The Influence of Different Parameters on the Electro Refining of Copper

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Abstract—**The experiments were performed using the acidic electrolyte composed of copper sulphate and sulphuric acid. The electro refining process was carried out at the temperatures of 40, 50, and 65^{0}C. On the basis of the experiments performed it was stated that the temperature of the electrolyte has significant influence on the copper consumption as well as the topography of copper deposited on the cathode. The influence of the temperature was explained by the increase in copper sulphate solubility and acceleration of the ions diffusion in the adjacent to the electrodes layer, which in consequence lead to the decrease in the resistances of Cu^{2+} ions deposition.**

It was also stated that increase in the current density beside the increase in the production rate causes the decrease in the current efficiency. The addition of gelatin to an electrolyte causes the smoothing the cathode deposit but increase in power consumption consequence of the increasing the resistances of Cu^{2+} ions deposition and as a result of it the increase in the cell voltage. The topography of the cathode deposit was observed using a metallurgical microscope. It was concluded that the optimum conditions for copper electro refining are: the consumption of the electrolyte- 50 kg Cu/m^3, 200 kg H$_2$SO$_4$/m^3 and gelatin-10 ppm, the temperature - 65^{0}C, current density-250A/m^2.

Index Terms: **Electro-refining, Current density, Temperature, Electrolyte, Copper.**

I.   INTRODUCTION

Copper is present in the earth's crust mainly in the form of sulphide minerals such as chalcopyrite (Cu Fe S$_2$) ,bornite (Cu$_5$FeS$_4$) and chalcocite (Cu$_2$S).The concentration of these minerals in an ore body is low and typical copper ores contain from 0% to 1or 2% Cu.

Copper also occurs in the form of oxidized minerals, (Carbonates, oxides, silicates, Sulphates) but to a much lesser extend, Ores containing these minerals are almost always treated by hydrometallurgical methods [1]. The efficiency of electro-refining of copper and the degree of its purity depend on many factors such as, the composition of electrolyte composed of copper sulphate, sulphuric acid, and some organic compounds, temperature of electrolyte and current density [1].

The last step of copper production is electrolytic deposition of high purity copper (99.9%) in the form of cathodes[1].

Electro-refining consists of electro-chemically dissolving copper from impure anodes and selectively plating the dissolved copper in pure form onto copper cathodes [2].

In ancient times, copper was available in nature as a free element. Today these natural deposits are more difficult to find , and copper is now extracted from ores that are mostly sulfides, such as chalcopyrite. The ore is crushed , concentrated by flotation and then smelted. The resulting copper is called blister copper, which is about 95% pure. Electrolysis is used to obtain higher purity levels suitable for commercial use [3].

The dry copper concentrate , containing as much as one- third copper , is traditionally smelted and refined. This process is known as pyrometallurgy , because heat is used to refine the metal. For applications such as electrical conductors, the copper is further refined electrolytically to a purity of at least 99.95% . A more recent technique for processing copper is hydrometallurgy, a process involving chemical and electrolytic reactions [4, 5].

Gelatin influences the polarization comes, the deposit morphology, the crystal structure, and the copper grain type. Addition of gelatin increases cathodic polarization but does not always lead to nodules formation [6].

This work aimed to determine the best conditions for electro-refining of copper taking into account the composition of electrolyte, the current density, and the temperature.

II. EXPERIMENTAL PART

A. Electrical Equipments

As a source of direct current, the selenic rectifier was used. This rectifier was separated from the 220 V power grid by means of transformer supplied by variable autotransformer allowed to change the voltage of DC current. Both the current intensity in the circuit of electrolyser and voltage between the cathode and anode were measured and registered by means of a pen-recorder.

The electrolysis was performed in a vessel of 400 cm^3 in volume filled with the electrolyte into which the anode and the cathode were immersed.

