INHIBITION OF AZ91D BY MOLYBDATE IONS
IN CORROSIVE WATER

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الملخص

تم دراسة سلوك سبيكة الماغنيسيوم (AZ91D) فــي المــاء الآكـل حــسب المواصــفة (ASTM D1384-87) عند أس هيدروجيني مقــداره 8.2 وبإضـــافة تركيـــزات مختلفــة مــن الموليبيدات، وأستعمل لذلك الطرق الكهروكيميائية، كما تم الإستعانة بتصوير المجهر الإلكتروني والتحليل بالأشعة السينية المرافقة له (EDS). أوضحت الدراســة أنــه يمكـن تحــسين كفــاءة الموليبيدات عند درجة الحرارة العادية وعند 82 م° بزيادة الأس الهيدروجيني إلى 9.0 ويلاحــظ أن الأكاسيد المتكونة عند درجة حرارة 82 م° أقل حماية للسبيكة، وأنه رغم مقدرة الموليبــدات على تخفيض التآكل المنتظم للسبيكة (AZ91D) عند أس هيدروجيني عالي ودرجة حرارة عادية، إلا أنها ليست قادرة على منع التآكل بالتنقير.

ABSTRACT

The corrosion behavior of AZ91D magnesium alloy in ASTM D1384-87 corrosive water (pH 8.2) inhibited by sodium molybdate was investigated using electrochemical and surface analysis techniques. It was shown that inhibition of AZ91 by molybdates at ambient and high temperature of 82 ^{o}C can be improved by buffering of the solution to higher pH values (pH>9). The protection afforded by the film formed at high temperature of 82 ºC was low and the corrosion rate was accelerated. It was concluded that eventhoug molybdate can reduce the general corrosion of AZ91 at high pH and low temperature it can not prevent formation of micro-pits on the metal surface.

KEYWORDS: Molybdate; Inhibitor; Magnesium alloys; AZ91D; Corrosion.

INTRODUCTION

Magnesium–aluminum zinc alloy (AZ91) represents the workhorse cast magnesium alloy not only in automobile industry but also in many low weight electrical and electronic devices. It has the same yield strength and ductility as its aluminium counterpart A380 and it can replace 319 and 356 in many casting components [1]. AZ91 is a dual phase alloy; the primary (α), eutectic (α) and (β) phase. The α-phase is an α Mg-Al-Zn solid solution and the β-phase is an intermetallic $Mg_{17}Al_{12}$ solidified at the grain boundary with high aluminum content of 45 to 58%. However AZ91 is the same

as many other magnesium alloys, it has a low corrosion resistance in aqueous environments which limiting its use.

The electrochemical behavior of magnesium alloys in neutral and alkali solutions have been investigated in the last decade [2,3]. Formation of magnesium hydroxide or magnesium hydroxide carbonate, which is a non conducting compound [4], can slow down the corrosion of magnesium alloys. In presence of chloride or sulfate ions, magnesium alloys form soluble compounds [5] such as MgO MgCl$_2$ and kieserite MgSO$_4$ 7H$_2$O.

In recent years, the search for more environmentally acceptable corrosion inhibitors has lead to identification of molybdates as a low toxicity [6] alternative. Molybdates are used in cooling systems, automotive coolants and organic coatings. They prevent corrosion of steel, aluminum and lead solders. The present study investigated the use of molybdate as a corrosion inhibitor for AZ91D alloy in ASTM D1384-87 Corrosive water. The inhibition by molybdate also compared with corrosion of AZ91D in LX7-001 commercial coolant used in Japan and china for automotive engines.

EXPERIMENTAL

Test specimens were prepared from ingot magnesium alloy AZ91D. The electrodes were embedded in epoxy resin leaving an exposed surface area of 1.21 cm^2. The exposed surfaces were grounded with silicon carbide paper to 1200 grit. They were then cleaned in distilled water, methanol and dried under a stream of air.

