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Purification of Copper Metal in Series Cells and Ways to Increase Efficiency

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Abstract: *Copper is the name of a periodic table element with the chemical symbol Cu.Copper is naturally occurring in pure copper, sulfide or oxide forms, most commonly found in sulfide minerals. In the present study examined the electric purification of copper. This method used series cells for the purification of copper. Faraday's first law describes the major electrochemical reaction during the electrolysis process. Since pure copper does not have the capability to be used in various industries, it will be refined. Copper metal treatment is done in two ways thermal and electric, which electrical treatment after copper thermal .In addition, energy losses during reactions have been investigated and their most important sources have been addressed. The electrical potential required for the purification operation obtained by the Nernst Law is described. During the purification processes, the impurity values are divided into two types of electronegative and electropositive which are fully described. The electrolyte flow cycle, which involves the electrolyte purification process in both crystallization and electrical methods, is described. Finally, suggestions for reducing energy loss during the mentioned processes are presented. In this paper, we have tried to identify copper impurities in the electrolyte and provide effective methods for reducing these impurities in the produced copper.*

Keywords: *Electrode, Electrolysis Cell, Anode, Cathode, Electrolyte, Electrical Refinement.*

INTRODUCTION

Copper uses can be classified, for example, into electrical, electronics and communications, construction, transportation, industrial machinery and equipment, and consumer and general products (Forsén, et al., 2017).

Electrical applications being the largest consumer of copper generates huge amount of scrap amenable to recycling (Randhawa, et al., 2016).

Pure copper, in the form of natural copper, is rarely found and it constitutes about 1% of all copper compounds (Pietrzyk & Tora, 2018).

Based on the results obtained from Sarcheshmeh Copper Company, the copper resulting from thermal refinement does not possess the purity required for electrical purposes and it has to be subjected to electrical refinement to overcome such a problem. The substantial impurities of copper are silver, gold, iron, zinc, lead, arsenic, sulfur and so forth.

In summary, the goals of electrorefining of copper are the followings:

1) Reducing the impurities of copper and increasing the degree of its purity
2) Retrieval of the more precious metals like gold and silver
3) Improvement of the copper’s conductivity when used in cables, generators, transformers and other electrical and electromagnetic devices

Electrical refinement of copper is the process within which copper is subjected to electrolysis inside a cell; the cathode segment of this cell is pure copper and the anode segment is impure copper (along with other metals). The most important electrochemical reaction that occurs in the course of copper electrolysis follows Faraday's first law.

During electrolyzing the copper and occurrence of the main reactions in anode and cathode, a number of unwanted reactions also take place in the cell that cause the considerable wastage of energy. Accordingly, the future and even the present copper industry needs to develop simulation and optimization instruments and application of effective methods for reducing these losses.

In the copper electrorefining process, copper is dissolved from impure copper anodes into the electrolyte bath and then subsequently deposited on to cathodes as high-purity copper (Kalliomäki, et al., 2016).

The energy required for electrorefinement of copper is supplied by the electrical currents and the cathode and anode's required potential during electrolysis can be calculated based on Nernst Law.

The amount of the impurities and their permissible limits in electrolyte are amongst the important considerations of the refinement process because the copper deposited in cathode should be completely pure; thus, the work conditions should be arranged so that the concentrations of impurities do not exceed a certain limit and they can be prevented from deposition on cathode.

The electrical refinement of copper is a process within which the electrolyte solution circulates in electrolysis ponds. Electrolytic solution undergoes changes in the course of work and it has to be subsequently subjected to certain purification actions for overcoming such a problem.

The present research utilized observational and laboratory methods and took advantage of the book "copper, the alchemical book" to investigate the electrical refinement of copper through electrolytic cells; in the end, suggestions have been presented for reducing energy wastes of the process as well as for increasing the copper production output.

Electrical Refinement:

In the present study, electrorefinement of copper using serial cells in Sarcheshmeh Copper Company's Refinery has been investigated in such a way that electrode pairs have been serially embedded in them and received the electrical currents but the potential difference is divided between them, hence only the first and the last electrodes are connected to the power source.

Each of the ponds contains 100-150 electrodes. The potential difference of the ponds ranges between 20V and 35V and the current intensity is from 80A to 500A.

The notable point regarding the serial connection of the anodes and cathodes is that each anode works as a cathode for the next electrode. In other words, each electrode works as a cathode in one level and as anode in the next level as shown in Figure (1).

