Packed Bed Electrolysis for Production of Copper Powder

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The electrolytic refining of pre-processed electronic scrap using the packed-bed electrolysis technology in both bench and semi pilot scales for production of copper powder were concerned in this paper. The process applied the actual industrial conditions as close as possible to the conventional electrolytic refining of copper anode plates employing a titanium basket to support and supply the applied current to anode particulates. The obtained results showed that the produced copper powder has a quality of about 98 % Cu with about 1.5 % Sn as a main alloying element with cathodic current efficiency of about 80 % and specific power demand from 0.4 to 0.5 kWh/kg.

Keywords:

Packed bed electrolysis – Electronic scrap – Electrolytic copper powder

Granulatelektrolyse für die Herstellung von Kupferpulver

Ziel dieser Arbeit ist die elektrolytische Raffination von Elektronikschrott durch eine Granulatelektrolyse in einer Labor- und Halb-Pilot-Maßstab Elektrolysezelle unter den gleichen Bedingungen wie in einer konventionellen Kupferraffinationselektrolyse. Als Anode wurde ein aus Titan gefertigter Korb benutzt der die Granalien enthält und der Stromzuführung dient. Es wurde Kupferpulver mit einer Reinheit (im Mittelwert) von 98 % Cu und ~ 1,5 % Sn bei einer kathodischen Stromdichte von 80% und einem spezifischen Energiebedarf von 0,4 – 0,5 kWh/kg produziert.

Schlüsselwörter:

Fest-Bett-Elektrolyse – Elektronikschrott – Elektrolytisches Kupferpulver

Franz. Titel: Electrolyse de granulés pour la production de cuivre en poudre

Span. Titel: Electrorefinación de gránulos para la producción de polvo de cobre

Copper powder has many industrial applications especially in the fields of abrasive wheels, agriculture, aerospace, automotive, building and construction, chemicals, coatings, coins, medals, medallions, electrical and electronics, joining, lubricants, machining, office equipments etc.

In general powder metallurgy has some basic advantages which can be summarized as follows: (a) metal powders are high purity materials (b) close dimensional tolerances can be maintained (c) high volume process with excellent reproducibility; (d) quality control is inherent in the process; (e) low labour input; (f) machining is eliminated or reduced; (g) scrap losses are eliminated or reduced; (h) segregation is avoided; (i) controllable porosity and density can be precisely controlled; (j) combines immiscible metals; and (k) complex shapes can be produced.

Granular copper powder can be produced by a number of methods, the most important being atomization, electrolysis, hydrometallurgy and solid state reduction. Each method yields a powder having certain inherent characteristics.

Electrolytic copper powder is produced by following principles used in electroplating with the conditions changed to produce a loose powdery deposit rather than a smooth adherently solid layer. The formation of powder deposits that adhere loosely to the cathode is favoured by low copper ion concentration in the electrolyte, high acid concentration and high cathode current density. The starting material is pure cathode copper. Properties of the powder depend on a number of variables including the concentration of sulfuric acid and copper sulfate, type and quantity of the addition agent, temperature of the electrolyte and the current density. After deposition, the powder is washed to remove all traces of the electrolyte, annealed in a reducing atmosphere, fed to high velocity impact mills to break up clusters, screened, classified and blended to the desired particle size distribution. The properties are influenced also by the temperature used in reducing the powder. The typical properties of the produced copper powder from different methods are shown in Table 1 and indicate that, a range of powders with different apparent densities and high green strengths is obtained. [1]

Table 1: Typical properties of copper powder produced by various methods

Parameter	Electrolytic	Atomized	Hydrometall	Solid state r
Copper, %	99 to 99.5	99 to 99.5	98.5 to 99.5	98.5 to 99.5
Weight loss in H_2, %	0.1 to 0.75	0.1 to 0.5	0.3 to 1.0	0.1 to 0.75
Acid insoluble, %	0.02 max.	0.1 max.	0.05 max.	0.3 max.
Apparent density, g/cm^3	1 to 3	2 to 4	1 to 4	1.5 to 4
Flow, s/50 g	25 to 40	25 to 35	25 to none	20 to 35
Green strength, psi	400 to 3000	400 to 2300	400 to 3000	400 to 2000
-325 mesh, %	15 to 90	25 to 90	35 to 90	15 to 90

The copper powder obtained by electrolysis is high purity material, averaging more than 99 % copper. The powder is dendritic in shape. A wide range of powders having different apparent densities and high green strengths can be obtained by this method. [1]

Production of electrolytic copper powder form the partially fire refined electronic scrap (~ 80 % Cu) avoiding the Cu loss to slag during the complete fire refining process is the main objective of this work. The electrolytic refining of a such scrap using the packed-bed electrolysis (PBE) technology was utilized. Two main steps were applied to reach this target: first, the mechanically pre-processed particles were pyrometallurgically treated to remove the adhesive non-metallic film covering the electronic particles, to separate some of the accompanied impurities by selective oxidation of the metal bath, and to granulate the particles to be suitable for application in PBE technology. The second step was the application of PBE technology utilizing conditions as close as possible to the conventional electrolytic refining of copper anode plates. The experimental work was carried out in a bench scale cell (~ 2 kg electronic scrap anode particulates sample) and a semi-pilot scale cell (~ 12 kg anode particulates sample) using galvanostatic technique in a titanium anode basket.

Fiure 1 shows the main steps used for production of copper powder from original electronic scrap raw materials. After collection and sorting of the electronic scrap raw material, it has two main ways to processing. The 1st way is the direct melting in a Cu-converter to produce Cu suitable for the conventional electrolysis process but with danger of Cu loss to slag. The 2nd proposed way (proposed to use in developing countries) is mechanical processing to resize and classify the materials and to separate some metals such as Fe (magnetic separation) and Al (eddy current separation). This step is followed by pyrometallurgical treatment for melting, fire refining and granulation of the preprocessed concentrates. The produced granulates will be subjected to packed bed electrolysis process to separate the noble metals in the slime phase and the non-noble metals in the electrolyte phase with Cu-Sn alloy in a powder phase. The produced anode slimes can be further processed in copper or precious metals factories.

