Int. J. Electrochem. Sci., 13 **(2018)** 8623 – 8632, doi: 10.20964/2018.09.45

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Investigation of AlMgCu Alloy Corrosion in 0.5M NaCl: Polarization and EIS studies

Jelena Šćepanović, Dragan Radonjić, Darko Vuksanović[*]

University of Montenegro, Faculty of Metallurgy and Technology, Cetinjski put, 81000 Podgorica, Montenegro
[*]E-mail: darkov@ac.me

Received: 14 March 2018 / *Accepted:* 29 June 2018 / *Published:* 5 August 2018

Analyzing the production and consumption of non-ferrous metals in the world, it can be stated that aluminum and its alloys are in the first place in the term of a growth rate. The accelerated rate of non-ferrous metals consumption, demands for high-quality castings, as well as the economic aspect, certainly have influenced some changes, certain improvements and innovations in casting technologies and their application in corrosive environments. In this sense the aluminum alloys with copper and magnesium occupy a significant place. Stability corrosion tests often use the Tafel's method of potentiodynamic polarization, as well as the electrochemical impedance measurements. Also, a certain corrosion stability enhancements and reducing the metal corrosion rates can be achieved with the addition of small quantities of inhibitors in the aggressive corrosion ambience.
A proper selection of inhibitors is very important for effective enhancement of the corrosion protection, bearing in mind that some types of the inhibitors slow down the corrosion only in a particular solution/metal system. Inhibitors are mainly used to improve the corrosion protection of metal parts in solvents and spaces of limited volume, such as: chemical devices, steam boilers, storage and etching equipment and similar devices. The inhibitors used in this study belong to anodic corrosion inhibitors whose role is to slow down the anodic process of metal dissolution, through creating an insoluble protective layer with the primary corrosion products that firmly adheres to the metal surface and thereby reduces the anodic surface.

Keywords: AlMgCu-alloys, corrosion rate, corrosion inhibition, polarization resistance, current density, aqueous solutions

1. INTRODUCTION

Due to the wide application of aluminum and Al-alloys and their technical and economical importance, significant attention is related to study of their corrosion behavior and protection. There is a significant interest in Al-alloys with copper and magnesium that behave steadily in a corrosive aggressive environment.

The design of the Al-alloys is related to fulfill of modern demands on mechanical and corrosion properties, through the interaction of the selected alloying elements, their quantitative presence, individual and mutual influence on the specific alloy properties. The corrosion rate, as one of the specific targeted characteristics of these Al alloys, dominantly depends on the major alloying elements.

The corrosion behavior of Al and Al alloys is commonly analyzed by monitoring the potential-pH variations [1,2]. Accordingly, the aim of this paper is to determine the corrosion rates of some Al-Mg-Cu alloys using the electrochemical impedance and Tafel's method of corrosion investigation, with a comparative analysis of the previously published results [3,4] and evaluation of the corrosion inhibition efficiency in 0.5M NaCl solution in the presence of $NaNO_2$, Na_2CO_3 and Na_2HPO_4 inorganic inhibitors. By analyzing these data, a clearer estimation of the possible increase of tested materials' working life in chosen exploitation conditions, as a result of the corrosion inhibition can be obtained.

In recent years some authors have examined the corrosion behavior of AA2024 and AA7075 types of alloys in chloride solutions using the electrochemical impedance and Tafel's method [5-7]. Some literature data explains the mechanisms of corrosion inhibitions [8] through the complex oxide-inhibition and forming the appropriate oxide film [9], as well as the influence of corrosion inhibitors on the corrosion behavior of Al and Al-alloys in acid and neutral solutions [10-12].

The selection of inhibitors depends primarily on the properties of the metallic material to be protected against corrosion, corrosive ambience (solution), required material efficiency, inhibitor's toxicity and costs. This study examines the use of environmentally-friendly corrosion inhibitors [13,14], with aim to determine the efficiency of the used inhibitors on the tested alloys, using the electrochemical impedance, Tafel's curves and linear polarization testing methods.

