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ASPECTS OF CORROSION AND ITS INHIBITION IN COOLING WATERS

Ioan Viorel BRÂNZOI[1], Ileana CAMENIȚĂ[2], Florina BRÂNZOI[3], Andreea BONDAREV[4]

În toate sistemle de răcire cu apă, la suprafața de contact metal / apă apar numeroase procese de coroziune care determină depunerea de produşi de coroziune sub formă de cruste. Datorită depunerilor pe suprafețele de transfer termic a crustelor formate din descompunerea bicarbonaților precum şi a produşilor de coroziune schimbul de căldură este îngreunat, fapt care deranjează funcționarea normală a instalațiilor industriale.

Această lucrare prezintă câteva aspecte ale fenomenelor de coroziune ce apar în sistemele de răcire cu apă şi se referă la protecția împotriva coroziunii a suprafețelor metalice cu ajutorul unui inhibitor ecologic, netoxic. A fost utilizat ca inhibitor de coroziune gluconatul de calciu (GCa), compus acceptat din punct de vedere ecologic. S-a obținut o bună eficiență a inhibitorului (87.81 %) la o concentrație de 2000 ppm GCa. Au fost effectuate analize electrochimice şi calculați parametrii cinetici de coroziune pentru oțelul OL37 în sisteme de răcire cu apă.

In all the cases of cooling water systems, at the metal / water interface appear frequently corrosion processes which lead to deposition of corrosion products, like scales. Due to these scales formation from the decomposition of bicarbonates and in the same time, of the corrosion products on the heat exchange surfaces, the heat exchange becomes more difficult, fact that disturbs the normal function of industrial installation.

This paper presents some attempts of analyzing the corrosion phenomena which occur in cooling water systems and relates to the protection of metallic surfaces from corrosion using an ecologically, non-toxic inhibitor. Calcium gluconate (GCa), ecologically acceptable compound, has been used as corrosion inhibitor. A good 87.81 % inhibition efficiency has been obtained with 2000 ppm GCa. Electrochemical data and corrosion kinetic parameters for OL37 steel in cooling water systems have been obtained.

Keywords: corrosion, calcium gluconate, ecological inhibitor, cooling water

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[1] Prof., Dept. of Phisical Chemistry and Electrochemistry, University "Politehnica" of Bucharest, Romania, E-mail: iv_branzoi@chim.upb.ro

[2] Lecturer, Dept. of Chemistry, "Petroleum – Gas" University of Ploiesti , Romania

[3] Superior research, "National Institute of Physical Chemistry „I.G. Murgulescu", Bucharest, Romania

[4] Assist., Dept. of Chemistry, "Petroleum – Gas" University of Ploiesti , Romania

1. Introduction

This paper presents the possibility of using of calcium gluconate (GCa), as corrosion processes inhibitor, in cooling waters. GCa a nontoxic and environmentally accepted product [1-3].

GCa is a salt of gluconic acid which could result by the controlled fermentation of glucose.

The presence of salts in cooling waters used in opened systems with recirculation determines the appearance of corrosion phenomena. They are accelerated by increasing the temperature. The oxygen solved in these waters increases also the corrosion processes. By the permanent contact between water and atmosphere, oxygen dissolved in recirculation waters is maintained at the maximum level of the saturation limit. The formation of scale by calcium carbonate precipitation can initiate corrosion processes under the deposited layer [4-7].

2. Experimental part

Experimental determinations have been done to establish the corrosion behavior of OL37 steel in cooling waters, in presence and absence of the ecological inhibitor, calcium gluconate. The chemical composition of OL37 steel is presented in Table 1.

Table 1

Chemical composition of OL37 steel

Chemical composition, (%)						
C	Si	Mn	P	S	Al	Fe
0.150	0.090	0.400	0.023	0.020	0.022	99.293

Water samples have been prelevated from opened cooling systems, with recirculation, from methane gas compression stations. Chemical composition of tested waters is presented in Table 2.

Table 2

Cooling water characterization

pH	HCO_3^- mg / L	D_T mval Ca^{2+}/L	Residue ppm	Cl^- ppm	Conductivity x 10^6 $ohm^{-1}\cdot cm^{-1}$
7.3	402.6	10	604	301.4	181.4

The metallic electrodes have been abraded with abrasive paper of different granulations (400-2000) to obtain a glassy and homogenous surface. Then, these electrodes have been degreased in benzene, at boiling temperature, cleaned in 5% HCl solution with inhibitor, washed with acetone and dried at room temperature.