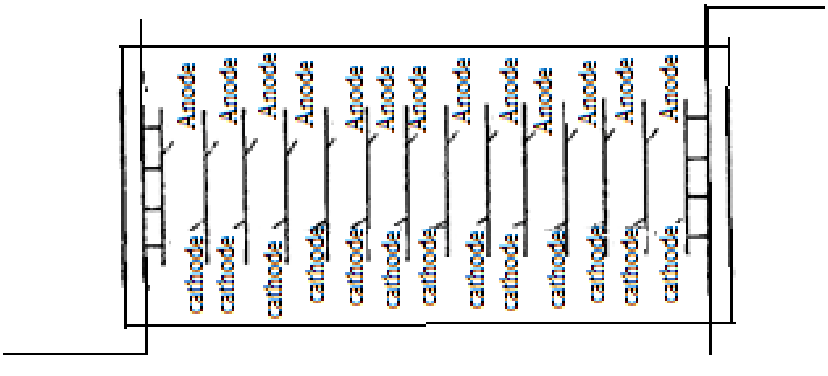

Figure 1. The serial anodic and cathodic system in electrolysis cell

The main electrochemical reaction occurs during electrolysis as shown in relation (1):

$$\mathbf{Cu^{\circ} \rightarrow Cu^{++} + 2e} \qquad (1)$$

During this reaction, the copper ion resulting from anode moves towards cathode and loses its negative electical charge and is deposited in the form of metal copper in cathode.

The reactions related to cathode and anode work as shown in the following relation[1]:

$$\boldsymbol{M} = \mathbf{KIt} \qquad (2)$$

Where, M is the mass of the deposited materials, I is the current intensity, t is the time and K is the proportionality constant[2] that is approximately equal to 1.9180mg for copper.

Using Faraday's first law, the mass of the deposited matter can be obtained based on the electrolysis time, the current flowing into the cells and the proportionality constant.

Energy Wastages:

Energy losses during electrolysis stem from several completely different sources. The followings are the most important of such wastages.

1) **Mechanical Loss:**

Mechanical losses come about due to the non-adhesion of the negative copper ions following neutralization to the cathode as a result of which an amount of copper that has used some energy in the prior processes does not deposit on the cathode in the last stage or is separated after deposition and this causes the wastage of a part of the energy.

2) **Electrochemical Losses:**

All of the reactions that consume electrone lead to the reduction in current's output. For example, as shown in relation (3), bivalent iron has been oxidized in anode and it is subseuently trasformed to trivalent iron which is again converted to bivalent iron in cathode.

$$Fe^{++} \rightarrow Fe^{+++} + e \rightarrow Fe^{+++} + e \rightarrow Fe^{++}$$

Anode Cathode

(3)

This set of processes consume electrone and account for part of the energy losses.

3) **Losses Resulting from Secondary Reactions:**

When a number of charged copper ions enter a combination with cathodic copper, they are transformed into univalent copper ions as shown in relation (4).

$$Cu^{++} + Cu \rightarrow 2Cu^{+} \qquad (4)$$

Therefore, an amount of copper that had received energy in the previous processes deposits on the cathode and turns to an aqueous solution and the univalent copper ions are oxidized by water as shown in the following relation:

$$2Cu^{+} + H_2o \rightarrow Cu_2o + 2H^{+} \qquad (5)$$

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[1] Faraday's first law

[2] The amount of copper mass released by one coulomb of charge

The formed copper oxide is deposited in cathode and causes the entry of an amount of oxygen into cathode, as a result of which the impurities are increased or entered to the sludge remover compartment (clarifier) of the electrolysis machine (figure 2) and increased the copper wastage.

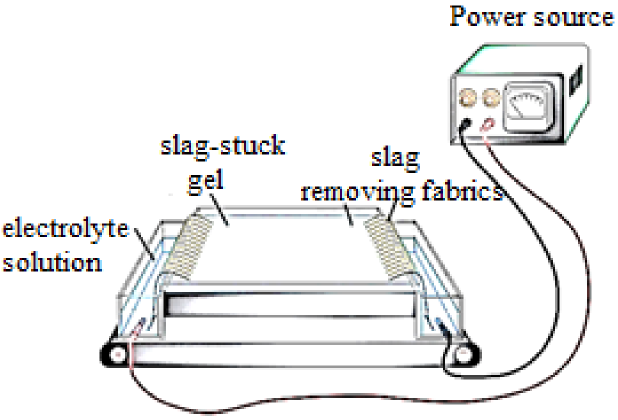

Figure 2. Electrolysis machine's sludge remover

The potential Required for Electrolysis:

