

# INFLUENCE OF THE INORGANIC SOLUTIONS ON THE CURRENT EFFICIENCY FOR IRON DISSOLUTION AT THE ELECTROCHEMICAL MACHINING

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**ABSTRACT.** At the processing by electrochemical erosion, an important influence has the working solution (electrolyte). This paper presented the results obtained by applying inorganic solutions at the machining by electrochemical erosion. There are analysed the process which takes place into the electrolytes during the anodic dissolution of the metal, the current efficiency at H generation and iron dissolution, as well as the modification of the pH values.

By comparing the obtained results has been established the best results for processing by electrochemical erosion of steels alloyed with chrome.

**KEYWORDS:** Electrolyte solution, anodic dissolution, electrochemical erosion, current efficiency, inorganic solutions.

## 1. INTRODUCTION

In the machining by electrochemical erosion, the anodic dissolution is the main process that depends on the type of the erosive agent. The processed object is connected at the anode of a source of continue current and the transfer object at the cathode of the same source. Between the two electrodes exists an electrolyte which in the presence of the electrical current promotes some physical and chemical processes that dissolved the processed object.

The transfer object is an output element in the transfer process of the energy necessary for the action of the erosive agent and it is the main parameter of the final stage of the erosive agent.

The anodic dissolution is followed by achieving of a protective layer on the work piece surface that decrease the dissolution rate. For a continuous processing by electrochemical erosion it is necessary a permanent activation of the electrodes surface.

In the metal machining by electrochemical erosion the most commune electrolytes are inorganic solutions:  $\text{NaNO}_3$ ,  $\text{NaClO}_3$ ,  $\text{Na}_2\text{CO}_3$ . Electrolytes assure the presence of the electrical charges in the working space and the anodic dissolution of the processed object [1], [4], [7].

In the case of inorganic solutions the anodic dissolution is very important [2] for removing the material. On the work piece surface is achieved a pellicle from oxides, hydroxides or salts, that protects the surface. In this case the surface is smooth, with a small roughness because the metal was removed by anodic dissolution.

An important influence on the electrochemical processing has also the flowing rate of the electrolyte, it must be rapidly to assure a low viscosity and a high ions mobility. Very good results

have been obtained with electrolyte with halogen ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ).

The main function of the electrolyte at the machining by electrochemical erosion is to assure the presence of the electric charges in the space between electrodes as well as the anodic dissolution of the work-piece. Generally are applied aqueous solutions of inorganic type [8].

At the electrochemical machining usually are applied salt solutions, with a smaller conductivity than acids and alkaline solution, but less corrosive. By anodic dissolution results metallic anions and the cathode reaction generates hydrogen and hydroxide ions [6].

The reaction products obtained at the anode and cathode interact between them and result some hydroxide insoluble that are removed by pumping the electrolyte outside the working space.

At the anode, the electrolyte has to assure a continuous dissolution of the work-piece and the electrolyte structure has to avoid the obtaining of the insoluble compounds that will achieve an insoluble pellicle on the anode surface.

The reaction that takes place at the cathode is important because the releasing of the positive ions shall not influence the anodic dissolution.

Iron alloys, are processed with very good results in inorganic solutions. Machining by electrochemical erosion has a great efficiency for alloyed steels [6].

The electrolyte flowing in the working space influences the increase of the hydrogen quantity at the cathode as well as the machining by electrochemical erosion [1]. The main effect of hydrogen releasing is the decreasing of the solution conductivity with a considerable effect on the processed surface. By adding of small quantities of additives ( $\text{Na}_2\text{CO}_3$ ) in the electrolyte solution will increase the metal dissolution from the anode because the electrolyte has a greater conductivity.

By hydrogen generation at the cathode decreases the electrolyte conductivity because is reduced the necessary volume for the conduction process. The modifications of the metal finished surface are due to the flowing type of electrolyte and some variation in the electrolyte conductivity. This is affected by the heating of the solution and releasing of the hydrogen.

## 2. EXPERIMENTAL METHOD

The material used for this work is steels alloyed with chrome, X210Cr12 (12% Cr) (anode) and brass (cathode), samples rods had 3 cm diameter and 30 cm length, time=5 min [1].

