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OLT – 35 LOW CARBON STEEL CORROSION IN PRESENCE OF SULFATE IONS

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ABSTRACT.The OLT-35 low carbon steel corrosion in aqueous NaCl solutions in the absence and the presence of sulfate ions by electrochemical methods (cyclic voltammetry and polarization curves) and metallographic microscopy has been investigated. From the corrosion parameters values, of the studied steel/electrolytic systems, and the analyzed micrographs results that the OLT –35 low carbon steel is most susceptible for corrosion in 1.5% NaCl + 1.5% Na_2SO_4 solution than in 3% NaCl due to the decreasing of polarization resistance.

Key words: carbon steel, sulfate ions, electrochemical corrosion, polarization curves, cyclic voltammetry, metallographic microscopy.

INTRODUCTION

The study of electrochemical behavior of an alloy, such as low carbon steel OLT – 35, may give relevant information about the corrosion of buried steel pipes or storage tanks in various media. Such studies serve as a rational basis for evaluation of coating performance and determination of controlling parameters.

The complexity of the corrosion processes of buried metallic structures results at first because of the multitude of metallic underground networks placed in the same environment, networks that can galvanicaly interact. Another factor in emphasizing the complexity of this problem is represented by chemical, electrochemical, biochemical, electromagnetic (stray currents) high pollution of the soil. The soil is a corrosive environment that has special characteristics from one place to another because of the variable humidity, the different percent of dissolved salts, various pH, the presence of microorganisms, the variable quantity of oxygen and stray currents presence.

In urban areas, residual wasters, containing carbonate, chloride and possibly sulfate ions, may be in contact with underground pipelines, made from mild steel bitumen coated, electrically insulating with paint and, sometime, cathodically protected. Any defects on these insulations permit corrosion. Depending on the ion concentration, potential, pH and temperature each ionic

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species has a different effect on the electrochemical behavior of mild low carbon steel. Studies of the corrosion of iron and its alloys are mainly focused on the effect of chloride ions [1-10]. By contrast, the literature for corrosion by sulfate ions is scarce [11-15]. The objective of this research was to investigate the electrochemical behaviour of low carbon steel OLT – 35 , in the range of anodic active potential of iron, in salted aqueous solutions containing Na_2SO_4.

EXPERIMENTAL

Electrochemical measurements were all carried out in a three-electrode type cell with separate compartments for reference electrode. The counter electrode, separated from the main compartment of the cell by a Nafion membrane, was a platinum sheet of 5 cm^2 in area. The working electrode was a disk of OLT – 35 steel (whose composition is (wt%): C 0.17, Si <0.35, Mn <0.4, P <0.05, S <0.05, Fe 98.98) with a surface area of 0.154 cm^2. Surface of the working electrode was prepared by grinding abrasive paper 400 – 1200 gradation. Next they were rinsed with distilled water and degreased with acetone. Before each experiment the OLT-35 steel electrode was cathodically polarized (for 5 minutes i.e.) in the range of hydrogen evolution potential, to provide a reproducible electroreduced steel surface.

The experiments were carried out at room temperature and cquiescent solutions. The volume of the used experimental cell was quite large (~ 0.35 l) so that the concentration of eventually dissolved iron compound in the bulk of the solution could be neglected

Potentials were measured vs. saturated calomel electrode (SCE) as reference. This was connected to the main compartment of the cell by a salt bridge and a Lugging capillary.

Aqueous solution of 3% NaCl, 1.5% NaCl, a mixture of 1.5% NaCl and 1.5% Na_2SO_4 were used as electrolyte. The electrolytes solution was prepared from analytical grade reagents using double distillated water.

The voltammograms at different scanning rate: 500mV/s, 200mV/s, 100mV/s, 50mV/s in the potential range between –1.8 and -0.25 V/SCE with an Autolab PGSTAT 10 system were recorded.