2. EXPERIMENTAL PART

Chemical compositions of investigated Al-Mg-Cu alloys are presented in Table 1. Alloys were produced in laboratory conditions by melting in an electro-resistant furnace, cast into a metal mould with subsequent cooling in the air. The chemical composition of the alloys is determined by use of the x-ray ARL 34000 type of quantometer.

The corrosion characteristics of tested alloys in as-cast temper, and inhibition effects, were analyzed in an aqueous NaCl solution, at room temperatures. The electrolyte employed in this study was 0.5M NaCl solution. This solution was prepared in laboratory, using analytical grade reagent and distilled water. The inorganic inhibitors employed in this experiment were $NaNO_2$, Na_2CO_3 and Na_2HPO_4 in the form of analytical grade reagent.

Tafel's method and electrochemical impedance method of electrochemical tests were performed using the "Gamini PCI-4G750" potentiostat. Linear polarization tests were performed using the "PAR system" with potentiostat-galvanostat model 273. Tests were conducted with scan rate of 1 mV/sec and with the recording the current density in a potential range of ± 250 mV in relation to the open circuit potential (OCP).

All samples were subjected to chemical preparation, followed by a corrosion test in uninhibited and inhibited solutions. Experiments were carried out in laboratory conditions at room temperature.

Table 1. Chemical compositions of investigated Al-Mg-Cu alloys, wt%, Al rest.

Alloy No.	Mg	Cu	Zn	Mn	Si	Fe	Cr	Ti
1	4,47	0,047	0,345	0,079	0,70	0,26	0,158	0,025
2	1,71	0,04	0,310	0,360	0,54	0,70	0,230	0,035
3	1,65	0,287	0,25	0,035	0,57	0,65	0,007	0,025
4	1,57	2,40	0,27	0,20	0,15	0,28	0,035	0,025
5	1,64	3,65	0,45	0,20	0,15	0,25	0,050	0,027
6	0,76	5,20	0,68	0,060	0,18	0,41	0,007	0,023
7	6,92	0,30	0,270	0,290	0,15	0,24	0,189	0,15

Before corrosion tests all samples were prepared in the same way:

- degreasing with detergent, rinsing with flow and distilled water and chemical degreasing for 3 min. at temperatures of 60-70° C in 25%Na_2CO_3, 25%$Na_3PO_4 \cdot 10H_2O$ solution;
- chemical preparation of the samples surfaces, after degreasing, was carried out using two corrosion agents, subsequently: the 5%NaOH, at temperatures of 50-55 ºC, for 3 min. and 20%HNO_3, 10%HF, for 5 min. at room temperature;
- after the chemical preparation, samples were washed with distilled water and 96% ethanol, followed by 5 min. of drying with fan heater.

The aim of the etching method, with two listed chemical agents, was to produce a fresh and active (oxide-free) electrode surface as much as possible.

3. RESULTS AND DISCUSSION

In order to evaluate the corrosion process of the tested Al-alloys in NaCl solution, corrosion rates and other corrosion parameters were estimated from potentiodynamic polarization, linear polarization and electrochemical impedance method as a function of a sample compositions. Corrosion investigations were carried out on seven Al-Mg-Cu alloys with different contents of Mg and Cu. The content of Mg ranged from 0.76% to 6.92%, while the content of Cu ranged from 0.04% to 5.20%.

Figure 1 shows potentiodynamic polarization curves of the investigated as-cast Al-Mg-Cu alloys in 0.5M NaCl solution. The current density is recorded in a potential range of ± 250 mV in relation to the open circuit potential (OCP), with the scan rate of 1mV/s.

Table 2 shows the values of corrosion current, corrosion potential and corrosion rate of the tested alloys in the conditions of potentiodynamic polarization. Small changes in current density with potentials variations in both, the anode and the cathode parts, were reported, which is in relation to the low corrosion rates of the alloys tested in the chloride solution.

The lowest corrosion rates were measured for alloys 1 and 7, which are characteristic by high presence of Mg (Mg content of 4.47% and 6.92%, and Cu content of 0.047% and 0.30% respectively).

