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# CORROSION INHIBITORY EFFECTS OF POTASSIUM DICHROMATE ON ALUMINIUM ALLOY IN CHLORIDE SOLUTION

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## ABSTRACT

Aluminium and its alloys have excellent corrosion resistance. When aluminium is exposed to the atmosphere, a thin invisible oxide $Al_2O_3$ is formed, protecting the metal from further oxidation. Compared to pure metals, alloys can have higher corrosion resistance depending on the content of certain alloying elements. Various substances such as organic or inorganic inhibitors can affect the corrosion of aluminium alloys and thus slow down the degradation of the material. In this paper, we studied the inhibitory effect of potassium dichromate on the corrosion processes of aluminium alloy. All measurements were performed in 0.5 M sodium chloride solution with the addition of different concentrations of inhibitors. The methods used were potentiodynamic polarization, cyclic voltammetry, and chronoamperometry.

Keywords: corrosion inhibition; potassium dichromate; aluminium alloy

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## 1. INTRODUCTION

Aluminium alloys have excellent mechanical properties: high strength and lower mass compared to the castings of other metals. They also possess good weldability, corrosion resistance, wear resistance, and machinability. Most aluminium alloys, in addition to the basic alloying element such as silicon, contain other alloying and trace elements, intentionally added to improve properties. Iron is one of the significant supporting influential elements increasing resistance to hot cracks. Nevertheless, the increase in iron content results in a decrease in elongation and toughness. Various substances such as organic or inorganic inhibitors can affect the corrosion of aluminium alloys and thus slow down the degradation of the material. The paper presents the influence of an inorganic inhibitor on the corrosion properties of AlFe alloy.

## 2. EXPERIMENTAL PROCEDURE

Electrochemical measurements were performed on a 263A potentiostat/ galvanostat and a Princeton Applied Research Lock – In 5210 amplifier with PowerCV software. The measurements were performed in a three-electrode electrochemical cell consisting of a saturated Ag/AgCl electrode used as a reference electrode, a Pt electrode as a counter electrode, and an AlFe alloy as a working electrode. The labels AlFe 1.2, AlFe

1.5, AlFe 1.9 indicate different iron content in the alloy. The methods used were potentiodynamic polarization, cyclic voltammetry, and chronoamperometry. A 0.5 molar solution of sodium chloride was used as the electrolyte. The method of linear polarization, i.e. determination of polarization resistance is based on potentiodynamic polarization, but in this case, it is polarized in a narrower potential range, than the open circuit potential about the reference electrode with a scanning speed of 1 mV/s. Corrosion kinetic parameters such as corrosion potential ($E_{\text{corr}}$), corrosion current density ($I_{\text{corr}}$), and Tafel constants ($\beta_{\text{anodic}}$ and $\beta_{\text{cathode}}$) were calculated using software installed on the instrument. The cyclic voltammetry method was used to examine the effect of different concentrations of inhibitors on the material, as well as to examine the diffusion processes between the electrolyte and the film on the electrode surface. All cyclic voltammetry measurements were performed in 0.5 molar sodium chloride solution and at a different potential range for each alloy with a scan rate of 50 mV/s. Also, the effect of different scanning speeds from 10 mV/s to 90 mV/s was examined by the cyclic voltammetry method. The chronoamperometric technique was used to determine the kinetic parameters at a constant potential of 0.65 V imposed on the working electrode, as well as at a constant stirring of 400 r/min. The reaction was observed in the absence and with the presence of different concentrations of potassium dichromate ($K_2Cr_2O_7$) 0.000045 mol/L, 0.00012 mol/L, and 0.0002 mol/L.

## 3. RESULTS AND DISCUSSION

The diagrams of potentiodynamic measurements of AlFe alloys are shown in Figure 1 in 0.5 M sodium chloride solution and at a scan rate of 0.166 mV/s. For AlFe 1.2 alloy, the range of recorded potential was from -2.0 V to 0.0 V, and for AlFe 1.5 and AlFe 1.9 alloys, it was the same potential range from -1.0 V to 1 V. For all three alloys different corrosion potential in the anode range was obtained, which indicates that the anodic passivity of the metal has occurred. Also, in Figure 1 can be seen that in the alloys AlFe1.5 and AlFe 1.9 passive segment occurs, while this process is not present in the alloy with lower iron content. In the case of AlFe 1.2, diffusion and corrosion processes take place unhindered in the corrosive environment. Figure 2 shows the effect of different concentrations of $K_2Cr_2O_7$ inhibitors on AlFe 1.2 alloy in 0.5 M sodium chloride solution, at a scan rate of 0.166 mV/s.