The instantaneous corrosion potential (ε_{corr}), the corrosion current density (i_{corr}) and polarization resistance (R_p) were determined from the Tafel plot using the Resistance Polarization measurement techniques developed by Stern et al [16]. A polarization sweep from –10 to 10 mV around the corrosion potential (in anodic and cathodic direction) at the scan rate of 1 mV s^{-1} was applied to OLT-35 steel electrode in studied electrolytes. The measurements were performed by using a SYCOPEL SCIENTIFIC – SCANING MINISTAT.

Metallographic microscopy was used to examine the morphology and the nature of corrosion on the OLT-35 steel surface after immersion, for 36 months, in various test solutions. The metallographic microscopy was performed with a NEOPHOT 21- CARL ZEISS JENA microscope with incorporated camera.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Figure 1 shows typical cyclic voltammograms for OLT –35 steel recorded at different scan rates in: a) NaCl 3%, b) NaCl 1.5% and c) NaCl 1.5% + Na_2SO_4 1.5% solutions. Such voltammograms in steady state could be obtained after a few cycles (20) over the whole potential range(–1.8 and -0.25V/SCE), Fig.1 d). The voltammetric profile changes with the number of sweeps in this range of potentials and well-defined anodic and cathodic peaks appear. All voltammograms shows two anodic (A_1 and A_2) and two cathodic (C_1 and C_2) peaks. Table 1 presents the values of the main electrochemical parameters.

Table 1.

Electrochemical parameters for OLT 35 in studied solutions

Electrolyte /Parameters	3% NaCl	1,5% NaCl	1,5%Na_2SO_4	1,5% NaCl + 1,5%Na_2SO_4
ε_{A1} (V)	-0.910	-0.939	-0.951	-0.918
I_{A1} (A)10^4	7.190	3.290	1.870	4.240
ε_{A2} (V)	-0.515	-0.535	-0.486	-0.515
I_{A2} (A)10^4	8.140	2.710	4.180	5.020
$\|I_{A1}/I_{C1}$	0.580	0.650	-	0.490
$\|I_{A2}/I_{C2}\|$	0.960	0.930	1.130	1.000

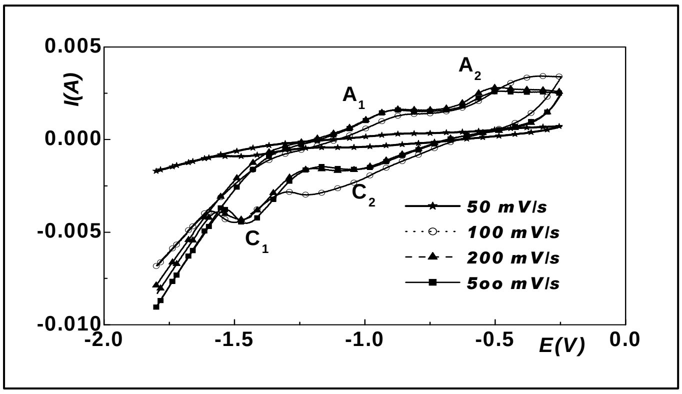
According to peaks potential values, there two processes can be identified [3-4]:

Process I – corresponding to oxidation of Fe(0) to Fe(II), peak A_1, coupled with the reduction of Fe(II) to Fe(0), peak C_1:

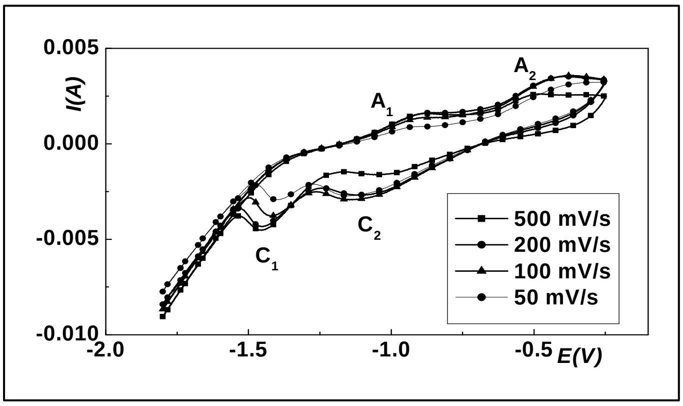
$$\mathrm{Fe} + 2\mathrm{H_2O} \leftrightarrow \mathrm{Fe(OH)_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \tag{1}$$

