Separation and Purification of Copper from a Hazardous Nickel Solution Using a Micro Controller Based Digital Electronic Switching System

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Abstract: In the present study, the effect of distribution of charge on the separation and purification of copper was investigated using Micro Controller based Digital Electronic Switching System (MCDESS). Mixtures of copper and toxic nickel salts with varying concentrations were injected into a free electrolytic diffusion apparatus (FEDA). The micro cathodes surrounding the central anode were programmed with MCDESS, which distributed the charge over the micro cathodes at time intervals of 100 µs - 900 µs or at the frequencies of 625 Hz - 70 Hz. Due to this charge distribution, the micro cathodes become electrodeposited with copper and toxic nickel metal, doing both separation and co-deposition. The purity of deposited metals was analyzed by Atomic Absorption Spectroscopy (AAS). The percentage purity of copper was found $99.38 \pm 0.041\%$ and $99.79 \pm 0.001\%$ at 70 Hz and 625 Hz respectively.

Key words: Charge distribution · Conducting electrolyte · Copper · Microcontroller · Purity · Separation

INTRODUCTION

Copper is one of the few metals to occur naturally as an un-compounded mineral. Copper was known to some of the oldest civilizations on record and has a round about 10,000 years old history of use. In the modern world, the metallic copper has wide applications as it is consumed to make electrical and electronic products, building construction, industrial machinery and equipments, transportation and general products. Copper is alloyed with many metals (e.g., zinc, tin) in the production of tubing, brass and bronze products. Electroplated copper has various applications as contacts and circuitry in the electronic industry, undercoating for Ni and Cr plating and the decoration of consumer goods. During the past decades, quantum improvements have been realized regarding the continuous purification process of copper [1].

There are many available methods for purification of copper such as beneficiate process with flotation, roasting and leaching stages for recovery of copper from sulfide oxide ores [2], anion exchange chromatography in hydrochloric media for overall purification of copper in a single-step operation [3-5], solvent extraction coupled with electro winning (SX-EW) for the production of high purity copper, copper electro winning from gold plant waste streams [6], preparation of high-purity copper films by non-mass separated ion beam deposition [7], electro gravimetery and pulsed electrophoresis in which separation of the cations was carried out by controlled cathode potential and voltage [8]. Modern refineries used an electrolytic step to effect further purification of the copper. The electrolytic purification step was the anodic dissolution of the blister copper and simultaneous deposition of pure copper at the cathode [9].

According to Kirk othomer encyclopedia [10] the conventional metal extraction procedures have limitations in one way or the other. They are laborious, time consuming and health hazardous and required special precautions for their application. The above stated techniques for separation and purification of copper are time consuming and less efficient. These techniques successfully are being used for the purification of copper.

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We also developed a new approach for separation and purification of metals, which was successfully used for purification and separation of nickel [11] and cadmium and lead from mixture [12].

In this approach for the first time, we coupled both electro deposition and micro controller in a Free Electrolytic Diffusion Apparatus (FEDA). We used a Micro Controller based Digital Electronic Switching System (MCDESS) to find the effect of distribution of charge on the percentage purities of deposited metals. The distribution of charge using MCDESS (a digital thruster), over the micro cathodes in a free electrolytic diffusion apparatus, to produce high purity metals is quite original and latest approach to separate and purify the materials [11, 12]. In the present work a Micro Controller based Digital Electronic Switching System (MCDESS) was used in FEDA for the separation and purification of copper.

MATERIALS AND METHODS

Chemicals and Glassware: KCl, H_2SO_4 and metal salts were of analytical grade. 1 M KCl was used as a conducting electrolyte and 0.2 M H_2SO_4 was used as a supporting electrolyte. Analytical grade HNO_3 (14M) was used in these experiments to dissolve the deposited metals. Volumetric flasks and beakers (100 mL) made of Pyrex glass were used. All glassware was carefully washed with 10 % HNO_3 (v/v) and double de-ionized water.