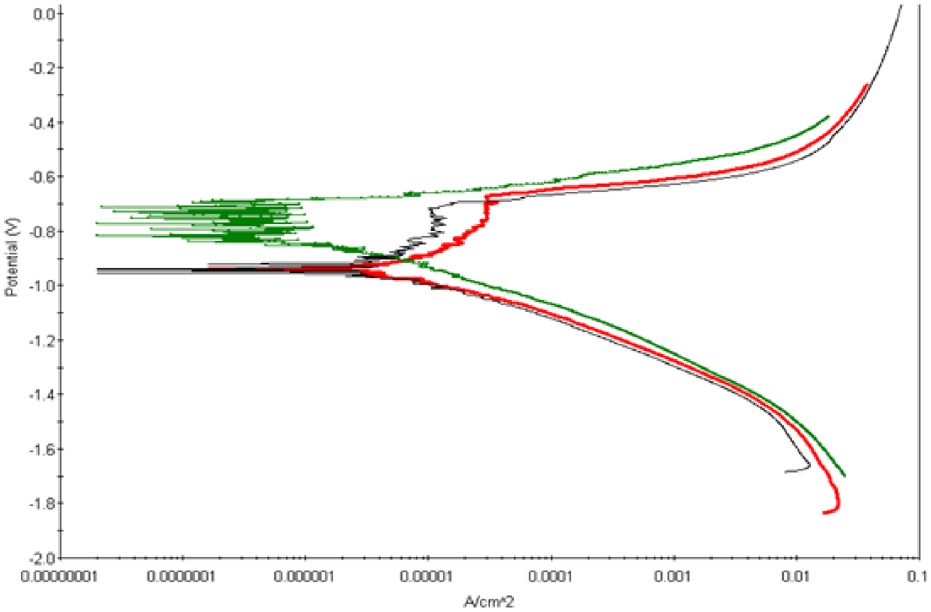

Figure 1. Tafel plots of — AlFe alloy 1.2; —AlFe alloy 1.5; —AlFe 1.9 alloy;

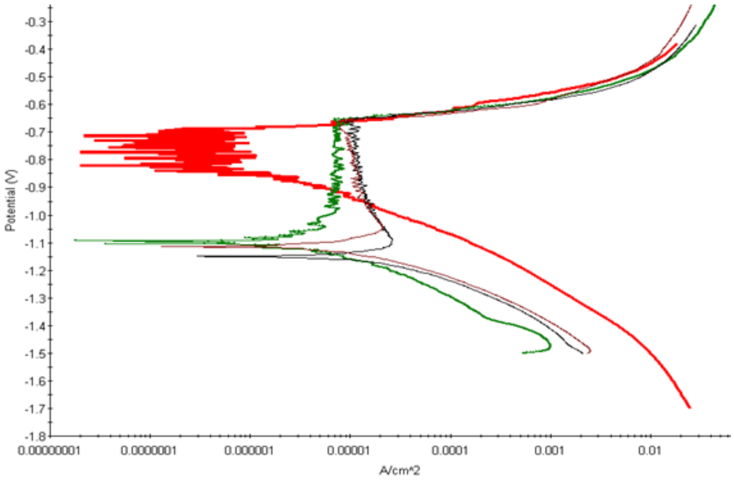

Figure 2. Tafel plots of AlFe alloys 1.2, — 0 mol/L; — 0.000045 mol/L;—0.00012 mol/L; —0.0002 mol/L

It can be concluded that all concentrations of potassium dichromate lead to corrosion inhibition of the alloys, and a lower value of the corrosion potential compared to the alloy without inhibitors. Figure 2 shows that at all used concentrations of inhibitors there is an occurrence of a passive process on the AlFe 1.2 alloy at potential – 0,7 V.

Loto et al. investigated the inhibitory effect of potassium dichromate on steel reinforcement, where they obtained an active potential of about -600 mV, passive at about -350 mV. In contrast to the values of active and passive potentials in this paper for AlFe 1.2 alloy, there is a difference in potentials because steel does not allow undisturbed diffusion of chloride ions [1].

Figure 3 shows the polarization curves of AlFe 1.5 alloy in 0.5 M sodium chloride solution at a scan rate of 0.166 mV/s, without and with the presence of different concentrations of potassium dichromate inhibitors.

Figure 4 shows the polarization curves of AlFe 1.9 alloy in 0.5 M sodium chloride solution, at a scan rate of 0.166 mV/s, without and with the presence of different concentrations of potassium dichromate inhibitors.

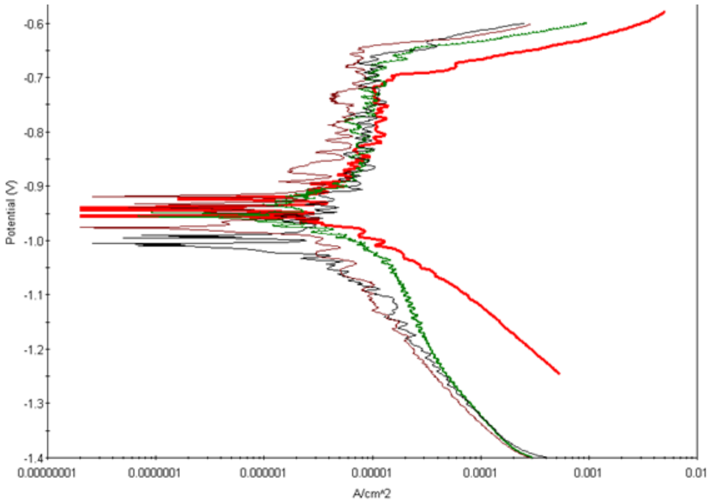

Figure 3. Tafel plots of AlFe 1.5,— 0 mol/L; — 0.000045 mol/L;—0.00012 mol/L; —0.0002 mol/L;

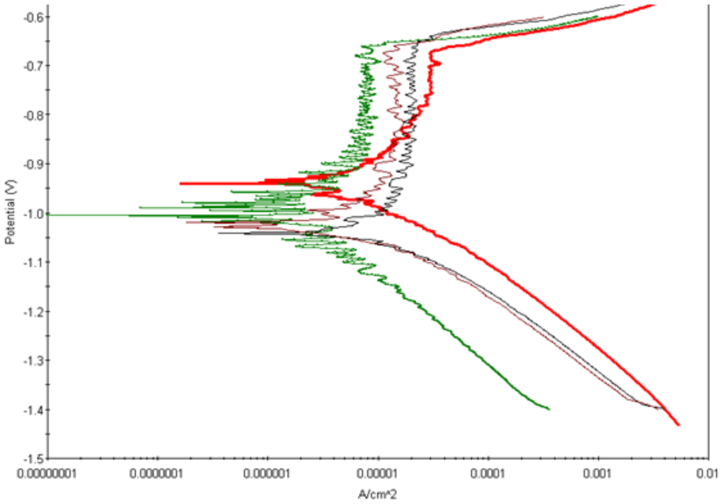

Figure 4. Tafel plots of AlFe 1.9, — 0 mol/L; — 0.000045 mol/L;—0.00012 mol/L; —0.0002 mol/L;