Process II – corresponding to oxidation of Fe(II) to Fe(III), peak $A_{2,}$ and to reduction of Fe(III) to Fe(II), peak C_2:

$$Fe(OH)_2 \leftrightarrow FeOOH + H^+ + e^- \qquad (2)$$



a)



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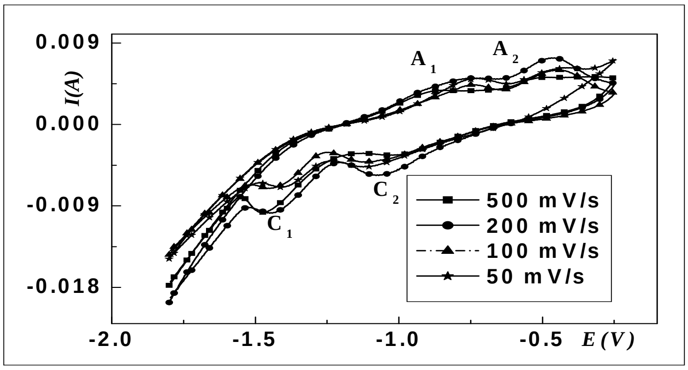

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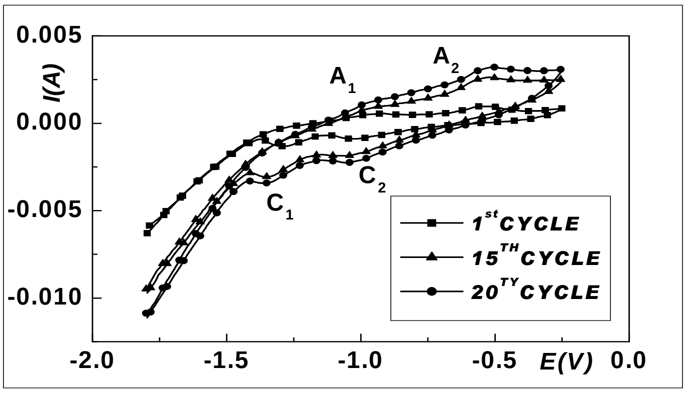


d)

Figure 1. Voltammograms recorded for OLT 35 steel in a) 3% NaCl .b) 1.5% NaCl and c) 1.5% NaCl +1.5 Na_2SO_4 solutions; *d)* influence of cycles number (3% NaCl)

In anodic scan direction three domains can be identified: a) the active zone of corrosion where the anodic peak A_1 can be pointed out; b) a relative passive zone, between –0.6 and –0.9V/ECS where appears a slow increase of current, so a reduced corrosion rate; c) a transpassive zone, over the potential value of –0.6V/ECS where the oxidation of Fe (II) to Fe (III) take place (peak A_2) followed by the oxygen evolution.

The increase of the scanning rate brings about an increase of the peak currents intensity in all three cases. A higher effect in the case of solution of 3% NaCl was observed. It results from the above figures that the cycle's number not influences the voltammograms shape.

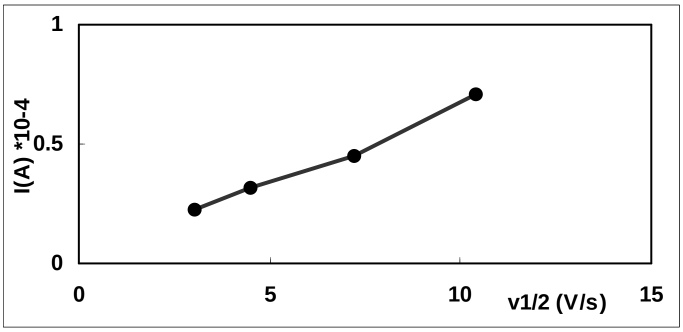


Figure 2. The peak current vs. (scan rate)$^{1/2}$ relations for the anodic peak A_1 for OLT 35/3% NaCl system

In the present experiments, all anodic observed peaks exhibited a relative linear relationship between the peak current and the square root of the scan rate (figure 2). This suggests that the processes are diffusion rather than kinetically limited.

