Asian Journal of Chemistry Vol. 21, No. 3 (2009), 2283-2292

Study of the Antideposit Effect of 2-Hydroxy-4-methylbenzylphosphonic Acid

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The scale inhibitor, 2-hydroxy-4-methylbenzylphosphonic acid (HMBP) appears efficient for desalination plants of sea water. A concentration of 26.5 ppm (131 µmol/L) prevents the calcareous magnesium deposits. The anti-scale effect of this inhibitor is achieved by chronoamperometry at imposed potential and complex impedance. SEM allows observation of the calcareous magnesium deposits with and without inhibitor 2-hydroxy-4-methylbenzylphosphonic acid (HMBP).

Key Words: Scaling, Organophosphonic inhibitor, Titanium electrode, Sea water.

INTRODUCTION

The use of sea water which is charged with salts, gas and solids in suspension, presents a certain number of operational difficulties related to the scaling, the organic deposits and the corrosion of the installations.

The owner of a desalination circuit of sea water is confronted with the presence of hard and adhering deposits on the evaporation and heating pipes walls, reducing the cross section and the water flow rate. Moreover, the formation of tartar in the exchanger of heat causes a decreasing of transfer thermal coefficient[1]. Previous workers[2] noted that the carbonated, sulphated and silicated deposit are 15 to 30 times less conductive than steel. A deposit of 1 mm in thickness and 1.7 W/m.K in thermal conductibility involves a loss of 41 % of effectiveness. The deposits encountered in sea water are essentially[3] calcium carbonates, dominating under 85 °C and magnesium hydroxide between 85 and 120 °C. The combination of these two deposits involves the calcomagnesian deposit. The latter is formed while changing the alkalinity of the medium in the vicinity of the material surface, by application to the interface metal/sea water of a cathodic potential.

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The electrochemical reaction will appear in two stages of reduction of dissolved oxygen[4]:

$$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^- \qquad (1)$$

$$H_2O_2 + 2e^- \longrightarrow 2OH^- \qquad (2)$$

The global reaction is:

$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^- \qquad (3)$$

For the reduction of the water which gives an evolution of hydrogen, we have:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (4)$$

The quantity of OH^- ions produced by these 3 reactions increases the interfacial pH. Indeed, the interface metal/sea water is the magnesium hydroxide precipitation site:

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2 \downarrow \qquad (5)$$

The bicarbonates, in the presence of OH^- ions, are transformed into less soluble carbonates by precipitation of calcium carbonate[5]:

$$HCO_3^- + OH^- \longleftrightarrow CO_3^{2-} + H_2O \qquad (6)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \downarrow \qquad (7)$$

It has been shown that the $CaCO_3$ precipitates for pH approximately from 8.35 whereas the $Mg(OH)_2$ appears from 9.5[6,7].

The study of the properties of the calcomagnesian deposits has been the subject of the several research studies. It was shown that these deposits are influenced by a number of parameters, such as: nature of material and its surface properties, temperature, pressure, the electrode exposure time, polarization potential, current density, rotation speed of the electrode and interfacial pH[4,8-11].

The aim of this work was initially to characterize the calcomagnesian deposit on a titanium electrode by electrochemical method in a natural sea water solution. Then, the behaviour of the synthesized inhibitor 2-hydroxy-4-methylbenzylphosphonic acid (HMBP)[12] were studied. The characteristic of this inhibitor is that it is thermostable due to its aromatic nucleus, in opposite to the other organic phosphonates whose radical is aliphatic[13].

EXPERIMENTAL

Measurements were carried out on samples of natural sea water taken on the site of the installation located at cap djenet site (60 km in the east of Algiers). In this study, a thermostated electrochemical cell is used, the working electrode was a titanium disc electrode (diameter = 3 mm), the counter electrode was platinum and the reference electrode was saturated calomel electrode (SCE).

To obtain reproducible results, the surface of the working electrode is treated chemically with sulphuric acid, then washed with acetone and distilled water.

