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# CYCLIC VOLTAMMETRIC STUDY OF COPPER IN ALKALINE SOLUTION

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The electrochemical reactions of a copper electrode in $Na_2S$ solutions were studied using cyclic voltammetry. Purification of working electrodes is determined by X-ray fluorescence. Also a surface examination and morphological studies were applied using scanning electron microscopy and X-ray diffractometer. There are three anodic peaks and, the cathodic branch also contains three peaks. These peaks correspond to the reduction of copper oxide and copper sulfide formed on the anode branch. These peaks may be corresponding successively to the formation of $Cu_2S$, CuS, $Cu_2O$ respectively. On the other hand are compounds formed by oxidation of the sulfide of metals using ethylenediaminetetraacetic acid.

***Keywords:*** copper, sodium sulfide, oxidation, ethylenediaminetetraacetic acid, cyclic voltammetry, copper oxide, copper sulfide

Copper is the one of the widely consumed metals in the world. It was found that different natural sulfide minerals such as chalcocite ($Cu_2S$), covellite (CuS) can be found in some copper mines, as well as metal sulfides obtained by chemical precipitation in aqueous solution of some acids and alkaline [1].

It is well known that the floatability of sulfide mineral is depressed by excessive oxidation. Former researchers indicate that sodium sulfide ($Na_2S$) would improve the floatability of many minerals. This process called as “sulfidization process” is used mostly in the flotation of oxidized sulfide mineral and oxide minerals. Sodium sulfide has been used to improve the floatability of copper oxide [2, 3] since 1970’s.

Sulfide mineral oxidation arises from the reaction of the species on the mineral surface with water and oxygen and it is inevitable during processing in plant conditions. It is now accepted that in the initial step of sulfide mineral oxidation, metal ions migrate to the surface and dissolve in acidic solutions, leaving behind a sulfur-rich surface; in alkaline conditions, these metal ions hydrolyze and form a layer of metal hydroxide above the sulphur-rich mineral surface. Equations 1 and 2 represent the initial oxidation step of the metal sulfide surface, MS, in acidic pH and in alkaline pH conditions, respectively [4, 5].

$$MS + 2n\,H^+ + n/2O_2 \rightarrow M_{n-1}S + nM^{2+} + nH_2O \quad \text{acidic pH} \quad (1)$$

$$MS + {}^1/_2nO_2 + nH_2O \rightarrow M_{n-1}S + nM(OH)_2 \quad \text{alkaline pH} \quad (2)$$

Bard et al. [6] has suggested some techniques (dissolution by changing the pH, extract by ethylenediaminetetraacetic acid) to remove oxidation products as oxide/hydroxide, sulfate and carbonate, particularly metal hydroxides, from mineral surface [4].

Ethylenediaminetetraacetic acid (EDTA) was used to extract metal oxidation products (e.g., oxide/hydroxide, sulfate and carbonate) from the mineral surface. Therefore, mineral flotation in the absence of collector depends on the type and proportion of surface species formed during the oxidation of that sulfide mineral [7].

The aim of the present work is studying electrochemical characteristics of copper and iron in sodium sulfide ($Na_2S$) using cyclic voltammogarms technique, and effects of EDTA as a complexion agent to extract metal oxidation products from the mineral surfaces, in copper and iron electrode.

## Experimental

A conventional three-electrode system was used for electrochemical measurements in which an Ag/AgCl electrode as reference, platinum as counter electrode and copper/iron electrode as working electrodes were used.

A small piece of copper rod, diameter 0.5 cm and length 2.0 cm was placed in a polyethylene shield. Electrical contact was achieved through a copper wire soldered to the end of the electrode not exposed to the solution. Before being used, the electrode surface was cleaned by mechanical and chemical methods as was polished with different grade emery papers until it appeared free of scratches and other defects. Then, it was rinsed with acetone and finally washed with twice distilled water.