Adding sodium sulphate to NaCl 1.5% solution produces an increase of A_1 and A_2 anodic peaks intensity of 1.3 and 1.85 fold respectively.

Polarization measurements

The ε_{corr}, i_{corr} and Tafel slops were determined from the Tafel plots of potentiodynamic measurements by extrapolation.

The polarization resistance (Rp) was calculated using the Stern–Geary equation:

$$i_{corr} = \frac{1}{2.303} \frac{b_a \cdot b_c}{(b_a + b_c)} \frac{1}{R_p} = \frac{B}{R_p} \tag{3}$$

where b_a and b_c are the Tafel slopes.

The corrosion rate, v_{corr}(mg/cm^2·h), was also calculated from the corrosion current, i_{corr} (A/dm^2), using Faraday's law:

$$v_{corr} = \frac{i_{corr} \cdot A}{26{,}8 \cdot z} \tag{4}$$

where 26.8 is the Faraday constant, A the average atomic weight of steel, z the number of electrons exchanged by metal ion (z = 2).

Figure 3 shows Tafel plots of OLT –35 steel in studied electrolytes.

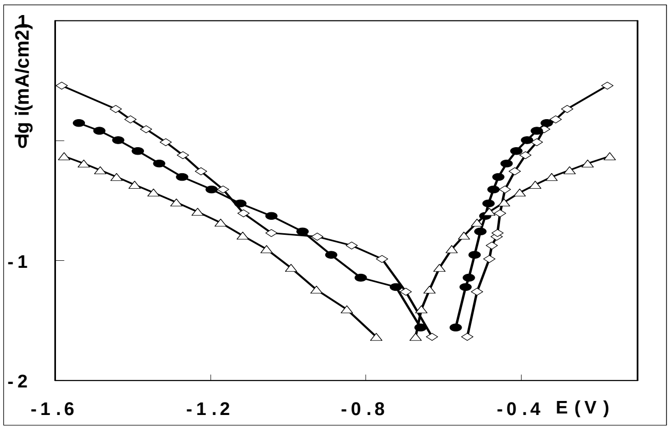


Figure 3. Polarization curves of OLT- 35 steel in: NaCl 3% (-○-);NaCl 1.5% (-●-) and NaCl 1,5% + Na_2SO_4 1,5% (- Δ -)

On the polarization curves of OLT- 35 in 3% NaCl solutions as well as in chloride and sulphate mixture, linear domains on the anodic and cathodic branches can be observed. The analysis of these curves reveals that, in all studied electrolytes, the corrosion of OLT –35 steel takes place by a kinetic control by the charge transfer typical reaction [5].

Table 2.

Corrosion parameters for OLT 35 in studied solutions

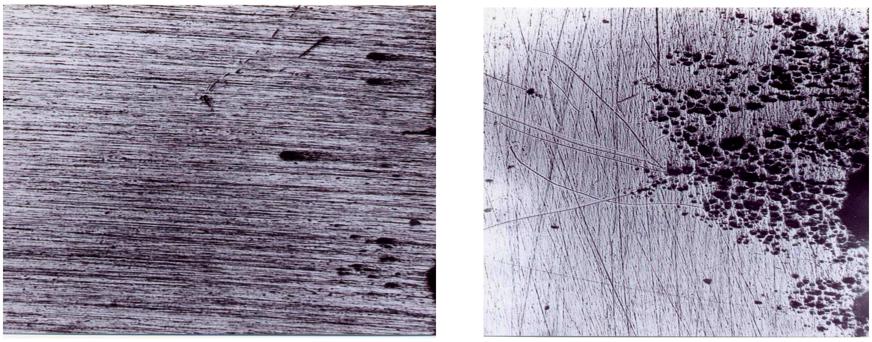
Electrolyte /Parameters	3% NaCl	1.5%NaCl	1.5% NaCl + 1.5% Na_2SO_4
I_{corr} x10^2 [mA/cm^2]	2.63	2.18	7.07
ε_{corr} [mV/ECS]	-620	-555	-580
b_a [mV/dec]	190	185	180
b_c [mV/dec]	160	195	280
R_p(kΩ cm^2)	1.424	1.890	0.673
V_{corr} x10^2 [mg/cm^{2}h]	2.74	2.27	7.38

