

CHARACTERIZATION OF CORROSION AND SCALE PROCESSES IN COOLING SYSTEMS

MAIOR I.* , COJOCARU A.* , VĂIREANU D. I.* , LINGVAY I.** , LINGVAY C.** ,
CĂPRĂRESCU S.*

* University Politehnica Bucuresti, Faculty i_maior@chim.upb.ro

** ICPE –BUCURESTI, lingvay@icpe-ca.ro

Abstract - Calcareous scales were deposited from a 0.7 M NaCl, 0.0025 M NaHCO₃, 0.028 M Na₂SO₄ and 0.01 M CaCl₂ solution by cathodic polarization of steel at – 0.95 V / SSCE at 40°C. Nucleation, crystal growth and coverage of steel with mineral scales were characterized by different impedance behaviour. The antiscalent effect of green inhibitors (AS, FC, CS, RO, JR) has been studied in 0.7 M NaCl solution using chronoamperometry, EIS and conductivity techniques. The metallic covered area decreases with addition of natural extracts solutions, the AS extract being the most efficient. The investigated extracts prevent the solution supersaturation with CaCO₃ and increase the nucleation time.

Keywords: scales, natural extracts, EIS, chronoamperometry

1. INTRODUCTION

Calcareous scaling on heat exchangers surfaces is often the persistent problem in cooling water systems, boilers and desalination plants [1–3] since it limit heat exchange and reduce tube diameter causing a significant decrease in water flow [4–9].

Currently plants extracts are employed as inhibitors in order to develop new cleaning chemicals for a green environment. A chemical is defined as being “green” according to three criteria: toxicity, bioaccumulation and biodegradation [10-14]. Plant extracts are viewed as a source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [12–15].

One of the most encountered scales is CaCO₃ formed by electrodeposition from a sequence of chemical reactions at the interface. By imposing a cathodic potential in the oxygen reduction regime the reaction (1) occurs. The production of OH⁻ at the interface shifts the pH and hence the equilibrium of the CO₂ – H₂O system. As a result the interface becomes supersaturated with CaCO₃ and the deposition can occur as in reaction (2):



The current density is proportional to the consumption of oxygen at the electrode surface and decreases when the active surface area decreases, due to blocking by the scale

formation [16-19]. The residual current density reaches a final value close to zero when the surface is completely covered by scale.

The aim of this study was to investigate different natural plant extracts as novel environmentally friendly antiscalent inhibitors for CaCO₃ calcareous deposits on steel surface in a neutral NaCl solution using electrochemical impedance spectroscopy (EIS), chronoamperometry and conductivity techniques.

2. EXPERIMENTAL

2.1. Solutions preparation

The neutral NaCl solution was prepared to a concentration of 0.7 M NaCl, 0.0025 M NaHCO₃, 0.028 M Na₂SO₄ and 0.01 M CaCl₂ [32]. The 0.7 M NaCl solution was chosen to produce the total ionic strength and pH of cooling water systems.

Tested solutions of natural plant extracts (allium sativum AS, ficus carica FC, castanea sativa CS, rosmarinus officinalis RO and juglans regia JR) of 400 ppm concentration, are ethylic alcohol extracts (50 % vol.), from the Romanian producers HOFIGAL S.A. and PlantExtract®.

2.2. Conductivity test

The experimental apparatus used for the conductivity measurements [10, 20] consists of a glass container, a mechanical stirrer and a conductivity-meter. Prior to each experiment, a volume of 5 mL of 0.1 M CaCl₂ solution is added to a volume of the natural extracts solution; then the mixture is completed to 100 mL with doubly distilled water. The conductivity is measured during titration by 0.1 M Na₂CO₃ solution that was added in portions of 0.2 mL.

