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# The influence of chloride ions on the *anti*-corrosion ability of binary inhibitor system of 5-methyl-1H-benzotriazole and potassium sorbate in sulfuric acid solution

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ABSTRACT

In this work, the effect of chloride ions on copper corrosion behavior in an acidic sulfate solution, in the presence of binary inhibitor system of azoles and potassium sorbate was studied. Electrochemical measurements, weight loss measurements and surface analysis (SEM/EDS) were used in this investigation. Results of potentiodynamic polarization experiments indicate that azoles and potassium sorbate, in appropriate concentration, act as mixed-type inhibitors. Surface analysis (SEM/EDS) of copper confirmed that the rate of copper dissolution in aggressive medium is reduced as a result of formation of the protective layer on its surface.

## 1. Introduction

Copper has been known to possess excellent thermal and electrical conductivity as well as good mechanical properties [1]. All of these features allow copper to be one of the most used metals in various industries such as microelectronics and electronic industry as well as in heating and cooling devices [2–4]. The corrosion of copper is investigated in different environments such as acidic solutions [5,6], neutral and alkaline solutions [7,8], synthetic sea water [9]. The presence of aggressive ions such as sulfate, chloride, sulfide ions can cause corrosion of copper so it is necessary to protect it in different ways. The dissolution of copper is very rapid in acidic solutions (pH range between 2 and 5) [10].

One of the most used methods for protecting copper is the application of organic compounds as corrosion inhibitors. Previous studies have demonstrated the possibilities of using heterocyclic organic compounds which in their structure contain S, N or O atoms as inhibitors of copper corrosion. Their inhibitory activity is based on the formation of coordinating bond between vacant d orbital of metal and a lone electron pair of the corresponding heterocyclic compounds [11,12]. The formed complexes have a polymeric structure and a protective role, which is reflected in preventing further dissolution of metals. This group consists of azoles and derivatives of azoles [13,14], imidazole and imidazole derivatives [15–18], amino acids [7,19–24], purine and adenine [5,6,25,26]. The efficiency of an organic compound as a corrosion inhibitor depends on its molecular structure as well as the nature of the metal surface. Also, the influence of pH values of solutions and temperature on inhibition ability of organic compounds has been a matter of different studies.

The efficiency of 1H-benzotriazole (BTAH) and its derivatives as the corrosion inhibitor of copper is well known for over 40 years [27–29]. It is known that molecules of BTAH contain N atom which can bind with vacant d orbital of copper [30]. As a consequence, the protective layer is formed on the copper surface which reduces a diffusion of aggressive ions onto metal surface [31].

According to previous studies [32,33], the potassium sorbate can be used as an inhibitor of copper corrosion in neutral and alkaline solutions. The ability of potassium sorbate to protect metal against corrosion is attributed to the carboxylate end group in its molecular structure. The corrosion process is prevented by the formation of hydrophobic protective layer on the metal surface [29]. Also, it was found that the sorbate protective film is more stable compared to BTAH protective layer in alkaline solutions.

Based on previous studies, some researchers believe that the presence of halide ions leads to increased corrosion rate [34], while others [35–37] found that halide ions act synergistically with inhibitors in the form of cations. Generally, it is proposed [38] that in the presence of halide ions, in the aggressive solutions, the adsorption ability of protonated organic compounds increases and the inhibition efficiency also increase. Halide ions are good ligands because they possess small electronegativity ($<3.5$) [39].

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In our previous study [40] it was found that a reduction in the inhibition efficiency MBTAH in acidic sulfate solution is due to the presence of various concentrations of $Cl^-$ ions. This paper examines the influence of $Cl^-$ ions on the corrosion behavior of copper in 0.01 M $H_2SO_4$ in the presence of a binary system inhibitors, MBTAH + potassium sorbate as well as BTAH + potassium sorbate.

## 2. Materials and methods

### 2.1. Electrochemical measurements

The working electrode of copper was prepared as follows: the copper wire was cut and sealed using a cold sealing material based on methyl methacrylate. Its exposed surface area was 0.49 $cm^2$. Before the beginning of each measurement process, copper electrode was polished with alumina (0.3 μm $Al_2O_3$, Buehler USA), washed with distilled water and dried.

For electrochemical testing of the corrosion behavior of copper potentiostat (IVIUM XRE, IVIUM Technologies) was used, with the appropriate software. The system is made up of three electrodes, copper electrode as working, platinum as the auxiliary electrode and standard calomel electrode as the reference electrode.

Electrochemical methods that were used are: open circuit potential (OCP) measurements, linear potentiodynamic polarization and cyclic voltammetry. Linear potentiodynamic polarization was recorded from the open circuit potential to ±0.25 V (vs. SCE), while the cyclic voltammetry was recorded in a wider potential range from −1 V (vs. SCE) to 1 V (vs. SCE). Scan rate was 1 mV/s for linear potentiodynamic measurements and 10 mV/s for cyclic voltammetric measurements.

For the preparation of tested solutions the following compounds were used: sulfuric acid ($H_2SO_4$, Zorka Pharmacy, Sabac, Serbia), hydrochloric acid (HCl, Zorka Pharmacy, Sabac, Serbia), 5-methyl-1H-benzotriazole (Sigma-Aldrich, Japan), 1H-benzotriazole (Sigma-Aldrich, Japan) and potassium sorbate (Sigma-Aldrich, Germany). Hydrochloric acid (37 mass %) was added to 0.01 M $H_2SO_4$ solution in order to obtain 0.05 M $Cl^-$ solution.

