Preparation and Purification of Copper Metal from Dross Scrap of the State Company for Electrical Industries by Electrochemical Technique.

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Abstract:

The copper metal was prepared and purified from dross scrap by electrochemical technique, using insoluble inert anode made of lead. The scrap was dissolved in 6M HCl. Cations of Al, Mn ,Ni, As, and Zn were separated by passing the solution of dross through strong basic anion exchanger (IRA 400) Column ,while the iron and copper were retained on column and then separated them by more dilute hydrochloric acid (0.005M) . Iron separated from copper by precipitating as basic ferric acetate and then heated to 600°C for one hour to obtain ferric oxide. Copper precipitated as copper nitrate hydroxide from acid solution at PH($_{4.5-5.5)}$. The copper nitrate hydroxide has been recrystalized by ethanol and dionized water and then heated to 900°C for one hour to obtain copper oxide. The copper metal has been prepared from copper oxide by electrochemical technique. The copper nitrate hydroxide, aluminum hydroxide, copper oxide and pure copper have been identified by X-ray diffraction (XRD), X-ray fluorescence (XRF) and elemental analysis by using flame and flameless atomic absorption spectrophotometer techniques.

Keywords: Copper metal, Dross scrap and electrochemical technique

Introduction:

Copper scrap was a major source in the most of countries .It was originated from foundries, fabricators and various industries waste. In general the scrap was classified by the according to the grade and composition , most of clean scrap was sent to brass and bronze foundries, wire and cable manufactures. Remelting process was carried out by using a rotary type furnace, which was used to melt and cast. The copper produce from re-rolling to wire rods. The elimination of iron contaminated copper – clad, was done by machine parts carrying brass and bronze by electromagnetic separation [1]. The recovery of copper and other metals from scrap requires less energy than the production of copper from main ore [2]. In addition to obtained cheap source of copper from scrap, it can obtained other metals such as Pb, Cu, Zn and Al source easily and a wide scope for increasing the tonnage[3] e.g. Se, Te, Bi and Cd, which can be obtained as a byproducts from main extraction process of Cu, Pd and Zn [4].The copper- aluminum alloys have appeared in dental marks in wide countries solid alternative alloy for conventional gold-rich alloys, which are applied for the fabrication economical crown and bridges [5]. The alloys have various elements of Fe, Ni and Sn, show quite color match to gold, which keep amazing brilliance in oral environment [6]. Effective technologies process have been proposed to eliminate contaminated metals in waste species, such as

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extraction of metals by modified silica, activated carbon and resin have been reported [7-11]. These materials have been subjected to a reaction with Lewis base molecules to act as a metal collector [12-18].Recently, copper Nano particles were synthesis by various methods, such as chemical reaction, electrochemical deposition [19] and the chemical and physical properties have been studied by X-ray diffraction (XRD) and thermal gravimetric-thermal analysis (TG-DTG) [20].The aims of this work involve separation and identification of pure copper from dross scrap.

Materials and Methods :

a- 10 grams of dross had been dissolved in 6 M HCl .Aluminum, zinc, nickel, arsenic and manganese were separated by passing the solution of dross through strong basic anion exchanger (amberlite IRA 400) column. Aluminum, zinc, nikel, manganese and arsenic were eluted while copper and iron were retained by the resin.

b- Separation of copper and iron

The copper and iron were eluted by (0.005M) hydrochloric acid.

C-Separation of iron: To the eluting solution, 30% the hydrogen peroxide was added slowly with sodium acetate at room temperature with stirring the solution immediately turned to reddish – brown.

The solution boiled until precipitation is complete. The solid was then collected by filtration, and then dried at 80°C for one hour, and then the solid heated to 600^0C to obtain red color which identified ferric oxide, Fe_2O_3.

d-Separation of copper The filtrate was treated with ammonium hydroxide to precipitate the copper as copper nitrate hydroxide $Cu_2(OH)_3NO_3$, as described in our previous paper [21] .The solid was collected by filtration and then dried at 100°C for half an hour and then purified by recrystalization from a mixture of deionized water and ethanol (1:2).