The electrochemical studies have been performed using a VoltaLab 40 potentiostat / galvanostat with multiple functions and data processing software. For the polarization curves drawing it has been used the potentiodynamic technique. In this case the electrode potential scanning has been performed at a rate of 2 mV/s and the working electrode potential has been measured in respect with the reference electrode, the saturated calomel electrode. Platinum electrode has been used as auxiliary electrode.

The metallographic analysis of OL37 steel working electrodes after the corrosion tests has been done using a metallographic/metallurgical microscope HUND H 600.

3. Results and discussion

To study the possibility of using calcium gluconate as corrosion inhibitor, there have been drawn the polarization curves of OL37 steel at a temperature of 20^{o}C, in absence and presence of different quantities of calcium gluconate.

There have been also determined some kinetic corrosion parameters: corrosion current (i_{cor}), corrosion potential (E_{cor}), polarization resistance (Rp), penetration index (P), coverage degree (θ) and inhibitions efficiency (I.E.); they have been presented in Table 3.

Table 3

Corrosion kinetic parameters determined from the polarization curves for OL37 steel in cooling water, at 20^{o}C, in presence of calcium gluconate inhibitor

Inhibitor (GCa) concentration (ppm)	i_{cor} (μA/cm^2)	E_{cor} (mV)	Rp (ohm·cm^2)	P (mm/an)	Θ	I.E. (%)
-	10.216	- 460.0	1470	0.108	-	-
300 GCa	6.812	- 455.7	2570	0.072	0.333	33.32
500 GCa	6.300	- 454.5	2960	0.066	0.383	38.33
800 GCa	3.752	- 452.4	3240	0.039	0.633	63.28
1000 GCa	2.023	- 450.2	5620	0.021	0.802	80.20
1500 GCa	1.836	- 430.6	5635	0.019	0.820	82.03
2000 GCa	1.245	- 427.1	5650	0.013	0.878	87.81

Because in Table 3 there are presented all the kinetic corrosion parameters, in Fig. 1 there are presented only some of the characteristic polarization curves, as example.

Analyzing the polarization curves from Fig. 1 there can be observed that, at reduced over voltages in cooling water, the corrosion process of OL37 steel is controlled by activation. There can be also observed that at high over voltages, on the anodic curve, the process is controlled by diffusion and at very high over voltages, a limit value of the diffusion current is achieved.

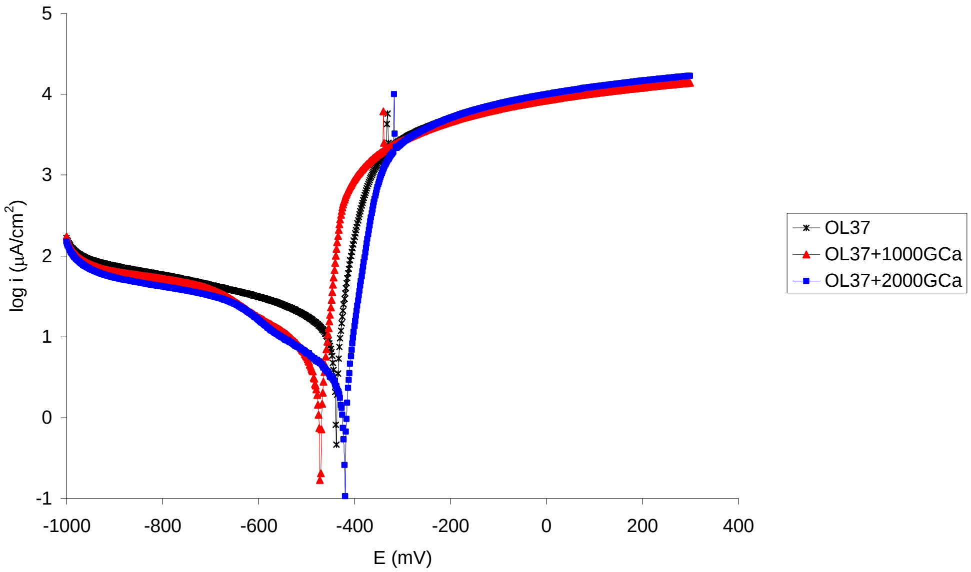

Fig. 1. Polarization curves for OL37 steel in cooling water with and without inhibitor (t=20°C)

If we analyze comparatively the cathodic and anodic curves, the potential domain where the cathodic process is controlled by activation is smaller than that on the anodic curve. The diffusion current density is smaller on the cathodic curve than in case of the anodic process and it covers a large potential domain. We assume that, on this domain of potential, depolarization is produced by oxygen reduction, this process being controlled by diffusion. Analyzing the shape of cathodic polarization curves, there can be observed that after the potential domain where the cathodic process is controlled by diffusion, a sudden increase of current takes place, which corresponds to hydrogen evolution.