2.3. Electrochemical techniques

The electrochemical measurements were carried out in a three-electrode glass cell (50 mL volume) with double walls. A platinum disk of 1.13 cm² (Radiometer Analytical) and a saturated silver/silver chloride SSC (Radiometer Analytical) electrodes were used as counter- and reference electrodes. The exposed area (0.50 cm²) of the working electrode which is made from carbon steel was mechanically abraded with a series of emery papers

of variable grades. The samples were then washed thoroughly with double distilled water.

Chronoamperometry and EIS measurements were achieved using a VoltaLab 40 PGZ301 potentiostat (Radiometer Analytical), connected with a computer that use VoltMaster 4.0 software for data acquisition and processing.

Chronoamperometry curves were carried out by polarizing the steel electrode to -0.95 V / SSC in the brine tested solution for a total time of 24 hours. The electrochemical impedance spectra were plotted at the OCP value during chronoamperometry measurements after 1, 3, 6 and 24 hours.

Electrochemical impedance spectroscopy (EIS) was carried out at the OCP in the frequency range 100 kHz – 100 mHz with a sinusoidal potential perturbation of 10

mV amplitude. The data of impedance spectra results were fitted using ZView software on several equivalent circuits.

3. Results and Discussions

3.1. Conductivity measurements

In order to evaluate the capacity of a certain compound to inhibit the scale formation, Drela et al. [10] developed a rapid and simple chemical test based on the solution conductivity measurements while CaCO_3 is being precipitated from CaCl_2 solution by addition of Na_2CO_3 .

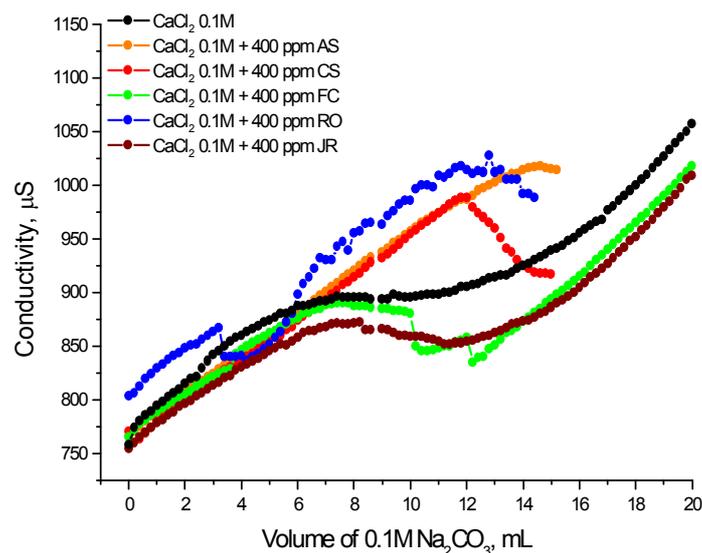


Fig. 1. Dependence of conductivity of 0.1M CaCl_2 solution with the amount of Na_2CO_3 added in the absence and in the presence of various natural extracts (AS, CS, FC, RO, JR)

Figure 1 shows the variation of conductivity for 0.1M CaCl_2 solution with the amount of added 0.1M Na_2CO_3 solution in the absence and in the presence of various investigated natural extracts (AS, CS, FC, RO, JR) of 400 ppm concentration. One can notice that the conductivity of the 0.1M CaCl_2 solution increases linearly with increasing the added amount of the 0.1M Na_2CO_3 solution; this increase continues up to a maximum point then the solution becomes supersaturated due to the rapid precipitation of CaCO_3 and results a conductivity decrease. After complete precipitation, further addition of Na_2CO_3 leads to more ions generation in the solution that increases again the conductivity.

However, Figure 1 reveals that the presence of 400 ppm AS, CS and RO extracts shifts the maximum point to a higher amount of Na_2CO_3 . These natural extracts impede the supersaturation; therefore the process may be attributed to the adsorption of the extracted molecules onto the active sites of the growing crystals and thus

causing the dispersion of suspended solids which reduces the rate of crystal growth [20].

The adsorption could take place on multiple paths: (a) electrostatic attraction between the charged particles and chemical extract constituents; (b) dipole-type interaction between unshared electrons pairs from extracted molecules and growing particles; (c) π -interaction with particles surfaces or (d) combination of all [20].