Cyclic voltammograms (CVs), potentiostatic and galvanostatic polarization techniques performed using $\mu_{\text{стат}}$ 400 that was connected to the computer with the Drop view 2.0 software by USB. This is a computer controlled electrochemical measurement system. It consists of data-acquisition system and a potentiostat/galvanostat. CV was used to study the corrosion of copper in sodium sulfide solutions ($Na_2S$) sweeping from 1.8 to 0.8 V. All measurements were taken at 25 ± 1C [8-10].

Scanning electron microscopy of the type scanning electron microscopy (SEM) track mini and X-ray diffractometr type of the MAXima x-ray diffractometer were used to study of oxidation products are formed from copper electrode in sodium sulfide solution.

## Result and discussion

Firstly, solutions with various concentrations were prepared by chemical purification sodium sulfide in order to determine the electrochemical behavior of copper and iron electrodes in sodium sulfide solution, and most suitable concentration of sodium sulfide was determined to become 0.8 M (Fig. 1). Therefore 0.8 M sodium sulfide solution was utilized in further experimental. All measurements were taken at

25±1ºC and the corrosion of copper and iron were studied with and without EDTA in 0.8 M sodium sulfide solution between -1.8 and 0.8 V.

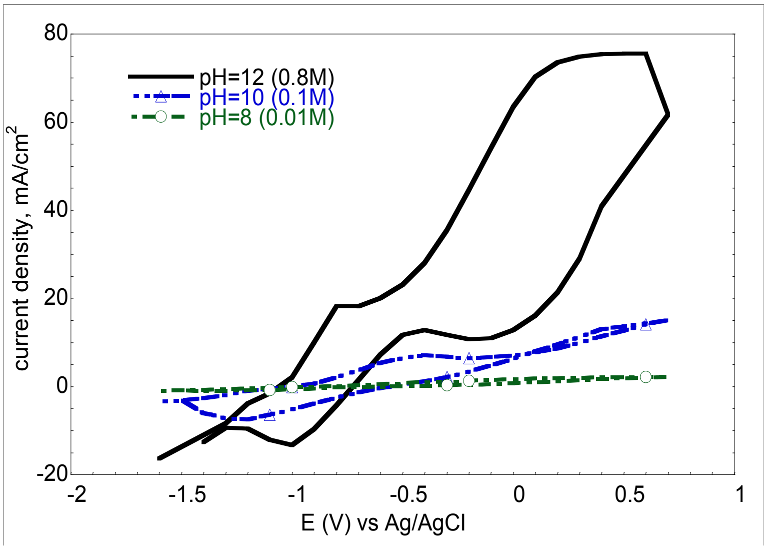

Fig. 1. Voltammograms of copper (left-scan rate 10 mV/s) electrode in different concentration of $Na_2S$ solution.

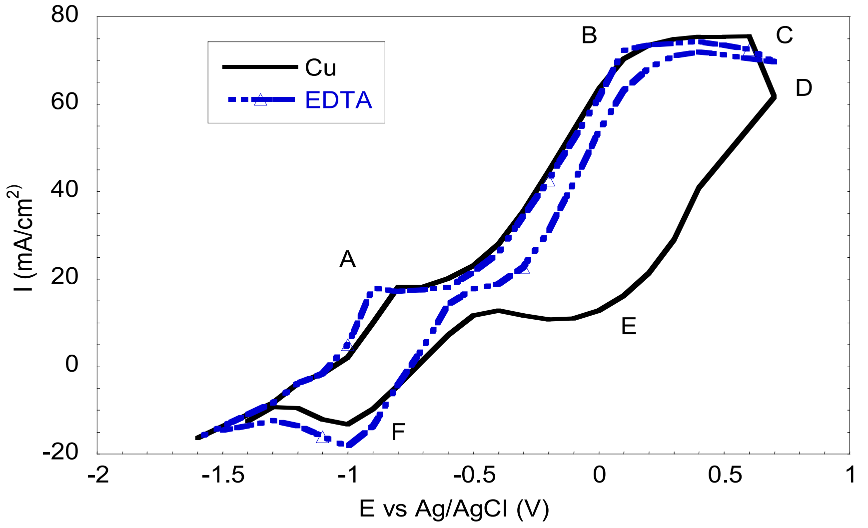

Fig. 2. Voltammograms of copper with and without EDTA in 0.8 M sodium sulfide solution.