B. Preparation of the Electrolyte

The electrolysis was prepared using a high purity of copper sulphate and sulphuric acid. These components were dissolved in distilled water. As an organic additive, gelatin was used. It was also dissolved in distilled water and dosed to the electrolyte in the form of solution.

C. Procedure of Electro-refining

The experiments consisted in electro-refining of crude copper using different compositions of electrolyte and temperatures. All experiments were carried out by means of the laboratory set-up. Each experiment comprised measuring the amount of copper deposited according to the current density and the temperature of the electrolyte. The started sheets for copper deposition were 0.2 mm + 99.99% copper sheets of the area of 60 cm^3 and these sheets before using were cleaned chemically with 10% hydrochloric acid and rinsed with distilled water. The weight of these cathodes before and after electrolysis was measured. The time of each experiment was two hours. The results obtained are presented in Figure 1 to Figure 6.

D. Investigation of the Topography of the Cathode deposit

According to the conditions of electro deposition of copper, the surface of the deposit had different structures. The differences in this structure consisted in differences in the size of deposited copper crystals. The topography of the deposited copper was investigated by means of the Richard's metallographic microscope using the objective Epi 8/0.15.The surfaces of the chosen deposit were photographed and the prints are presented in Figure 7 to Figure 17.

III. RRESUTS AND DISCUSSION

As shown in Figures 1 to 6, the power consumption of electro refining process depend strongly on the current density and the temperature of the electrolyte. however, the power consumption increases more than the current density for typical conditions of electro refining process (Figure 6). A 4 times increases in the current density

causes a 4.4 times augmentation of the power consumption nearly 4.4 times. In the case of the lower temperature of electrolyte (Figure 4), the same increase in current density causes an increase in the power consumption as far as 5.4 times. This fact can be explained by increasing in the anode passivation.

This passivation consists in the fact that rapid dissolution of copper at high current densities leads to an excessive concentration of power adjacent to the anode surface and to the precipitation of a solid $CuSo_4. 5H_2O$ layer on the anode. This copper sulphate film inhibits further dissolution of the anode, the voltage between the electrodes must be increased and it leads to increase the power consumption. In this case , because of the higher cell voltage, oxygen and hydrogen can be produced as a result of water electrolysis which causes the decrease in current efficiency. Besides the current density, the temperature has also significant influence on the power consumption during the copper electro refining process. If one compare the data presented in Figure 1 to Figure 6 it can be clearly seen that the decrease in temperature (for the same current density) also leads to the increasing in power consumption both for low and high current densities.

The electrolysis process consists of three main stages:

a) Electrochemical dissolving of copper from the anode into the solution.
b) The migration by diffusion and convection of Cu^{2+} cations in the solution to the negative electrode.
c) The depositions of Cu on the cathode as a result of the reaction:

$$Cu^{2+} + 2e^- \longrightarrow Cu^0$$
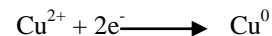
It must be noted here that, the Cu^{2+} ions can pass through the adjacent to electrode layer by diffusion only, so all the factors affecting the diffusion process will also affect the migration of Cu^{2+} ions in the electrolyte and in consequently affect the rate of copper deposition. The diffusion process is strongly affected by the temperature (the higher temperature the higher rate of diffusion). Thereby an increase in temperature of electrolyte causes an decrease in resistance of ions which leads to decrease of cell voltage and the power consumption as shown in Figure 1 to Figure 6.
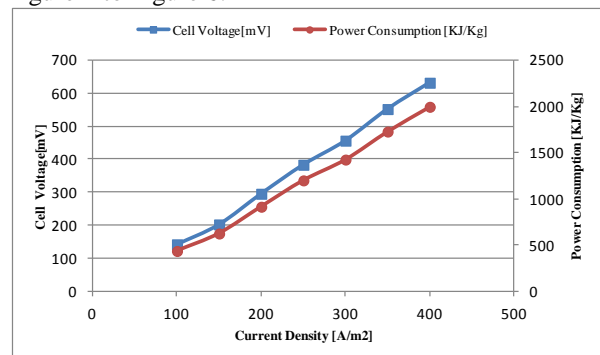
Figure 1. Efficiency of Electrolyte Refining of Copper. (electrolyte - 50 kg Cu/m^3, 200 kg H$_2$SO$_4$/m^3 , T= 40^{0}C).