At the machining by electrochemical erosion were applied inorganic solutions: NaClO<sub>3</sub> 20% , NaClO<sub>4</sub> 3%+NaNO<sub>3</sub> 10%, NaNO<sub>3</sub> 10%, NaNO<sub>3</sub> 10% +Na<sub>2</sub>CO<sub>3</sub> 3%. There were processed steel bars as anode in different inorganic solutions.

The inorganic solutions at the processing by electrochemical erosion has the rule to assure the presence of the electrically charges in the space between the electrodes [6] as well as the dissolution of the work piece surface.

### a) NaClO<sub>3</sub> 20%

In this case good results were obtained at low potential values. During the anodic dissolution results an oxide film Fe<sub>2</sub>O<sub>3</sub> with a great porosity that allows the rapid passing of the metal cations through it. The rate of metal removal thereby decreased proportional with the thickness of the anode oxide. For this electrolyte the anodic process takes place because of iron dissolution as Fe<sup>+2</sup> ions that can be transformed by oxygen in Fe<sup>+3</sup>. During the process of erosion the anode surface is covered with an oxide pellicle of Fe<sub>2</sub>O<sub>3</sub>.

The anodic reaction is:

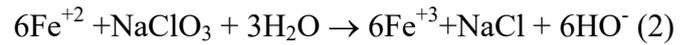


In table 1 are given the values of current efficiency for steel processing in an electrolyte of NaClO<sub>3</sub>:

**Table 1** Current efficiency for iron dissolution in NaClO<sub>3</sub> electrolyte

NaClO <sub>3</sub> conc. [%]	Current intensity I [A]	Current efficiency for iron dissolution	pH modification from	
20	75	155,38	7,7	7,4
20	100	163,99	8,1	6,1
20	125	220	7,9	6,5
20	150	262	8,5	6,3
20	200	240	8,9	6,1

The result shows that the cathode reaction is hydrogen evolution the overall chemical reaction is:



These results show that the current efficiency for the metal removal from anode increases with the current density, with a corresponding decrease in current efficiency for oxygen releasing.

The oxide pellicle achieved on the anode surface is porous and permits the rapid passing of the cations through it. In the same time the pellicle acts like a barrier that hinder the migration of the reaction products. The removing rate of the metal decreases in time and is dependent on the thickness of the oxide layer [1].

By decreasing the quantity of removed metal a part from the electrical current is consumed at the oxygen releasing:



By increasing of the current intensity the oxide layer became thinner so that increases the removing rate of the metal. Because the oxide layer has a great solubility at low values of pH, the decreasing of the oxide thickness can be the result of the smaller values of pH near the cathode surface.

### b) NaClO<sub>4</sub> 3% + NaNO<sub>3</sub> 10%

In the case of an electrolyte solution of NaClO<sub>4</sub>, for current densities between 26-47 A/cm<sup>2</sup>, the current efficiency for the hydrogen releasing is approximately 100%.

At the anode the current efficiency at the metal removing and oxygen releasing is 90%. In the case when brass is the cathode, hydrogen is not released. The current efficiency in the case of NaClO<sub>4</sub> electrolytes are smaller than the results obtained in NaClO<sub>3</sub>, a part of the electrically current is consumed at the oxygen releasing. At the anode the current efficiency at the metal removing and oxygen releasing is almost 90%. The small amount of oxygen released in an electrolyte of NaClO<sub>4</sub> than the oxygen released in a NaClO<sub>3</sub> electrolyte is because of the thinner pellicle of oxide obtained for this solution.

The main effect of NaClO<sub>4</sub> solution is the decreasing of the oxidation power of sodium chlorate, NaClO<sub>3</sub>. At high concentrations of NaClO<sub>4</sub>, it will attack the oxide pellicle and will cause the pitting process (conc.> 0,25M).

c) NaNO<sub>3</sub> 10%

These solutions have the properties to achieve on the anode surface a porous pellicle of Fe<sub>3</sub>O<sub>4</sub> that assures an advanced dissolution of the components from steel. Because at the process beginning has been achieved an efficient contact between electrolyte and the work-piece from steel the roughness value measured in the contact zone is relatively small ( $r_1 = 0,58 \mu\text{m}$ ) that evidenced the preponderance of the anodic dissolution.