Electrochemical measurements were carried out using a programmable electrochemical system, analytical radiometer PGZ301, driven by voltmaster 4. The deposits formed after potentiostatic control were analyzed by SEM. The samples were observed with Philips XL30 ESEM. The ESEM is capable of operating as conventional highest vacuum SEM, or under low vacuum in ESEM mode for imaging of wet and non conductive samples using the gaseous secondary electron detector. The ESEM is fully equipped with arrange of secondary electron (SE) and back scattered (BSE) detectors. Additionally, the ESEM is equipped with a fully integrated EDAX analyzer.

RESULTS AND DISCUSSION

Polarization curve: In order to determine the potential effect applied on the cathodic reactions of reduction of oxygen and water, the intensity-potential curves is plotted (Fig. 1), by using a titanium rotating electrode. This test is carried out in natural sea water under stirring at a speed of 500 rpm. This curve shows a wave of oxygen reduction followed by the characteristic water reduction.

Influence of the imposed potential on the calcomagnesian deposit: The effect of cathodic overpotential on the kinetics of scaling is followed by chronoamperometry. The curves obtained with the potentials: -1.5, -1.6, -1.7 and -1.8 V/SCE are represented in Fig. 2.

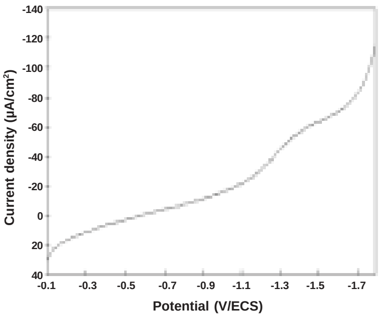


Fig. 1. Linear Voltammetry curve of sea water

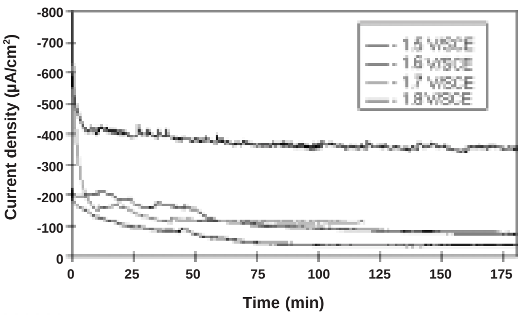


Fig. 2. The influence of the applied potential on the calcomagnesian deposit at 500 rpm

It is noticed that as the imposed potential gets low with time, the current decreases in a monotonous way and the deposit is formed quickly. The time of scaling is *ca.* 40 to 60 min. When the applied potential is cathodic, the residual current increases. This phenomenon is related to the hydrogen release which makes the deposit friable (crumbly). Thus, for the presentation of this study, we have chosen to work with a potential of -1.7 V/SCE.

Characterization of calcomagnesian deposit: Electrochemical measurements of impedance are carried out *versus* time on a revolving electrode with 1500 rpm under a potential of -1.7 V/SCE and amplitude of 10 mV with frequencies of measurements ranging between 100 KHz and 50 MHz (10 points/decade).

The obtained diagrams (Fig. 3) show that the resistance of polarization R_p increases with time of deposition. This can be explained by the fact that the electrode surface is increasingly covered and blocked. This is confirmed by an analysis of the state of electrode surface by scanning electron microscope. Indeed, the photos made after 1 h of deposition at room temperature showed that the electrode surface is completely covered (Fig. 4). The deposit is composed of platelets brucite weakly linked, seeded with aragonite and calcite crystals[14,15]. The cracks and pores are assigned to the observed evolution of hydrogen.

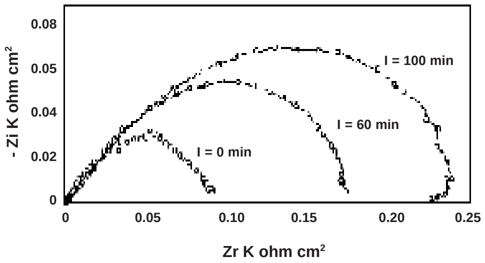


Fig. 3. Layouts of Zac impedance of the calcomagnesian deposit *vs.* time at -1.7 V/SCE and at 1500 rpm with scanning frequency from 100 KHz to 50 mHz (10 points/decade)

