

## INVESTIGATION OF THE GENERAL CORROSION OF COPPER IN HYDROCHLORIC ACID

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**Key words:** copper, hydrochloric acid(HCl), general corrosion, Tafel extrapolation method, potentiostat/galvanostat.

### ABSTRACT

*In this paper were investigated the effect of hydrochloric acid concentration and addition of oxidizing agents on the rate of general corrosion of copper. For comparison, the corrosion rate in distilled water was also tested. Tafel extrapolation method was used for investigation of general corrosion of copper. Tafel extrapolation method implies scanning of working electrode potential on the order of  $\pm 250$  mV in relation to its Open Circuit Potential ( $E_{OCP}$ ), at the speed of  $0.5$  mVs<sup>-1</sup>. Investigations of corrosion were conducted in the corrosion cell according to Standard ASTM G5[5], on instrument potentiostat/galvanostat, Princeton Applied Research, model 263A-2, with the software PowerCORR®. Tests were performed at room temperature,  $20 \pm 1$  °C.*

### 1. INTRODUCTION

Copper is characterized by its high electrical and thermal conductivities and good mechanical workability. The metal has been widely used as a material in pipelines for domestic and industrial water utilities, heat conductors, heat exchangers, in electronic industries, and communications as a conductor in electrical power lines [1]. It is classed with silver and gold as a noble metal and can be found in nature in element form. Copper occurs as two natural isotopes <sup>63</sup>Cu and <sup>65</sup>Cu.

In nature, copper is mainly found in the form of sulfide ores (chalcopyrite-CuFeS<sub>2</sub>, covelin-CuS, chalcocite-Cu<sub>2</sub>S and bornite-Cu<sub>3</sub>FeS<sub>3</sub>), oxide ores (cuprite-Cu<sub>2</sub>O) and carbonate ores (malachite-CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> and azurite-Cu(OH)<sub>2</sub>·2CuCO<sub>3</sub>) [2]. Copper has good corrosion resistance. It is completely dissolved in nitric acid, as well as in mineral acids of oxidizing character, in acidic solutions of chromium salts and in warm concentrated sulfuric acid.

Copper is stable in dilute nitric and sulfuric acid. Copper is stable in aggressive organic acids [2]. Corrosion products have a negative effect on heat transfer, and cause a decrease in the heating efficiency [3].

Generally, copper has high resistance to industrial and marine atmospheres, seawater, alkalis and solvents [4]. However, corrosion of copper may still occur in two circumstances [4]:

1. Pitting corrosion of copper in natural water or less aggressive environments.

- Corrosion of copper in corrosive media such as acid or alkaline solution, or to presence of strong oxidizing reagent and complexing ions.

Copper is so sensitive to chloride ions, and even traces amount of  $\text{Cl}^-$  ions can cause corrosion problem [4]. At low chloride concentrations, the dissolution of copper occurs through formation of  $\text{CuCl}$  that transforms to the soluble  $\text{CuCl}_2^-$  by reacting with excess chloride. While, at high concentrations, cuprous complexes such as  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$  are formed, in addition to the ones with fewer chlorides such as  $\text{CuCl}$  and  $\text{CuCl}_2^-$  [1].

In this paper were investigated the effect of hydrochloric acid (HCl) concentration and addition of oxidizing agents on the rate of general corrosion of copper. For comparison, the corrosion rate in distilled water was also tested.

## 2. EXPERIMENTAL PART

Copper of purity 98,1 % was used for testing. The tests were carried out in the following solutions: 0.1 M HCl; 0.5 M HCl; 1 M HCl; 0.1 M HCl + 0.1 M  $\text{H}_2\text{O}_2$ ; 0.1 M HCl without  $\text{O}_2$  and distilled water. Tafel extrapolation method was used for investigation of general corrosion of copper. Tafel extrapolation method implies scanning of working electrode potential on the order of  $\pm 250$  mV in relation to its Open Circuit Potential ( $E_{\text{OCP}}$ ), at the speed of  $0.5 \text{ mVs}^{-1}$ . Investigations of corrosion were conducted in the corrosion cell according to Standard ASTM G5 [5], on instrument potentiostat/galvanostat, Princeton Applied Research, model 263A-2, with the software PowerCORR®. Tests were performed at room temperature,  $20 \pm 1$  °C.