Designing of Free Electrolytic Diffusion Apparatus (FEDA): FEDA (Figure 1) has only one chamber, which is 6 inch long, 6 inch wide and 2 inch high. In the center of the chamber there was a large cylindrical hollow anode (containing sample mixture) made of platinum with side longitudinal slit. The diameter of the cylindrical anode was 3.0 cm and the height was 5.0 cm. The position of the slit was just before the position of first micro cathode. The slit was filled with cellulose material to pass the metallic cations slowly outside the cylinder. Cylindrical platinum anode was further surrounded by a grid of anodes for the eddy diffusion of metallic cations toward the micro cathodes. Micro cathodes were made of platinum wire of 0.2 mm diameter. The length of every micro cathode was 5 cm and each micro cathode was 1.0 mm apart from each other. Micro cathodes were arranged parallel to the anode in a circular fashion. Every micro cathode was at equal distance from each other and
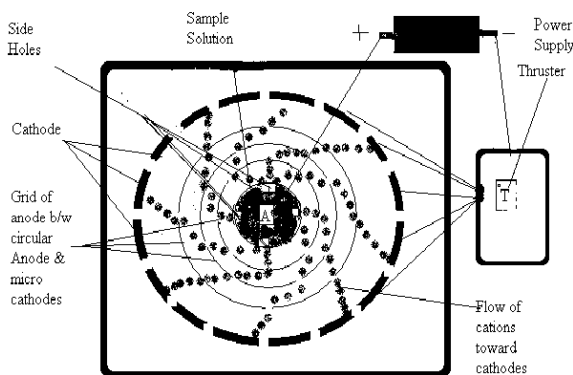

Fig. 1: Free Electrolytic Diffusion Apparatus

7.0 cm away from the anode to keep the equal attraction between anode and micro cathodes. A total of 150 micro cathodes were used in all of these experiments. They were divided into 15 groups and each group contained 10 micro cathodes. Each group was weighed before and after the metallic deposition to find the weight of deposit.

Micro Controller based Digital Electronic Switching System (MCDESS): The micro cathodes were programmed with the Micro Controller based Digital Electronic Switching System (MCDESS), in such away that a thrust of charge was repeated at the time interval of 100 μs to 900 μs. MCDESS distributed the charge at a frequency of 70 Hz to 625 Hz at an applied direct current of 1.0 A - 3.0 A. MCDESS has 16 terminals to be connected with micro cathodes. When terminal 1 was in the "ON" position then remaining 15 terminals were in the "OFF" position. After the selected time interval (100 μs - 900 μs) terminal 2 was in the "ON" position and remaining 15 terminals were in the "OFF" position and so on. Thus charge was distributed from terminal 1 to terminal 16 in a regular fashion to complete a cycle [11, 12].

Programming of MCDESS with Micro Cathodes: The micro cathodes surrounding the central anode were programmed with MCDESS. It was a repeating thrust programming in which every 17th micro cathode was connected to every 4th terminal of MCDESS. It means that micro cathode numbers 1, 17, 33, 49, 65, 81,--- were connected to the terminal numbers T1, T4, T8, T12. Similarly micro cathode numbers 2, 18, 34, 50, 66, 82,--- were connected to the terminal numbers T2, T5, T9, T13 and so on. The programming of the microelectrodes was shown in Table 1.

Table 1: Programming of Micro Controller based Digital Electric Switching System with Micro cathode

Serial No.	Micro Cathode Number	Terminal Number
1	1, 17, 33, 49, 65, 81, ---	T1, T4, T8, T12
2	2, 18, 34, 50, 66, 82, ---	T2, T5, T9, T13
3	3, 19, 35, 51, 67, 83, ---	T3, T6, T10, T14
4	4, 20, 36, 52, 68, 84, ---	T 4, T7, T11, T15
5	5, 21, 37, 53, 69, 85, ---	T5, T8, T12, T16
6	6, 22, 38, 54, 70, 86, ---	T6, T9, T13, T1
7	7, 23, 39, 55, 71, 87,---	T7, T10, T14, T2
8	8, 24, 40, 56, 72, 88, ---	T8, T11, T15, T3
9	9, 25, 41, 57, 73, 89, ---	T9, T12, T16, T4
10	10, 26, 42, 58, 74, 90, ---	T10, T13, T1, T5
11	11, 27, 43, 59, 75, 91, ---	T11, T14, T2, T6
12	12, 28, 44, 60, 76, 92, ---	T12, T15, T3, T7
13	13, 29, 45, 61, 77, 93, ---	T13, T16, T4, T8
14	14, 30, 46, 62, 78, 94, ---	T14, T1, T5, T9
15	15, 31, 47, 63, 79, 95, ---	T15, T2, T6, T10
16	16, 32, 48, 64, 80, 96, ---	T16, T3, T7, T11