Figures 3 and 4 show the inhibitory effect without and in the presence of potassium dichromate on AlFe 1.5 and AlFe 1.9 alloys. As shown in the figures, the corrosion potentials for both alloys are about -0.9 V, while the potential with different concentrations of inhibitors decreases. Tables 1-3 show the results of different alloys in 0.5 M sodium chloride solution without and with the presence of different concentrations of potassium dichromate. The correct dependence of the decrease in the corrosion current at different concentrations of potassium dichromate was observed in the AlFe 1.5 alloy (Table 2).

Table 1. Results of the corrosion parameters of AlFe 1.2 alloy in 0.5 M sodium chloride solution without and with the presence of different concentrations of potassium dichromate

| Alloy | [$K_2Cr_2O_7$] (mol/L) | E (mV) | $I_{corr}$ (µAcm$^{-2}$) | $\beta_K$ (mVdec$^{-1}$) | $\beta_A$ (mVdec$^{-1}$) |
|---|---|---|---|---|---|
| AlFe 1.2 | 0 | -784.54 | 1.013 | 142.77 | 75.88 |
| | 0.000045 | -1092.49 | 4.102 | 137.99 | 368.571 |
| | 0.00012 | -1143.42 | 21.5 | 135.44 | 513.511 |
| | 0.0002 | -1104.06 | 15.02 | 149.73 | 321.43 |

Table 2. Results of corrosion parameters of AlFe 1.5 alloy in 0.5 M solution of sodium chloride without and with the presence of different concentrations of potassium dichromate

| Alloy | [$K_2Cr_2O_7$] (mol/L) | E (mV) | $I_{corr}$ (µAcm$^{-2}$) | $\beta_K$ (mVdec$^{-1}$) | $\beta_A$ (mVdec$^{-1}$) |
|---|---|---|---|---|---|
| AlFe 1.5 | 0 | -963.770 | 3.830 | 125.72 | 262.62 |
| | 0.000045 | -954.93 | 3.718 | 160.149 | 229.66 |
| | 0.00012 | -990.01 | 2.65 | 189.10 | 203.84 |
| | 0.0002 | -995.11 | 2.132 | 205.63 | 277.73 |

Table 3. Results of corrosion parameters of AlFe 1.9 alloy in 0.5 M sodium chloride solution without and with the presence of different concentrations of potassium dichromate

| Alloy | [$K_2Cr_2O_7$] (mol/L) | E (mV) | $I_{corr}$ (µAcm$^{-2}$) | $\beta_K$ (mVdec$^{-1}$) | $\beta_A$ (mVdec$^{-1}$) |
|---|---|---|---|---|---|
| AlFe 1.9 | 0 | -937.881 | 6.76 | 140.030 | 240.09 |
| | 0.000045 | -989.85 | 2.127 | 192.53 | 192.53 |
| | 0.00012 | -1021.45 | 9.41 | 140.55 | 251.96 |
| | 0.0002 | -1014.50 | 5.76 | 123.81 | 274.77 |

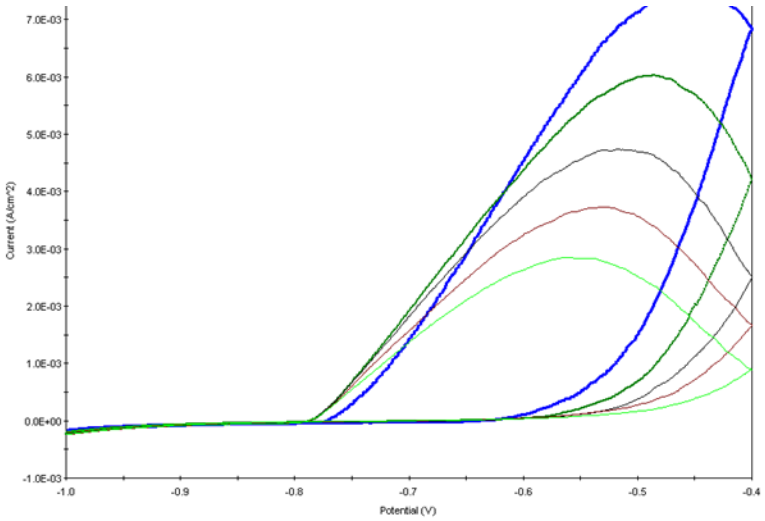

Figure 5. Cyclic voltammogram of AlFe 1.2 alloy; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

Unlike AlFe 1.2 alloy without inhibitors, AlFe 1.5 and AlFe 1.9 alloys have a passive process in the anode polarization region. Figures 3 and 4 show the reaction of oxidation of aluminium and reduction of chromate to Cr (III) on the surface of the alloy. Chromate ions on the surface of the alloy prevent corrosion processes in the chloride medium by affecting and changing the kinetics of the solution and the alloy. Chromates are very soluble, so due to this property, they are adsorbed on the surface of the alloy, not allowing the electrolyte to diffusely penetrate the pores of the alloy and cause any form of corrosion. Zhao et al. suggest that chromates had an inhibitory effect on Al alloy 2024-T3, and only high concentrations of chromates change the kinetic and corrosion processes [2].