3.2. Chronoamperometry measurements

The mineral scales formed on metal surfaces under cathodic polarization at the diffusion limiting current density of oxygen cover the active surface area available for the electrochemical reactions and consequently reduce the current density [11-13, 20].

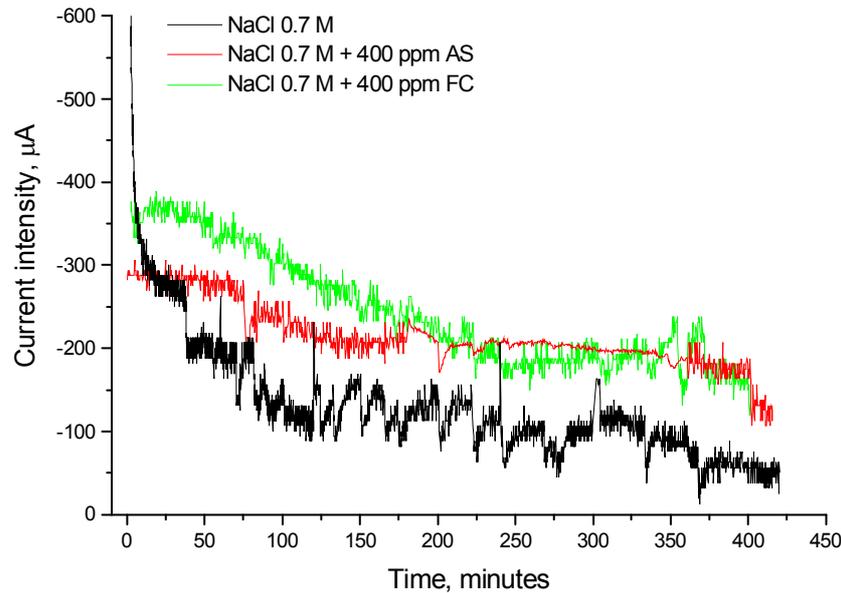


Fig. 2. Chronoamperometry curves plotted for polarized steel electrode in the 0.7 M NaCl brine solution in the absence and the presence of AS and FC natural extracts at 40°C

The chronoamperometry curve plotted for polarized steel electrode in the 0.7 M NaCl brine solution in the absence and the presence of AS and FC natural extracts at 40°C is shown in Figure 2. As can be seen, the plot can be separated into three regions: (1) nucleation, (2) crystal growth and (3) total coverage of the electrode surface. During the first stage, the initial current decrease is attributed to the decrease of the oxygen reduction rate.

The cathodic scaling process is initialized by increasing the pH near the electrode surface due to the reduction of the dissolved oxygen. The resulting HO⁻ ions determine the CaCO₃ nuclei to begin the nucleation and crystallization on the electrode surface. In the second stage, the current decreases linearly indicating that the constituted nuclei were growing and partial cover the electrode surface.

In the third stage, the current reach a limiting value of 35 µA and 150 µA, respectively, after 7 hours that practically define the deposition time when total coverage of metal surface was obtained. The lower value of limiting current suggests that the surface coverage is porous.

From Figure 2 results that the addition of 400 ppm natural extract of AS and FC to the brine solution first increases the nucleation time and then decreases the crystals growth rate. On the other hand, a better behavior presents the AS extract, because changing in the current values is very low, between 300 and 150 µA, and it became rapidly constant (after 180 minutes).

3.3. Electrochemical impedance spectroscopy measurements

In Figure 3 are presented the Nyquist diagrams plotted at the OCP value in 0.7 M NaCl brine solution for the steel electrode after cathodic polarization at -0.95

V / SSC, initial, after 1 and 3 hours (nucleation and crystal growth, respectively) and after 24 hours (complete coverage of the electrode surface).