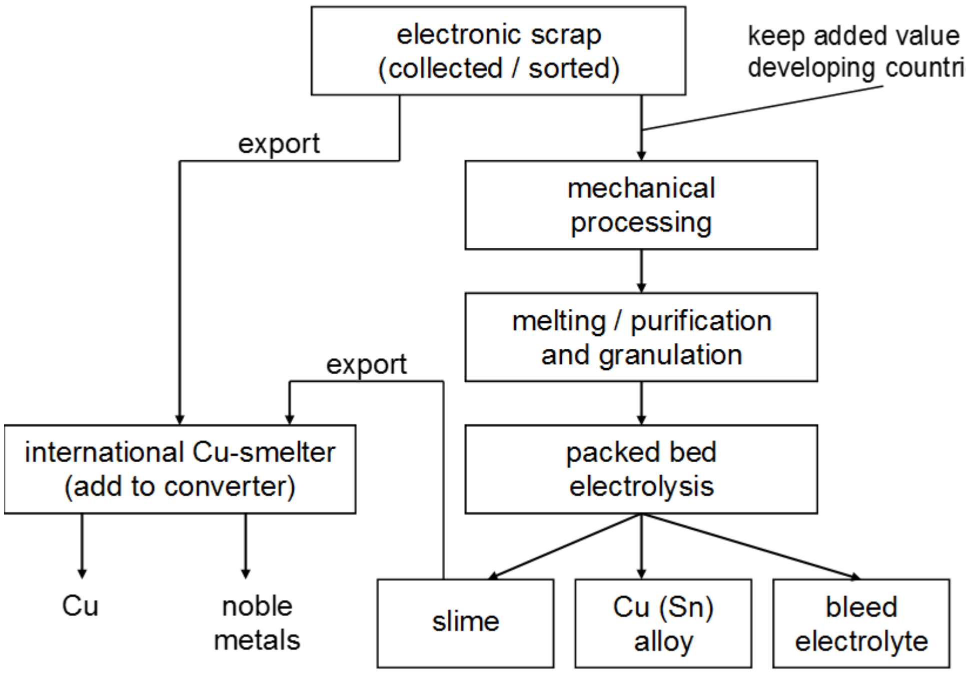

Fig. 1: Mass flow alternatives of electronic scrap recycling

1 Experimental details

1.1 Materials characteristics and process parameters

The main anode materials used in this study were particulates processed from electronic scrap (obtained from IFA, Institute for Processing and Recycling of Solid Waste Material, RWTH) and from a synthetic alloy containing a similar composition. A partial fire refining of the recycling alloy was carried out in an open gas furnace by injection of air in the metal bath for 1 hour at 1200 °C and continually skimming up of the slag layer every 15 min to avoid the backward of the impurities to the melt. Table 2 shows the chemical analysis of electronic scrap before and after the partial fire refining step.

Table 2: Percentage chemical analysis of electronic scrap before and after fire-refining step

	Cu	Al	Sn	Pb	Zn	Fe	Ag	Ni	Sb	As	Bi
before refi	75.02	7.72	7.73	4.83	3.96	0.24	0.06	0.15	0.26	< 0.01	0.03
after refini	79.26	7.0	7.5	2.6	2.9	0.2	0.11	0.15	0.25	< 0.01	0.03

Granulation of the molten alloy was carried out in a water bath without bottom - air agitation throughout a hot graphite sieve with 4 mm ϕ holes. The obtained particulates were classified into three main size fractions (see Figure 2). Each size fraction was subjected to an electrolysis process, which showed that the optimum electrolysis results were obtained from the size fraction <5 >2 mm. Such size fraction was electrolysed in both bench scale and semi pilot experiments. Table 2 shows the main specifications and the studied parameters of the bench scale experiments. While the technical data of semi pilot scale runs were collected in Table 3.

Fig. 2: A view of the different anode particle sizes (20 g each sample)

Table 3: Technical data of the bench scale experiments

Description	Parameter
One Ti basket (112 mm×80 mm×20	Anode basket
Two permanent stainless steel plates (122 mm×100 mm×3.25 mm)	Starting cathode sheet
25 mm	Anode-cathode distance*
<5 >2 mm	Anode particle size*
8 l	Total electrolyte volume
65 ± 0.5 °C	Electrolyte temperature
1.6 l/h (cell volume exchange 2.5 h)	Electrolyte circulation
250 A/m^2	Cathodic current density*

* at the beginning of the experiment

XRD analysis of the anode particulates before the electrolysis process were carried out. The main obtained phases were Cu, $AlCu_3$, $Al_3Cu_{12}Sn$, Al_3Ni_2, Cu-Sn, Zn and Pb.

316 L stainless steel plates with 3.25 mm thickness were used as starting cathodes. The main experimental data of the semi pilot runs were illustrated in Table 4.

Table 4: Technical data of the semi-pilot runs

Description	Parameter
one Ti basket (250 mm×170 mm) with 7	Anode basket and active are
Two permanent stainless steel plates (26	Starting cathode and active
21 mm	Anode-cathode distance*
<5 >2 mm	Anode particle size*
21.6 l	Electrolyte volume in each c
65 ± 0.5 °C	Electrolyte temperature
12 l/h (cell volume exchange 2.5 h)	Electrolyte circulation
250 A/m^2	Cathodic current density*

* at the beginning of the experiment

The starting electrolyte was prepared with the composition of Cu (5 g/l), 168 g/l H_2SO_4 and with/without 40 mg/l Cl. The electrolysis process was carried out at a constant temperature of 65 °C (± 0.5 °C).

1.2 Experimental apparatus and procedure

The electrolytic cell constructed for the bench scale experiments consists of two 5 l beaker glasses (Figure 3). A precise electrolyte pump (Heidolph Type 641) was projected between the two beaker glasses to recirculate the used electrolyte beside the electrolyte convection in the main cell. The electrolyte overflow was recirculated using a special glass bridge (ϕ 7mm) positioned between the two electrolyte baths. Electrolyte temperature was controlled by two heating plates (type: IKA Werk 7813 Staufen) with a magnetic field rotator to agitate the electrolyte.

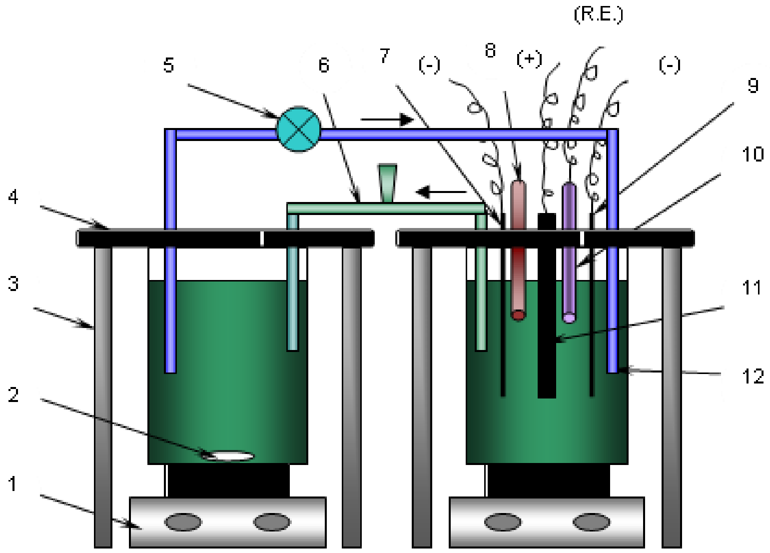

Fig. 3: Schematic representation of the experimental bench scale set up
1 = heater with magnetic rotator, 2 = rotating fish, 3 = steel stand, 4 = PVC cell cover, 5 = electrolyte pump, 6 = electrolyte bridge, 7 = cathode 1, 8 = thermometer, 9 = cathode 2, 10 = reference electrode, 11 = Ti-basket (anode), 12 = electrolyte inlet