The potential required for electrolysis is as shown below:

$$U = e_{anode} - e_{cathode} + e_{pol}anode + e_{pol}cathode + IR_{1+}IR_2$$

Anode and cathode's potentials can be calculated according to the following formula based on Nernst Law:

$$e_{cathode\,/\,anode} = e_{\circ} - \frac{RT}{ZF}\log a_{cu} + + \qquad (6)$$

As for the copper electrode cell, since both of the cathode and anode are made of copper (anode with impurities), the potential difference between anode and cathode is resultantly $e_{anode} - e_{cathode}$ with the nearly zero normal current.

In the above relation, U is the general voltage in V, e_{pol}[3] is the polarization electrode, IR_1[4] is the potential difference in the electrodes and connection and IR_2[5] is the potential difference in the electrolute.

We also have:

$$e_{pol}anode = 0 - 0/1 \text{ volts}$$

$$e_{pol}\text{cathode} = 0/04 - \frac{0}{08}\text{volts}$$

Therefore, the potential required for electrolysis includes the sum of the aforementioned potentials which is in a range from 0.20 to 0.25 volts. In practice, the main factor determining this potential difference is the electrolytic impedance between the two electrodes.

The Impurities Existent along with Copper in Electrolyte:

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[3] Potential difference in action and ideal state

[4] About 0.04-0.08V

[5] About 0.11-0.13V

The impurities accompanying copper can be divided into two general electronegative and electropositive sets.

1) **Electronegative impurities:**

This set of impurities are Sb, As, Bi, Fe, NiCo, Mn, Cd and Zn that, as summarized in Table (1), featuring a lower potential than copper hence they are more likely to dissolve in the electrolutic solution.

Table 1. Standard potentials of the important elements in electrolyte in 25ºC

Potential difference	Electrochemical actions and reactions
1.42	$Au^{+++} + 3e^{-} = Au^{\circ}$
0.8	$Ag^{+} + e^{-} = Ag^{\circ}$
0.34	$Cu^{++} + 2e^{-} = Cu$
0.32	$BiO^{+} + 2H^{+} + 3e^{-} = Bi + H_2O$
0.25	$HAsO_2 + 3H^{+} + 3e^{-} = As^{\circ} + 2H_2O$
0.21	$SbO^{+} + 2H^{+} + 3e^{-} = Sb^{\circ} + H_2O$
0	$2H^{+} + 2e^{-} = H_2$
-0.13	$Pb^{++} + 2e^{-} \rightarrow Pb^{\circ}$
-0.23	$Ni^{++} + 2e^{-} \rightarrow Ni^{\circ}$
-0.43	$Fe^{++} + 2e^{-} \rightarrow Fe^{\circ}$

This set of elements form a layer on the anode and prevent anode's dissolution in acid.

2) **Electropositive Impurities:**

The most important elements of this group of impurities are Au, Ag and Pt.

This set of metals have a higher potential than copper as shown in Table (1). Due to the insufficiency of their energy levels, they do not dissolve on anode and enter the slag-removing compartment of the electrolysis device in the form of other metals and ingredients. For example, gold is mostly electrolized in the form of inter-metal compounds and enters the slag-removal part of the electrolysis machine whereas silver is dissolved if the current's density is high.

Table (2) gives the dissolution percentage and deposition of the electronegative and electropositive elements in the important parts of the cell.

Table 2. The solubility, deposition and sedimentation percentages of the electronegative and electropositive elements in the electrolytic solution, cathode and slag-remover (clarifier)

Impurities	Electolyte percentage	Cathode percentage	Clarifier percentage
Ag	0	2.3	97.7
Au	0	¼	86.6
Se	0	2.4	97.6
Pb	0	1.7	98.3
Ni	94.9	¼	3.7
As	73.8	1.5	24.7
Sb	40.4	2	57.6
Fe	100	0	0

Electrolysis, Electrolyte Circulation and Electrolyte Purification:

Electrolyte circulation is generally as shown in Figure (3). In this cycle, the electrolyte solution enters the electrolysis ponds and performs the electrolysis. The electrolytic solution dissolves and carries some impurities out with it and loses some amounts of its acid contnet and this free acid is transformed to copper sulfate ($CuSo_4$).