For determining the pitting potential and growth of the separated oxidized and reduced peaks, the cyclic voltammetry method was used. Cyclic voltammetry was also used for studying various redox processes, to determine the stability of reaction products, electron transfer kinetics, etc. [3]. In Figures, 5–7 different cycles for the tested alloys at scanning speeds of 10 mV/s, 30 mV/s, 50 mV/s, 70 mV/s, and 90 mV/s in 0.5 M sodium chloride solution can be seen. As the scanning speed increases, so does the separation peaks. The current density increases from the corrosion potential and changes the sign in the anode peak in all diagrams. At the anode tip, an oxide film may have formed on the alloys as a corrosion product. When the surface of the alloy is completely covered with an oxide passive film, a sudden drop in the anode current occurs, which indicates the process of passivation. In Figure 5 for the AlFe 1.2 alloy can be seen that the Epitt is almost the same for all scan speeds and is about -0.83 V, while for the other alloys it had an approximate potential value. Studies performed by Pandiarajan et al. also indicated a sharp drop in anode current during precipitation of passive film oxide on steel and in 3.5% sodium chloride solution [4].

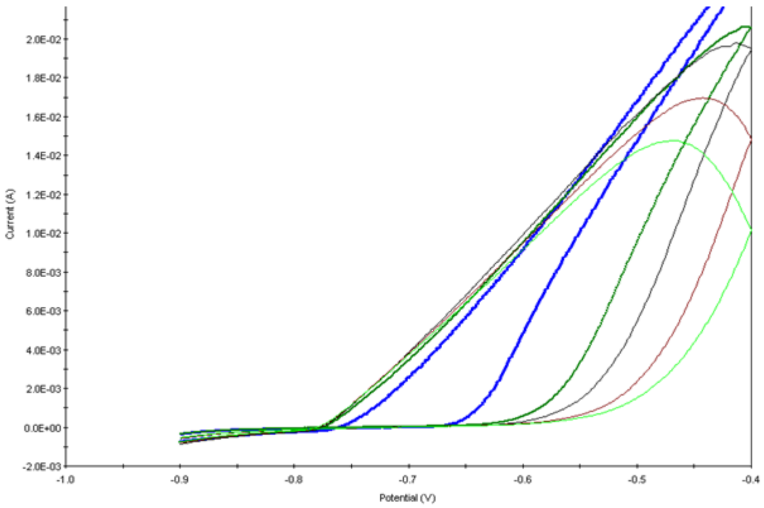

Figure 6. Cyclic voltammogram of AlFe 1.5 alloy; scan rate: – 10 mV/s; –30 mV/s;–50 mV/s; – 70 mV/s; –90 mV/s;

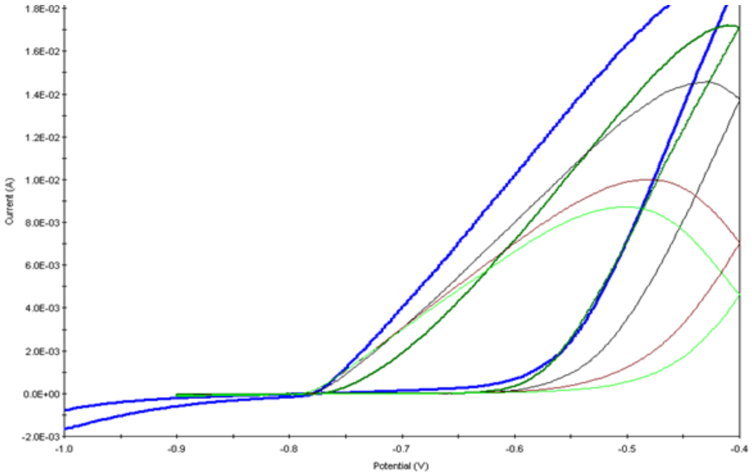

Figure 7. Cyclic voltammogram of AlFe 1.9 alloy; scan rate: – 10 mV/s; –30 mV/s;–50 mV/s; – 70 mV/s; –90 mV/s;

In addition to Tafel diagrams, redox processes that occur in the presence of different concentrations of potassium dichromate inhibitors by cyclic voltammetry were examined, Figures 8-16. With AlFe 1.2 alloy and the lowest inhibitor concentration, the anode peak is the most pronounced, and passivation occurs at all scan speeds to about -0.78 V. At higher inhibitor concentrations, Figure 8 and Figure 11 show that the potential shifts toward more positive values. Figure 9 (AlFe 1.5 alloy) shows that Epitt is about -0.53 V at a scanning speed of 10 mV/s. At the same scan rate and the same inhibitor concentration of 0.000045 mol/L Epitt in Al Fe 1.2 alloy is about -0.6 V, which indicates that the inhibitor has more influence on the kinetics and rate of formation of passive oxide films on the alloy surface. Chloride ions participate in the re-passivation process of all tested alloys, which can be removed by the diffusion process [5]. As the concentration of dichromates increases, the transfer of electrons from the electrolyte and the surface of the alloys slows down in all alloys. Increasing the scanning speed leads to a slow formation of the corrosion product, which leads to a shift of the potential towards more positive values (Deyab and Keer) [6]. This trend occurs due to the short incubation time [7]. At higher scanning speeds, pitting initiation can only be observed at a higher noble potential, which corresponds to a short incubation time. The incubation time to initiate passivity is caused by the time it takes for chloride ions to destroy the passive layer and adsorb to the alloy surface. In all alloys, increasing the concentration of inhibitors leads to a linear dependence and a decrease in the formation of corrosion products. The chromate ions formed on the surface of the alloys lead to less solubility of corrosion products and thus protect the alloys [8,9]. Chromates are anodic inhibitors that protect the material from the corrosive environment and thus the formation of a passive film, prevent the cracking of the passive oxide film leading to uniform corrosion.