Preparation of Standards and Standard Calibration:
3.798 g of $Cu(NO_3)_2.3H_2O$ was dissolved in 250 mL of de-ionized water followed by dilution with de-ionized water to prepare 1000 ppm stock solution. Further standard solutions with concentrations of 2, 4, 6, 8 and 10 ppm were prepared using this stock solution. Health Safety and Environmental Training Center, Lahore, Pakistan provided the standard solutions to make standard calibration. Different dilutions of deposited metals were prepared and their absorbance compared with standards. After this the standard deviation values at λ 327.4 nm for copper and λ 341.5 nm for nickel were calculated.

ICP Analysis of Sample Mixture: The starting material was an industrial effluent. It was analyzed by inductive couple plasma (Perkin Elmer Optima 2100). ICP analysis showed that 92.25% copper was present as a major element, 4.63 % Ni as major impurity and S, Fe, Ag, Ca, Zn and Pb are the minor impurities while Ca, Na, K and Cadmium are in traces about 1.0 ppm as described in Table 2. Determination of trace impurities in high-purity metals and alloys was an important part of the quality control process in the manufacture of these materials [13].

AAS Determination: Both the copper and nickel were deposited on microelectrodes indicating their spectrum on 150 microelectrodes. In order to find out the percentage purity of copper and nickel on the respective 150 electrodes, it was difficult to analyze all the micro electrodes by AAS ((Perkin Elmer AAnalyst 100), so microelectrodes were then grouped (sub grouped) based on the visibility of spectrum. Each group of microelectrodes was then weighed on an analytical balance and a sample solution of a group of 15 microelectrodes was then prepared. A total of 15 samples were thus obtained from the spectrum. Each sample was dissolved in extra pure concentrated HNO_3 separately and was diluted up to 1000 times. These dilutions were run in AAS (Perkin Elmer AAnalyst 100). The values were compared with the Perkins Elmer and Aldrich standards. A graph between concentration and absorption was plotted to find the concentration of desired metal and the percentage purity of the metallic deposits were determined. The wavelengths used for copper and nickel was 327.4 nm and 341.5 nm respectively. The fuel pressure was 15 PSI and spectral band pass was 0.2 nm.

Table 2: ICP analysis of industrial effluent

Element	Concentration (ppm)	Concentration (ppm) at 70 Hz	Concentration (ppm) at 625 Hz
Na	0.11	0.1	0.010
K	1.10	0.01	0.010
Cu	92.25	99.39	99.790
Cd	0.10	0.1	0.001
Mg	0.20	0.01	0.010
Ca	0.09	0.01	0.010
S	0.20	0.11	0.010
Pb	0.20	0.01	0.010
Zn	0.30	0.01	0.010
Ag	0.12	0.1	0.010
Fe	0.30	0.09	0.100
Ca	0.40	0.02	0.010
Ni	4.63	0.0.004	0.001

RESULTS AND DISCUSSIONS

If we compare this new method reported with other methods described in introduction section, the following points or differences were observed. In this method we applied constant voltage from DC supply to purify copper from toxic nickel as compared to other methods such as controlled cathode potential technique. Second difference is that we distributed charge over micro cathodes in a circular fashion to separate the metallic ions from each other and to deposit on separate cathode. This differentiates the new technique to other technique such as pulse field electrophoresis in which cathode moves from one direction to opposite side. So this new technique is better than pulse field electrophoresis as instead of cathode displacement, we distributed charge over the cathodes and cathodes were at fixed positions. For the first time we used microcontroller based switching system (Digital thruster) for the distribution of charge in a circular fashion to separate metals from impurities [11, 12]. So this technique is a new addition in separation and purification of metals, which has some advantages.