The electrolyte used in this study was ASTM D1384-87 Corrosive Water (CW) [7] composed of 148 mg/l sodium sulfate, 165 mg/l sodium chloride and 138 mg/l sodium bicarbonate, which gives an 8.2 pH value. Sodium molybdate [Na$_2$MoO$_4$ 2H$_2$O] at concentrations of 2 and 3 g/l were used which are the typical concentrations used in automotive coolants [8]. Some corrosive water and molybdate solutions were buffered to pH10 by magnesium hydroxide. The electrochemical tests were done at ambient temperature of 20 ºC or higher temperature of 82 ºC. For comparison one of the most used coolants in China and Japan (LX7-001A) was tested. The electrochemical cell consisted of a three electrode Pyrex glass cell. A saturated calomel electrode (SCE) was used as a reference electrode and platinum sheet was used as the auxiliary electrode. All experiments have been done without de-aeration nor stirring and the potential values quoted on the SCE scale.

The open circuit potential (OCP) was measured for the first hour of immersion followed by potentiodynamic scan. The scan rate was 0.2 mV/s recorded from -2000 mV to a potential higher than the anodic breakdown or to the current density which does not exceed a value of 20 mA/cm^2.

The polarization measurements were conducted using a potentiostate Model (PS-168) operated with computer driven software.

Surface photographs and elemental analyses of AZ91D alloy were done after exposure to the CW inhibited by sodium molybdate. The exposure time was four hours at 82 ºC. Optical microscope (Olympus Bx60M) and scanning electron microscopy (SEM) (model: Cambridge S-360) equipped with energy dispersive spectrometer (EDS) analysis facilities were used.

RESULTS

Electrochemical methods

Potential values gathered during the hour immediately preceding the potentiodynamic polarization measurements for each molybdate concentration indicated that an hour was sufficient to allow the potential to equilibrate.

Figure (1) shows an increase in OCP of AZ91D with immersion time. This behavior was observed for all formulations. In the case of corrosive water inhibited by 0.2 w% sodium molybdate (pH 8.6) and that buffered with magnesium hydroxide (pH10), the potential values were slightly higher than that in the blank corrosive water. As the inhibitor concentration increased to 0.3 w% the OCP rose to 270 mV, this shift of the OCP in the positive direction indicates that, a protective film was formed on the metal surface. However, as the temperature increased to 82 °C (Figure 1-5) the OCP was shifted to more active values (-250 mV) which indicate the loose of the protective properties of the film formed.
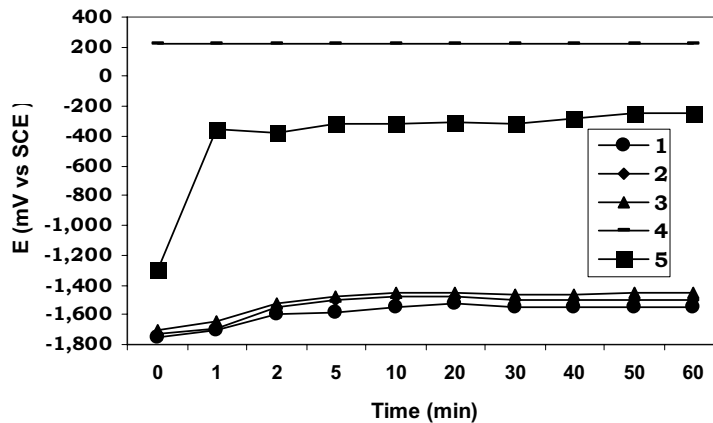

Figure 1: Open circuit potential of AZ91D in CW inhibited by Na₂MoO₄.2H₂O: (1) blank CW, (2) 0.2 w%, (3) 0.2 w% at pH 10, (4) 0.3 w% and (5) 0.3 w% at 82 °C.

The potentiodynamic polarization curves of AZ91D in corrosive water inhibited by 0.2 and 0.3 w% sodium molybdate are shown in Figure (2). Increase in molybdate concentration appears to shift the corrosion potential to the positive direction. The largest shift (1.7 V) was observed in the case of AZ91D inhibited by 0.3 w% sodium molybdate. In this environment, the alloy also shows an anodic passivation tendency and a cathodic limiting current density. The electrochemical data of the Figure (2) are presented in Table (1).