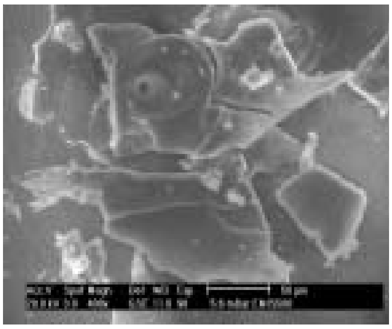


Fig. 4. SEM photograph of calcomagnesian deposit at 25 °C, -1.7V/SCE and 1500 rpm

The analysis of the composition of the deposit by EDAX reveals at the crystal level the presence of calcium, magnesium, oxygen and carbon (Fig. 5a), while the spot analysis on a plate, in the vicinity of the crystal, indicates that the plate is mainly composed of magnesium and oxygen as shown in Fig. 5b.

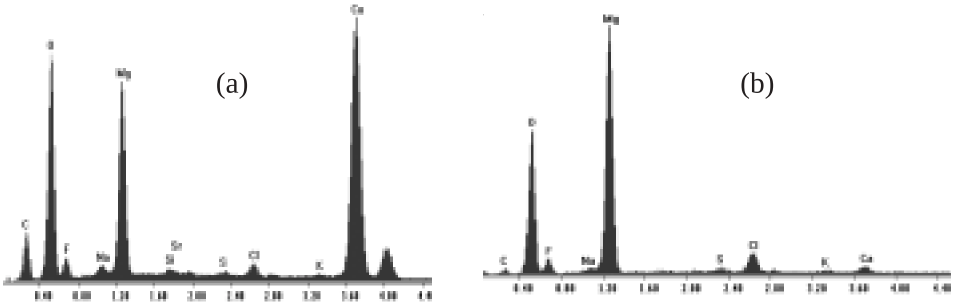


Fig. 5. X analysis of a cubic crystal deposited at 25 °C

Study of the inhibition of scale: To avoid the problems of scale observed in industrial installations, a number of solutions have been proposed. The acid injection, physical processes, tartrifuges, *etc.* are some of them[13]. The tartrifuges are chemical compounds that slow germination and growth by changing the morphology of the deposit and thus leading to non-members of crystals. These compounds are variable; the phosphonates are frequently used, they are active at low contents (a few ppm).

In this paper, it is proposed to use 2-hydroxy-4-methylbenzylphosphonic acid (HMBP) as an inhibitor of scale. In order to evaluate its performance we have proceeded, first, by electrochemical techniques and then analyzed the state of the surface with the SEM and determined the chemical composition of deposits by EDAX.

Chronoamperometry: Fig. 6 shows the curves current density *vs.* time of the calcomagnesian deposit in presence of increasing amounts of inhibitor 2-hydroxy-4-methylbenzylphosphonic acid at 25 °C.

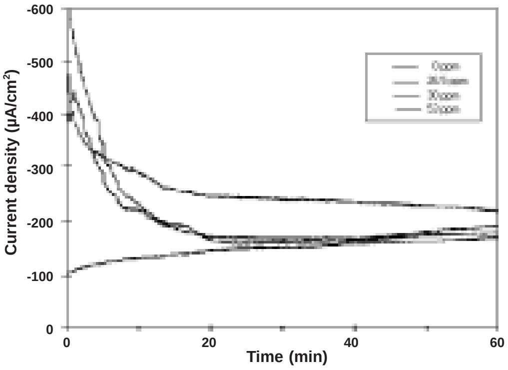


Fig. 6. Chronamperometric curves showing the influence of the 2-hydroxy-4-methylbenzylphosphonic acid addition on the scaling of the titanium electrode in the sea water at -1.7 V/SCE, 500 rpm and 25 °C

Scaling time, defined by the intersection of the inflexion tangent at the point of each chronoamperometric curve with the time scale in abscissa[16,17], increases with the 2-hydroxy-4-methylbenzylphosphonic acid concentration, while the deposition rate decreases. This is probably due to the fact that a film of this inhibitor is formed on the surface of the electrode and delays germination of tartar crystals. A concentration of 26.5 ppm of the 2-hydroxy-4-methylbenzylphosphonic acid is sufficient to inhibit the deposition.