The solid copper nitrated hydroxide was heated to 900° C by using muffle furnace for one hour to obtain black color which identified as copper oxide by XRD.

e-Extraction and purification of copper metal : The pure copper was obtained from copper oxide using electrochemical technique .The dimension of cell 15 × 11× 8 cm^3(made of Teflon), had been used in this technique. The cell was manufactured by take in account the minimum space with maximum cathode and anode areas. The anodes were made of crude copper, while the inert anode was made of leads weighted 150 grams for each .The cathode was manufactured from pure sheet of copper coated was coated with graphite to eliminate the copper deposited. To increasing the electrical conductivity, the electrolyte were prepared from copper oxide (10 g/L), and 2M Sulphuric acid by using current density of $1A/cm^3$ to reach the electrolyte temperature to $40\text{-}50^0$C.

Results and Discussion:

All the samples red, ferric oxide, dark green copper nitrate hydroxide, $Cu_2(OH)_3NO_3$ dark black, copper oxide and red copper metal after extraction were taken to quantitative analysis using X-ray techniques The X-ray fluorescence spectrophotometer, oxford twinx (XRF) technique was used for inspecting the elemental analysis for copper and its oxide .The qualitative analysis was carried out at department of materials, Ministry of Science and Technology by using wavelength disperse spectrometry (WDS) of siemens type SRS-200 sequential X-ray spectrometer with the following operation conditions:

1- X-ray tube target : Nb-Mo

2- Power :35 Kv, 25mA

3- Filter :Al-foil

4- Analyzing crystal :Lif (100) with 2d=4.03 A° and ADP with 2d=10.684A°

5- Detector: scintillation counter.

6- Vacuum :10^3 mbar in both sample and analyzing chambers.

In this work ,the acid solution of dross pass through strong anion exchanger resin (amberlite IRA400) to isolate iron and copper from other metals in dross (Mn,Ni,Zn,Al,As,Pb) not form stable chloro acid , so they were eluted through the strong anion exchanger. Because copper and iron form stable choloro complexes, , they were retained in column[21,22]. All the results were illustrated in table (1) and figure (1).

Table (1): The analysis of the dross, copper oxide, copper nitrate hydroxide, metal copper and Ferric oxide after extraction from dross.

Sample Color	Atomic absorption	XRF	XRD
Scrap (grey)	16%Cu 30%Zn 1%Mn 11.5%Fe 0.01%pb 0.04%Ni 0.101%As	Cu Zn Mn Fe Pb Ni As	Al,Cu,Zn,Mn,Fe,Pb,Ni
White Precipitate $Al(OH)_3$	58.6%	100%Al	$Al(OH)_3$
Green Precipitate $Cu_2(OH)_3NO_3$	53%Cu	100%Cu	$Cu_2(OH)_3NO_3$
Black CuO	80%Cu	100%Cu	CuO
Red Cu	99.9967% Cu	100% Cu	Cu