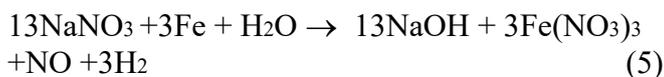
By electrolytic dissociation [4] of the NaNO<sub>3</sub> solution results NO<sub>3</sub><sup>-</sup> ions that under the influence of the electrical current migrates toward anode (work piece surface) where meets the metallic ions Me<sup>z+</sup> resulted by anodic dissolution of the material. By chemical reactions that takes place on the work piece surface will be achieved a pellicle that includes also inorganic components. So at the anodic dissolution of steel the protective pellicle has in the structure oxides ( Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>) and nitrates Fe(NO<sub>3</sub>)<sub>3</sub>, Cr(NO<sub>3</sub>)<sub>3</sub> [2].

At the cathode the main reaction is nitrate reduction appearing iron nitrates.

In this case the metal processing by electrochemical erosion takes place on a great surface of the anode. The machining rate is smaller than the obtained rate in the case of NaClO<sub>3</sub> solution. On the anode is obtained a pellicle of Fe<sub>3</sub>O<sub>4</sub> that allows the passing of the electrical current [3]. The reaction that takes place in an electrolyte of NaNO<sub>3</sub> at the metal dissolution is:



The global reaction that takes place is:



The current efficiency obtained in a NaNO<sub>3</sub> electrolyte for iron dissolution by electrochemical erosion is given in the following table:

**Table 2** Current efficiency at iron dissolution in NaNO<sub>3</sub> electrolyte

NaNO <sub>3</sub> conc. [%]	Current intensity I [A]	Current efficiency at iron dissolution Q <sub>p</sub> [mm <sup>3</sup> /min]	pH changing from to	
10	75	120,35	5,3	11,4
10	100	165,08	6,3	11,3
10	125	225	6,2	11,2
10	150	272,06	6	11,4
10	200	260,30	6,1	11,5

It is observed that the current efficiency at the metal removing increase with the current intensity.

By chemical analysis of the obtained precipitate, for this working solution, the obtained products obtained by anodic dissolution are less in the protective pellicle and more in the precipitate as ferrous nitrate Fe(NO<sub>3</sub>)<sub>3</sub>. It can be concluded that by adding NaNO<sub>3</sub> the anodic dissolution is significantly influenced but it does not appear in the protective pellicle.

d) NaNO<sub>3</sub> 10% + Na<sub>2</sub>CO<sub>3</sub> 3%

In the case of NaNO<sub>3</sub> electrolytes with additives were obtained good results at the metal machining by electrochemical erosion. In the following table are presented results obtained for iron dissolution in a mixture of NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> at different values of the current intensity:

**Table 3** Current efficiency in a NaNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> electrolyte

NaNO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> conc. [%]	Current intensity I [A]	Current efficiency at iron dissolution Q <sub>p</sub> [mm <sup>3</sup> /min]
10 + 3	75	253,66
10 + 3	100	299,79
10 + 3	125	328
10 + 3	150	353,11
10 + 3	200	300,5

The presence of inorganic substances as additives in an electrolyte of NaNO<sub>3</sub> accelerates the anodic dissolution of the metal and influences the obtaining of the passive pellicle on the anode surface. The current efficiency values at hydrogen generation for the three types of electrolytes at the metal dissolution by electrochemical machining are presented in table 4:

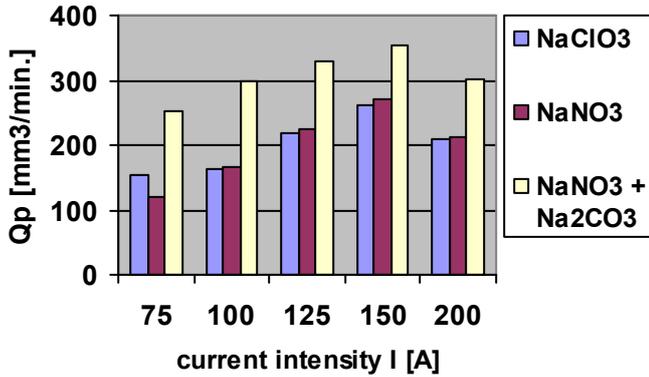
**Table 4** Current efficiency at H generation in NaClO<sub>3</sub>, NaNO<sub>3</sub>, NaNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub>