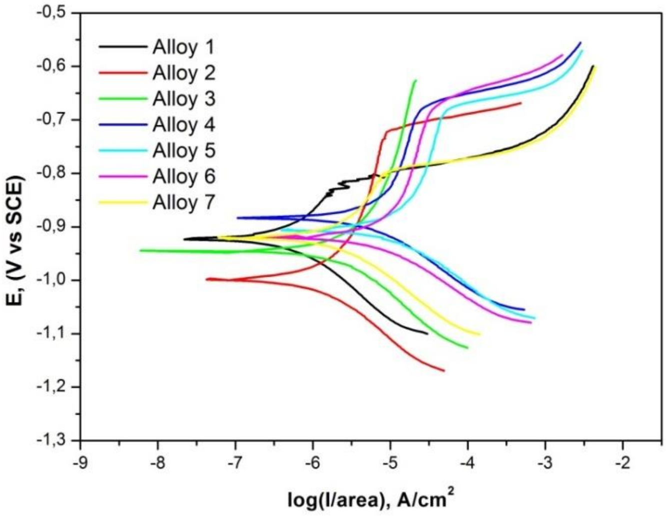

Figure 1. Potentiodynamic polarization curves of the investigated Al-Mg-Cu alloys in 0.5M NaCl; scan rate of 1 mV/sec; current density recorded in a potential range of ± 250 mV in relation to the OCP

Table 2. Values of corrosion current, corrosion potential and corrosion rate of tested alloys; potentiodynamic polarization; solution: 0.5M NaCl; room temperature; scan rate 1mV/s.

Alloy	I_{corr} [µA]	E_{corr} [mV]	Corrosion rate [mm/year]	b_k [mV/dec]	b_a [mV/dec]
1	0.17	-921	0.01	114	31
2	2.05	-998	0.07	108	38
3	3.45	-944	0.12	114	-
4	7.32	-883	0.25	95	36
5	11.60	-906	0.39	84	31
6	8.60	-920	0.29	87	46
7	0.52	-921	0.02	101	30

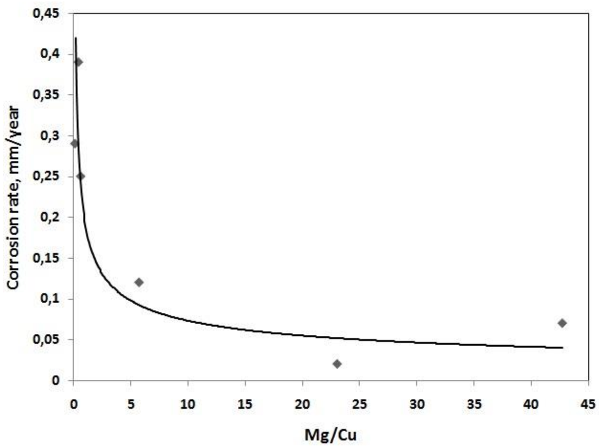

Figure 2. The influence of Mg/Cu ratio on the corrosion rate of tested alloys; potentiodynamic polarization; solution: 0.5M NaCl; room temperature, scan rate 1mV/s

The analysis of Mg/Cu ratio influence on the corrosion behavior of tested alloys has shown that the corrosion rate decreases exponentially with increasing of the Mg/Cu ratio, Figure 2.

The influence of the increase of Cu content on the corrosion rates of the alloys with approximately the same content of Mg was also analyzed. Alloys designated as 2, 3, 4 and 5 have a similar content of Mg (between 1.57-1.71% wt), while the content of Cu increases in the range between 0.04-3.65% wt. The increasing of Cu content up to 3.65 %wt causes a significant increase in the corrosion rate of the tested alloys containing the similar amount of Mg (Figure 3).