From Table 3 is observed a maximum efficiency (I.E. = 87.81%) of the corrosion process inhibition when 2000 ppm GCa is used.

There have been performed electrochemical impedance spectroscopy measurements (EIS) for OL37 steel in cooling waters, with and without adding GCa corrosion inhibitor, at open circuit potential. The obtained results are presented in Nyquist diagrams from Fig. 2 and the characteristic measures for these diagrams are presented in Table 4.

Table 4

Characteristic measures of Nyquist diagrams for OL37 steel in cooling water in presence of GCa inhibitor

Inhibitor (GCa) concentration (ppm)	R1 [*] (ohm·cm^2)	R2 [**] (ohm·cm^2)	C [***] (μF/cm^2)	D [****] (ohm·cm^2)
-	62.02	49.79	527.2	51.08
300	56.70	54.07	449.0	54.93
500	62.34	95.07	439.5	96.77
800	59.61	135.20	378.1	138.20
1000	64.31	470.40	234.0	483.00
1500	59.25	446.10	186.7	450.10
2000	61.75	906.10	78.4	909.80

[*] R1 – solution resistance; [**] R2 – metal polarization resistance; [***] C – double layer capacity; [****] D – capacitive loop diameter

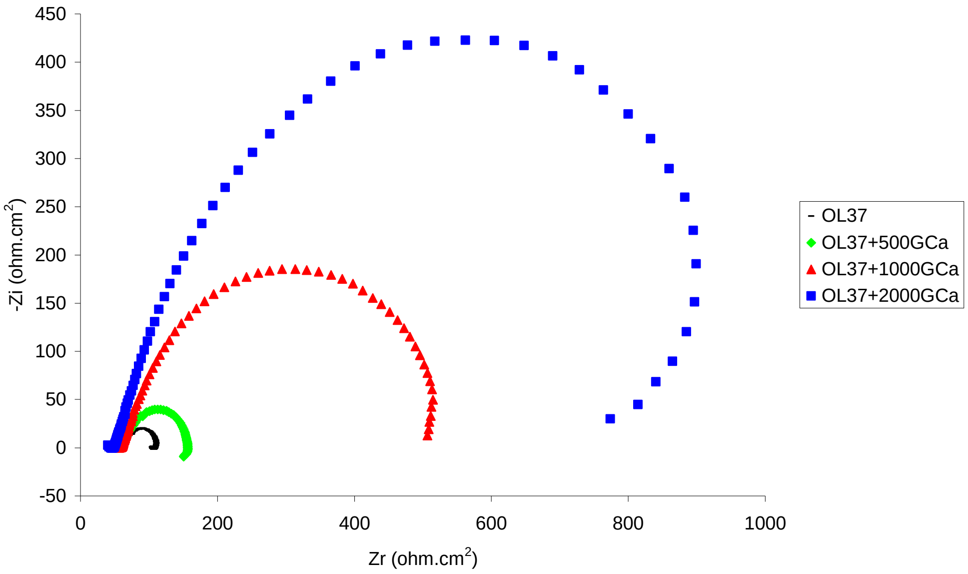

Fig. 2. Nyquist diagram for OL37 steel in cooling water with and without inhibitor (t=20°C)

By analyzing Nyquist diagrams from Fig. 2 there can be observed that in all studied cases, both in cooling water without inhibitor and in cooling water with different adds of inhibitor, the appearance of capacitive loops, very well defined in the domain of very high and medium frequencies.

The diameter of these capacitive loops represents a measure of polarization resistance and it is larger when the charge transfer is more difficult and this fact is because of GCa inhibitor presence. From Fig. 2 it can be observed that the diameter of capacitive loop is larger in the presence of inhibitor, than in its absence. The largest diameter, respectively the highest polarization resistance is obtained at a concentration of 2000 ppm GCa in cooling water which corresponds with data obtained from polarization measurements (see Fig. 1 and Table 3).