Electrolyte	Current intensity I [A]	Current efficiency at hydrogen generation Q <sub>p</sub> [mm <sup>3</sup> /min]
NaClO <sub>3</sub> 20%	75	98.2
	100	99.3
	125	99.8
	150	98.6
	200	98.3
NaNO <sub>3</sub> 10%	75	87.4
	100	88.8
	125	98.3
	150	96
	200	95.4
NaNO <sub>3</sub> 10% + NaClO <sub>3</sub> 3%	75	99.6
	100	100.9
	125	102
	150	99.8
	200	99.3

#### 4. RESULTS AND DISCUSSIONS

With the obtained results have been achieved a comparative analysis of the current efficiency  $Q_p$  [mm<sup>3</sup>/min] at the iron dissolution in correlation with the electrical current intensity  $I$  [A] at the processing of steel bars alloyed with chrome.

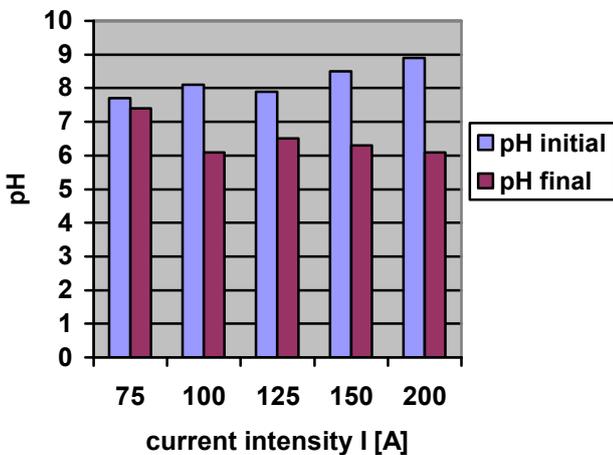
In figure 1 is achieved comparative analyses at the processing of steel bars of type X210Cr12 in the inorganic electrolytes presented above:



**Figure 1** Dependence of the process efficiency  $Q_p$  on the current intensity for steel X210Cr12, in NaClO<sub>3</sub>, NaNO<sub>3</sub>, NaNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> electrolytes

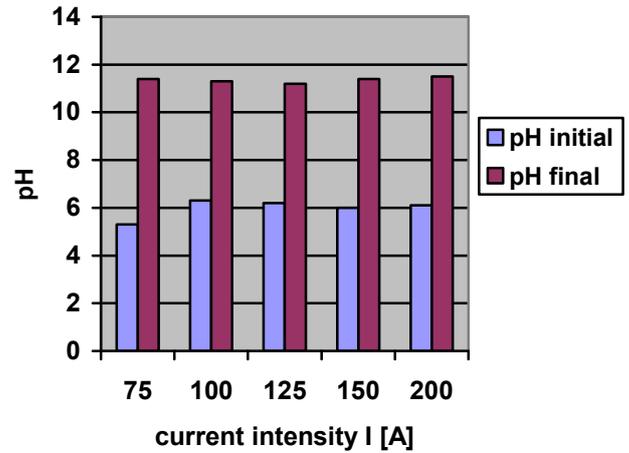
The best results at the iron dissolution from the work piece were obtained for the electrolyte NaNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> because NO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>-2</sup> ions promote the metal dissolution. By increasing of the current intensity [200 A] the protective pellicle with different structures hinders the anodic dissolution and the current efficiency at iron dissolution.

In the case of NaClO<sub>3</sub> electrolyte, the hydrogen releasing modifies the pH value, which decreases with the increasing of the solution acidity and the current intensity.



**Figure 2** Dependence of the pH values on the current intensity for steel X210Cr12, in NaClO<sub>3</sub> electrolyte

In the case of NaNO<sub>3</sub> electrolyte it can be observed that the pH values increases because the passive pellicle achieved on the anode surface hinders the hydrogen releasing as well as pH decreasing.