While for the semi pilot scale apparatus, the main parts were a plexiglas cell which divided into two equal containers (with an active volume of 685 mm × 224 mm × 135 mm which corresponds to 20.71 l practical electrolyte volume for each container). The outer surface of the two container was surrounded by a circulating water bath heated to about 65 °C to supply a constant and a homogeneous heat distributions in the electrolyte bath. The utilized heating system consists of the main thermostat (ThermoHaake B7), which heats up the distilled water filled a stainless steel (S.S.) container and hence the main electrolyte container (200 l plastic container) which immersed in a such S.S. container, together with heating up the water bath surrounded the two plexiglas cells which circulated with another pump. Another thermostat (Haake F) coupled with a glass heat exchanger was used to heat the electrolyte directly before its inlet to the cell. This system has always supplied a constant electrolyte temperature of 65 ± 0.5 °C. A complete view of the used semi pilot arrangement is illustrated in Figure 4.

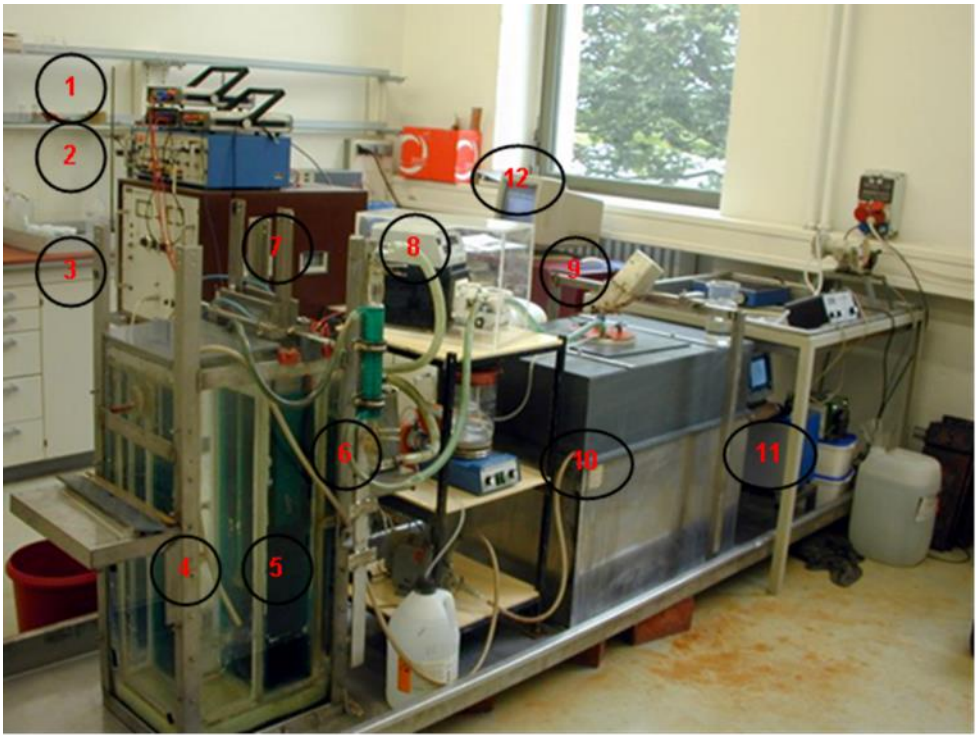

Fig. 4: A complete illustration of the used cell for semi-pilot runs
1 = millimetres, 2 = scanner, 3 = galvanostat, 4 = cell 1, 5 = cell 2, 6 = heat exchanger, 7 = anode basket, 8 = electrolyte pump, 9 = electrorotator, 10 = 200 l electrolyte container, 11 = thermostat, 12 = data recording system

The employed electrolyte was always circulated from the 200 l electrolyte container to the employed cell at a constant rate of 12 l/h (2.5 h for a complete circulation of the cell electrolyte) by using a precise pump (Ismatec BVP). The continually conducting of the used bath additives (bone glue and thiourea) was carried out using another pump (CFG type A2001). While the compensating water arises from both electrolyte evaporation and heating water was supplied using another two pumps (B. Braun Melsungen AG) and (CFG type A2001) respectively.

The anode particulates were washed with concentrated H_2SO_4 followed by distilled water and air drying to remove the oxide layers formed on the particulate surfaces during the granulation process. The utilized Ti-basket with and without anode particulates was weighed and fixed in the cell. The stainless starting sheets were isolated the non-reactive surface area, cleaned, feted with ethanol and dried before taking their position in the cell. The strong electrolyte evaporation was continuously compensated with distilled water through a pump (type B. Braun Melsungen).

All experiments were carried out using a constant direct current supply (galvanostat type Heinzinger TNB 10-500). To assure a constant supply and a good controlling of the current feeding to the cell, a Double Pulse Control Generator (Wenking model DPC 72) was used. The cell current was directly measured with the help of a suitable shunt (0.1 Ohm, 50 W). The anodic and cathodic potential were measured against Ag/AgCl reference electrode (Inlab 301 with standard potential of 207 mV at 25 °C and 176.4 mV at 65 °C – data obtained from Dr. W. Ingold KG company, Frankfurt, Germany). Experimental data were measured using different digital multimeters. Recording of the different measurements was carried out using an analog digital modifier type DT 2811-AL (measuring level up to 2 V ± 0.5 % error range) connected to a computer to save the resulted data continuously by a Diadem computer software.

At the end of the experiment the electrodeposited copper powder, anode -particulates or -plates and anode slimes were washed, dried, weighed and chemically analysed. A method of a quantitative cations analysis by ICP, Spectro Flame D (Fa. Spectro) was employed for analysis of the daily electrolyte samples, anode slimes and copper powder. While analysis of sulphur were carried out using Leco CS-400 respectively.

2 Results and discussion

2.1 Bench scale experiments (proof of principle)

Three typical tests with particulates (<5 >2 mm), conducted at the same electrolysis conditions are shown in Table 5 (experimental data). The same electrolyte was continually employed for all operated experiments (depletion of Cu content).