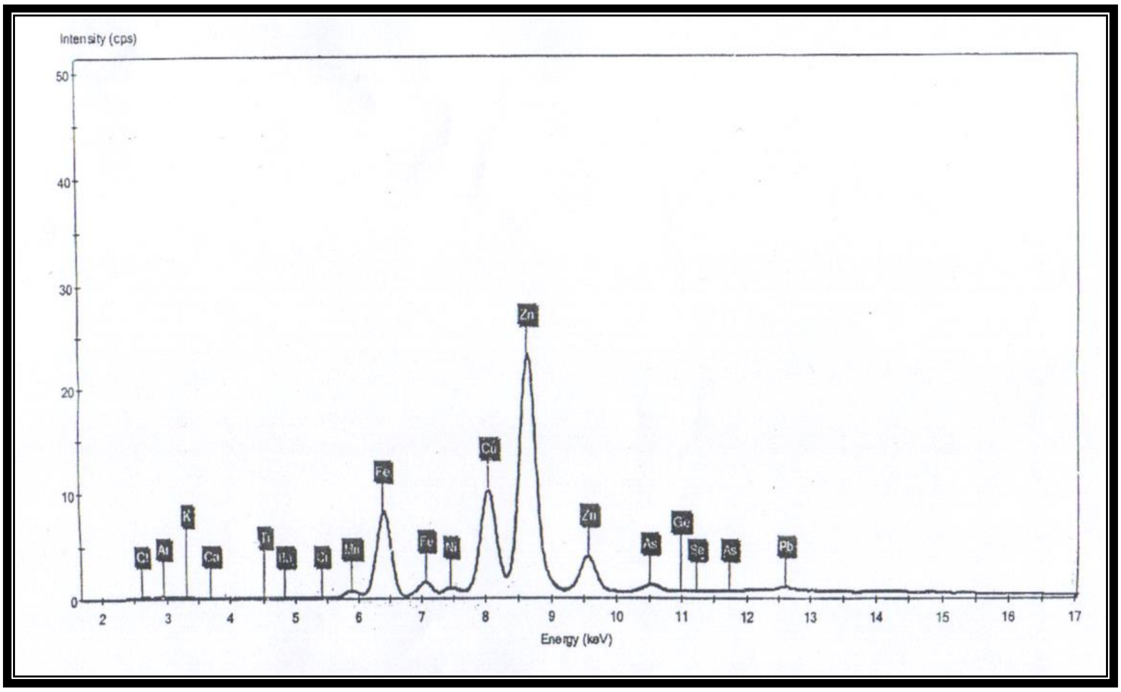

Fig.(1):X-ray fluorcence analysis of dross of the state company for electrical industries

The copper has been eluted at 0.005M hydrochloric acid and precipitated at pH4.5-5.5 as copper nitrate hydroxide (dark green color). The copper nitrate hydroxide heated to 900°C for three hours to get copper oxide. Copper metal was prepared and purified from copper oxide by using electrochemical technique. These samples were analyzed by many techniques because the X-ray diffraction (XRD) technique can not identified from samples less than 2%.X-ray fluorescence and atomic absorption spectrophotometer (shimadzu 670 AA) were also conducted in this work. These are summarized in figures (2,3) and the analysis of XRD in tables (2-5). Copper metal was analysis for elemental impurities using flameless atomic absorption spectrophotometer technique .Copper is conveyed from anode to pure cathode during the analysis. It impurities in the crude copper such as Fe ,Co,Ni,Mn,As,Pb,and Zn go into solution and the precious collected below the anode in which is called as the anode slime. As progresses some difficulties are likely to happen to the vicinity of the cathode, the concentration of copper ion decreases and the water in electrolyte is electrolyzed, releasing hydrogen, which lowers the current efficiency. More over, in the vicinity of the anode, the concentration of copper ion increases and copper sulphate has the ability to crystallize. In order to overcome these setbacks, these must be continous stirring and circulation of copper. This is illustrated in table (6).

Table (2): X-ray diffraction analysis of ferric oxide , Fe_2O_3

$D(^0A)$	2θ	I(C/S)
2.69	33.3	310
2.52	35.7	350
2.19	41.2	220
1.83	49.7	220
1.68	54.5	240
3.67	24.2	240

Table (3):X-ray diffraction analysis for copper nitrate hydroxide.

$D(^0A)$	2θ	I(C/S)	$D(^0A)$	2θ	I(C/S)
3.041	29.5	1200	6.946	12.7	2000
2.790 2.668	32.0 33.5	1568 2000	4.121	21.5	1356
2.529	35.4	1780	3.628	24.5	1294
2.465 2.256	36.3 39.8	2000 1709	3.465	25.6	2000

Table (4): the X-ray diffraction analysis for copper oxide

$D(^0A)$	2θ	I(C/S)
2.74	32.7	400
2.52	35.7	510
2.32	39.0	530

Table (5) X-ray diffraction analysis for pure copper

D(^{0}A)	2θ	I(C/S)
2.152	41.9	1600
2.080	43.3	2000
1.847	49.2	1152
1.779	51.2	1231
1.715	53.3	1427
1.587	58.0	1450
2.072	43.6	2000
1.795	50.7	1388