***Voltammogram of copper.*** Voltammograms of copper electrode taken with and without EDTA in 0.8 M sodium sulfide solution are given Fig. 2.

Three peaks (A-C) were observed the anodic branch of voltammograms and three peaks in the cathodic branch (D-F).

The initial peak A in the anodic branch appears at about -0.8 V and that is supported by two electron transfer reaction. There seems to be a general agreement between different authors that when copper electrodes comes in contact with sulfide ions in solution, the corrosion product, developing spontaneously is mostly cuprous sulfide ($\Delta G = -86.2$ KJ) which thickens on anodic polarization.

This process can be looked upon as occurring through the ionization of Cu metal followed by a combination of cuprous ions and sulfide with the precipitation of a porous black-scale of cuprous sulfide on the surface [11].

$2Cu = 2Cu^{2+} + 2e$ (3)

$2Cu^{+} + S^{2-} = Cu_2S$ (4)

$2Cu + S^{2-} = Cu_2S + 2e$ (5)

The second anodic peak B appears at nearly 0.1 V. This peak is through to correspond to the partial transformation of the thick corrosion product $Cu_2S$, formed under peak A to copper monosulfide as CuS:

$Cu_2S + S^{2-} = 2CuS$ (6)

Some CuS might be also formed by the direct combination between $Cu^{2+}$ ions and sulfide ions that could block some pores in the sulfide-type film:

$Cu + S^{2-} = CuS + 2e$ (7)

The third anodic peak (C) at about 0.5 V, correspond to the thick cuprous sulfide scale is transformed to copper oxide, elemental sulfur is produced. Nevertheless, the electronic and ionic conduction of the growing film decease because of the low $S^{2-}$ ion content:

$CuS + OH^{-} = Cu_2O + 2S+H^{+}+2e$ (8)

However the three cathodic peaks (D–F) and (D) could be attributed to the successive reduction of the copper oxide layer giving eventually metallic copper. On the other hand, the two cathodic peaks (E) and (F) could be attributed to the reduction of copper sulfide.

The electrochemical behavior of copper how it effects of EDTA, was illustrated in 0.8 M sodium sulfide solution. There were no changes in the CuS type compounds which anodic branch voltammogram. This result showed that EDTA, which complexing agent did not affect sulfide-type film, however, it was extracted and removed of copper oxide from metal surfaces.

***Surface and structural analysis.*** In the result of electrochemistry experimental, insoluble films were formed on the surface of copper and iron electrode. These surfaces examinations and morphological studies were applied using scanning electron microscopy (SEM) and X-ray diffractometer.

Size of copper electrode film was from 1.65 μм to 11.94 μм and size of the iron electrode film was from 1.00 μм to 14.50 μм was shown in Fig. 3.

Also structure of these surfaces was analyzed by X-ray diffractometer (Fig. 4).

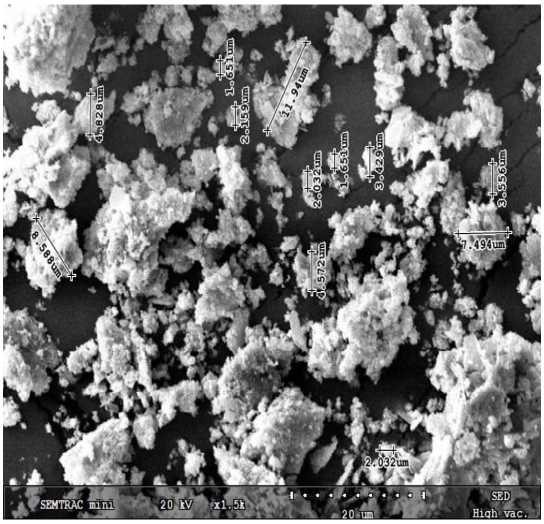

Fig. 3. Scanning electron photomicrographs of copper electrode surface in 0.8 M sodium sulfide