Figure 2. Efficiency of Electrolyte refining of Copper. (Electrolyte - 50 kg Cu/m^3, 200 kg H$_2$SO$_4$/m^3 , T= 50^{0}C).
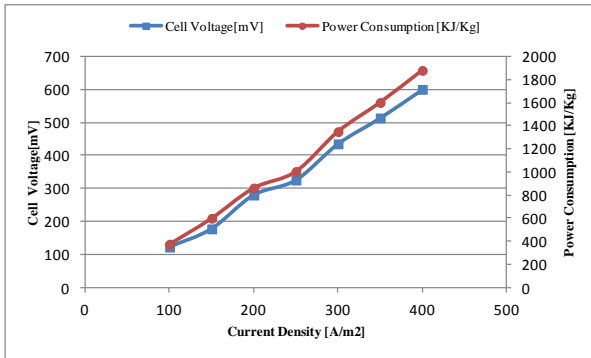

Figure 3. Efficiency of Electrolyte Refining of Copper. (Electrolyte - 50 kg Cu/m3, 200 kg H2SO4/m3 , T= 650C).
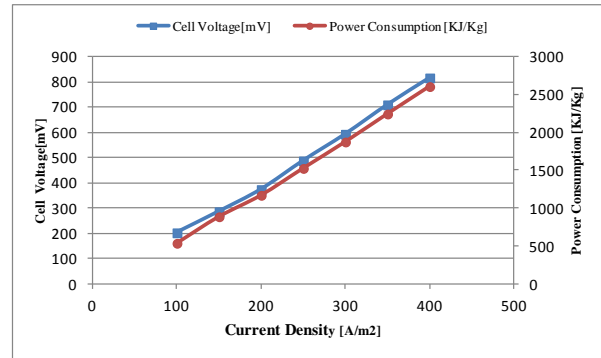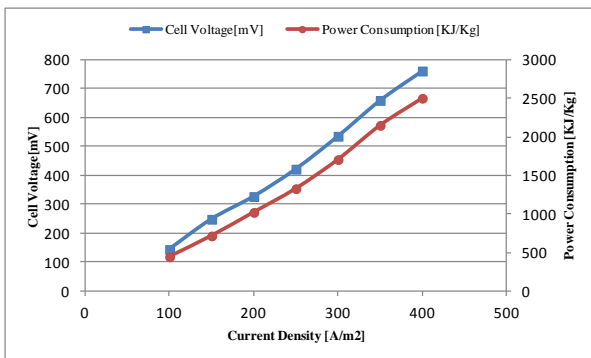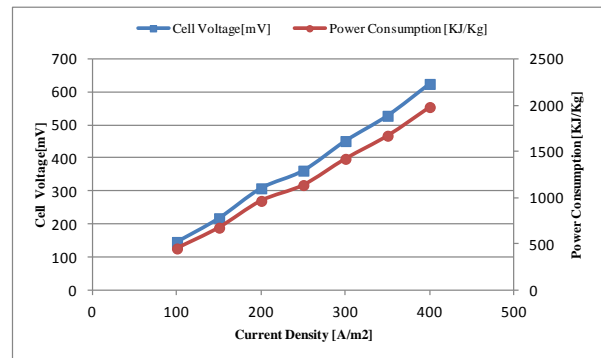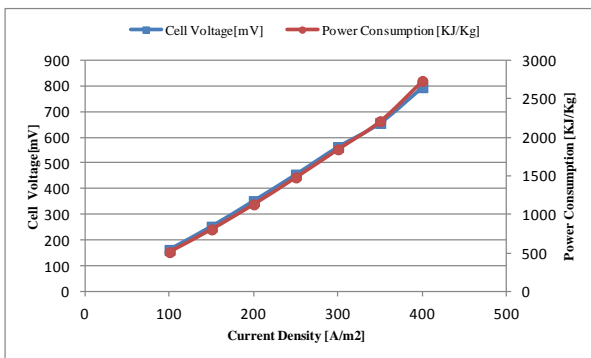