Effect of Charge Distribution at 70 Hz and 625 Hz: The ICP analysis of the industrial effluent showed that it contained only 92.25 % pure copper while nickel was the main impurity present as shown in Table 2. In FEDA there was a set of pre weighed 150 micro cathodes. In the start, on first ten micro cathodes the percentage purity of nickel was 97.44 ± 0.002, while the percentage purity of copper was 2.56 ± 0.0254 at 70 Hz. The percentage purity of nickel was 96.89 ± 0.084, while the percentage purity of copper was 3.11 ± 0.054 at 625 Hz as shown in Table 3. At 70 Hz, an alloy of copper and nickel with varying composition formed at the micro cathodes (30-140) as shown in Figure 2. While at 625 Hz, the copper-nickel alloy formed on the earlier group of micro cathodes (20-130) as shown in Figure 3. It was found that at a higher frequency (625 Hz) copper-nickel alloy formation took place at earlier microelectrodes due to enhanced ionic mobility of Cu^{+2} and Ni^{+2} cations. At the last ten micro cathodes the percentage purity of nickel decreased to 0.062 ± 0.023, while the percentage purity of copper increased to 99.38 ± 0.041, at low frequency (70 Hz) and copper separated from nickel in the purified form was 99.79 ± 0.001 at higher frequency (625 Hz) as shown in Table 3.

Effect of Voltage: In the production of pure copper at high voltage (18-30 V), the conductivity of electrolyte increased. But the evolution of hydrogen gas at the micro cathodes also increased. The rapid reduction of hydrogen ions at the micro cathodes not only increased the temperature of the apparatus but also affected the pH of the conducting electrolyte. The experiments were performed at a voltage of 6.8 V at which less evolution of hydrogen took place. Deposition is usually overlapped by the reduction of hydrogen ions during electro deposition of less noble metal. This normally led to a large increase of the pH value close to the electrode surface and to a change in the deposition behavior and the properties of the deposits. The hydrogen reaction was minimized normally by buffering the electrolyte.

Table 3: Separation of copper from nickel by using FEDA

MCG No.	70 Hz		625 Hz	
	PP of Ni + SD	PP of Cu + SD	PP of Ni + SD	PP of Cu + SD
1	97.44±0.0020	2.56±0.0254	96.89±0.0840	3.11±0.054
2	96.35±0.0230	3.65±0.0130	94.58±0.0960	5.42±0.650
3	95.65±0.0360	4.35±0.0150	93.14±.06200	6.86±0.150
4	91.25±0.4750	8.75±0.0740	86.47±10.032	13.53±0.630
5	82.65±0.0150	17.35±0.0120	74.96±0.0850	25.04±0.110
6	71.54±0.0620	28.46±0.0410	62.58±0.0040	37.42±0.050
7	65.54±0.0410	34.46±0.0620	57.89±50.070	42.11±0.030
8	59.14±0.0470	40.86±0.0380	48.56±0.0900	51.44±0.005
9	55.65±0.0310	44.35±0.0190	41.99±0.0360	58.01±0.006
10	48.59±0.0850	51.41±0.0420	31.69±0.0340	68.31±0.460
11	43.51±0.0280	56.49±0.0310	22.65±0.0340	77.35±0.036
12	31.25±0.0180	68.75±0.0920	10.02±0.0540	89.98±0.064
13	23.87±0.0150	76.13±0.0410	5.04±0.0190	94.96±0.004
14	16.02±0.0150	83.98±0.0150	2.58±0.0240	97.42±0.087
15	0.62±0.0230	99.38±0.0410	0.21±0.0240	99.79±0.001

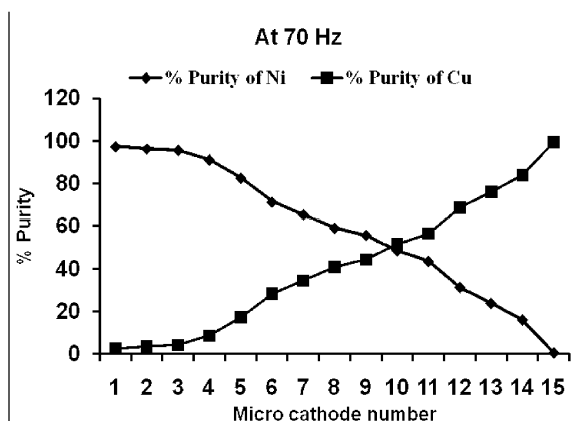MCG No: Micro Cathode Group Number; SD: Standard Deviation; PP: Percentage Purity