Table 5: Experimental data of powder production experiments

Exp.	Particle s	Apparent curre	Period	Cell voltag	Cathodic c	Sp. energ	Productivity
	[mm]	[A/m^2]	[h]	[V]	[%]	[kWh/kg]	[g/A.h]
A	<5 >2	250/280	27.55	0.8757	83.35	0.857	1.02
B	<5 >2	250/280	40.48	0.9886	74.9	1.070	0.92
C	<5 >2	250/280	21.533	1.17650	91.52	1.047	1.12

As shown in Figure 5, the cell voltage was started with a higher value and after about two hours reached a steady state level. The reason could be the higher superficial current density at the beginning of the electrolysis process (low cathode surface area), which decreases with the gradual formation of the powder on the cathode surface as well as the reduction of the anode cathode distance which leads to lower polarization. Another reason could be a 20 mV higher hydrogen overvoltage on the stainless steel starting cathode compared to copper (25 °C, 2N H_2SO_4) [2]. This H_2 overvoltage together with the other accompanied polarizations (such as diffusion, crystallization, electrolyte ohmic resistance, cable contact, etc.) will rise the overall cell voltage throughout the electrolytic process course in the all operated experiments [3].

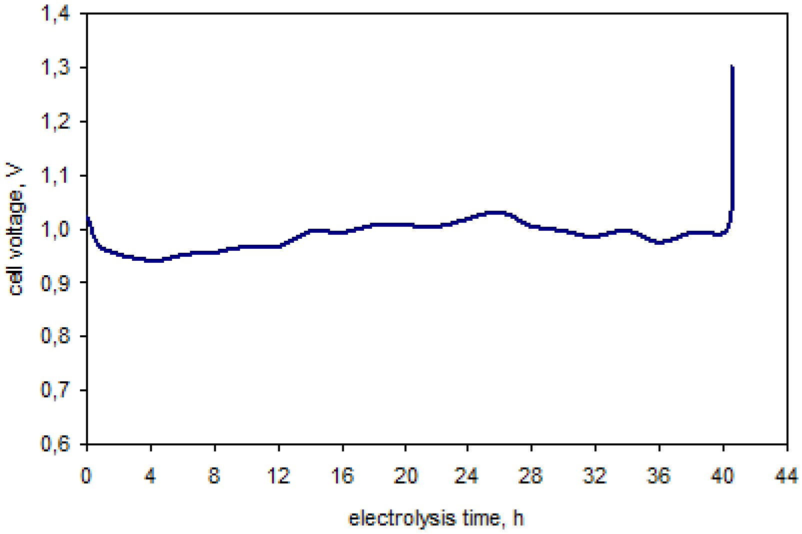

Fig. 5: Cell voltage with time of copper powder production (Exp. B, <5 >2 mm,1.6 l/h, 250 A/m^2)

At different time intervals, the cell voltage increased slightly. This effect resulted from the removing of the formed powder from the cathode surface, which decreased the cathodic surface area (increase of the current density).

XRD of the anode particulates before and after the electrolysis process were detected and the main phases were still $AlCu_3$ and Cu (only after electrolysis process). The reason for appearing of Cu after the electrolysis process is the formation of copper cement around the anode particulates leading to a decrease of the less noble metals (comparing to Cu) contents in the electrolysed particulates during the cementation process.

Electrolysis of the particulate anode led to cathodic current efficiencies more than 90 % (see Table 5). The calculated anodic current efficiency was in the average value of 84 % in the all cases. This could be due to (a) the lower real anodic current density (higher particulate surface area) in a comparison to the calculated apparent current density (280 A/m^2), (b) the formation of a thick slime layer around the anode particulate [4,5], (c) the lower content of Cu ions in the electrolyte beside its high impurities content, which increased with the electrolysis time, and (d) the permanent resulted light short circuits.

The produced powder (Table 6) has a high content of Sn (the primary deposited powder at the cathode surface reached up to 59 % and the secondary Cu-powder had up to 5.7 % after fall to the cell bottom). Its high content in the anode (7.5 %) gives a good possibility to deposit with Cu at the higher cell voltage as existent in the all experiments (from 0.825 to 1.177 V). Much less noble metals are Sb, Bi and As. As and Bi were not detected because of its very low content in the starting anode. Sb has a measurable content of about 0.3 %. The contamination of Cu powder with Pb (~ 0.6 %), Al (~ 0.15%), Zn (~ 0.06 %) and Fe (~ 0.02 %) comes from their high contents in the electrolyte resulted from the anodic dissolution and from the extreme low copper concentration. Another reason for the powder contamination can be the anode slime, which fall with the produced powder to the cell bottom.

Table 6: Chemical analysis of the deposited powder at cathode surface and that fall to the cell bottom

Exp. No.	Cu	Sn	Sb	Pb	Zn	Al	Ag	Fe	Ni	Bi	As	S
											[%]	
A (bottom)	95.31	2.92	0.32	0.24	0.02	0.06	0.01	0.02	<0.01	<0.05	<0.05	1.10
A(cathode)	82.80	16.5	0.33	0.20	<0.01	<0.01	<0.01	0.02	<0.01	<0.05	<0.05	0.15
B (bottom)	92.26	5.69	0.30	0.75	0.02	0.10	0.01	0.02	<0.01	<0.05	<0.05	0.85
B(cathode)	48.28	50.8	0.35	0.33	<0.01	<0.01	0.01	0.01	0.74	<0.05	<0.05	0.23
C (bottom)	92.93	4.64	0.26	0.59	0.06	0.17	0.01	0.01	<0.01	<0.05	<0.05	1.33
C (cathode)	39.40	59.2	0.34	0.83	<0.01	<0.01	0.02	0.01	0.83	<0.05	<0.05	0.20

It is also observed that, the colour of the deposited powder on the cathode surface has changed from the black to brawn (cupric) after dropping to the cell bottom. The black colour could be due to the oxidation of the powder by the entrapped oxygen from air to electrolyte and by the evolution of oxygen from the winning process. The most viable reason could be the cementation of Cu ions present in the electrolyte with Sn powder to form Cu-cement throughout this reaction:

$Cu^{2+} + Sn^{\circ} \rightarrow Cu^{\circ} + Sn^{2+}$

or

$2Cu^{2+} + Sn^{\circ} \rightarrow 2Cu^{\circ} + Sn^{4+}$

These reactions are seemed to be fast at the utilized conditions because of higher reacting surface area of copper powder and the used process temperature (65 °C). The obtained results from the XRD analysis of the produced powder showed no significant differences and indicated that, the main detected impurity phases were Cu_2O, $Cu_{40.5}Sn_{11}$ and CuZn (Figure 6).

