# Synergist Action of Some Inhibitors Mixtures for Anticorrosive Protection of Steel in Cooling Waters

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*It was studied the anticorrosive action of some inhibitors mixtures for steel protection in cooling waters. By X-rays analysis it was determined the composition of solid deposits formed in coolers. Inhibitor mixtures containing magnesium lignosulphonate, sodium tripolyphosphate and zinc sulphate present a synergist action in the process of corrosion inhibition for OLC 45 steel in cooling waters, obtaining increased efficiencies.*

*Keywords: corrosion inhibitors, magnesium lignosulphonate, synergist action, cooling waters*

In systems using water as cooling agent, there appear complex corrosion processes at the contact surface metal/ water and crust deposition processes. The initiation and the development of these processes are determined by physical and chemical factors which exist permanently in the system [1-3].

In open recirculating cooling systems, cooling water is made by partial evaporation of this in cooling towers, which determines the increase in salt concentration.

The contact of water to the atmosphere maintains the quantity of oxygen dissolved in circulating water, closed to the saturation limit.

In the same time, because of the instability of calcium and magnesium acid carbonates, there appear depositions which are added to corrosion products.

Factors which determine the formation of crusts have a complex action. The formation of calcium carbonate is determined by the fact that waters are not subjected to a softening process before entering in cooling system. This leads to the maintenance in waters of calcium and magnesium ions. Calcium and magnesium acid carbonate are decomposed in neutral, insoluble carbonates at increasing temperature.

Another factor is temperature, which accentuates the process of crust increasing, because the process of acid carbonates decomposition is accelerated [4-5].

The experimental determination studied the behavior of OLC 45 steel at corrosion taking place in water recirculating cooling systems, from the station of natural gases compression.

There was studied also the behaviour of some compounds or mixtures as corrosion inhibitors in waters which were tested:

-LGS-Mg – magnesium lignosulphonate,

-LGS-Mg + TPF– magnesium lignosulphonate + tripolyphosphate;

-LGS-Mg + TPF + $ZnSO_4$ – magnesium lignosulphonate + tripolyphosphate + zinc sulphate.

## Experimental part

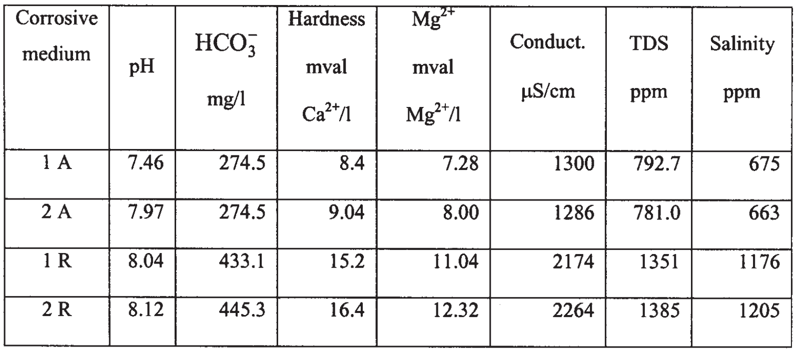
In order to identify the factors which determine the apparition of corrosion phenomena, there were analyzed raw water and waters from different areas of heat exchange. The characteristics of waters are presented in table 1.

The crust from the cooler pipes was analyzed also by X-ray diffraction (fig. 1.).

Experimental determinations were performed in laboratory, using assay-samples made of OLC 45 steel. Chemical composition of tested steel is presented in table 2.

The electrochemical corrosion studies were performed using a „VSP" – Princeton Applied Research laboratory equipment, which represents an assembly potentiostat/ galvanostat with multiple functions and software for calculation of electrochemical parameters.

**Table 1**
CHARACTERIZATION OF THE STUDIED COOLING WATERS



| Corrosive medium | pH | $HCO_3^-$ mg/l | Hardness mval $Ca^{2+}$/l | $Mg^{2+}$ mval $Mg^{2+}$/l | Conduct. µS/cm | TDS ppm | Salinity ppm |
|---|---|---|---|---|---|---|---|
| 1 A | 7.46 | 274.5 | 8.4 | 7.28 | 1300 | 792.7 | 675 |
| 2 A | 7.97 | 274.5 | 9.04 | 8.00 | 1286 | 781.0 | 663 |
| 1 R | 8.04 | 433.1 | 15.2 | 11.04 | 2174 | 1351 | 1176 |
| 2 R | 8.12 | 445.3 | 16.4 | 12.32 | 2264 | 1385 | 1205 |