Electrochemical impedance spectroscopy: The measurement of the electrochemical impedance characterizes the ability of the deposit and its adhesion to the electrode[18,19]. In this way, we studied, *in situ* at -1.7 V/SCE, the effect of the inhibition of 2-hydroxy-4-methylbenzylphosphonic acid on the scale of the electrode according to increasing concentrations in 2-hydroxy-4-methylbenzylphosphonic acid. The diagrams have been drawn at the initial time (t = 0 min) of the immersing electrode in the solution and after 1 h (Fig. 7). The resistance of polarization R_p increases with the addition of increasing amounts of the inhibitor. This shows that insulating film is probably formed on the electrode surface, thus it becomes blocking. This phenomenon has already been observed by Göhr[20].

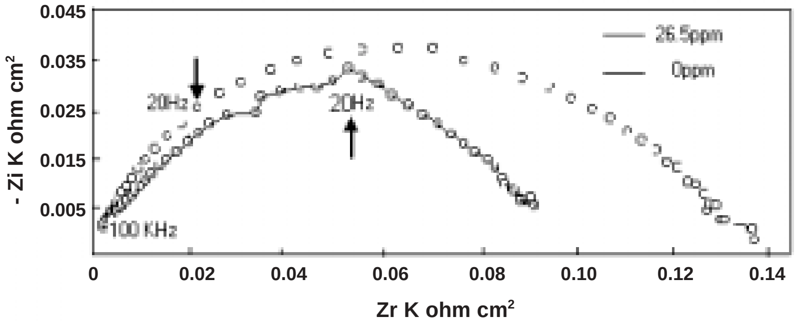
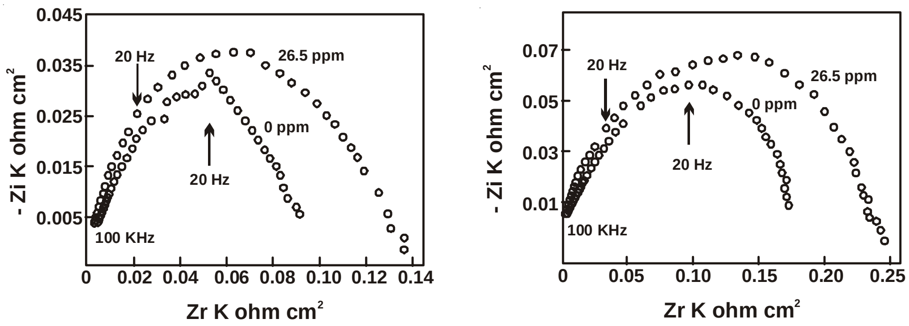


Fig. 7. Relaxation frequencies obtained on the Zac diagrams of calcomagnesian deposit with and without 2-hydroxy-4-methylbenzylphosphonic acid at -1.7 V/SCE and 1500 rpm, at t = 0 min, scanning frequencies from 100 KHz to 50 MHz (10 points/decade)

The line of the impedance diagrams is, in present case, expressed by a loop high frequency due to the deposit of tartar and low frequency loop in the case of the formation of a film of the inhibitor. These may be identified by the values of the capacity of the double layer C_{d1} given by the $2\pi f_{max} R_t C_{d1} = 1$ (where f_{max} is the relaxation frequency at a maximum and R_t is the charge transfer resistance).

The analysis of both diagrams corresponding to 0 and 26.5 ppm 2-hydroxy-4-methylbenzylphosphonic acid curves t = 0 min and t = 1 h (Fig. 8a and 8b), a shift in the bias resistor R_t of the loop - f_{max} = 20 hz- in the absence of inhibitor up 0.18 KΩcm² is observed.



(a) (b)

Fig. 8. Relaxation frequencies obtained on Zac diagrams of calcomagnesian deposit with and without 2-hydroxy-4-methylbenzylphosphonic acid at -1.7V/SCE and 1500 rpm, scanning frequencies from 100 KHz to 50 MHz (10 points/decade); (a) at t = 0 min and (b) at t = 1 h

In the presence of the inhibitor, the R_t of the loop - f_{max} = 20 Hz - corresponding to the tartar deposit changes slightly from 0.06 to 0.07 KΩcm². This suggests that the inhibitor slows the deposition. The increase in the overall resistance on the Fig. 8b (deposition and film inhibitor) after 1 h deposition can be explained by the spreading of the film the 2-hydroxy-4-methylbenzylphosphonic acid on the electrode surface. These interpretations will be verified by the analysis of the surface of the electrode realized on SEM.