Potassium chromates can also act as cathodic inhibitors by accelerating the cathodic reaction that produces a catalytic process that leads to the evolution of hydrogen. In addition to the evolution of hydrogen, they should lead to a reduction of chromate ions to the trivalent state $CrO_3^{3-}$ absorbed on the metal surface, while the tetravalent state $CrO_4^{4-}$ acts as a mediator between the metal surface and the corrosive medium, as described by Afolabi [10], and shown by reactions:

$$CrO_4^{2-} + 2e^- = CrO_4^{4-} \tag{1}$$

$$CrO_4^{4-} + 2H_2O = CrO_4^{2-} + H_2 + 2OH \tag{2}$$

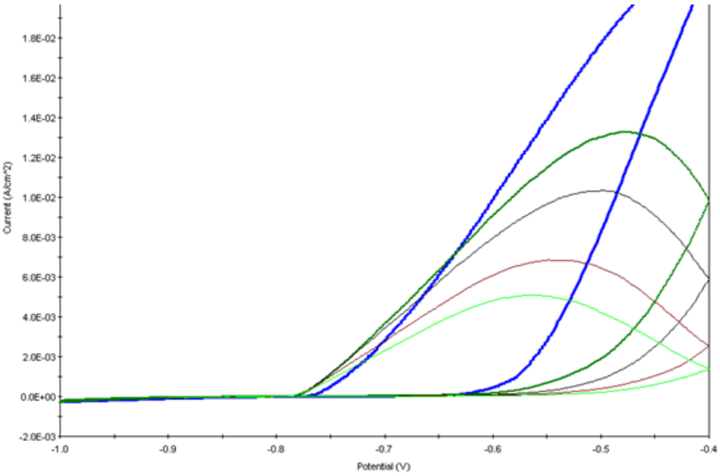

Figure 8. Cyclic voltammogram of AlFe 1.2 in the presence of inhibitors of concentration 0.000045 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

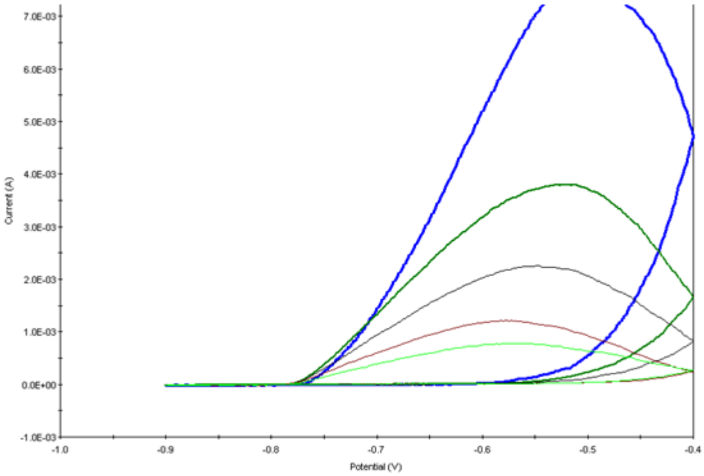

Figure 9. Cyclic voltammogram of AlFe 1.5 in the presence of inhibitors of concentration 0.000045 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

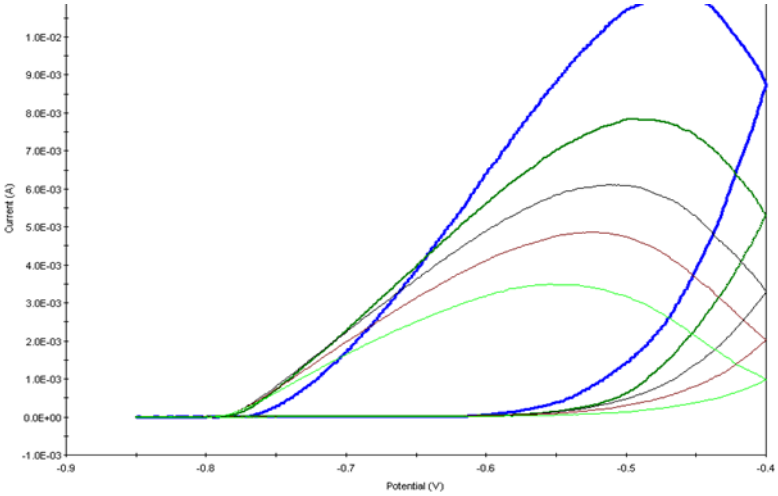

Figure 10. Cyclic voltammogram of AlFe 1.9 alloy in the presence of inhibitors of concentration 0.000045 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