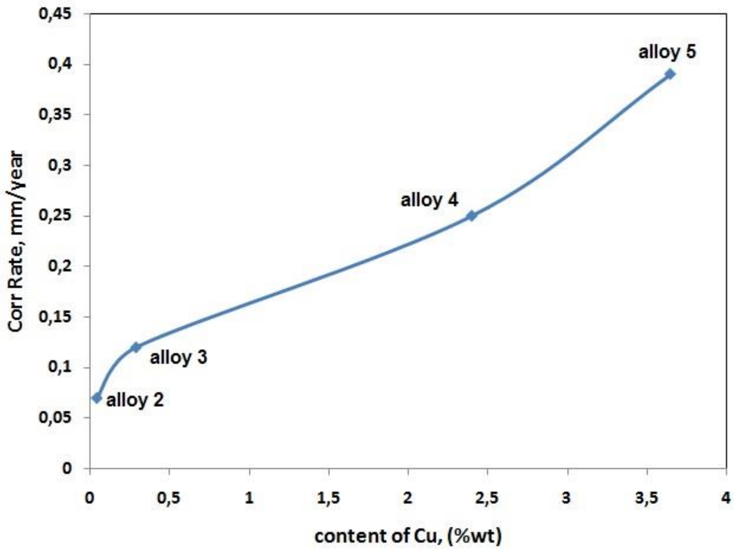

Figure 3. The influence of Cu content on the corrosion rate of tested alloys containing the similar amount of Mg (1.57-1.71% wt); potentiodynamic polarization; solution: 0.5M NaCl; room temperature, scan rate 1mV/s

The alloy no. 6, containing the 5.2% wt of Cu and 0.76%wt of Mg (the lowest ratio of Mg/Cu=0.15), also showed an increased corrosion rate, which is comparable to the rates measured for alloys 4 and 5, with Mg/Cu ratios of 0.45 and 0.65. According to these data, the lowest corrosion resistance was shown by alloys 4, 5 and 6, in accordance with the increase in Cu content (from 2.4 to 5.2% wt) and simultaneously reducing of Mg content from 1.64 to 0.76% wt. Alloys with higher Cu content are less corrosion resistant, since Cu is more electropositive metal than Al and behaves as a cathode in the micro galvanic couple with Al. Aluminum behaves like an anode in this conditions, and consequently there is its faster dissolution. Based on the results listed in Table 2, the values of the cathode slopes are in the range which corresponds to the cathode reaction of oxygen reduction (101-114 mV/dec). The anode slope does not occur as a kinetic parameter in the passive area (area of the chemical dissolution of passive film mainly). After reaching the critical pitting potential, it is possible to speak about the anode slopes of active dissolution and, for all tested alloys, they are in the range of 30-46 mV/dec, indicating anode oxidation of Al to Al^{3+}. [15]

The results of the electrochemical impedance measurement (Nyqvist curves), adapted by complex nonlinear least-squares method [16], are presented in Figure 4 and Table 3.

Figure 4 shows the interdependencies between the Z_{imag} and Z_{real} (Nyqvist curves) recorded by the electrochemical impedance measurement method of corrosion testing. According to these results, the lowest corrosion rates show alloys 1 and 2, while the lowest resistance to corrosion is measured for alloys 4, 5 and 6.