Figure 4. Efficiency of Electrolyte refining of Copper. (Electrolyte - 50 kg Cu/m^3, 200 kg H$_2$SO$_4$/m^3 , T= 40^{0}C, gelatin- 10ppm).

Figure 5. Efficiency of Electrolyte Refining of Copper. (Electrolyte - 60 kg Cu/m^3, 100 kg H$_2$SO$_4$/m^3 , T= 40^{0}C).

Figure 6. Efficiency of Electrolyte refining of Copper. (Electrolyte - 50 kg Cu/m^3, 200 kg H$_2$SO$_4$/m^3 , T= 65^{0}C, gelatin- 10ppm).

The structure of cathode deposit which can be seen from a topography of the surface of this deposit, strongly depends on the conditions of electrode deposition. In this study the effects of current density, temperature of the electrolyte and gelatin content were investigated, it can be seen from Figure 7 to Figure 17 that the surface of deposited copper has coarse crystal structure when low temperature and high current density were applied. For the same current density the increase in temperature of the electrolyte leads to deposition of finer crystals of copper. Similarly for the same temperature of the electrolyte a lower current density gives finer crystals of copper.

It must be noted here, that the higher roughness and sponginess of the cathode deposit the more impurities are occluded on the cathode and purity of the deposit is deteriorated. The addition of some organic additives (gelatin is used) causes the deposition of smaller copper crystals that leads to the formation of denser and non-porous cathode deposit, thereby, the occlusion of impurities by the cathode is decreased and the purity of deposit increases. The action of the gelatin in smoothing the cathode deposit is due to its adsorption on the surfaces of the newly forming of copper grains. Therefore, any copper grains which is tending to grow out excessively from the cathode adsorbs a non-conductive film of gelatin.

This renders the protruding grains less conductive than reminder of the cathode surface and its growth is thereby

hindered. The result is a smoother and harder deposit of improved purity.

Figure 7 . The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density – 400 A/m^2, Temp. – 40^{0}C.

Figure 8 . The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density – 400 A/m^2, Temp. –50^{0}C.

Figure 9.The Surface of Deposited Copper. /Objective Epi 8/0.1./, Current Density – 400 A/m^2, Temp. – 65^{0}C.

Figure 10. The surface of deposited copper. /Objective Epi 8/0.15/, Current density – 400 A/m^2, Temp. – 40^{0}C. gelatin – 10 ppm.
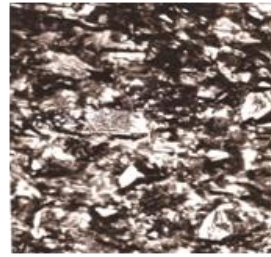

Figure 11 . The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density – 400 A/m^2, Temp. – 65^{0}C. gelatin – 10 ppm.
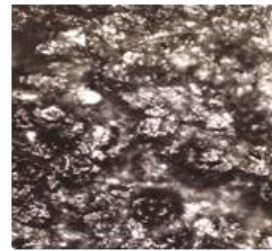

Figure 12 . The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density –100 A/m^2, Temp. – 40^{0}C.
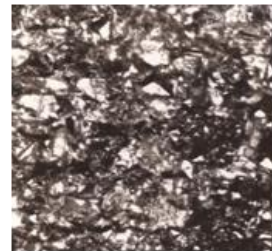

Figure 13 . The Surface of Deposited Copper./Objective Epi 8/0.15/, Current Density –100 A/m^2, Temp. –50^{0}C.
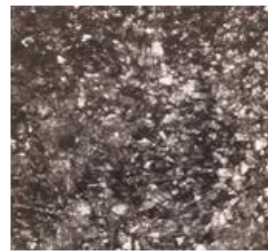

Figure 14 . The surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density –100 A/m^2, Temp. – 65^{0}C.