At 70 Hz

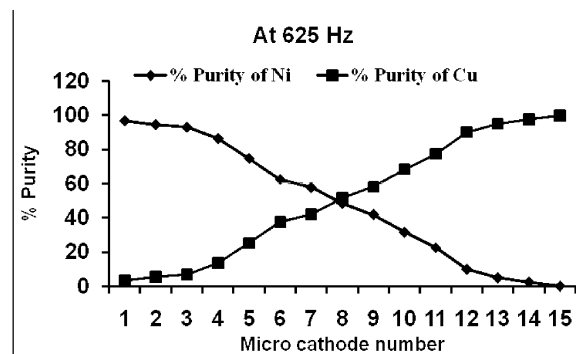Fig. 2: Comparison of percentage purities of copper from nickel at 70 Hz

At 625 Hz

Fig. 3: Comparison of percentage purities of copper from nickel at 625 Hz

Distance Between Micro Cathodes and Anode: The distance between a cathode and an anode plays very important role during electro deposition. Usually decreasing their distance decreased the resistivity with an accompanying increase in conductivity. However a small distance (2-3 cm) between the micro cathodes and anode was not suitable for the separation of cations present in our mixtures. A small distance usually results in co deposition. It was found that separation of copper from the impurities was good when the micro cathodes and anode were at a distance of 7.0 cm.

Distance Between Micro Cathodes: In these experiments a total of 150 micro cathodes were arranged around the cylindrical platinum anode in a circular fashion. Each micro cathode was 1.0 mm apart, similar distance used in our previous work for the purification of nickel [11]. It was found that micro cathodes at this distance show good separation of copper from the matrix. When the distance between micro cathodes was increased to more than 1 mm then co deposition of copper and impurities took place on all micro cathodes.

Conducting and Supporting Electrolytes: Gokhan Orhan and coworkers [14] studied the behavior of organic components in copper recovery from electrodes plating bath effluents using 3D electrodes systems. In order to enhance the electrical conductivity for purification of copper, KCl (1.0 M) was used as a conducting electrolyte. The supporting electrolyte used for these experiments consisted of 0.2 M H_2SO_4. This supporting electrolyte was used at negative electrode potential, which was necessary for these experiments. The other supporting electrolytes for copper electro deposition were (i) 0.3 M HCl + 4.0 M $NH_2OH.HCl$ (ii) 0.7 M HNO_3(iii) 0.4 M Sodium tartarate + 0.1 M NaH tartarate (iv) 1.2 M NH_4OH + 0.2 M NH_4Cl (v) 0.4 M KCN + 0.2 M KOH (vi) 5g NH_4NO_3 + 2g $NH_4OH.HCl$ + 200 ml H_2O + EDTA (Molar ratio of metal to EDTA was 1:3) (vii) 5g CH_3COONH_4+ 200 ml H_2O + EDTA (pH = 5, Molar ratio of metal to EDTA was 1:3) (viii) 2g NH_4Cl + 20 ml NH_4OH + 180 ml de-ionized water + EDTA (Molar ratio of metal to EDTA was 1:3). Experimentally it was found that 1.0 M KCl as conducting electrolyte and 0.2 M H_2SO_4 was sufficient for the separation and purification of copper from a hazardous solution using a MCDESS (digital thruster).

Concentration of Sample: A method was reported about the electrochemical treatment of copper from aqueous citrate solutions using a cation-selective membrane [15]. An economically acceptable current efficiency (>50 %) and recovery of Cu (II) and citrate (96%) was obtained when the feed concentration of chelated Cu (II) was sufficiently high. It was found that a higher concentration of sample mixture (1.0 M) caused the co deposition of copper and impurities on all available micro cathodes. The rapid release of copper ions in the conducting electrolyte did not allow their complete separation. For better purification, 1.0 ml of sample mixture (0.2 M) was diluted 20 times with de ionized water. The diluted sample mixture diffused into the outer conducting electrolyte drop wise. The observed optimum conditions for the copper purity were the use of a supporting electrolyte solution containing 0.2 M H_2SO_4 (pH = 3.0) and 1.0 M KCl was used as a conducting electrolyte.

CONCLUSION

Previous research described the effect of rotation of disc electrode on the geometry and structure of electrodeposits. In this work, for the first time rotation of charge at higher cycles per second over the multi cathode system employed for the separation and purification of copper. Usually distribution of charge at

the rate of 625 Hz shows better results as compared to 70 Hz. The results obtained showing the percentage purity of copper, which was 99.38 ± 0.041 % and 99.79 ± 0.001 % at 70 Hz and 625 Hz respectively.

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