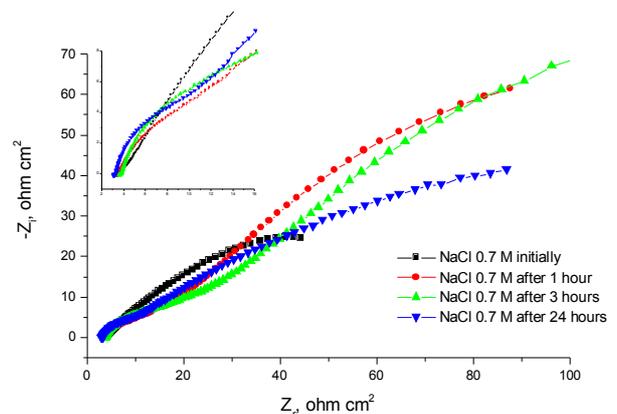


Fig 3. Nyquist diagrams plotted at OCP value in 0.7 M NaCl solution for the steel electrode after polarization at -0.95 V/SSC at different exposure time

In all cases, the Nyquist plots consists of two depressed capacitive semicircles, first at higher frequencies followed by another one at low frequencies corresponding to the crystal growth step. As seen from Figure 3, the diameter of the obtained semicircles increases with exposure time that means a significant increase of electrode impedance modulus. This suggests that the electrode surface has been changed by exposure to a scaling environment due to the formation of an adherent and compact deposit with insulator character [15].

Notice that there are two time constants in these plots. This fact leads to the conclusion that at the interface

are taking place simultaneously multiple stages of the process [7, 8]: formation and growth of CaCO_3 layer (associated with deposition resistance R_f and capacity CPE_f); uncovered steel surface due to deposited layer porosity (associated with charge transfer resistance R_{ct} and respective capacity CPE_{dl}); diffusion of oxygen through the calcium carbonate formed layer (associated with the diffusion impedance, Z_{diff}).

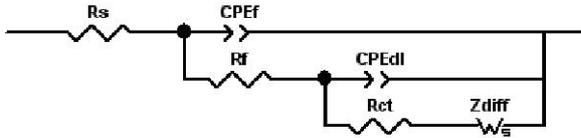


Fig. 4. The equivalent circuit used to determine the impedance parameters for scale process in the NaCl solution in absence and in presence of natural plant extracts

In order to determine the impedance parameters for steel surface corrosion and scale process in neutral media several authors [7, 15–18, 20] have used the equivalent electrical circuit model shown in Figure 4.

In Figure 5 are represented the Nyquist diagrams plotted at the OCP value in 0.7 M NaCl brine solution in presence of the investigated natural extracts – (a) 400 ppm AS and (b) 400 ppm FC – for the steel electrode after cathodic polarization at $-0.95 \text{ V} / \text{SSC}$, initially, after 1, 3 and 24 hours, respectively.

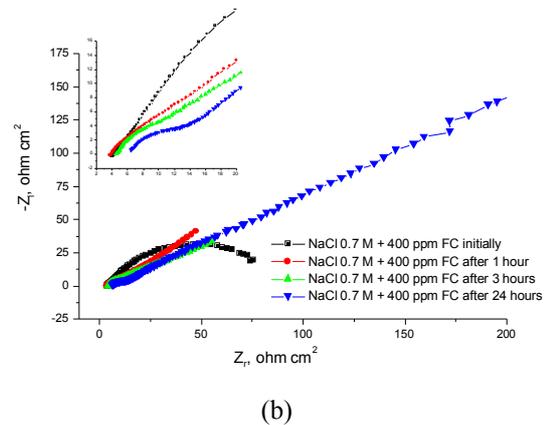
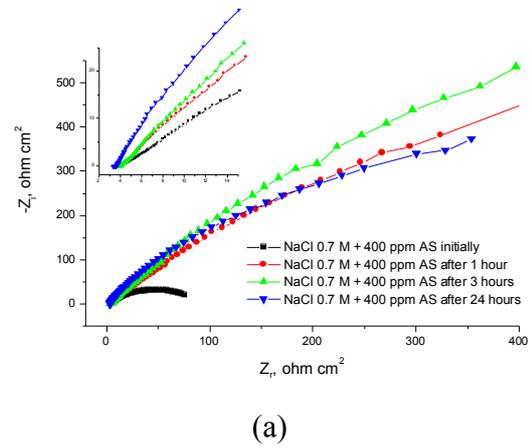