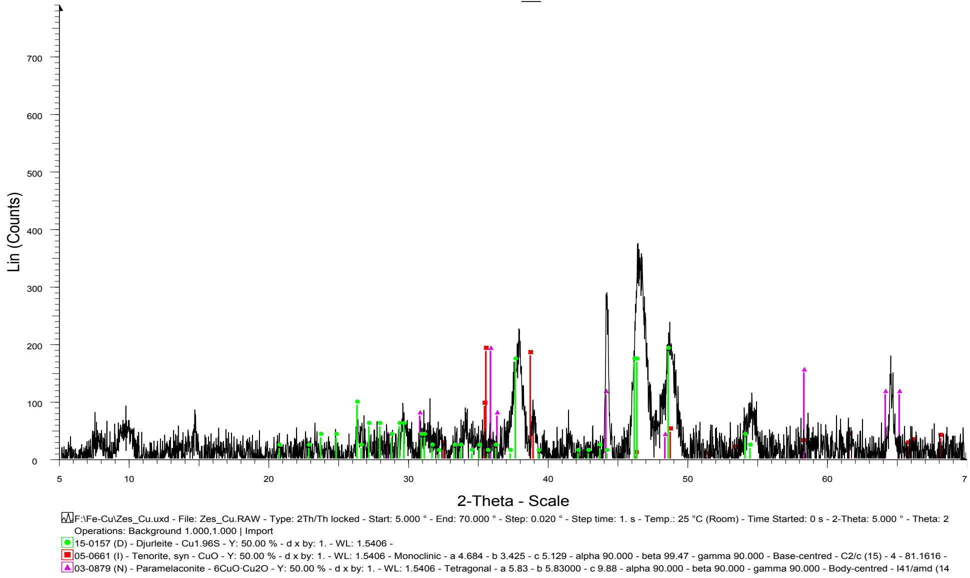

Fig. 4. Roentgenogram of oxidation products on the copper electrode.

## Conclusion

We have studied electrochemical activity of copper electrode in the 0,8M sodium sulfide solution by cyclic voltammograms technique. The result showed that outside of copper electrode, surface formed insoluble film. It was determined that oxides of copper and iron, which had been formed on copper and iron electrode surface could be removed by EDTA.

By the XRD analyze identified that the copper surface was formed $Cu_{1.96}S$, cupric oxide, CuO, paramelaconite $6CuO \cdot Cu_2O$.

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# ЦИКЛИЧЕСКОЕ ВОЛЬТАМПЕРОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ МЕДИ В ЩЕЛОЧНЫХ РАСТВОРАХ

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С помощью метода циклической вольтамперометрии было изучено влияние реагенга этилендиаминтетрауксусная кислота на электрохимическое поведение медных электродов в растворе сульфида натрия. Для выяснения природы слоя который образуется на поверхности металлов, в результате гидролиза, были использованы методы рентгенографии и сканирующей электронной микроскопии На вольтамперной кривой измеренной на медных электродах имеются три анодных и катодных пика, которые соответствуют $Cu_2S$, $CuS$ и $Cu_2O$. Эти пики показывают уменьшение окиси меди и сульфида меди, сформированных на аноде. Пики показывают соответствующие последовательное образование $Cu_2S$, $Си_2O$, соответственно. С другой стороны соединения образуются путем окисления сульфида металла и с помощью этилендиаминтетрауксусной кислоты.

*Ключевые слова:* медь; сульфид натрия; окисление; этилендиаминтетрауксусная кислота; циклическая вольтамперометрия; оксид меди; сульфид меди.