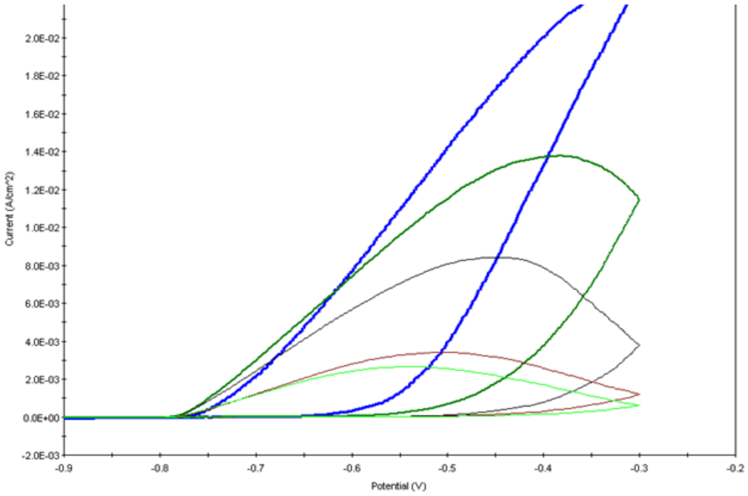

Figure 11. Cyclic voltammogram of AlFe 1.2 alloy in the presence of inhibitors of concentration 0.00012 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

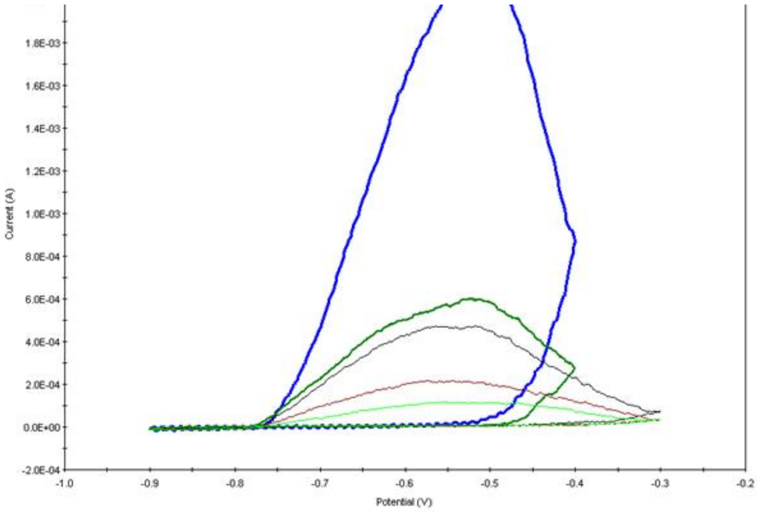

Figure 12. Cyclic voltammogram of AlFe 1.5 alloy in the presence of inhibitors of concentration 0.00012 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

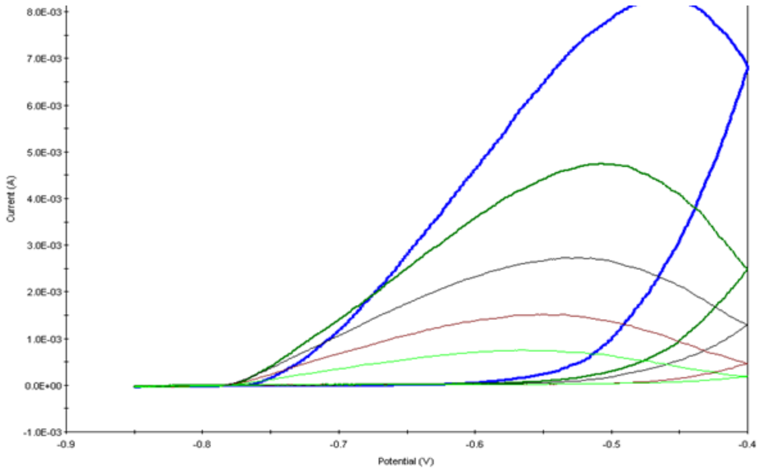

Figure 13. Cyclic voltammogram of AlFe 1.9 alloy in the presence of inhibitors of concentration 0.00012 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

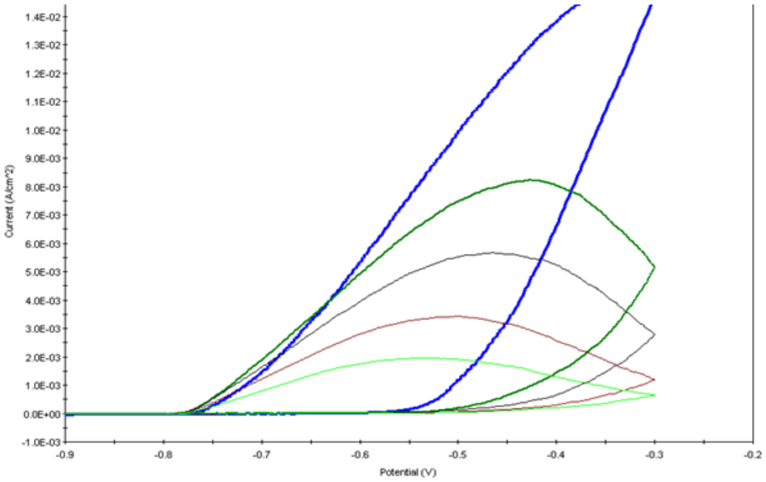

Figure 14. Cyclic voltammogram of AlFe 1.2 alloy in the presence of inhibitors of concentration 0.0002 mol/L; scan rate:— 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