Fig. 5. Nyquist diagrams plotted at open circuit potential value in 0.7 M NaCl solution for the steel electrode after polarization at $-0.95 \text{ V} / \text{SSC}$ in presence of (a) 400 ppm AS natural extract solution and (b) 400 ppm FC natural extract solution at different exposure time

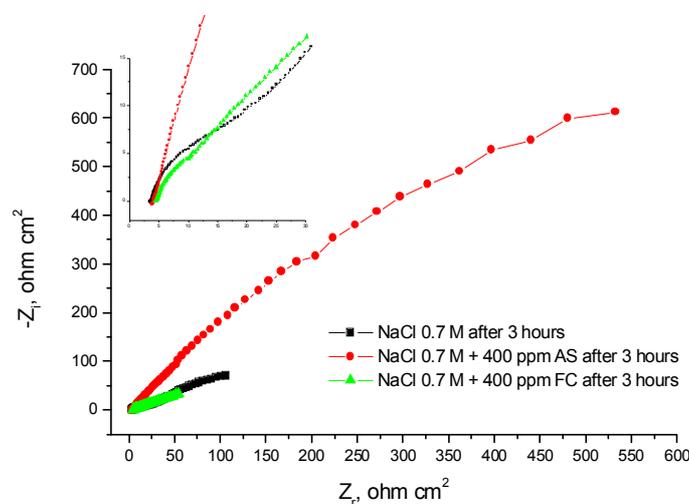


Fig. 6. Nyquist diagrams plotted at open circuit potential value in 0.7 M NaCl solution for the steel electrode after polarization at $-0.95 \text{ V} / \text{SSC}$ at 3 hours exposure time in absence and in presence of both investigated natural extracts

As can be seen in Figure 5a, the impedance spectra present a complete semicircle in high frequency region,

followed by a second incomplete semicircle at low frequencies. Increasing exposure time up to 24 hours

decreases the size of the depressed semicircle, indicating that it can inhibit the scale growth rate.

In Figure 6, the Nyquist diagrams obtained after polarization of steel over a longer period shows a capacitive depressed semicircle at high frequencies domain, followed by a specific line to the diffusion phenomenon in the low frequencies domain that corresponds to the crystal growth step. Therefore, the scaling process occurs under the control of the oxygen diffusion.

The circular regression results of the impedance spectra measured at OCP in 0.7 M NaCl solution at different times show that the R_p resistance increases while the non-ideal double layer capacitance C_{dl} decrease with the exposure time. These results could be possibly correlated to increasing the diffusion thickness.

This fact suggests that the electrode surface has changed by immersion in the neutral media due to the formation of deposit with protective qualities. At low frequencies, due to irregular shape of Nyquist curves, it is assumed that appears the diffusion phenomenon of two species simultaneously (iron ions and oxygen) through the porous surface [8, 20].

4. CONCLUSIONS

The investigated natural plant extracts decrease the rate of scale formation by bonding off the active chemical constituents to the cations from the neutral solution, thus forming a soluble complex or by dispersion of the suspended solids through an adsorption process.

In comparison with the FC extract, the AS solution significantly change the scale growth rate, since the slope of the lines representing the growth stage have different values, while the nucleation time show notable increase. However, a complete coverage of the electrode surface was not observed within the exposure time in presence of neither tested inhibitors.

Therefore, a porous morphology of the scale layer can be predicted since the dissolved oxygen has to cross the scale layer through pores between the CaCO_3 crystals. Thus, the increase of the electrode impedance can be attributed to the decrease of surface porosity or to decrease of the active area due to the scale deposition that increases the charge transfer resistance.