By analyzing Nyquist diagrams from Fig. 2, in the domain of small and very small frequencies, it is observed the appearance of an inductive area which evidences the adsorption of some ionic species at metal surface and the production of relaxation phenomena at the interface metal/solution.

When adding 2000 ppm GCa in cooling waters it is observed an increased capacitive loop diameter, thus, an important increasing of the polarization resistance in comparison with the system OL37 steel in water without inhibitor.

In Figs 3- 8 there are presented the structural micrographs of OL37 steel before polarization and OL37 steel in cooling water, with and without inhibitor GCa, obtained with the metallographic microscope.

From the analysis of surfaces structural micrographs there can be observed that corrosion processes are reduced when GCa inhibitor of 2000 ppm is used in cooling water, this concentration corresponding to a maximum efficiency of the inhibition of corrosion processes.

By a comparative analysis of micrographs from Figs 3-8, there can be observed that for cooling waters with inhibitor (GCa) corrosive destroying is much smaller and less severe than for cooling waters without inhibitor. This is caused by the fact that the inhibitor from solution is adsorbed at the metallic electrode surface forming an adsorption layer which behaves as a barrier for the aggressive agents [6, 7] and leads to the corrosion process inhibition, this being observed by EIS and electrochemical polarization measurements.

Calcium gluconate has an inhibition effect for corrosive processes, because of the formation of a less soluble calcium/iron gluconate or of calcium hydroxide, acting as a protective layer.

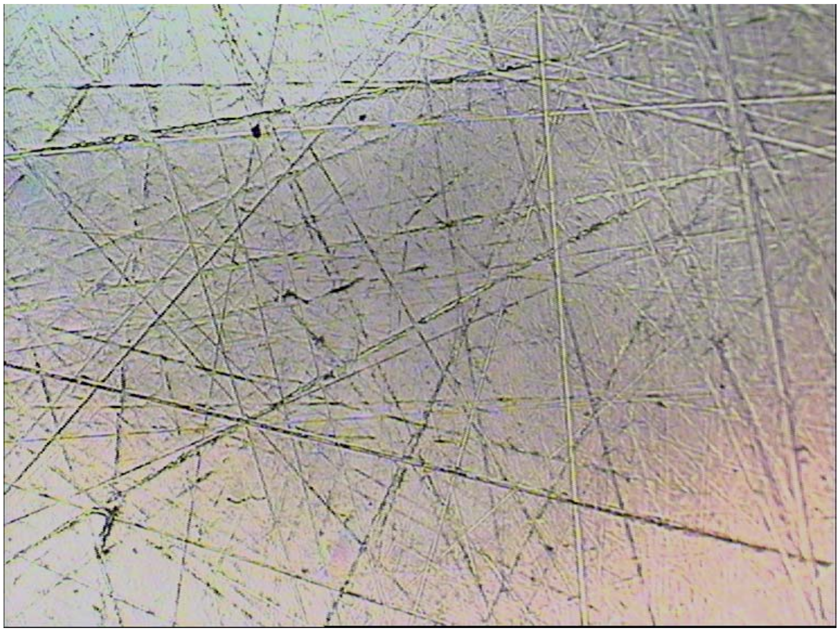

Fig.3**.** Metallographic analysis for OL37 steel before polarization (200 x)