The polarized cathodic curves to less current values (bc> 240 mV/dec) were more clear in the case of buffered solutions at 10 pH, and this effect seems to lower the corrosion current density. The positive shift of corrosion potential indicates formation of a protective film on the metal surface, which is probably composed of magnesium hydroxide, magnesium carbonate and reduced molybdate. Unfortunately, the film breakdown potential was low in high pH solutions and the alloy showed micro-pits covered by corrosion products after exposure to the experiment conditions.
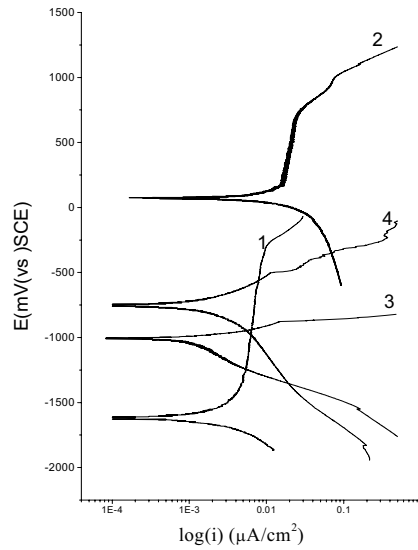
Figure 2: Potentiodynamic polarization curves of AZ91D in CW inhibited by Na₂MoO₄.2H₂O at 20 °C: (1) blank CW, (2) 0.3 w% at pH8.6, (3) 0.2 w% at pH10 and (4) 0.3 w% at pH10.

Table 1: Electrochemical corrosion data of AZ91D from Figure (2).

Solution (w% Molybdate)	OCP (mV)	E_{cor} (mV)	i_{cor} ($\mu A/cm^2$)	E_b (mV)	i_p ($\mu A/cm^2$)
Blank CW (pH 8.2)	-1540	-1625	3	-375	0.01
CW + 0.3 (pH 8.6)	200	100	9	700	12
CW + 0.2 (pH 10)	-1460	-1000	1.1	- 900	15
CW + 0.3 (pH 10)	-1333	-780	1.4	-500	15

The polarization curves of AZ91D in CW inhibited by 0.3 w% sodium molybdate at 82 °C are presented in Figure (3). In blank solution the polarization curve shows a positive shift of corrosion potential of more than 350 mV compared to the ambient temperature (see Figure 2). The anodic curve shows a tendency for passivity with no change in the corrosion current. For AZ91D in CW inhibited by 0.3 w% molybdate (pH 8.6) at 82 °C, the corrosion current increased to 70 $\mu A/cm^2$ and the anodic curve shows no signs of passivity. For higher pH value of 10, the potential was moved to the positive direction with a steady increase of the anodic current, and the cathodic curves showed a similar behavior with Tafel slope of 240 mV/dec.

Regarding the AZ91D exposed to LX7.001A solution (pH10), which is an inorganic coolant composed of water, ethylene glycol and corrosion inhibitors, the polarization curve at ambient temperature in Figure (4) shows a high breakdown potential of -700 mV and a low corrosion rate with a steady increase of anodic current. In the case of high temperature of 82 °C the corrosion potential was shifted to more positive value and corrosion current decreased to 0.7 $\mu A/cm^2$.
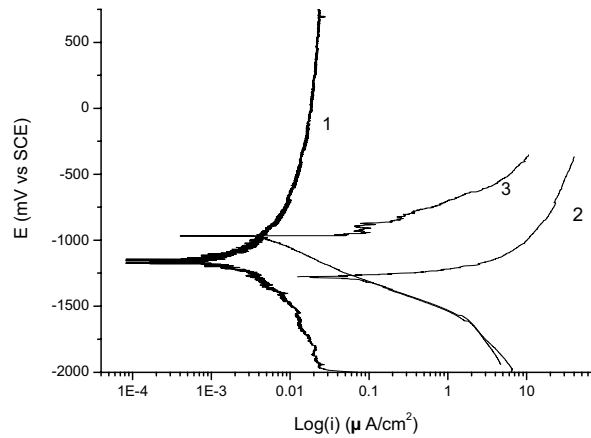
Figure 3: Potentiodynamic polarization curves of AZ91D in CW inhibited by $Na_2MoO_4.2H_2O$ at 82 ºC: (1) blank CW, (2) 0.3 w% at pH8.6 and (3) 0.3 w% at pH10.