Adding a small quantity of natural studied extracts in the NaCl solution prevents complete coverage of the electrode surface, indicating that these compounds can be used with good results as antiscalants.

5. ACKNOWLEDGMENTS

This research is financially supported by The National University Research Council CNCSIS in

Romanian Partnerships Program provided by the PLANTINHIB Project no. 72-166/2008.

For the logistic support the authors express their gratitude to Mr. Corneliu Andrei and Mrs. Mariana Andrei from University Politehnica of Bucharest.

REFERENCES

- [1]. A.P. Morizot and A. Neville, *J. Coll. Interf. Sci.*, 2002, 245, 40-49.
- [2]. D.J. Choi, S.J. You and J.G. Kim, *Mat. Sci. Eng., series A*, 2002, 335, 228-235.
- [3]. A. Martinod, A. Neville, M. Euvrad, K. Sorbie, *Chem. Eng. Sci.*, 2009, 64, 2413-2421.
- [4]. D. Darling, R., Rakshpal, *Material Performance*, 1998, 37, 42-45.
- [5]. J. Marin-Cruz and I. Gonzalez, *J. Electrochem. Soc.*, 2002, 149, 1, B1-B3.
- [6]. J. Marin-Cruz, E. Garcia-Figueroa, M. Miranda-Hernandez and I. Gonzalez, *Water Res.*, 2004, 38, 1, 173-183.
- [7]. J. Marin-Cruz, R. Cabrera-Sierra, M.A. Prech-Canul and I. Gonzalez, *J. Appl. Electrochem.*, 2004, 34, 3, 337-343.
- [8]. J. Marin-Cruz, R. Cabrera-Sierra, M.A. Prech-Canul and I. Gonzalez, *Electrochim. Acta*, 2006, 51, 8-9, 1847-1854.
- [9]. C. Gabrielli, M. Keddad, A. Khalil, G. Mourin, H. Perrot, R. Rosset and M. Zidoune, *J. Electrochem. Soc.*, 1998, 145, 7, 2386-2396.
- [10]. I. Drela, P. Falewicz and S. Kuczkowska, *Water Res.*, 1998, 32, 10, 3188-3191.
- [11]. C. Deslouis, C. Gabrielli, M. Keddad, A. Khalil, R. Rosset, B. Tribollet and M. Zidoune, *Electrochim. Acta*, 1997, 42, 8, 1219-1233.
- [12]. C. Deslouis, D. Festy, O. Gil, V. Maillot, S. Touzain and B. Tribollet, *Electrochim. Acta*, 2000, 45, 11, 1837-1845.
- [13]. C. Gabrielli, M. Keddad, A. Khalil, R. Rosset and M. Zidoune, *Electrochim. Acta*, 1997, 42, 8, 1207-1218.
- [14]. M. Sfaira, A. Sghiri, M. Keddad and H. Takenouti, *Electrochim. Acta*, 1999, 44, 24, 4395-4402.
- [15]. T. Hong, Y.H. Sun and W.P. Jepson, *Corros. Sci.*, 2002, 44, 1, 101-112.
- [16]. L. Bousselmi, C. Fiaud, B. Tribollet and E. Triki, *Corros. Sci.*, 1997, 39, 9, 1711-1724.
- [17]. Y. Chen, T. Hong, M. Gopal and W.P. Jepson, *Corros. Sci.*, 2000, 42, 6, 979-990.
- [18]. L. Bousselmi, C. Fiaud, B. Tribollet, E. Triki, *Electrochim. Acta*, 1999, 44, 24, 4357-4363.
- [19]. J.B. Bessone, D.R. Salinas, C.E. Mayer, M. Ebert and W.J. Lorenz, *Electrochim. Acta*, 1992, 37, 12, 2283-2290.
- [20]. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, E. Khamis and D.E. Abd-El-Khalek, *Desalination*, 2008, 230 (1-3), 314-328.