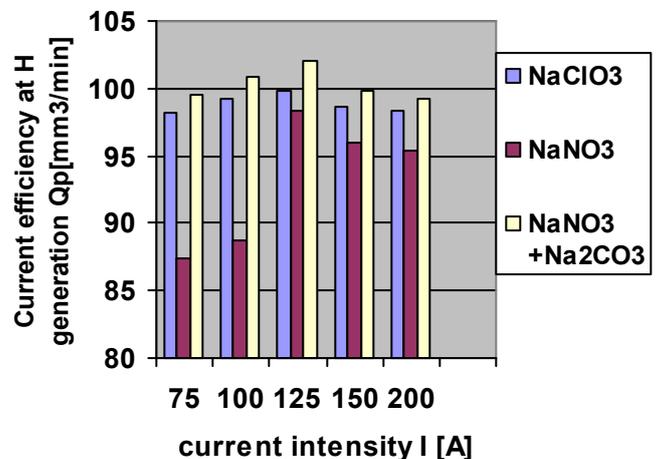


**Figure 3** Dependence of the pH values on the current intensity for steel X210Cr12, in NaNO<sub>3</sub> electrolyte

The alkaline character of the electrolyte, in this case (high values of pH) is due to NaOH which is obtained in the chemical reactions at the iron dissolution from the work piece, in NaNO<sub>3</sub> electrolyte.

The hydrogen released at the cathode influences the machining by electrochemical erosion. The main effect of hydrogen is the decreasing of the solution conductivity after a current intensity of 125 A, but by adding of small quantity of Na<sub>2</sub>CO<sub>3</sub> (3%) increases the iron dissolution from the work piece and the electrolyte will have a greater conductivity.

The hydrogen generation in the three types of electrolytes at different values of the current intensity is presented in figure 4:



**Figure 4** Dependence of the current efficiency at H generation on the current intensity for steel X210Cr12, in NaClO<sub>3</sub>, NaNO<sub>3</sub>, NaNO<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> electrolytes

## 4. CONCLUSIONS

Among the studied electrolytes, the best results were obtained in a mixture of  $\text{NaNO}_3$  with  $\text{Na}_2\text{CO}_3$  electrolyte, mainly because of the  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  ions that promotes the anodic dissolution. The current efficiency at the metal removing by anodic dissolution decreases in all cases with the concentration decreasing. At the metal machining by electrochemical erosion for a proper current efficiency is necessary that the electrolyte solutions to have a concentration between 3-10% and the current intensity to be at high values.

The electrolytic dissociation of the inorganic salts influences the increasing of the dissociation ions in the working space. Negative ions  $\text{NO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{CO}_3^{2-}$  under the influence of the electrical current are migrating towards the processed object (anode) where they are in contact with the metallic ions that results from the anodic dissociation. Because of the chemical reactions that occurs on the anode surface will be obtained a pellicle from inorganic compounds [5] that can present different structures. At the anodic dissolution of steel in the presented electrolytes the structure of the pellicle is different:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{ClO}_3)_3$ .

The main effect of hydrogen releasing is the decreasing of the solution conductivity with a considerable effect on the processed surface. By adding of small quantities of additives ( $\text{Na}_2\text{CO}_3$ ) in the electrolyte solution will increase the metal dissolution from the anode because the electrolyte has a greater conductivity.

The insoluble compounds can achieve an insoluble pellicle on the anode surface therefore to assure the metal erosion, they have to be removed by pumping the electrolyte outside the working space.

In inorganic solutions the anodic dissolution is very important [2] for removing the material, the obtained surface is smooth, with a small roughness.

In conclusion, the inorganic electrolytes applied at the machining by electrochemical machining presents the following advantages:

- because of the electrochemical process of anodic dissolution the obtained surface of the processed object has a small roughness, so there are not necessary some finishing process;
- on the machining tool is not obtained an adherent pellicle.
- the presence of the electric charges in the space between electrodes assures a great rate of the anodic dissolution of the work-piece.
- at the electrochemical machining are applied salt solutions because they are less corrosive than acids and alkaline solutions.

The drawbacks of these electrolytes in the electrochemical machining are:

- the small resistance of the passive pellicle limits the increasing of the electrical current and reduces the precision of machining;
- chemical reactions that takes place during the anodic dissolution generates corrosive compounds that corrodes the machining equipment.
- there are released toxic gases.
- acid and alkaline solution have a corrosive effect on the machining equipment.
- for a continuous processing by electrochemical erosion it is necessary a permanent activation of the electrodes surface by electrolyte pumping.

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