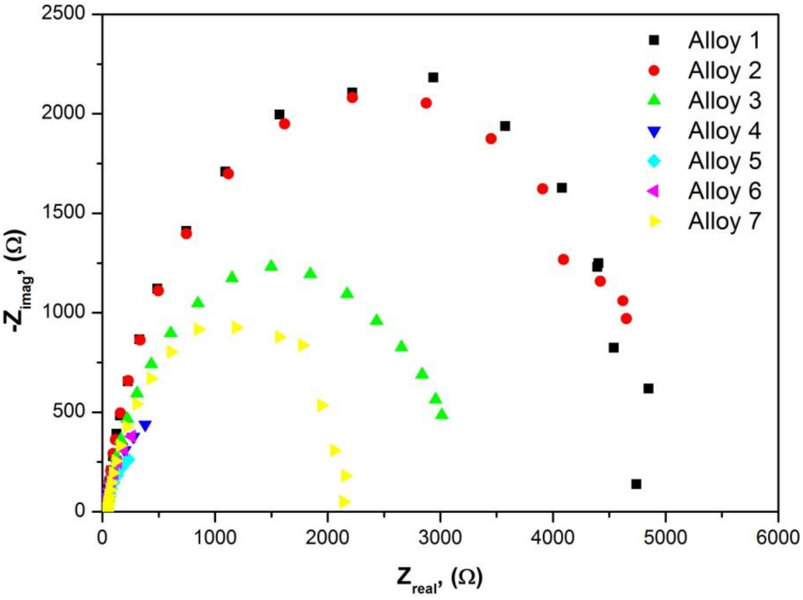

Figure 4. Electrochemical impedance measurement of the tested Al alloys; solution: 0.5M NaCl; room temperature

Table 3. presents the measured electrochemical impedance measurement parameters. The electrolyte resistance (R_s) is a significant factor in the impedance of an electrochemical cell, and depends on the type of ions, ionic concentration, temperature and the geometry of the current carrying area. The R_s values were approximately the same, in the range from 31.25 to 33.77 Ω. The highest polarization resistance (R_p) values, and consequently the lowest values of double layer capacity (C_{dl}), were measured on alloys marked with 1 and 2, i.e. on the alloys with high Mg/Cu ratios.

Table 3. Electrochemical impedance parameters: electrolyte resistance (R_s), polarization resistance (R_p), double layer capacity (C_{dl}), open circuit potential (OCP) vs SCE; solution: 0.5M NaCl; room temperature

Alloy	**R_s [Ω]**	**R_p [Ω]**	**C_{dl} [μF/cm^2]**	**OCP vs SCE [mV]**
1	33.77	4706.23	11.3	-841
2	34.32	4619.68	11.5	-874
3	34.31	2978.69	34.5	-793
4	31.25	347.65	3059	-801
5	34.75	196.95	5416	-826
6	33.24	226.66	4697	-816
7	31.57	2108.43	68	-824

The influence of Cu content on the polarization resistance during the electrochemical impedance measurements on Al-alloys with approximately the same content of Mg was also analyzed (alloys designated as 2, 3, 4 and 5 have a similar content of Mg, while the content of Cu increases in the range between 0.04-3.65% wt). Figure 5 illustrates the changes in polarization resistance caused by the increasing of Cu content up to 3.65 %wt. The polarization resistance of the alloy no. 6 (containing the 5.2% wt of Cu and 0.76%wt of Mg) is comparable to the R_p values obtained for alloys 4 and 5.

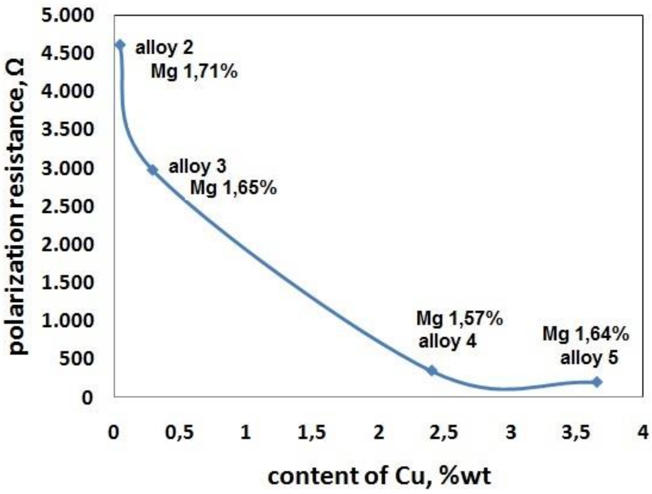

Figure 5. Polarization resistance (R_p) of tested Al-alloys as a function of Cu content; electrochemical impedance measurements on Al-alloys containing the similar amount of Mg (1.57-1.71% wt); solution: 0.5M NaCl; room temperature, scan rate 1mV/s

The determination of the corrosion inhibition efficiency in 0.5M NaCl solution in the presence of $NaNO_2$, Na_2CO_3 and Na_2HPO_4 inorganic inhibitors has also been involved in this experiment. All samples were subjected to a corrosion test in uninhibited and inhibited solutions. Figure 6 illustrates the influence of the inhibition on the corrosion behavior of two selected alloys, designated as 4 and 6, in 0,5M NaCl solution.