The polarization parameters (table 2) shows that the OLT –35 steel is more corrodible in 1.5% NaCl + 1.5% Na_2SO_4 solution than in 3% NaCl due to the decreasing of polarization resistance.

The higher corrosion rate in the mixture of salts, in our experiments, suggests that Na_2SO_4 acts as a corrosion accelerator.

Metallographic microscopy

Samples surfaces aspects obtained by metallographic microscopy are presented in the figure 4.



a) b)

Fig.4. Micrographs of the corroded surface of the OLT- 35 steel in the presence of a) NaCl 3%, b) mixture of NaCl 1,5% + Na_2SO_4 1,5%

The metallographic microscopy observations confirms, by the higher localized attack of the metal surface (Fig.4 b) that NaCl 1,5% + Na_2SO_4 1,5% mixture solution is more aggressive than NaCl 3%.

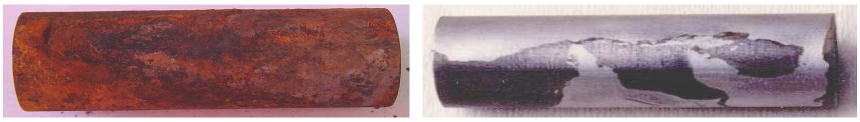
Micrographs recorded for OLT- 35 steel in NaCl 3% solution denote a relative generalized corrosion, with a thickness of the corrosion products layers around 0, 2 mm. No rusts are seen from the micrograph. The surface morphology of the samples immersed in mixture of NaCl 1, 5% + Na_2SO_4 1, 5% solution is different. Localized corrosion takes place, in the plague forms, with larger depth and diameters, on the most of the surface. Dark green rust was observed on the electrode surface.

According to Genin et al. [17] the green rust may be a transient compound with the following formula: $4Fe(OH)_2 2FeOOH.FeSO_4.nH_2O$, with *n* of probable 4 value. The formation of a passive layer may be considered according to:

$$4Fe(OH)_2 2FeOOH.FeSO_4 + 2\ H_2O = 7\ \gamma FeOOH + SO_4^{-2} + 7H^+ + 5e^- \quad (5)$$

Although the surface oxidation in the presence of sulfate ions induces the formation of a passive film, the precipitation of a sulfate product alone can not protect the steel against localized attack or uniform dissolution.

These are confirmed by the surfaces aspect of the samples macroscopically analyzed with the help of a magnifier [18], Fig. 5.



a) b)

Fig.5. The aspect of the corrosion products formed on the OLT 35 carbon steel in 1.5 % NaCl + 1.5% Na_2SO_4: a) before and b) after removing the corrosion products

CONCLUSIONS

Results of this investigation showed that buried pipeline systems made from OLT – 35 low carbons steel in presence of sulfate ions will develop surface corrosion problems.

By analyzing the corrosion parameters values, obtained from electrochemical measurements, a greater susceptibility for corrosion of OLT – 35 low carbons steel in presence of sulfate ions was demonstrated.

A good agreement between electrochemical measurements results and surface morphological studies was observed.

A relatively uniform corrosion for samples immersed in NaCl solutions was observed in comparison with those exposed in a mixture of NaCl + Na_2SO_4 where the localized corrosion is predominant.