where: 1 A, 2 A – feed water; 1 R, 2 R - water from the cooler

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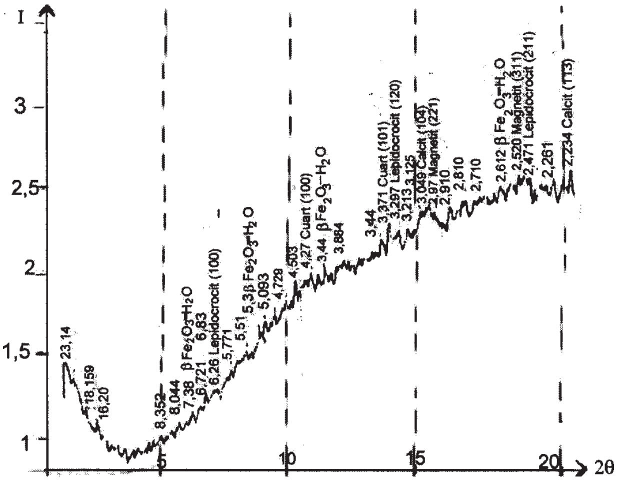

Fig. 1. X-ray diffraction spectrum of the crust (radiation Cu $K_\alpha$, I = 1.54Å)

**Table 2**
CHEMICAL COMPOSITION OF OLC 45 STEEL

| Chemical composition, (%) | | | | | | |
|---|---|---|---|---|---|---|
| C | Si | Mn | S | P | Cr | Ni |
| 0.48 | 0.030 | 0.79 | 0.025 | 0.020 | 0.060 | 0.050 |
| Cu | Mo | V | Ti | Al | As | Sn |
| 0.180 | 0.004 | 0.0 | 0.001 | 0.027 | 0.007 | 0.012 |

**Table 3**
CORROSION KINETIC PARAMETRES DETERMINED FROM THE POLARIZATION CURVES FOR OLC 45 STEEL IN COOLING WATER, IN PRESENCE OF LGS-Mg INHIBITOR

| Inhibitor conc. (ppm) | $i_{cor}$ (μA) | $E_{cor}$ (mV) | Rp (ohm) | ϴ | E.I. (%) |
|---|---|---|---|---|---|
| - | 12.984 | - 637.85 | 2009.24 | - | - |
| 100 LGS-Mg | 8.663 | - 628.29 | 3011.35 | 0.333 | 33.28 |
| 300 LGS-Mg | 7.629 | - 751.07 | 3419.52 | 0.412 | 41.24 |
| 500 LGS-Mg | 5.699 | - 615.61 | 4577.75 | 0.561 | 56.11 |
| 1000 LGS-Mg | 5.297 | - 620.42 | 5432.63 | 0.592 | 59.20 |

Working electrode had a cylindrical shape with the section area of 1 $cm^2$.

In all cases the electrochemical polarization started after 30 minutes from the electrode immersion in solution, to obtain the stabilization of the stationary potential.

Polarization tests were made in presence of air, in stagnant solutions, at 25°C.

Polarization curves were registered always starting from the stationary potential. By graphic representation of current density function of the potential of working electrode, there were obtained the anodic and cathodic polarization curves.

In order to reduce ohm resistance we used a single compartment cell, where working electrode was situated in cell center and closed to this - the counter electrode.

By using Evans method and the method of slopes extrapolation, it was determined the rate of the corrosion process, namely it was determined the density of the corrosion current: polarization resistance (Rp), corrosion potential $E_{cor}$, cover degree (ϴ) and the inhibitors efficiency (E.I.).

There were studied the corrosion processes of OLC 45 steel in cooling water with and without LGS-Mg as inhibitor, at concentrations between 100 and 1000 ppm and the synergist effect of mixtures LGS-Mg, TPF, $ZnSO_4$ in different proportions.

There were drawn the polarization curves of OLC 45 steel at the temperature of 25°C in cooling water 1 A, with and without of different quantities of inhibitors.

## Results and discussions

Kinetic corrosion parameters which were determined from the polarization curves for OLC 45 steel in cooling water, in presence of the LGS-Mg inhibitor are presented in table 3. Some characteristic polarization curves are presented in figure 2.