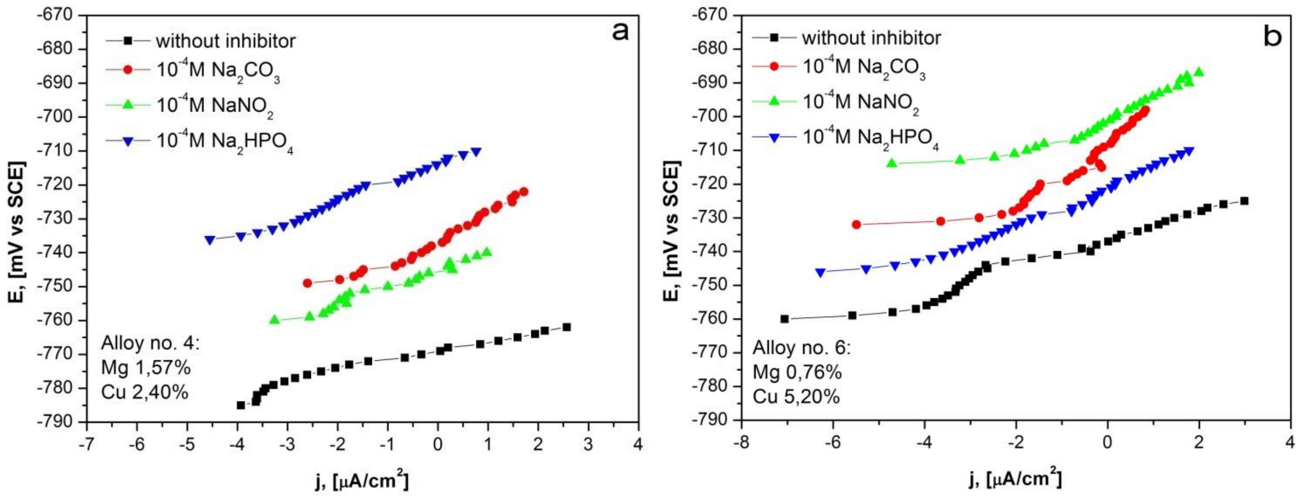

Figure 6. The influence of the type of the inhibitor on the behavior under linear polarization conditions of (a) alloy no. 4 containing Mg 1,57% and Cu 2,4% and (b) alloy no. 6 containing Mg o,76% and Cu 5,2%. solution: 0.5M NaCl; room temperature

Using the inhibitor supplements in the 0,5M NaCl solution causes the moving of corrosion potentials for all tested alloys toward less negative values, and it is indicated for all of three inhibitors used. In the case of alloy no. 4 (Mg/Cu=0.65) the increase of measured potential or the displacement of curves to less negative values due to inhibition was for 23-55 mV, with the highest influence shown by Na_2HPO_4 type of inhibitor. In the case of the alloy no. 6, where the Mg/Cu ratio was 0.15, the measured increase in potential or displacement of curves to less negative values due to inhibition was somewhat lower, 15-36 mV, with the highest influence shown by $NaNO_3$ type of inhibitor.

Figure 7. illustrates the efficiency of the used inorganic inhibitors on the corrosion of tested Al alloys in 0,5M NaCl solution. The inhibitor efficiency is calculated by the equation:

$$\eta = \frac{j_{corr} - (j_{corr})_{inh}}{j_{corr}}$$

where the j_{corr} is the corrosion current in uninhibited and $(j_{corr})_{inh}$ corrosion current in inhibited solution. The corrosion current values used to calculate the inhibitor efficiency were obtained from the linear polarization test [3,4].