Figure 15. The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density –100 A/m^2, Temp. – 40^{0}C. gelatin – 10 ppm.
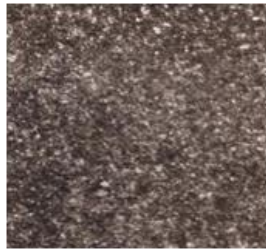

Figure 16. The Surface of Deposited Copper. /Objective Epi 8/0.15/, Current Density –100 A/m^2, Temp. –65^{0}C. gelatin – 10 ppm.

Figure 17. The Surface of Electrochemically Dissolved Copper Objective Epi 8/0.15/, (Anode).

IV.   CONCLUSIONS

The following points can be concluded:

1. The temperature of electrolyte has significant influence on the power consumption during electrolysis. The higher temperature leads to the lower power consumption.
2. The temperature affects the structure of copper deposited. The higher temperature leads to the smaller size of crystals of copper deposit.
3. The current density affects the size of crystals of copper deposited. The higher current density leads to coarser crystal-line and the more nodular deposit.

4. The current density influences the power consumption in electro refining of copper. higher current density leads to the higher power consumption and the lower current efficiency.
5. The addition of gelatin to electrolyte improves the copper deposit which makes it smoother and denser that prevents its contamination.
6. The addition of gelatin increases the power consumption but this is outweighed by purity of copper deposited.
7. The best conditions for electro refining rate: - 50 kg Cu+/m3, 200 kg H2SO4/m3 and gelatin-10ppm, the temperature-650C, current density-250 A/m2.

REFERENCES

[1] A.K. Biswas, and W. G. Davenport, *Extractive   Metallurgy of Copper*, 2nd ed, Pergamon Press, 1980.
[2] I. Park, S. hyung, and Y. K, Sung*, Electrolytic* refining for Copper, Humsok Hakhoe Chi, 1975,pp .444- 453
[3]M.P.   Groover,   *Fundamental   of   modern Manufacturing , Materials, Processes, and   Systems*, 2nd ed, John Wiley & Sons, Inc, 1999.
[4]S.   Kalpakjian   and   S.R.   Schmid,   *Manufacturing Engineering and Technology*, 4th ed., USA, Prentice-   Hall, ,Inc, 2001.
[5]M. E. El-Dahshan*, Fundamentals of Extractive Metallurgy*, King Abdulaziz University,1996.
[6]B.   Veilleux,   Am   Lafront,   E.   Ghali,   Pr.Roberge, "Influence of Gelatin on Deposit Morphology During   Copper Electrorefining Using Scaled Industrial Cells"   *Journal of Applied Electrochemistry*, 2002.

BIOGRAPHIES

Musbah Kharis received the PhD in Industrial Engineering and Technology from Huddersfield University, Uk, in 2015. He graduated in 1988 with a BSc Degree in Metallurgical Engineering from the Tripoli University, Libya and attained an MSc in Production and Quality Control from the Industrial Technical College, Misurata, Libya in 2002. He worked as a Supervisor in Libyan iron and steel company between 1989 and 2005 with responsibility for quality and product conformance after which he worked as a Lecturer from 2006 to 2008 at the Faculty of Engineering in the University of Misurata,. Currently he is head of Department of Materials Science and Engineering at the Faculty of Engineering in the University of Misurata. He has presented many papers in national and international conferences and he has a paper published in the Journal of Quality and Reliability Management. His current research interests include production of iron and steel, metal shaping, quality control, ISO 9000 standards, cement industry, welding metallurgy.