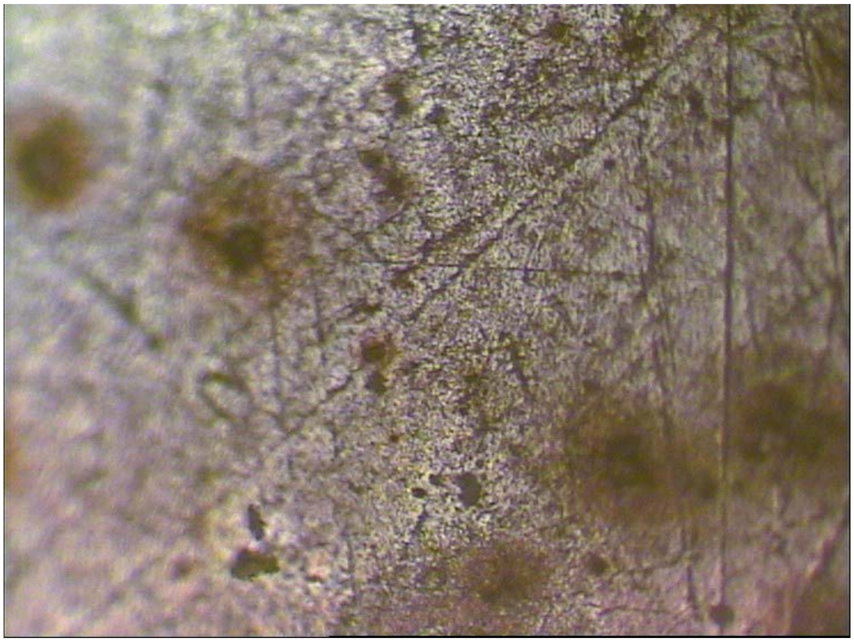

Fig.4**.** Metallographic analysis for OL37 steel in cooling water (200 x)

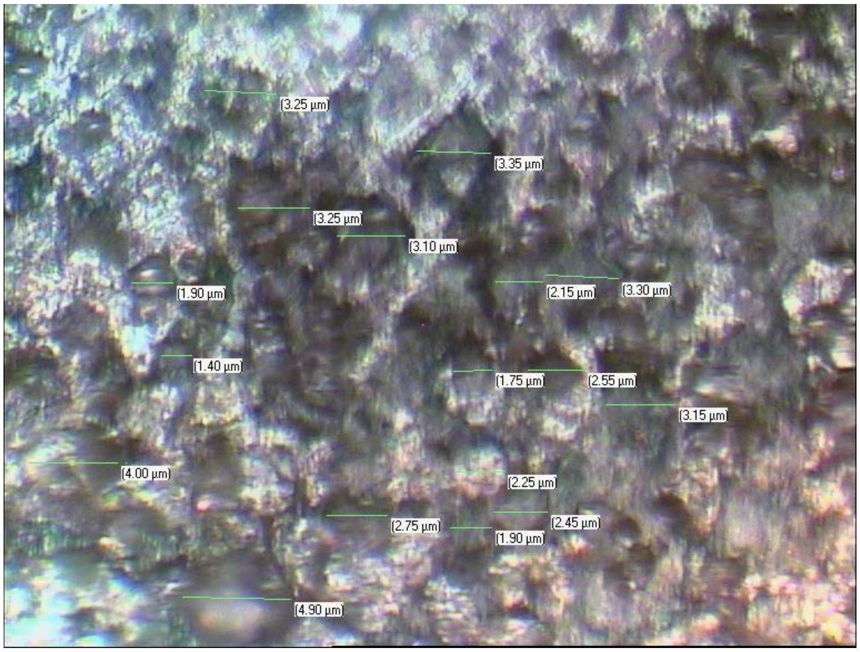

Fig.5. Metallographic analysis for OL37 steel in cooling water with 500 ppm GCa (400 x)

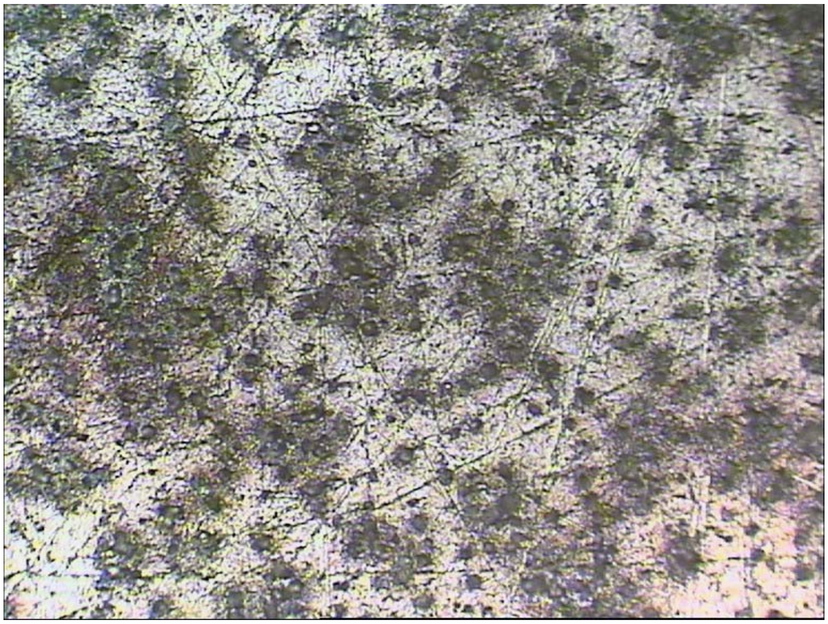

Fig.6. Metallographic analysis for OL37 steel in cooling water with 1000 ppm GCa (200 x)