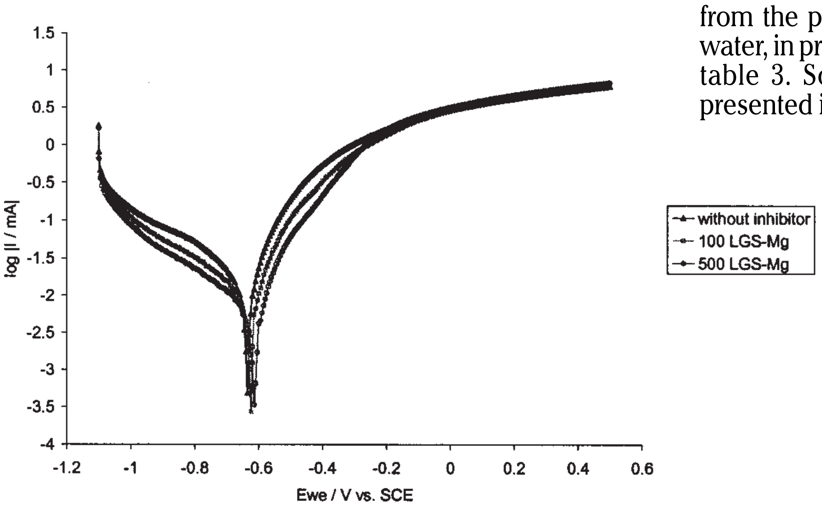

Fig. 2. Polarization curves for OLC 45 steel in cooling water with and without inhibitor LGS-Mg

**Table 4**
CORROSION KINETIC PARAMETERS DETERMINED FROM THE POLARIZATION CURVES FOR OLC 45 STEEL IN COOLING WATER, IN PRESENCE OF DIFFERENT SYNERGIST INHIBITORS MIXTURES

| Inhibitor conc. (ppm) | $i_{cor}$ (μA) | $E_{cor}$ (mV) | Rp (ohm) | θ | E.I. (%) |
|---|---|---|---|---|---|
| - | 12.984 | - 637.85 | 2009.24 | - | - |
| 500 LGS-Mg | 5.699 | - 615.61 | 4577.75 | 0.561 | 56.11 |
| 500 LGS-Mg +100 TPF | 3.408 | - 750.97 | 7655.39 | 0.738 | 73.75 |
| 500 LGS-Mg +100 TPF+25 $ZnSO_4$ | 2.910 | - 685.48 | 8963.44 | 0.776 | 77.59 |

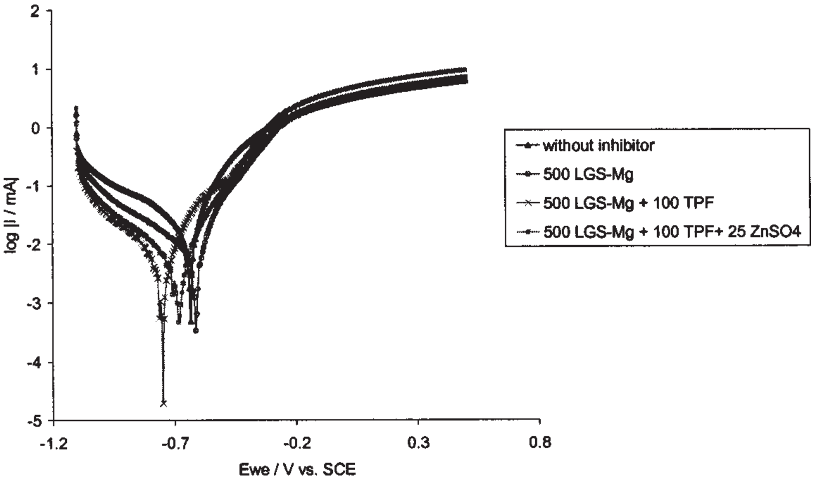

Fig. 3. Polarization curves for OLC 45 steel in cooling water with different synergist inhibitors mixtures

**Tabelul 5**
CORROSION KINETIC PARAMETERS DETERMINED FROM THE POLARIZATION CURVES FOR OLC 45 STEEL IN COOLING WATER, IN PRESENCE OF DIFFERENT SYNERGIST INHIBITORS MIXTURES

| Conc. inhibitor (ppm) | $i_{cor}$ (μA) | $E_{cor}$ (mV) | Rp (ohm) | θ | E.I. (%) |
|---|---|---|---|---|---|
| Fără inhibitor | 12.984 | - 637.85 | 2009.24 | - | - |
| 100 LGS-Mg | 8.663 | - 628.29 | 3011.35 | 0.333 | 33.28 |
| 100 LGS-Mg +100 TPF | 4.110 | - 695.10 | 6347.75 | 0.683 | 68.35 |
| 100 LGS-Mg +100 TPF+25 $ZnSO_4$ | 1.937 | - 523.16 | 13466.6 | 0.851 | 85.08 |