Morphological analysis and chemical composition: After 1 h of deposition in the presence of 26.5 ppm of the 2-hydroxy-4-methylbenzylphosphonic acid, the Fig. 9 is compared to the Fig. 4 and shows a less covered surface. These results are similar to those reported by Gabrielli[21].

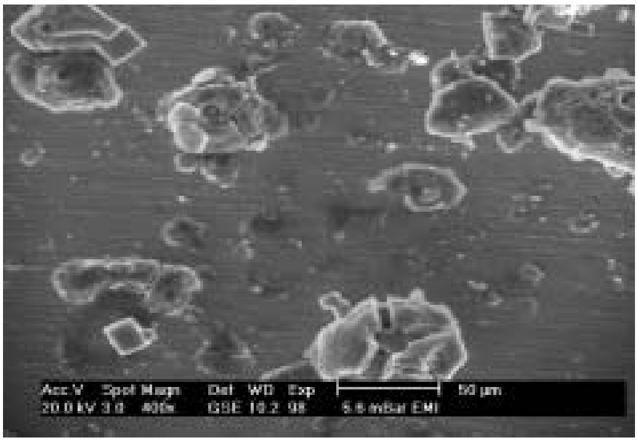


Fig. 9. SEM photograph of calcomagnesian deposits with 26.5 ppm of 2-hydroxy-4-methylbenzylphosphonic acid obtained at 25 °C, at -1.7 V/SCE and 1500 rpm

The chemical composition of the deposit in the presence of the inhibitor, produced by EDAX, Fig. 10, shows that this deposit is made up mostly of Na, Mg, Cl and traces of Ca. The appearance of a peak of Ti is also observed, which indicate that the thickness of the deposit is low (< 1 µm).

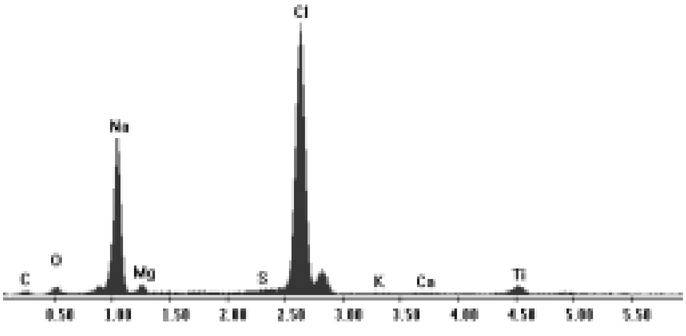


Fig. 10. X-Analysis on a layer in the vicinity of cubic crystal of 26.5 ppm deposit of 2-hydroxy-4-methylbenzylphosphonic acid at 25°C

Tests were performed to determine the behaviour of the 2-hydroxy-4-methylbenzylphosphonic acid at elevated temperature (85 °C). The pictures of the electrode in the absence and presence of the anti-scaling have been taken (Fig. 11). The photo (Fig. 11a) shows a surface covered with a thick and compact deposit on the borders of the electrode, while the photo (Fig. 11b) shows in opposite a naked surface of the electrode.