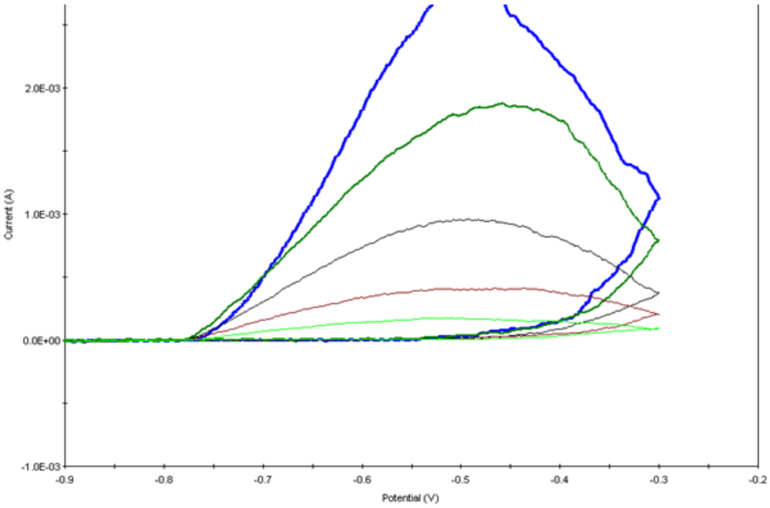

Figure 15. Cyclic voltammogram of AlFe 1.5 alloy in the presence of inhibitors of concentration 0.0002 mol/L; scan rate: — 10 mV/s; —30 mV/s;—50 mV/s; — 70 mV/s; —90 mV/s

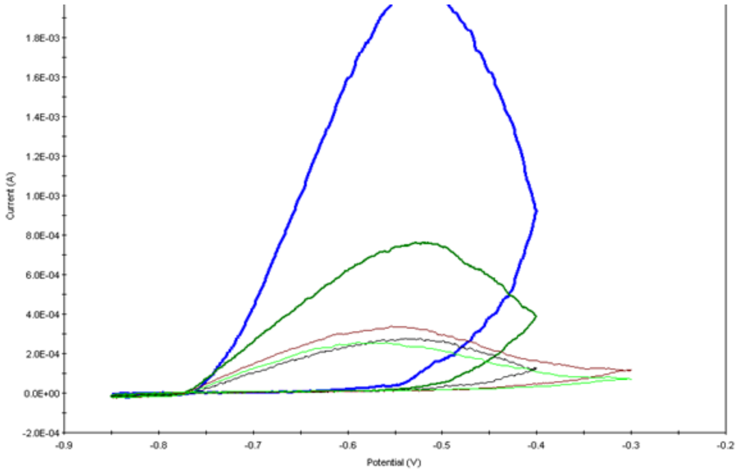

Figure 16. Cyclic voltammogram of AlFe 1.9 alloy in the presence of inhibitors of concentration 0.0002 mol/L; scan rate: – 10 mV/s; –30 mV/s;–50 mV/s; – 70 mV/s; –90 mV/s

The mass transport, controlled by diffusion in the time interval and under the influence of chloride ions, by the chronoamperometry method, was monitored, Figures 17 – 19. From the Figures, can be seen that oxidation processes occur briefly, and reduction processes occur somewhat longer on the alloy surfaces. Electron transport between the electrolyte and the surface area of AlFe 1.5 and AlFe 1.9 alloys takes slightly longer than in AlFe 1.2 alloy due to the solubility of the oxide film and the different content of iron ions. In the research, small current values were obtained by the chronoamperometric method, which indicates the compactness of the film on the surface area of the alloys. Scendo and Uznanska were recorded higher current values because they investigated the inhibitory effect of Cu – alloy in an acidic medium, and a linear dependence when increasing the inhibitor concentration [11].

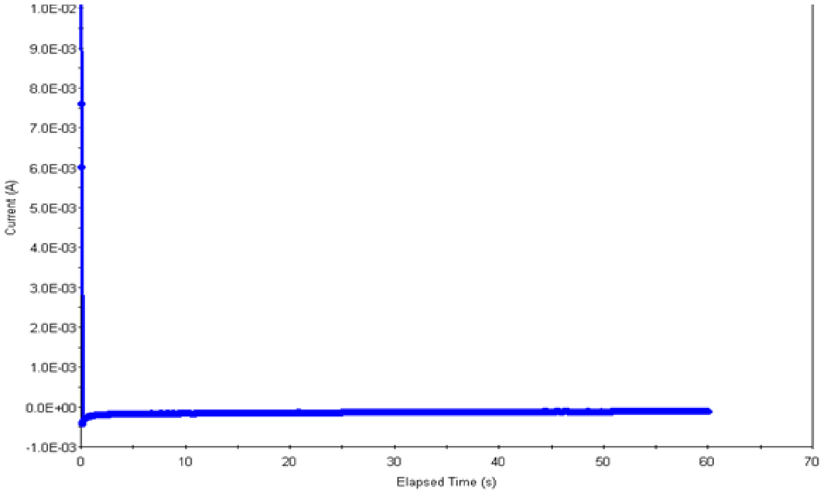

Figure 17. Chronoamperogram of Al-Fe alloy 1.2. alloys in 0.5 M sodium chloride solution

