfuric acid media using some benzimidazole derivatives", Materials Chemistry and Physics, Vol.12. pp.320-325, 2010.

[7] M.A. Hegazy, H.M. Ahmed, A.S. El-Tabei, "Investigation of the inhibitive effect of p-Substituted 4-(N,N,N-dimethyldodecyl-Ammonium bromide) benzylidene-Benzene 2-yl-amine on corrosion of carbon steel pipelines in acidic medium", Corrosion Science, Vol.53. pp.671-678, 2011.

[8] M.M. Solomon, S.A. Umoren, I.I. Udosoro, A.P. Udoh, "Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid olution", Corrosions Science, Vol.52. pp.1317-1325, 2010.

[9] I.B. Obot, N.O. Obi-Egbedi, "Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation", Corrosion Science, Vol.52. pp.198-204, 2010.

[10] I. A. Aiad, N. A. Negm, "Some schiff Base surfactants as steel-corrosion inhibitor" Journal of Surfactants Detergents Vol.12.pp.313-319, 2009.

[11] K. F. Khaled, "Electrochemical behavior of nickel in nitric acid and its corrosion inhibition using some thiosemicarbazone derivatives", Electrochimica Acta Vol.55, pp.5375-5383.2010.

[12] P.C. Okafor, Y. Zheng, "Synergistic inhibition behaviour of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H2SO4 solutions", Corrosion Science, Vol.51.pp. 850-859, 2009.

[13] Y.F. Yan, X.Q. Xu, D.Q. Zhou, H. Wang, Y. Wu, X.J. Liu, Z.P. Lu, "Hot corrosion behaviour and its mechanism of a new alumina-forming

austenitic stainless steel in molten sodium sulphate", Corrosion Science, Vol.77, pp. 202-209, 2013.

[14] F. Kellou, A. Benchettara, S. Amara, "Temperature and microstructure effects on corrosion behavior of annealed Fe–xTi–yC alloys in sulphuric acid solution", Materials Chemistry and Physics, Vol.106, pp. 198-208, 2007.

[15] M.A. Hegazy, H.M. Ahmed, A.S. El-Tabei, "Investigation of the inhibitive effect of p-substituted 4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-benzene-2-yl-amine on corrosion of carbon steel pipelines in acidic medium", Corrosion Science, Vol.53, pp. 671-678, 2011.

[16] G.E. Badr, "The role of some thiosemicarbazide derivatives as corrosion inhibitors for C-steel in acidic media", Corrosion Science, Vol.51, pp. 2529-2536, 2009.

[17] L. Elkadi, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenée, "The inhibition action of 3,6-bis(2-methoxyphenyl)-1,2-dihydro-1,2,4,5-tetrazine on the corrosion of mild steel in acidic media", Corrosion Science, Vol.42, pp. 703-719, 2000.

[18] M. Tourabi, K. Nohair, M. Traisnel, C. Jama, F. Bentiss, "Electrochemical and XPS studies of the corrosion inhibition of carbon steel in hydrochloric acid pickling solutions by 3,5-bis(2-thienylmethyl)-4-amino-1,2,4-triazole", Corrosion Science, Vol.75, pp.123-133, 2013.

[19] A. Popova, M. Christov, A. Vasilev, A. Zwetanova, "Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part I: Gravimetric and voltammetric results", Corrosion Science, Vol.53, pp. 679-686, 2011.

[20] A. Popova, M. Christov, A. Vasilev, "Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part II: Electrochemical impedance and polarisation resistance results", Corrosion Science, Vol.53, pp.1770-1777, 2011.

[21] A. Popova, E. Sokolova, S. Raicheva, M. Christov, "AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives", Corrosion Science, Vol.45, pp.33-58, 2003.

[22] A Popova, M Christov, S Raicheva, E Sokolova, "Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion", Corrosion Science, Vol.46, pp.1333-1350, 2004.

[23] E. E. Oguzie, V .O. Njoku, C. K. Enenebeaku, C. O. Akalezi, C. Obi, "Effect of hexamethylpararosaniline chloride (crystal violet) on mild steel corrosion in acidic media",Corrosion Science, Vol.50, pp.3480-3486, 2008.

[24] Emeka E. Oguzie, "Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel",, Corrosion Science, Vol.50, pp.2993-2998, 2008.

[25] R. Shukla, S.K. Ghosh, D. Chakrabarti, S. Chatterjee, "Microstructure, texture, property relationship in thermo-mechanically processed ultra-low carbon microalloyed steel for pipeline application", Materials Science and Engineering, Vol.587, pp.201-208, 2013.

[26] A.K. Shukla, R. Balasubramaniam, S. Bhargava, "Effect of replacement of V by Fe and Nb on passive film behavior of Ti–6Al–4V in simulated body fluid conditions", Journal of Alloys and Compounds, Vol.389, pp.144-152, 2005.

[27] P. Suresh, A. K. Shukla, S. A. Shivashankar, N. Munichandraiah, "Electrochemical behaviour of aluminium in non-aqueous electrolytes over a wide potential range", Journal of Power Sources, Vol.110, pp.11-18, 2002.

[28] A. Chetouani, B. Hammouti, T. Benhadda, M. Daoudi, "Inhibitive action of bipyrazolic type organic compounds towards corrosion of pure iron in acidic media" ,Applied Surface Science, Vol.249, pp.375-385, 2005.

[29] J. O'M. Bochris, A. K. N. Reddy, "Modern Electrochemistry", Vol.2, Plenum Press, New York, 1977.

[30] E. Hamed, "Studies of the corrosion inhibition of copper in Na_2SO4 solution using polarization and electrochemical impedance spectroscopy", Materials Chemistry and Physics, Vol.121, pp.70-76, 2010.

[31] M. Lebrini, M. Lagrenée, H. Vezin, M. Traisnel, F. Bentiss, "Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds", Corrosion Science, Vol.49, Issue 5, pp.2254-2269, 2007.