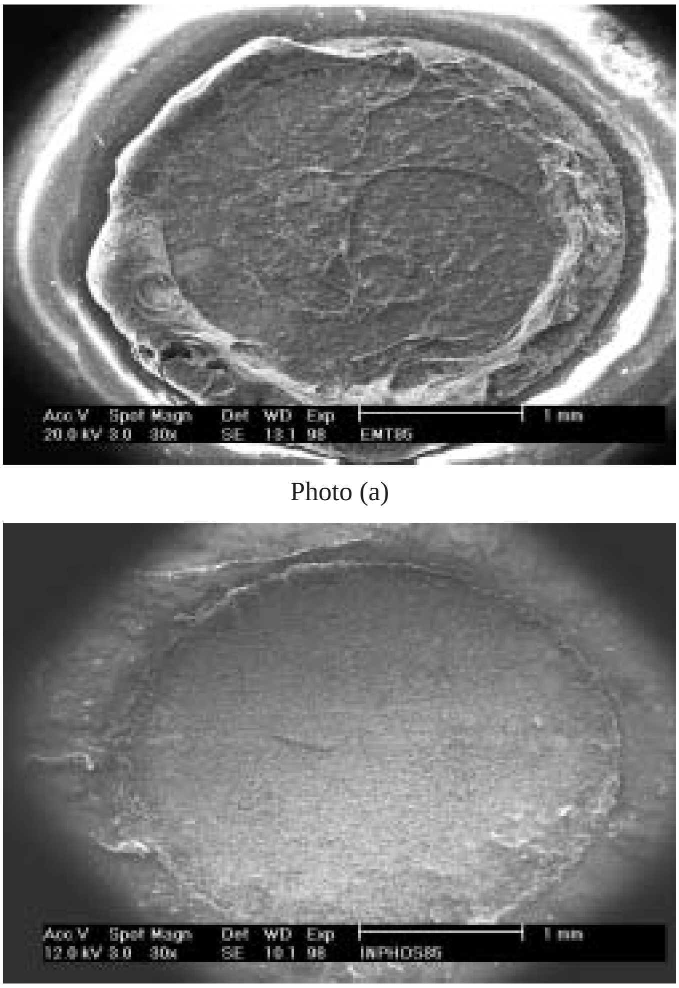
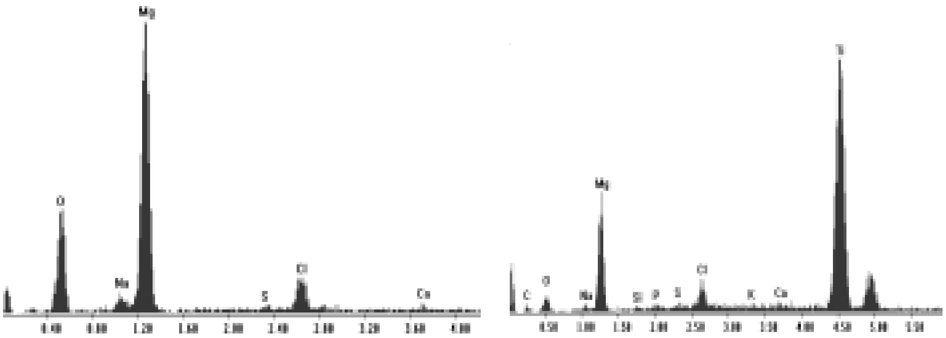


Photo (a)

Photo (b)

Fig. 11. General view of the sample after 1 h of filling

At 85 °C, the spectra EDAX, in the presence and absence of inhibitors (Fig. 12), show on the one hand, that the chemical composition of the deposit consists essentially of $Mg(OH)_2$ and on the other hand, the thickness of the coating is largely reduced in the presence of inhibitor. This shows the effectiveness of 2-hydroxy-4-methylbenzylphosphonic acid used at 85 °C, where the deposit consists mainly of aragonite[22,23].



(a) (b)

Fig. 12. X-Analysis of the deposit layer at 85 °C; (a) in the absence of 2-hydroxy-4-methylbenzylphosphonic acid (b) in the presence of 2-hydroxy-4-methylbenzylphosphonic acid

Conclusion

The results show that 2-hydroxy-4-methylbenzylphosphonic acid used in small amounts (26.5 ppm) slows down the calcomagnesian deposit. Its effect is more pronounced towards the $CaCO_3$. However, traces of $Mg(OH)_2$ remain. The used chemical and electrochemical methods converge to explain this phenomenon. Present results carried out at 85 °C, show that 2-hydroxy-4-methylbenzylphosphonic acid is not affected by temperature.

ACKNOWLEDGEMENT

The authors acknowledge to CRNA Center of Nuclear Research of Algiers, Algeria for scanning electron microscopy.

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(*Received*: 2 May 2008; *Accepted*: 20 November 2008) AJC-7056