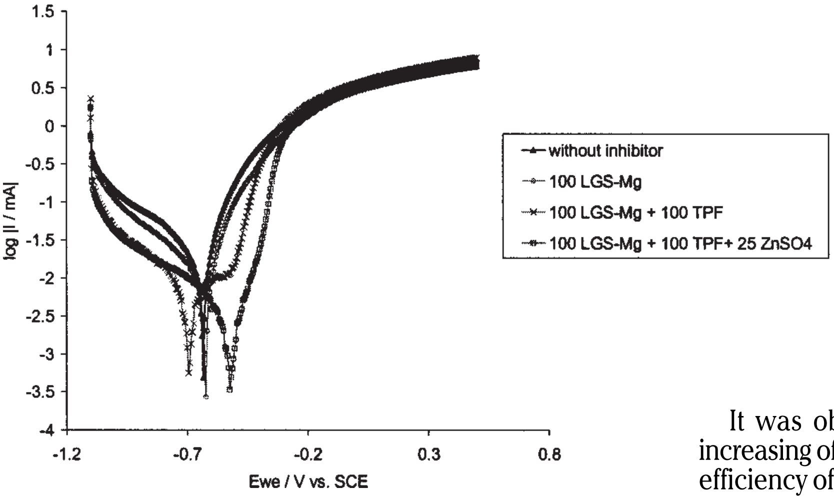

Fig. 4. Polarization curves for OLC 45 steel in cooling water with different synergist inhibitors mixtures

It was observed that the corrosion processes of OLC 45 steel in cooling water take place with relatively high rates. For all concentrations, the addition of LGS-Mg inhibitor leads to increasing of polarization resistance and leads to the decrease of the corrosion current and to corrosion inhibition of OLC 45 steel in cooling water 1A.

It was observed an increase of the efficiency with increasing of inhibitor concentration, obtaining a maximum efficiency of inhibition of the corrosion process for OLC 45 steel, using 500 ppm LGS-Mg.

For the corrosion inhibition of OLC 45 steel in cooling waters which is used in gases compression stations, there were synthesized in laboratory mixed inhibitors based on sodium tripolyphosphate, adding magnesium lignosulphonate and zinc sulphate with inhibition and antiscale properties, having different composition, to study their synergistic effect.

All kinetic parameters of corrosion are presented in tables 4-5 and in figures 3-4 there are presented only some characteristic polarization curves.

For all studied cases, when sodium tripolyphosphate was added in cooling water with magnesium lignosulphonate, at high tensions there is observed the apparition of two sections on the anodic curves, two domains of potential where the rate determining step is the diffusion process, the diffusion of the aggressive ions from solutions at interface and the diffusion of ions by the layer of products formed on the metal surface.

## Conclusions

Feeding water of the cooling system is high hardness water. In the recirculation process there is a concentration in salts, which determines an increase of hardness from 8 mval $Ca^{2+}$/L to 16 mval $Ca^{2+}$/L.

Solid deposits from condensers have a complex structure and they contain calcium carbonate, iron oxides, silica and amorphous substance, data which were evidenced by X-rays analyses.

Based on these analyses, there can be observed that waters used in the open circuit cooling systems from gases compression station have a great contribution at crusts formation for the corrosion processes, determined by the salt content of waters, by oxygen which is present – the system being in direct contact with the atmosphere – and also by the modification of waters composition in different treatment processes.

Tests on corrosion processes of OLC 45 steel in cooling water indicate relatively high corrosion rates.

Magnesium lignosulphonate behaves as an inhibitor in case of corrosion processes which appear in cooling waters, with an inhibition efficiency of about 56% at a content of 500 ppm LGS-Mg. Because of its hydrophile-hydrophobe structure, it leads to the formation of a protection physical barrier at the interface metal/ corrosive medium. Magnesium lignosulphonate presents also dispersant properties, avoiding fouling formation. It is a non toxic product, ecologically tested.

Sodium tripolyphosphate delays the precipitation process of calcium carbonate, by the complexation in its chain of the crystallization germs and initiates the formation of hard deposits, influencing the increase of the inhibitor efficiency.

Inhibitor mixtures containing magnesium lignosulphonate, tripolyphosphate and zinc sulphate present increased efficiencies, by their synergist action in the inhibition process of OLC 45 steel corrosion in cooling waters. The components of the inhibitor react with $Ca^{2+}$, $Mg^{2+}$ or even $Fe^{2+}$ions, resulting complexes which form a protecting film on the metal surface which must be protected and stable suspensions because of the dispersant behaviour of the polymer. The efficiency of the corrosion inhibition increases from 56% to 78-85%.

Mixed inhibitors action as cathodic and anodic inhibitors, in the same time.

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