When a coolant is used for a long time; (two years or 30,000 miles) its composition changes because of decomposition of glycol to organic acids, dissolution of cooling system metals and accumulation of salts in the coolant. In order to investigate the effect of ageing of LX7 on corrosion of AZ91D, the ASTM D1384-87 CW salts were added at the same concentration to the LX7 coolant and tested at 82 ºC. The polarization curve shows a decrease in breakdown potential and increase in corrosion current, which is a typical corrosion behavior in chloride solutions [9].
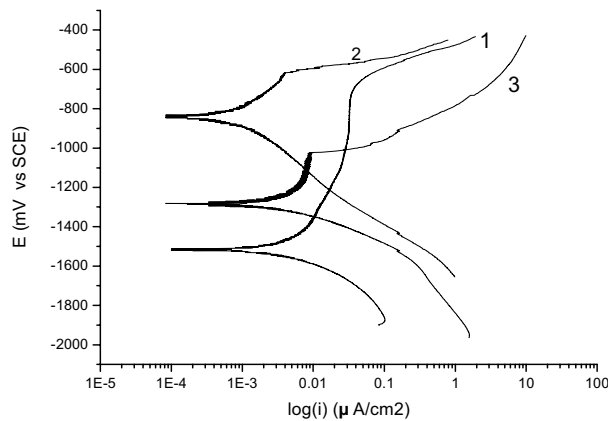

Figure 4: Potentiodynamic polarization curves of AZ91D in LX7-001A coolant: (1) at 20 ºC, (2) at 82 ºC, and (3) CW salts added.

Table 2: Electrochemical corrosion data for LX7 coolant and CW inhibited by molybdate (w%) derived from Figure (3 and 4).

Solution	E_{cor} (mV)	i_{cor} ($\mu A/cm^2$)	E_b (mV)	i_P ($\mu A/cm^2$)
CW (pH 8.2) at 82 ºC	-1150	2.8	225	20
CW+ 0.3 at 82 ºC	-1270	70	-	-
CW +0.3 (pH 10) at 82 ºC	-980	5	-	-
LX7 (pH 10) at 20 ºC	-1520	2.5	-700	32
LX7 (pH 10) at 82 ºC	-830	0.7	-620	4
LX7 + CW salts at 82 ºC	-1290	3	-1040	8

Surface morphology

Despite a low corrosion rate measured for AZ91D in CW or that inhibited by molybdate at room temperature as well as the coolant LX7, SEM and optical microscope revealed many micro-pits formed on the metal surface, and most of the pits were covered by corrosion products as shown in Fig. 5. Analyses of the pits by EDS (in the case of 0.3 w% molybdate solutions) showed that it contained molybdenum, iron, silicon, sulfur and chloride. This may suggest that the compounds formed in the pits are $MgMoO_4$, $MgCl_2$ and $MgSO_4$. It is also clear that most of the pits were located in (α) phase near to the boundaries of the (β) phase (the white area around the pits in Figure 5-a). The β-phase was almost unaffected. This indicates that β-phase represents the cathodic area which confirms the finding of previous works [10,11].

The topography of AZ91D after immersion in CW inhibited by 0.3 w% sodium molybdate and in LX7 for four hours at 82 ºC (Figure 5 and 6) showed many pits and cracks. These cracks can explain the higher reactivity of the alloy at high temperature presented in Figure (3).
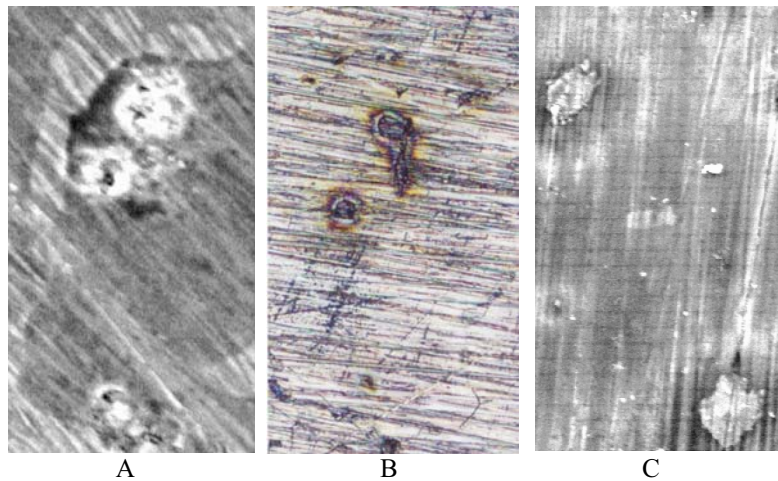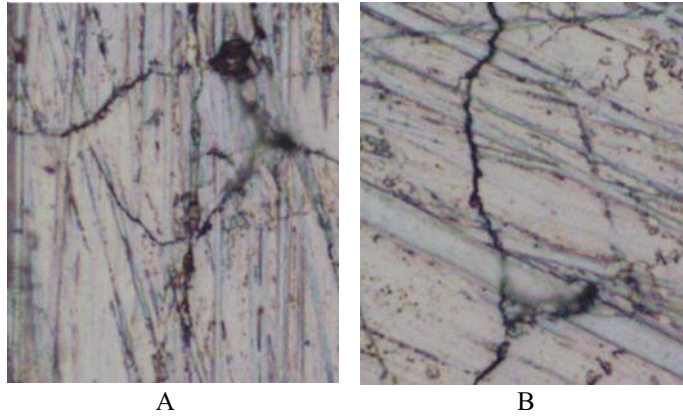