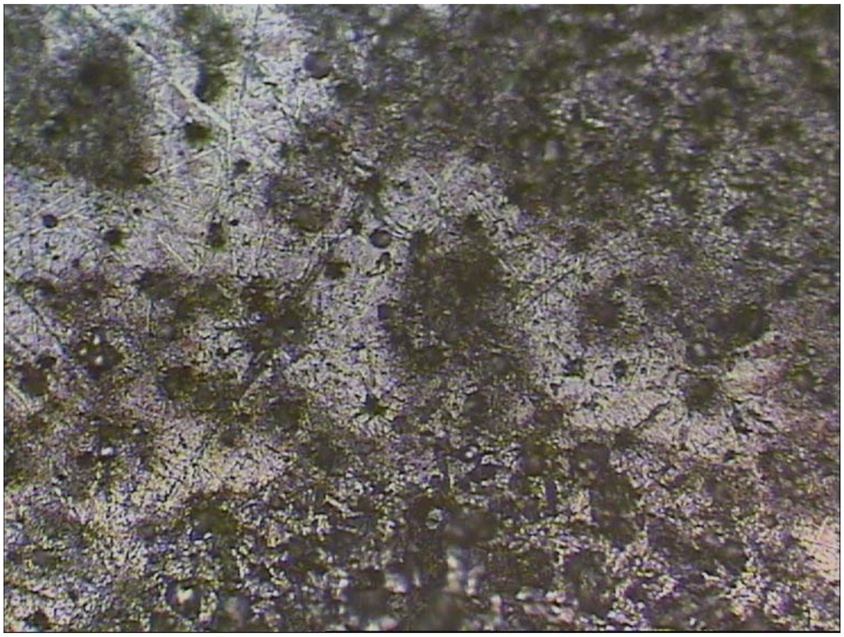

Fig.7. Metallographic analysis for OL37 steel in cooling water with 2000 ppm GCa (200 x)

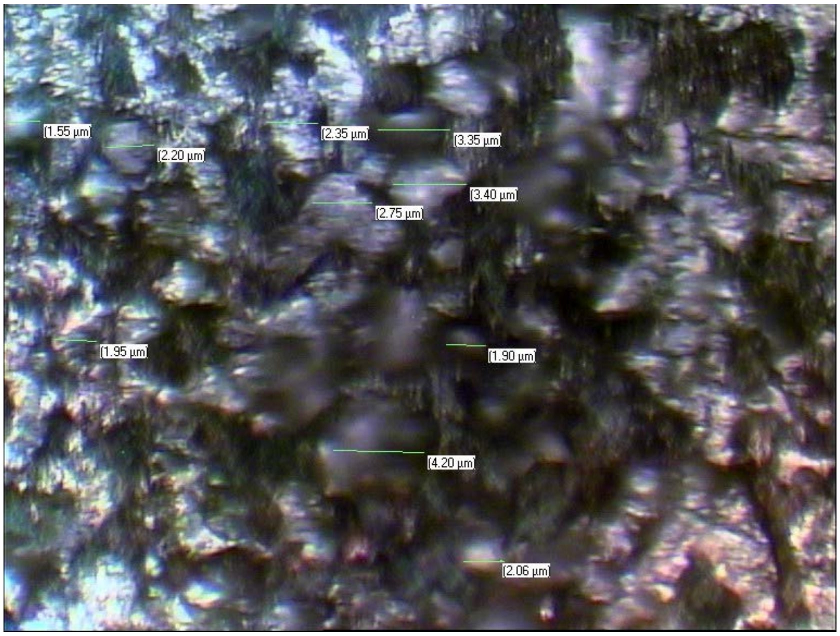

Fig.8. Metallographic analysis for OL37 in cooling water with 2000 ppm GCa (400 x)

4. Conclusions

It has been studied the behaviour of calcium gluconate (GCa), an ecologically and non-toxic product as corrosion inhibitor.

Tests made on OL 37 steel corrosion processes in cooling waters, demonstrate important rates of corrosive processes.

The optimal content of inhibitor GCa is of 2000 ppm and corresponds to a maximum efficiency of the corrosion processes inhibition of 87.81 %, this meaning that it can be recommended as inhibitor for this system.

EIS measurements have evidenced the capacitive behaviour of OL 37steel at high and medium frequencies and an inductive behaviour at small and very small frequencies.

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