### 2.2. Analysis of copper samples surface (SEM-EDS analysis)

The copper surface was examined after exposing the sample to an acidic sulfate solution (0.01 M $H_2SO_4$) and in the presence of MBTAH + potassium sorbate + $5 \cdot 10^{-2}$ M $Cl^-$ for a period of 7 days. The tests were conducted by using a scanning electron microscope Tescan VEGA 3 LM with Oxford EDS X-act 350 Inca system.

### 2.3. Weight loss measurements

The copper specimens of the following dimensions: 20 × 20 × 0.5 mm were used for weight loss measurements. Each coupon was polished with emery paper, rinsed with distilled water and ethanol and weighted. The copper specimens prepared as described were immersed into beakers containing 0.01 M sulfate solution, azoles ($8.4 \cdot 10^{-3}$ M MBTAH, $8.4 \cdot 10^{-3}$ M BTAH) with potassium sorbate (1% *w*/*v*) and with addition of different concentrations of $Cl^-$ ion ($1 \cdot 10^{-4}$–$5 \cdot 10^{-2}$ M). After 7 days, the coupons were removed from the solutions, washed, dried and weighted.

## 3. Results and discussion

### 3.1. The open circuit potential measurements

The open circuit potential (OCP) of copper is measured in 0.01 M $H_2SO_4$ in the presence of different concentration of $Cl^-$ ions as well as in the presence of appropriate inhibitors and $Cl^-$ ions. The obtained results are shown in Fig. 1. As the concentration of $Cl^-$ ion increases, the OCP values in acidic sulfate solution are shifted toward negative values in comparation with the OCP value in bare sulfate solution ($E_{OCP} = -0.03$ V vs. SCE). The similar behavior was observed in earlier investigation by Milic and Antonijevic [41]. This can be explained by the formation of $CuCl^-_{(ads)}$ intermediates on the copper surface which led more negative charges on the electrode surface [42].

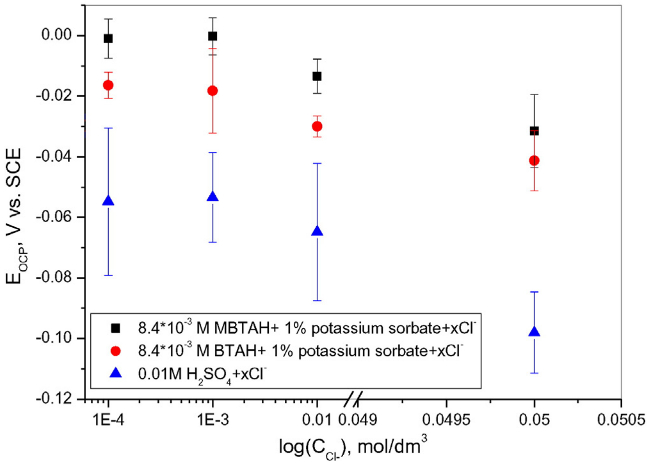

**Fig. 1.** Open circuit potential of copper in 0.01 M $H_2SO_4$ in the presene of different concentrations of $Cl^-$ ions and $8.4 \cdot 10^{-3}$ M MBTAH with 1% potassium sorbate as well as $8.4 \cdot 10^{-3}$ M BTAH with 1% potassium sorbate.

Also, the OCP values of copper are measured in inhibited sulfate solutions in the presence of different concentrations of $Cl^-$ ions. As the concentration of chloride ions is increased, the OCP values are shifted toward negative values indicating the adsorption of $Cl^-$ ions on the surface of the electrode which leads to more negative charge [43].

### 3.2. Cyclic voltammetric measurements of copper

The cyclic voltammograms of copper in an acidic sulfate medium without and with the addition of different concentrations of $Cl^-$ ions are shown in Fig. 2. The obtained CV curve of copper in 0.01 M $H_2SO_4$ indicates that copper undergoes oxidation to $Cu^+$ ions [44]. In the cathodic direction, reduction peak was observed which represents a reduction of generated copper ions. According to the literature [45] copper dissolution in naturally aerated acidic solution can be presented by the reactions (1) and (2):

$$Cu \rightarrow Cu^+ + e^- \tag{1}$$

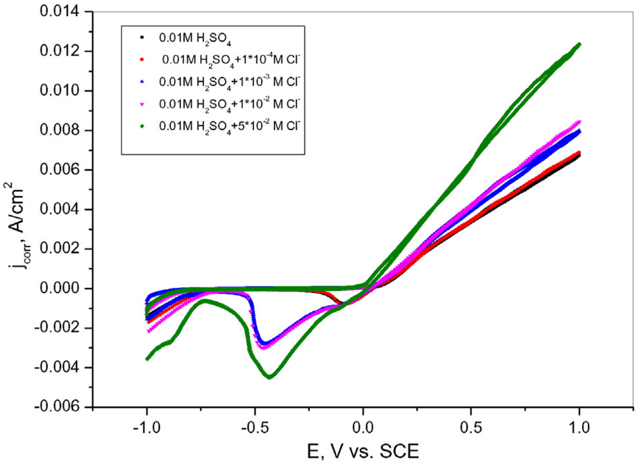

**Fig. 2.** Cyclic voltammetric curves of copper in 0.01 M $H_2SO_4$ solution without and with the addition of different concentrations of $Cl^-$ ions.