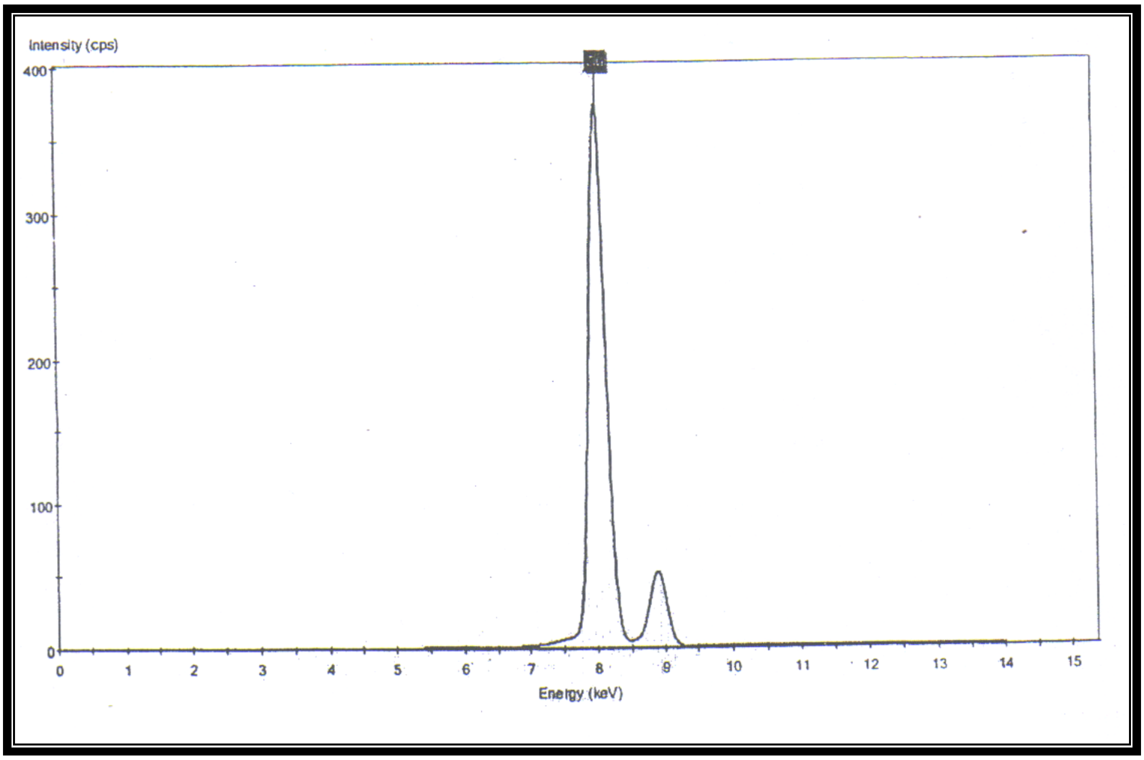

Fig.(2) X-ray fluorcence analysis of pure copper

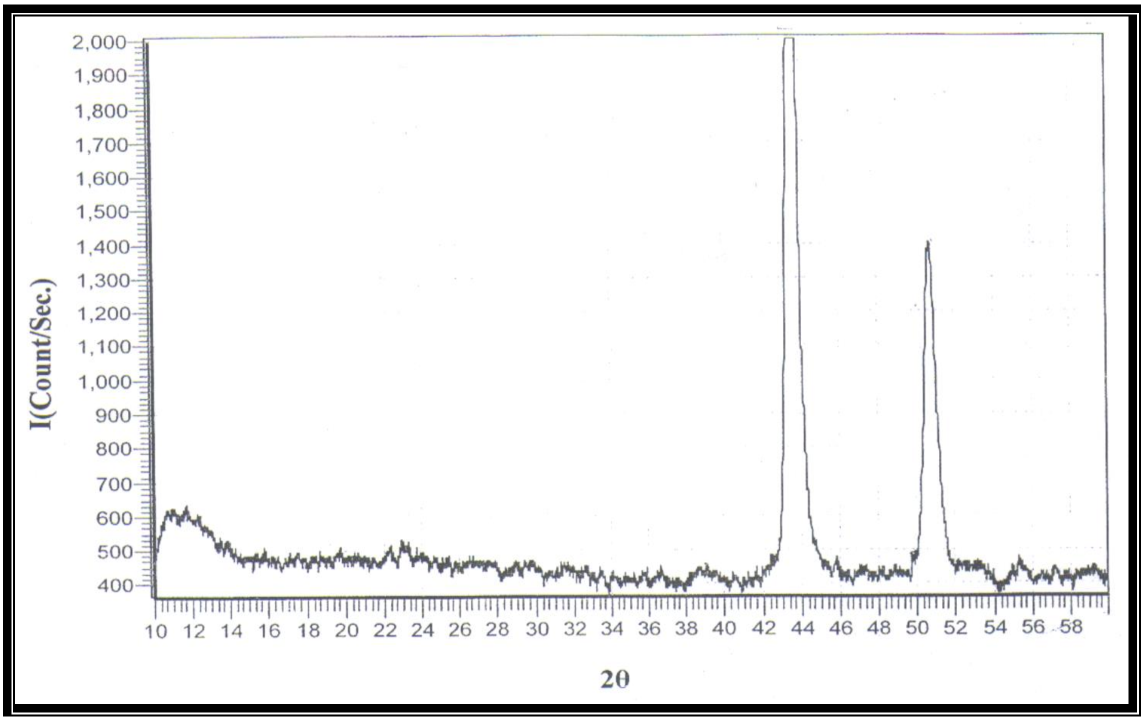

Fig. (3) X-ray diffraction analysis of pure copper.

Table (6): concentration of impurities in ppm

Concentration in ppm	Element
o.82	Fe
0.55	Co
0.31	Ni
0.28	Zn
0.21	Se
0.21	Te
5.00	As
2	Ge
5	Mn

Conclusions:

1- The extraction and purification of copper by electrochemistry technique can be considered as the best method for obtaining high purity copper.

2- A lot of dross has been produced in this country, which has high percentage of copper and can be extracted and purified using this method.

3- The composition of the anode slim (sludge) the last purification of copper was analyzed by different techniques, which is listed in table (7).

Table (7): analysis of the anode slime, after final extraction and purification of copper.

Concentration	Element
7%	Cu
5ppm	Ag
15ppm	Au
1%	Pb
0.1%	As
0.3%	Te
2.8%	Ni
1%	S
0.22%	Fe
1%	Se
12ppm	Al
20ppm	Mn
5ppm	Ge
10PPm	Zn

These elements harm both the mechanical and electrical properties of copper and have to be removed during purification. Removing these elements was discussed in detail in our previous papers [21, 22].

4- Using the Teflon for cell because it is not affected by both aqueous acid and base.