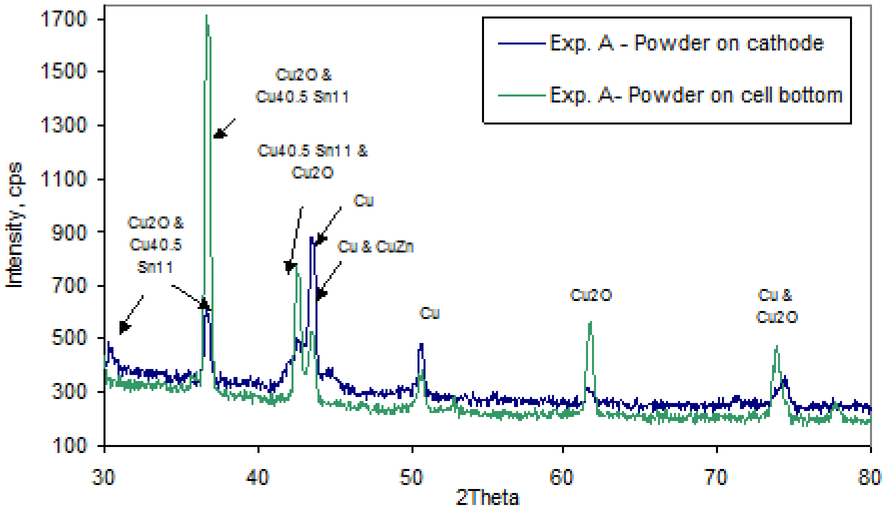

Fig. 6: XRD of the produced powder

Figure 7 presents the morphology of the produced powder using scanning electron microscope. As expected the obtained particles have a dendritic shape as that always obtained from the powder produced by electrolysis [1]. The agglomeration of the powder particles could be due to the presence of Cl^- ions in the utilized electrolyte, which enhance the agglomeration of the particles [6].

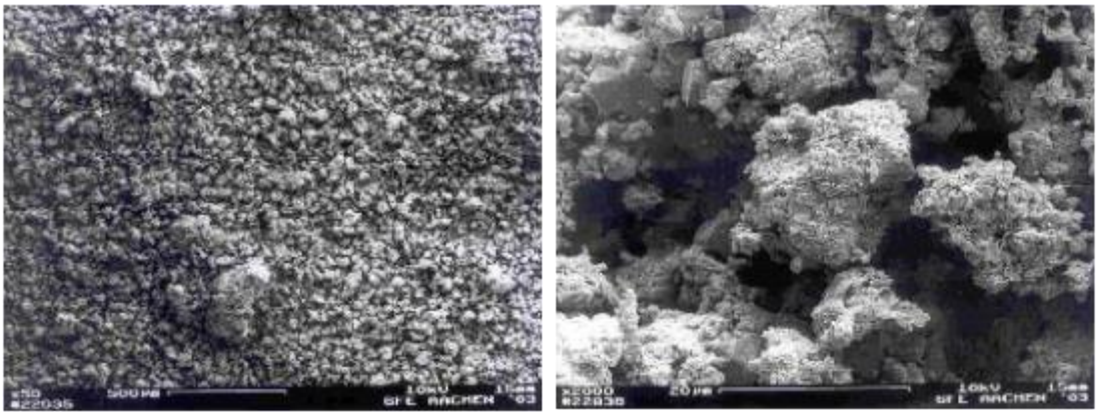

Fig. 7: SEM photomicrographs of the bench - scale electrodeposited copper powder from electronic scrap (Exp. No. B) (a) 50 X (b) 2000 X

As shown in Table 7, the concentration of the different electrolyte components except Cu and Sn was increased throughout the electrolysis course. The starting copper concentration was 5 g/l and decreased gradually in the first day to 168 mg/l and stayed constant till the end of the electrolysis course. The reason is the low anode content from Cu (~ 79 %) which supplies less Cu ions to the solution than required for depositing on the cathode surface. The equilibrium amount of Cu (~ 170 mg/l) is a result of which deposited copper on cathode surface comes directly from the anode dissolution. It is also important to state that, due to this very low level of Cu ions in the solution a significant amount of copper will be substituted by H_2 deposition on the cathode surface [7]. The concentration of Sn keeps stable at about 2 g/l.

Table 7: Chemical analysis of the electrolyte before and after the electrolysis process (bench scale experiments)

Exp.	Al	Zn	Sn	H_2SO_4	Cu	Fe	Ag	Sb	Pb	Ni	Bi	As	Cl
No.													[m
A(before)	0	0	0	167	5550	0	< 0.1	0	0	16.6	< 2	< 1	47
A (after)	2.63	1.06	1.28	168	168	42.2	< 0.1	16.4	6.66	56.1	< 2	< 1	32.3
B (before)	2.17	0.879	1.1	168	168	35.6	< 0.1	13	6.96	39.4	< 2	< 1	28.6
B (after)	5.65	2.31	2.17	169	169	91.9	< 0.1	33.7	12.3	120	< 2	< 1	33.6
C (before)	5.19	2.14	2.08	171	171	84	< 0.1	29.2	11.7	108	< 2	< 1	34.6
C (after)	6.91	2.68	1.72	172	172	103	< 0.1	39.2	12.6	138	< 2	< 1	22.4

The concentration of H_2SO_4 has the trend to the gradual increase. This is due to the winning process of the different electrolyte impurities, which increases continuously the sulphuric acid concentration [3]. Otherwise, the concentration of Cl ions has the trend to decrease as shown in the experiments. The reason is the high affinity of copper powder to react with Cl, together with the main reaction of Cl with silver [8].

The chemical analysis of the formed anode slimes on the particulate surfaces are illustrated in Table 8. The analysis of the very fine electrolyte slimes was very rich in Sn (77.2 %). It is most likely that, very light Sn compounds float in the electrolyte and settle outside in the electrolyte system.

Table 8: Chemical analysis of the anode slimes (bench scale experiments)

Exp. No.	Cu	Al	Fe	Ni	Zn	Sn	Ag	Sb	Pb	Bi	As	S	Cl
												[%]	
A (particulate)	40.2	1.88	0.04	0.05	0.81	6.46	0.36	0.72	30.7	0.02	< 0.01	5.90	0.07
B (particulate)	32.4	1.51	0.02	0.03	0.62	10.4	0.47	0.86	31.1	0.03	< 0.01	6.12	0.08
B (electrolyte) (cell 2)	0.26	0.03	0.02	< 0.01	0.07	77.2	0.43	0.69	0.07	<0.01	< 0.01	1.71	-
C (particulate)	33.4	0.81	0.02	0.02	0.38	23.9	0.42	1.16	20.6	0.04	< 0.01	4.19	0.09

2.2 Semi-pilot scale runs

The same experimental technique was applied to produce electrolytic copper powder in a semi pilot scale. An electrolyte was prepared with 5 g/l Cu (run D) utilizing the same other conditions. Cl was not added to avoid CuCl formation which comes from the following two reactions ($Cu_2O + 2HCl \rightarrow 2CuCl + H_2O$ and $Cu^+ + Cl^- \rightarrow CuCl$) [12, 13]. Also bath additives (Thiourea and glue) were not used to prevent the contamination of the produced powder with sulphur and to avoid polarization effects on the anode [9]. In both runs pre-used anode particulates were subjected to the electrolysis process. Short circuits which occurred from time to time due to the short distance between anode and cathode (20 mm) were removed manually. Table 9 illustrates the technical data of the semi pilot runs.