The metallographic microscopy shows that a NaCl + Na_2SO_4 mixture solution is more aggressive than NaCl solution. This fact is confirmed by the higher localized attack of the metallic surface which is covered by corrosion defects (pitting and plague type with higher depth and diameters).

REFERENCES

1. Daksh Baweja, Harold Roper, and Vute Sirivivatnanon, *Materials Journal,* **2003**,100, 228-238.
2. C. Calin, I. Lingvay, Georgeta Rus, I. Baldea, Eleonora Maria Rus,"Study on corrosion behaviour of carbon steel in salted media", *The 1st International Corrosion Conference-Study and Control of Corrosion in the Perspective of Sustainable Development of Urban Distribution Grid*, Constanta, June 6-8, **2002**, 96-101
3. M. Fathy, W. Bayoumi, A. Ghanem and B. G. Ateya*, Int. J. Electrochem. Sci.,* **2006,** 1, 258-267.
4. Eleonora Maria Rus, Georgeta Ţarălungă, Delia Maria Constantin, *Studia Universitatis Babes-Bolyai, Chemia L(1),* **2005**, 261 – 270.
5. C. Calin, I. Baldea, Eleonora Maria Rus, " Steel corrosion and its control in neutral media", *The 2nd International Corrosion Conference-Study and Control of Corrosion in the Perspective of Sustainable Development of Urban Distribution Grid*, M. Ciuc, june 19-21, **2003**, 138-144
6. C. Calin, I. Baldea, Eleonora Maria Rus, "Annals of West University of Timisoara*", Series Chemistry,* 12(3), **2003**, 747-756
7. Gui-Fang Huang, Wei-Qing Huang, Ling-Ling Wang, Bing-Suo Zou, Di-Ping Chen, De-Yi Li, Jia-Mou Wei, Jian-Hui Zhang, *Int. J. Electrochem. Sci.,* **2007,** 2, 321 - 328
8. Y. M. Liou, S. Y. Chiu and C. L. Lee, *J. Appl. Electrochem.,* **1999**, 29, 1977 – 1981
9. J. A. Bardwell, J. W. Fraser, B. MacDougall and M. J. Graham, *J. Electrochem. Soc.,* **1992**, 139, 366 - 375.
10. Dae-Kyeong Kim, J. D. Scantlebury, Srinivasan Muralidharan, Tae-Hyun Ha, Jeong-Hyo Bae, Yoon-Cheol Ha and Hyun-Goo Lee, (http://www.umist.ac.uk/corrosion/jcse) *Journal ofCorrosion Science and Engineering,* **2004***,* 9 – 14.
11. G. Vatankhah, M. Drogowska, H. Menard and L. Brossard, *J. Appl. Electrochem.,* **1998**, 28, 173 - 183.
12. Bore Jegdič, Dragutin Dražič and Jovan P. Popič, *J. Serb. Chem. Soc.*, **2006***,* 71 (5) 543–551.
13. C. Calin, Eleonora Maria Rus, I. Baldea, Analele Universitatii Oradea, Fascicola Chimie, **2001,** VIII, 5 – 10.
14. M. Drogowska, H. Menard and L. Brossard, *J. Appl. Electrochem.,* **1996**, 26, 217 - 225.

15. M. Drogowska, L. Brossard and H. Menard, *J. Appl. Electrochem.,* **1998**, 28, 491 - 501.
16. M. Stern and A. L. Geary, J. Electrochem. *Soc*., **1957,** 104, 56.
17. Ph. Refait, M. Abdelmoula and M. R. Genin, *Corrosion Science,* **1994**, 36,55-63.
18. C. Calin, I. Baldea, Eleonora Maria Rus, "Analysis of underground gas pipelines corrosion by optical methods. Corrosion control and its efficiency"*, The 4th International Conference URB-CORR- Study and Control of Corrosion in the Perspective of Sustainable Development of Urban Distribution Grid*, Sibiu, Romania, June, 9-11, **2005**, 182-194.