## 3. RESULTS AND DISCUSSION

Figure 1 and Table 1 shows the effect of concentration of HCl solutions on the rate of general corrosion of copper.

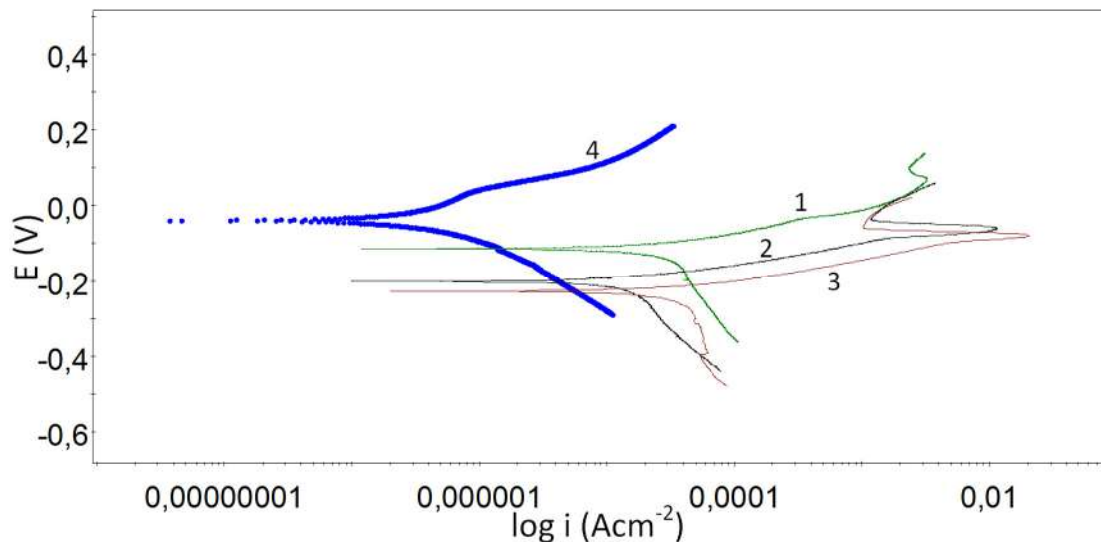


Figure 1. Tafel curves samples of copper

1 – sample treated in 0.1 M HCl; 2 – sample treated in 0.5 M HCl; 3 – sample treated in 1 M HCl; 4 – sample treated in distilled water

Table 1. The values of open circuit potential and corrosion current density of copper samples treated in HCl

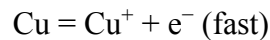
The type of HCl solutions	$E_{\text{ocp}}$ (mV)	Corrosion current density, $i_{\text{cor}}$ ( $\mu\text{Acm}^{-2}$ )
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0.1 M HCl	-114,118	$4,994 \cdot 10^1$
0.5M HCl	-199,160	$1,69 \cdot 10^1$
1 M HCl	-225,623	$5,125 \cdot 10^1$
0.1 M HCl without O <sub>2</sub>	-125,717	$2,126 \cdot 10^1$
0.1 M HCl + 0.1 M H <sub>2</sub> O <sub>2</sub>	28,232	$2,177 \cdot 10^1$
Distilled water	-38,263	$3,778 \cdot 10^{-1}$

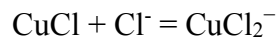
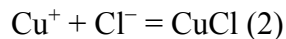
Oxygen removal from solution of 0.1 M HCl (sample 0.1 M HCl without O<sub>2</sub>) was made by blowing the solution with pure argon 20 minutes. The results shown in Figure 1 and Table 1 show that the rate of general corrosion of copper generally increases with increasing HCl concentration. Table 1 shows that with increasing HCl concentration there is an increase in corrosion current density, a key parameter for estimating corrosion rate, except for 0.1 M HCl solution. The fact that the corrosion rate of copper increases with increasing HCl concentration is also evidenced by the move of the open circuit potential to negative values in proportion to the increase in HCl concentration in all three tested samples (Table 1).

For comparison, Figure 1 and Table 1 also show the corrosion rate of copper in distilled water. The corrosion rate of copper is the lowest in distilled water, which was to be expected.