5- The unique method which is presented in this study for the extraction and purification of copper was economic because this metal has varied applications.

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تحضير وتنقية معدن النحاس من الخبث المعدني الناتج من مخلفات الشركة العامة للصناعات الكهربائية بتقنية الكيمياء الكهربائية

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*** كلية العلوم للبنات /جامعة بغداد**

الخلاصة :

تم تحضير وتنقية معدن النحاس من مخلفات الخبث المعدني وباستخدام انود محايد مصنوع من الرصاص وبالطريقة الكهربائية تم اذابة المخلفات في محلول 6 مولر حامض الهيدروكلوريك وتم فصل الالمنيوم المنغنيز النيكل الزرنيخ والخارصين بامرار محلول الخبث خلال عمود التبادل الايوني السالب القوي (IRA400) بقى النحاس والحديد محملين على عمود التبادل الايوني ومن ثم فصلهما بحامض الهايدروكلوريك المخفف جدا (0,0005 مولر)

تم فصل الحديد عن النحاس بالترسيب على هيئة خلات الحديديك القاعدية ثم التسخين الى 600 م^{0} ولمدة ساعه واحدة للحصول على اوكسيد الحديديك تم ترسيب النحاس على هيئة نترات هيدروكسيد النحاس من المحلول الحامضي بداله حامضية تراوحت من 4,5 الى 5,5 ثم تنقيتها بتقنية اعادة البلورة بالايثانول ثم التسخين الى درجة حرارية مقدارها 900 م^{0} للحصول على اوكسيد النحاس ثم استخلاص معدن النحاس بتقنية الكيمياء الكهربائية