| A | B | C |

Figure 5: AZ91 immersed for 4 hours at 82 ºC in: A. CW, B. CW inhibited by 0.3 w% molybdate and C. LX7 coolant.

Figure 6: Optical micrographs of AZ91 at 82 ºC for four hours in:
A. CW inhibited by 0.3 w% Molybdate, B. LX7 coolant.

DISCUSSION

When magnesium alloys are immersed in water at ambient temperature they form a partially protective layer of magnesium hydroxide [12,13]. As the pH or temperature increases, magnesium hydroxide deposited grows to form more coherent film. It is well known that $Mg(OH)_2$ has a tendency to become less soluble as the temperature increases beyond 60 ºC. The corrosion reaction (1) has an intermediate stage of magnesium hydride Mg_2H_2 at low potentials, which react with water to form Mg^{2+} and hydrogen gas.

$$Mg + 4H_2O + 2e^- \rightarrow Mg^{2+} + 4OH^- + 2H_2 \tag{1}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \tag{2}$$
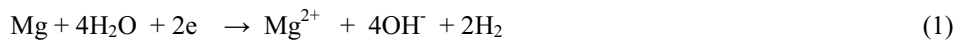
In the case of AZ91D in corrosive water another important compound which is nesquehonite (magnesium hydroxide carbonate) may form on the metal surface because of reaction of magnesium ions with bicarbonate in the solution at ambient temperature [14,15].

$$Mg^{2+} + HCO_3^- \rightarrow Mg(HCO_3)_2 \tag{3}$$

This magnesium bicarbonate decomposes at higher temperature of 82 to 100 ºC to form perfect hemisphere crystals of hydromagnesite and carbon dioxide gas librated [14].

$$5\,Mg(HCO_3)_2 \rightarrow 4\,MgCO_3.Mg(OH)_2.4H_2O + 6\,CO_2 \tag{4}$$
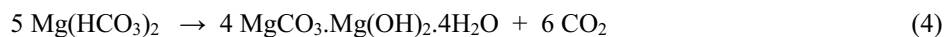
It is evident that the observed inhibition dependence of AZ91D on pH of the solutions as shown in Figure (2 and 3) is in qualitative agreement with equation one, this means that hydroxide ions may act as an inhibitor by stimulating magnesium hydroxide formation in equation (2). The role of molybdate at ambient temperature

(Figure 2) appears to adsorb on the metal surface and to enhance accumulation of Mg $(OH)_2$ to an extant that stifles the alloy corrosion reaction.

Considering electrochemistry of molybdenum, it becomes evident that this metal can dissolve at relative low potentials due to the formation of soluble MoO_4^{2-} species [16]. The potential region for this reaction is situated in the active region of magnesium based alloys and hence the buffering ability of sodium molybdate is low, the inhibition efficiency of this compound is expected to be low at pH values less than 9. This analogy is in agreement with the low inhibition efficiency at 0.3 w% molybdate and low pH of 8.6 compared to 0.2 w% and 0.3 w% at higher pH value of 10.

Increase in temperature appears to hinder the adsorption of molybdate and oxygen (which is vital for inhibition in this case) on the metal surface and hence no further repairing of the defected area will take place. A similar behavior of high corrosion rate was observed on inhibition of steel by molybdate [17] at 70 ºC.