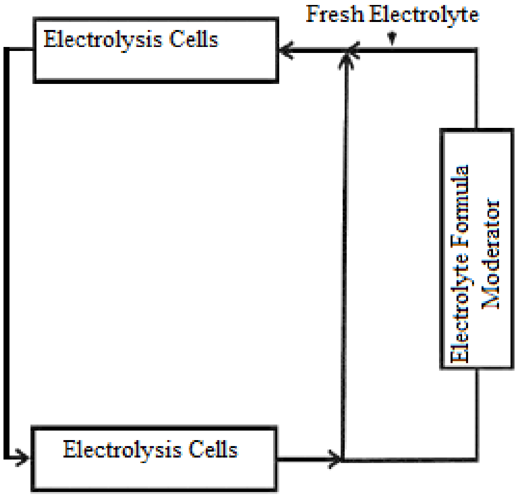

Figure 3. Electrolytic solution's circulation in copper electrolysis

Electrolyte undergoes changes in the work progress as explained below:

A) An amount of water is vaporized from electrolyte as a result of which the concentration of the solutes is increased therein.
B) The amount of copper sulfate is increased and its free acid is reduced.
C) The impurities become more condensed and their amounts are increased.
D) The electrolyte is cooled in the work course and loses its temperature.

To refine electrolyte, there are two general methods, including:

1) Crystalization
2) Electrical Method

In the refinement based on crystalization, the electrolyte is seminally passed over the small copper particles so that its acid content combines with copper upon being exposed to the peripheral air as a result of which copper sulfate is produced as shown in relation (7):

$$H_2SO_4 + Cu + \frac{1}{2}H_2o \rightarrow CuSO_4 + Ho_2 \qquad (7)$$

This action is performed so repeatedly that the free acid reaches amounts below 1%. Then, the resulting product is vaporized so that the copper sulfate's concentration is increased.

In electrolyte purification based on electrical method, the electrolytic solution is firstly allowed to enter the electrolysis ponds wherein the anodes are made of insoluble copper and cathodes are made of pure copper. These ponds are usually consisted of two series of separate ponds and the electrolyte circulates in a speed about 1400l/h which is very high. Under such conditions, the arsenic existent in the electrolyte is not capable of depositing on cathode. This way, the substantial fraction of copper is practically taken in these ponds from electrolyte. Then, electrolyte enters the second series of the ponds wherein the anode is made of impure copper and cathode is made of pure copper. The electrolyte's circulation speed in these ponds is reduced to

250l/h, as a result of which the conditions become appropriate for the simultaneous deposition of arsenic and copper on cathode.

Suggestions for Reducing the Energy Loss:

To reduce the extents of the secondary reactions, the electrolyte environment should be intensively acidified so that water cannot oxidize the univalent copper ions. It is in the course of these processes that an amount of oxygen is dissolved in electrolyte due to its being exposed to air, which brings about wastage of energy. To overcome this problem, the amount of oxygen dissolved in electrolyte should be minimized to the lowest possible amount. Due to the same reason, it is suggested that the purification action has to be carried out in a temperature between 40ºC and 50ºC.

As for the reduction of losses originating from electronegative and electropositive materials, the following cases can be suggested:

1) Addition of gelatine (for about 40g to 60g per every copper ton) and chlorine (for 110g per every ton of copper) in the form of hydrochloric acid or table salt so that the arsenic's deposition is delayed.
2) Addition of bismuth and antimony to the electrolytic solution for bismuth has a normal potential of 0.23, and antimony has a normal potential of about 0.21V that is close to copper's normal potential and causes reduction in energy wastage.
3) Addition of some organic matters like glue and thiourea and others cause uniformness and fineness of the crystals on cathode surface and generally regulate the copper deposition on cathode.

Conclusion

CuO is a semiconductor type-n with conductivity equal to 10^{-4} s/cm, 1.2 eV band gap and many applications in field emission, photovoltaic, catalysis and electrochemistry (Mahmoud, et al., 2018).

After the electrical refinement of copper, its electric conductivity was increased and the cathodic copper was delivered to the market in the form of cathodic plates. Additionally, the electrorefinment of the coppper enabled the separation of its impurities making it applicable in the other industries. In the serial connection method, the accuracy was very much increased because the first and the last electrodes were connected to the circuit, which brought about a reduction in the energy losses.

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