Table 1 shows that the corrosion rate of copper according to both tested parameters (corrosion current density and open circuit potential) is highest in 1 M HCl. At this condition the copper cations go to the solution (Eq. 1) and then react with chloride ions from the solution to form cuprous chloride (Eq. 2) on the copper surface. The formed CuCl does not give enough protection to the copper surface and transforms to the soluble copper chloride complex, CuCl<sub>2</sub><sup>-</sup> as can be seen from (Eq. 3) [1, 6-12].



(1)

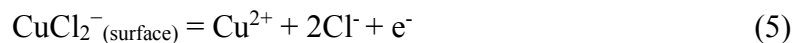


(3)

According to our previous work [1], if this formed CuCl<sub>2</sub><sup>-</sup> is adsorbed on the surface, its dissolution into the solution will go as follows,



The formed CuCl<sub>2</sub><sup>-</sup> might further oxidize to cupric ions according to the reaction;



The rate of corrosion of copper in HCl should increase with the increase in the addition of oxidizing agents, knowing that copper very poorly corrodes in non-oxidizing acids such as HCl. Figure 2 and Table 1 show the results of the influence of the addition of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> oxidizing agents on the corrosion rate of copper in HCl.

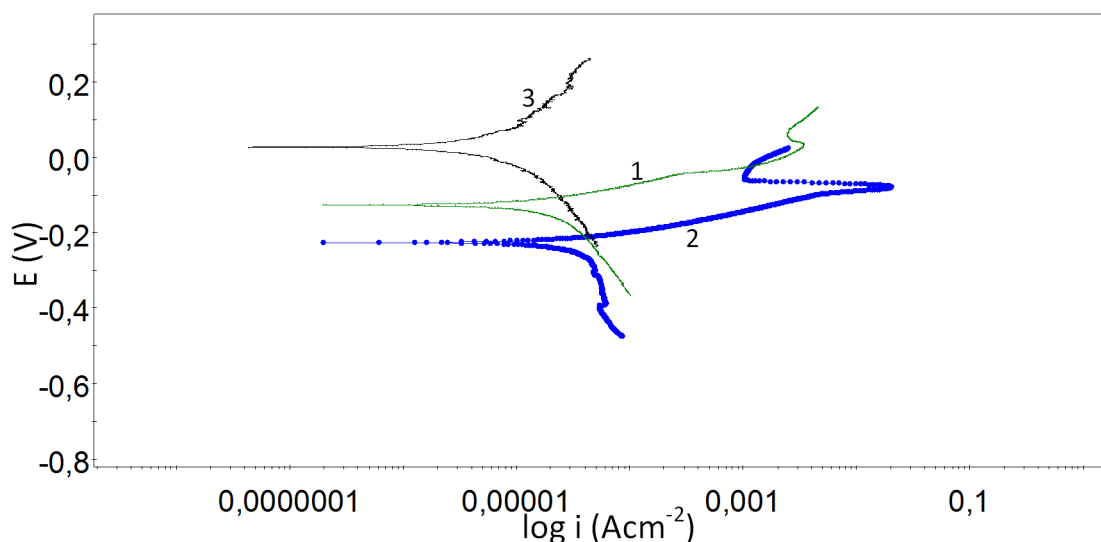


Figure 2. Tafel curves samples of copper

1 – sample treated in 0,1 M HCl without O<sub>2</sub>; 2 – sample treated in 0,1 M HCl with O<sub>2</sub> (sample 0.1 M HCl in table 1); 3 – sample treated in 0.1 M HCl + 0.1 M H<sub>2</sub>O<sub>2</sub>

The results expressed by the corrosion current shown in Figure 2 and in Table 1 show that with the addition of H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> in HCl, the corrosion rate of copper is increased. Copper corrodes poorly in non-oxidizing acids such as HCl because it has a positive reduction potential. This is the reason why the addition of oxidizing agents influence the increase of the corrosion rate of copper in HCl.

#### 4. CONCLUSION

Examining the effect of HCl concentration and the addition of oxidizing agents on the rate of general corrosion of copper, it was found that by increasing the concentration of HCl as well as by adding the oxidizing agents H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>, the corrosion rate of copper was increased. The highest corrosion current density was recorded in 1M HCl and the lowest in distilled water.

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