The observed cracked film at higher temperature (Figure 7) suggested that it was disturbed by the hydrogen gas evolved. Indeed, the observed hydrogen evolution bubbles at ambient temperature can be accelerated at higher temperature of 82ºC to cause cracks or even partial removal of the surface film. This means that, the film can not be formed (as continuous film) before the hydrogen evolution rate is sufficiently suppressed by an increase in the electrode potential. However, it is quite clear that further work is needed to explain the factors affecting pitting and cracks formation in inhibited corrosive water.

CONCLUSION

The corrosion of AZ91D in ASTM D1384 corrosive water inhibited by Molybdate and LX7-001A coolant was studied, and the following points can be emphasized:

- AZ91D shows a tendency for passivation when it immersed in CW due to magnesium hydroxide deposited on the metal surface. However, a network of pits was formed at α -phase of the alloy.
- Molybdate seem to be an effective corrosion inhibitor to stifle pitting corrosion for AZ91D at ambient temperature and high pH value. Where's, at higher temperature of 82ºC the corrosion rate was accelerated rather than reduced.
- In spite of the high efficiency of LX7-001A at ambient temperature, AZ91D alloy suffers from pitting corrosion and formation of cracks at higher temperature of 82 ºC. This may indicate that most of the traditional inorganic coolants may not be suitable for inhibition of AZ91D and many other magnesium alloys.

REFERANCES

[1] A.A. Luo, Materials composition and potential applications of magnesium in automobiles. Magnesium Tech. (2000), Edit. H.I. Kaplan et.al., The minerals, metals and materials Soc. (2000) 89.

[2] S. Mathieu, C. Rapin, J. Hazan and P. Steinmetz, Corrosion behavior of high pressure die-cast and semi-solid cast AZ91D alloys. Corrosion Sci. 44 (2002)2737.

[3] G. Song, A. Atrens, X. Wu and Bo. Zhang, Corrosion behavior of AZ21, AZ501 and AZ91 in sodium chloride. Corrosion Sci., 40(1998)1769

[4] A. Froats and W. Unsworth, Metals handbook Vol.13. "Corrosion" Pub. ASM, 13(1985) 744.

[5]   M.G. Lopez and B. Natta, Evidence of two anodic processes in the polarization curve of magnesium in aqueous media. Corrosion, 57(8) (2001)712.

[6]   B. A. Shaw, G.D. Davis, T.L. Fritz, and K.A. Oliver, A molybdate treatment for enhancing the passivity of aluminum in chloride-containing environments., J. Electrochem. Soc., 137(1990)359.

[7]   ASTM D1384-87, Annual book of ASTM standards, ASTM Philadelphia, PA19103(1986)

[8]   T. Gilles, Automotive Service, Inspection, Maintenance, Repair. Pub. Delmar ITP,(1999)253

[9]   V. Mitrovic-Scepanovic and R. J. Brigham., Localized corrosion initiation on magnesium alloys. Corrosion, 48(9)(1992) 780

[10]   O. Lunder, T.K.R. Aune and K. Nisancioglu, The role of the $Mg_{17}Al_{12}$ phase in the corrosion of Mg alloy AZ91. Corrosion 45 (9)(1989) 741.

[11]   R. Ambat, N. N. Aung and W. Zhou, Evaluation of microstractural effects on corrosion behavior of AZ91D magnesium alloy. Corrosion Science, 42(2000)1433.

[12]   J. L. Robinson and P.F King, Electrochemical behavior of the magnesium anode. J.Electrochem. Soc., 108(1954)36.

[13]   G. Song, et. al., Anodic dissolution of magnesium in chloride and sulphate solutions, Corrosion. Sci. 39(1997)1981.

[14]   E. Gulbrandsen, Anodic behavior of Mg in HCO_3^- /CO_3^{2-} buffer solutions. Quasi-steady measurements. Electrochemica Acta., 37(8)(1992)1403.

[15]   C. Henrist, et. al., Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. J. Crystal growth, 249(2003)321.

[16]   M. Pourbaix, Atlas d' Equilibres Electrochimiques, Gautiers- Villars and Vie, Paris(1963).

[17]   A. M. Shams Eldin and L. Wang, Mechanism of corrosion inhibition by sodium molybdate. Desalination, 107(1996)29.