Table 9: Experimental data of the operated electronic scrap anode runs (semi pilot runs)

Run	Anode pa	Cell cu	Apparent c	Period	Cell voltage	Cathodic c	Anodic cu	Sp. energ	Productivit
	[mm]	[A]	[A/m^2]	[h]	[V]	[%]	[%]	[kWh/kg]	[g/A.h]
D	<5 >2 m	26	250/270	48.24	0.374	63.23	86.42	0.511	0.75
E	<5 >2 m	26	250/270	117.92	0.459	67.67	81.23	0.405	0.79

The obtained results from the semi pilot runs indicated that the average cell voltage is 0.42 V in comparison to 1.01 V in bench scale experiments. The reason for this difference is the lower anode cathode distance in the case of semi pilot runs (20 mm in comparison to 25 mm in bench scale experiments) beside the lower electrolyte contamination in semi pilot runs and the better electrical contact and lower oxygen overvoltage due to utilizing of a platinized Ti current distributor in comparison to graphite distributor in bench scale experiments [7]. The average cathodic current efficiencies in semi pilot runs are 65.45 % and 83.25 % in bench scale experiments. This difference can be attributed to the strong short circuits in the case of semi pilot runs as well as the loss of Cu-powder in cell bottom after the end of the electrolysis coarse. In both cases the evolution of hydrogen on the cathode surface due to the extreme lower Cu concentration in the electrolyte is a cause for the lower cathodic current efficiencies. At higher electrolysis time (Run E) the anodic current efficiency is lower due to the formation of a thicker slime layer around the anode particulates which hinder the diffusion of dissoluted ions to the bulk solution.

The composition of the produced powder is illustrated in Table 10. The average content of copper was in the range of 98 % while Sn was in the average range of 1.5 %.

Table 10 Average percentage chemical analysis of the produced powder resulted from semi-pilot runs

Run No.	Cu	Sn	Sb	Pb	Zn	Al	Ag	Fe	Ni	Bi	As
(D)	97.8	1.81	0.04	0.24	0.03	0.02	< 0.01	0.03	0.01	0.02	< 0.01
(E)	98.55	0.905	0.17	0.39	0.11	0.3	< 0.1	<0.01	0.017	0.03	< 0.01
(E) (on c	98.22	1.07	0.037	0.65	<0.01	<0.1	< 0.1	<0.01	<0.01	0.033	< 0.01

In comparison to bench scale experiments, the produced powder has a higher copper content (average 98.2 % in comparison to 93.5 %) and lower Sn content (1.36 % in comparison to 4.4 %). Also the copper powder deposited on cathode surface has a lower Sn content (1.07 % in comparison to 42.2 %). This could be due to the lower cell voltage which decrease the deposition of Sn on cathode surface. The other elements have lower contents than the bench scale experiments which attributed to the lower cell voltage and lower electrolyte contamination in semi pilot runs in comparison to bench scale experiments.

The microstructure of the electrodeposited powder is shown in Figure 8 and is similar to that resulted from the bench scale experiments (dendritic shape). But the obtained particle sizes were coarser. The reason may be attributed to the absence of Cl in the semi pilot runs [6].

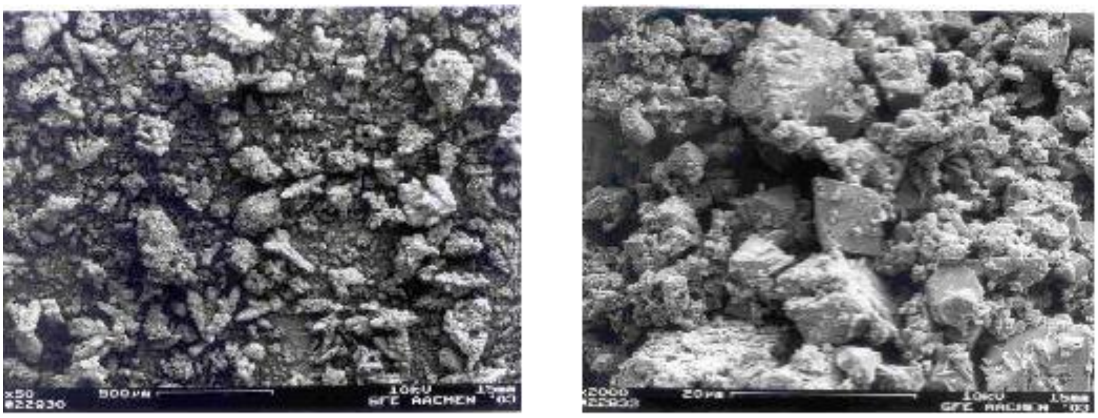

Fig. 8: SEM photomicrographs of the semi-pilot electrodeposited powder (run No. E) (a) 50 X (b) 2000 X

The apparent density of the produced powder as well as the powder sieve analysis are illustrated in Table 11.

Table 11: Sieve analysis and apparent density of the produced copper powder

Exp. No.	Apparent d	Sieve fraction	Amount	Percentage
	[g/cm³]	[µm]	[g]	[%]
E (semi pilot)	4.25	> 500	20.61	26.9
		< 500 > 250	12.86	16.8
		< 250 > 125	17.33	22.6
		< 125 > 90	7.70	10.1
		< 90	18.10	23.6
B (bench scale)	4.28	> 500	12.95	24.6
		< 500 > 250	10.07	19.1
		< 250 > 125	8.81	16.7
		< 125 > 90	3.74	7.1
		< 90	17.05	32.4

From Table 11, the finest size fraction (< 90 µm) and the coarsest one (> 500 µm) have the greatest amount in both bench and semi pilot scales with mean particle size of 275 µm. The obtained apparent densities in size fraction > 500 µm are similar in both scales and has an average value of 4.26 g/cm^3.

The gradual variation of the electrolyte composition with the course of the dissolution time is presented in Table 12 and Figure 9. The copper ions concentrations were always decreased with electrolysis time while the other components were gradually increased. The reason for this effect is the deposition of copper ions on the cathode surface as a copper powder as well as the dissolution of the other constituents from anode and enriched in the electrolyte.

Table 12: Electrolyte composition at different electrolysis periods

Run No.	Cu	Al	Ni	H_2SO_4	Fe	Zn	Sn	As	Ag	Sb	Pb	Bi	
													[ı
(D) befor	4.66	0.024	0.017	158	3.23	9.04	11.8	< 1	< 0.1	< 2	4.07	< 1	
(D) after	1.95	1.04	0.163	162	20.5	387	26	< 1	< 0.1	10.8	9.1	< 1	
(E) befor	1.46	0.924	0.125	169	15.9	350	20.5	< 1	< 0.1	8.45	2.86	< 1	
(E) after	0.667	1.95	0.445	173	32.2	727	33.2	< 1	< 0.1	13.7	8.5	< 1	

Run E was carried out for a longer time (117.92 h) employing a pre-used electrolyte after run No. D using the same conditions to see the effect of the electrolysis process on the electrolyte composition (Figure 9). The electric parameters and data are illustrated in Table 8 and showed in Figure 10. As in the bench scale experiments, accompanied short circuits between the anode basket and cathode were taken place due to the accumulation of the electrodeposited powder on the cathodic surface. The removal of powder resulted in sharp peaks of the cell voltage.