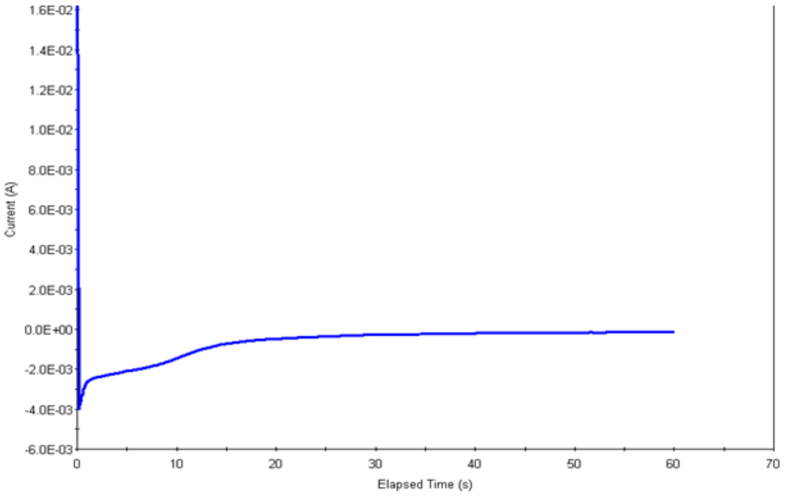

Figure 18. Chronoamperogram of Al-Fe 1.5 alloy in 0.5 M sodium chloride solution

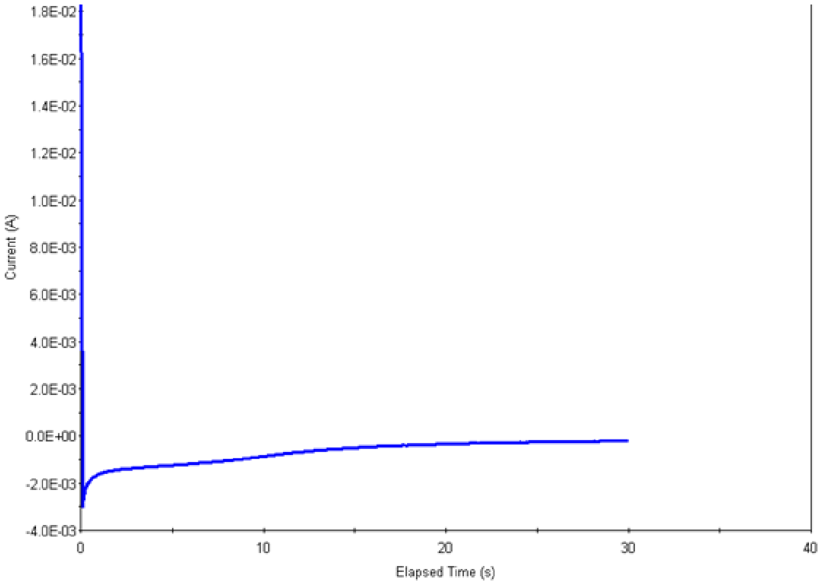

Figure 19. Chronoamperogram of AlFe 1.9 alloy in 0.5 M sodium chloride solution

## 4. CONCLUSIONS

Investigation of the effect of potassium dichromate on AlFe alloy by electrochemical methods showed an inhibitory effect. The formation of passivity depends on the chloride ions adsorbed on the surface of the alloys. The presence of potassium dichromate with chloride ions has an inhibitory effect and leads to the active dissolution of corrosion products. Also, in the presence of chromate ions, the potential shifts to more positive values. Cr(III) that occurs on the surface of alloys prevents the local corrosion, and an inorganic inhibitor such as potassium dichromate can be used in the process of alloys protecting.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

[1] C.A Loto, O.A. Omotosho. API Popoola, Inhibition effect of potassium dichromate on the corrosion protection of mild steel reinforcement in concrete, *International Journal of the Physical Sciences*, 6 (2011), p. 2275-2284

[2] J. Zhao, L. Xia, A. Sehgal, D. Lu, R. L. McCreery, G. S. Frankel, Effects of chromate and chromate conversion coatings on corrosion of aluminium alloy 2024-T3, *Surface and Coatings Technology,* 140*(*2001), p. 51-57

[3] R. Mark Wightman, Probing Cellular Chemistry in Biological Systems with Microelectrodes, *Science*, 311 (2006), p. 1570

[4] M. Pandiarajan, S. Rajendran, J. Sathiya bama, R. Joseph Rathis, S. Santhana Prabha, Applications of Cyclic voltammetry in Corrosion inhibition studies*, Int J Nano CorrSci and Engg.*, 3 (2016), p. 166-180

[5] S.A.M. Refaey, S.S. Abd El-Rehim, F. Taha, M.B. Saleh, R.A. Ahmed, Inhibition of chloride localized corrosion of mild steel by phosphate, chromate, molybdate and nitrate anions, *Appl. Surf. Sci.*, 158 (2000), p. 190

[6] M. A. Deyab, S. T. Keera, Cyclic voltammetric studies of carbon steel corrosion in chloride-formation water solution and effect of some inorganic salts. *Egyptian Journal of Petroleum,* 21(2012), p. 31–36

[7] S. S. Abd El-Rehim, S. M. Abd El-Wahab, E.E. Fouad, H.H. Hassan, Passivity and Passivity Breakdown of Zinc Anode in Alkaline Medium, *Mater. Corros.*, 46 (1995). p. 633

[8] A. Q. Fu, Y. F. Cheng, Electrochemical polarization behavior of X70 steel in thin carbonate/bicarbonate solution layers trapped under a disbonded coating and its implication on pipeline SCC, *Corrosion Science*, 52 (2010) p. 2511-2518.

[9] Seif Mohammad Meshari, Potassium Chromate as a Corrosion Inhibitors for Carbon Steel Alloy In HCl Media, *Basrah Journal of Science (A),* 30 (2012), p. 142-148

[10] Ayo Samuel Afolabi, Synergistic Inhibition of Potassium Chromate and Sodium Nitrite on Mild Steel in Chloride and Sulphide Media, *Leonardo Electronic Journal of Practices and Technologies*, 11 (2007), p. 143-154

[11] M. Scendo and J. Uznanska, The Effect of Ionic Liquids on the Corrosion Inhibition of Copper in Acidic Chloride Solutions, *International Journal of Corrosion,* Volume 2011, Article ID 718626, 13 pages doi:10.1155/2011/718626