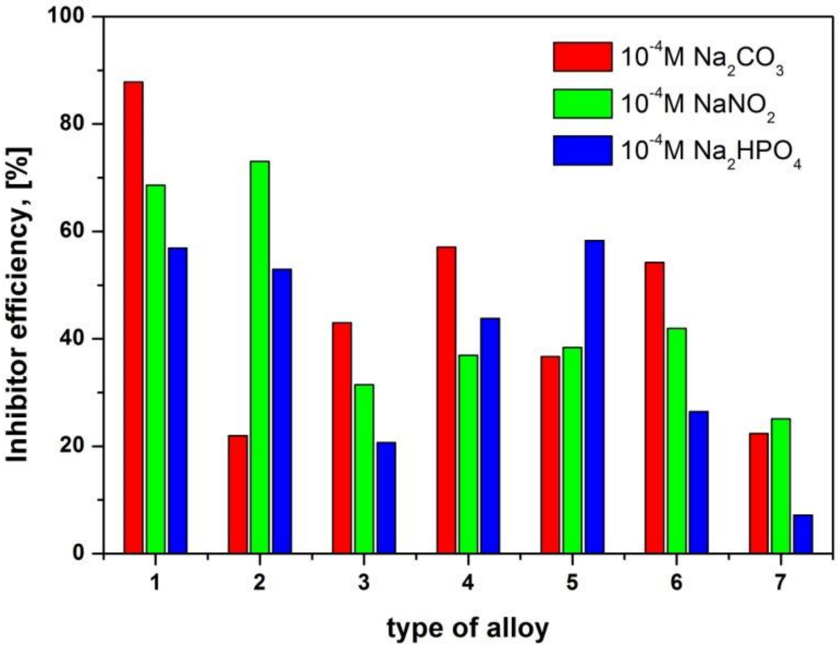

Figure 7. Efficiency of the used inorganic inhibitors on the corrosion of tested Al alloys in 0,5M NaCl solution, based on the corrosion currents in uninhibited and inhibited solution

According to data from the Figure 7, the presence of any of the three inhibitors, used in the experiment, reduces corrosion rates of the tested Al alloys in the chloride solution, through the causing the corrosion currents decrease, and increasing of the polarization resistance. The efficiency of the inhibitors depends on the chemical composition of the alloys. Increasing of the content of Cu causes a decrease in both, the corrosion resistance of the tested alloys and the inhibitor efficiency. Although the increase of Cu content in this type of alloy decreases the inhibition efficiency in the chloride solution, the achieved inhibition level satisfies the overall efficiency of the inhibitory system and the corrosion behavior of the investigated Al alloys in 0,5M NaCl solution. If the average inhibitors efficiency is analyzed it can be concluded that the best performances is shown by Na_2CO_3 (10^{-4}M) type of inhibitor for all the alloys used in the experiment. The lowest efficiency was demonstrated by Na_2HPO_4.

5. CONCLUSION

Corrosion behavior of some Al-Mg-Cu alloys has been studied in uninhibited and inhibited 0.5M NaCl solutions. Measurements were performed using potentiodynamic polarization, electrochemical impedance measurements and linear polarization tests. Corrosion rates and other corrosion parameters were estimated as a function of a sample compositions. The lowest corrosion rates were measured for alloys 1 and 7, which are characteristic by high content of Mg (Mg content of 4.47% and 6.92%, and Cu content of 0.047% and 0.30% respectively). Corrosion rate decreases exponentially with increasing of the Mg/Cu ratio in this type of alloys. Using the inhibitor supplements in the 0,5M NaCl solution causes the moving of corrosion potentials for all tested alloys toward less negative values, and it is indicated for all of three inhibitors used ($NaNO_2$, Na_2CO_3 and Na_2HPO_4). The efficiency of the inhibitors depends on the chemical composition of the alloys. Increasing of the content of Cu causes a decrease in both, the corrosion resistance of the tested alloys and the inhibitor efficiency. If the average inhibitors efficiency is analyzed it can be concluded that the best performances is shown by Na_2CO_3 (10^{-4}M) type of inhibitor for all the alloys used in the experiment. The lowest efficiency was demonstrated by Na_2HPO_4.

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