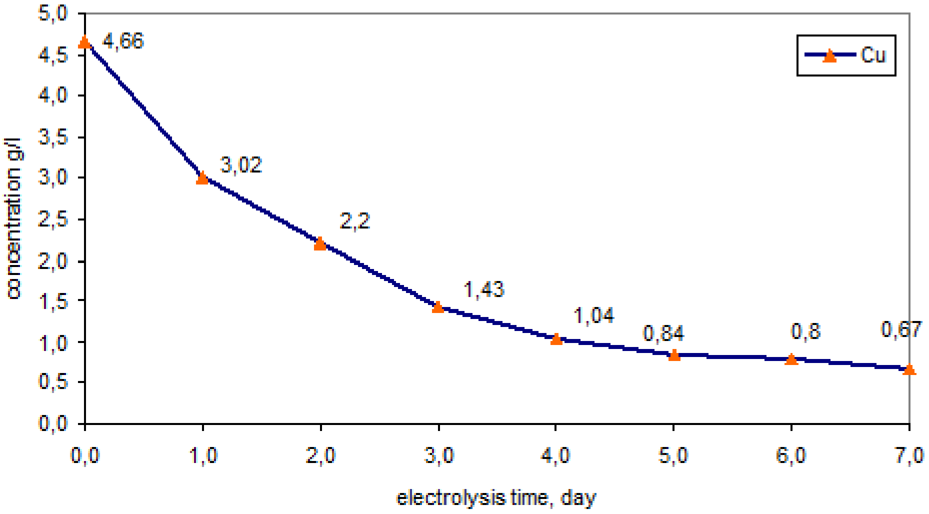

Fig. 9: Variation of the Cu ions concentration during powder production (run No. D & E)

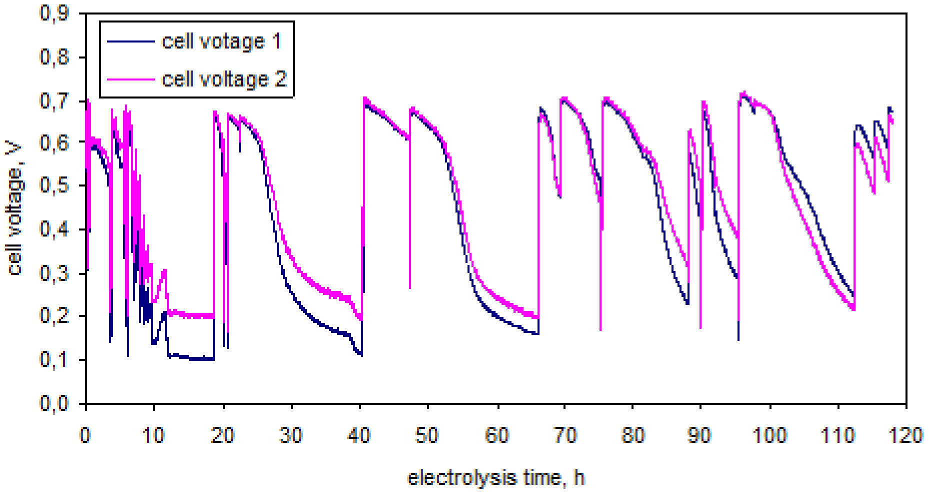

Fig. 10: Dependence of cell voltage on electrolysis time (semi pilot scale run D)

The average composition of the produced anode slimes formed on the anode particulates are listed in Table 13.

Table 13: Average percentage chemical composition of the produced slimes

Run No.	Cu	Sn	Sb	Pb	Zn	Al	Ag	Fe	Ni	Bi	As	S
D	18.24	32.68	1.16	14.23	0.44	2.14	0.50	0.07	0.02	0.09	0.03	3.60
E	15.78	39.53	1.258	15.35	0.208	0.43	0.586	0.018	0.0135	0.077	0.02	3.5

From the above Table (Table 13), it was observed that, the content of the main slime components were Sn, Pb and Cu. This is due to the high amount of these elements in the anode particulates and their distance to Cu in the electrochemical potential. Presence of these elements will form slime compounds such as $PbSO_4$ and $Sn(OH)SO_4$ [3, 10]. While for Cu, the reason could be from cemented copper on the anode particulate surfaces and from Cu intermetallics beside the anode rest powder fall to the bottom after the reduction in the particle sizes with the coarse of the electrolysis process [11, 12]. Another source for Cu is the disproportionating reaction ($2\,Cu^+ \rightarrow Cu^{2+} + Cu$) which is a typical source of slime Cu in the electrolytic refining of Cu [9]. In comparison to the slimes formed on anode particulates from the bench scale experiments, the content of the most elements such as Sn, Ag, Sb, Bi and As is higher. This could be due to the higher cell voltage (~ 1.2V in comparison to ~ 0.4 V in semi pilot runs) which gives a possibility of dissolution of these metals Sn more than precipitation in the slime phase. This is proofed from their higher content in the deposited copper powder in bench scale experiments.

Figure 11 illustrates senky diagram (run E) to show the distribution of different elements between the process phases (powder, slime and electrolyte). It is shown from the diagram that, Al, Zn, Fe and Ni transfer completely to electrolyte phase, while Sn, Ag, Pb and Sb prefer to settle with slime phase. This can be attributed to the nobility of the different elements in comparison to Cu.

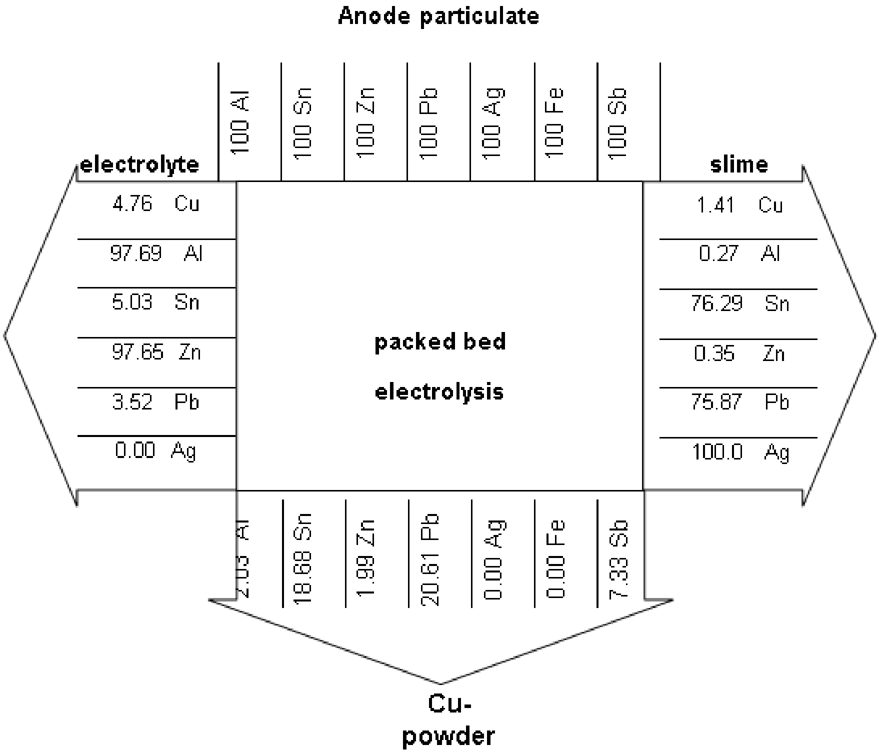

Fig. 11: Senky diagram for production of Cu-powder from electronic scrap recycling

3 Conclusion and outlook

From the obtained results, it can be concluded that, packed bed electrolysis technology without external copper sulphate additions and the other bath additives can be used to produce copper powder with min. 98 % Cu, and the main alloying element 1.5 % Sn. The process was carried out without serious polarization, but with tendencies for short circuits occurred after a definite enough time to accommodate the powder on the cathode surface. This causes a slight contact with the anode surface or the anode basket. The cell voltage was higher than that of the normal electrolysis process utilizing the typical conventional electrolyte composition. This could be due to the lower content of Cu ions in the utilized electrolyte, which causes H_2 deposition instead of Cu on the cathode surface. The obtained cathodic current efficiencies exceeded slightly only 80 % with a specific energy demand in the range from 0.4 to 0.5 kWh/kg and a ‘productivity’ ranging about 0.8 g/Ah.

From Figure 12, the resulted cathodic and anodic current efficiencies of both individual Cu and Cu with other metals contained electronic scrap materials were illustrated. Also the main specifications of the process were represented.

This work is a part from extended investigations to apply this new technology in production of electrolytic copper powder from electronic scrap materials. The next work will be concerned with the investigation of the different affecting factors on the process (e.g. current density, electrolyte temperature, anode cathode distance, starting cathode type etc. …).

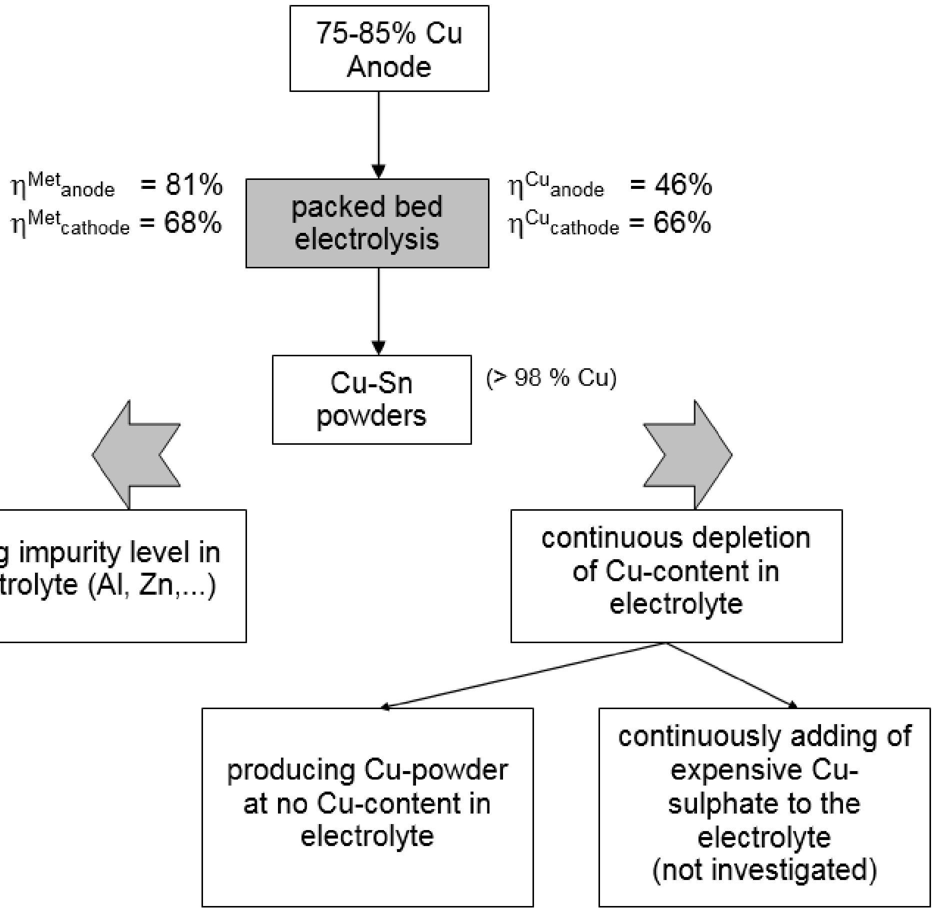

Fig. 12: Yields of the process and driving force to produce powders

Literature

[1] TAUBENBLAT, P.W. (1974): Importance of copper in powder metallurgy. – Int. J. Powder Metallurgy & Powder Technology, **10**: 169-184.

[2] JOHN, H.P. (1950): Chemical engineering handbook: p. 1788; New York, Toronto, London (McGRAW-Hill Book Co.).

[3] BISWAS, A.K. & Davenport, W.G. (1994): Extractive metallurgy of copper: 3rd Edition.

[4] LÜCK, M. (1985): Granulate electrolysis of copper scrap containing 10-15 % Ag. Ph.D. submitted to RWTH-Aachen

[5] FRIEDRICH, B. (1988): Electrolytic refining of strong contaminated tin with packed bed anode. Ph.D. submitted to RWTH-Aachen

[6] PEISSKER, E. (1984), Production and properties of electrolytic copper powder. – Int. J. Powder Met. & Powder Technology, **20**: 87-101.

[7] GREENAWALT, W. (1912): The hydrometallurgy of copper: 1st ed., 4th impression; New York (McGraw-Hill Book Company, Inc.).

[8] BOMBACH H. et al. (1997): Anode passivity – basis and meaning for electrolytic refining. – In: GDMB-Schriftenreihe, Heft 81: Elektrolyseverfahren in der Metallurgie: pp. 97-112.

[9] KNUUTILA, K., FORSEN, O. & PEHKONEN, A. (1987): The effect of organic additives on the electro-crystallization of copper. Proceedings of the symposium sponsored by the TMS Copper, Nickel, Cobalt, Precious Metals and Electrolytic Processes Committees, and held at the TMS 116th Annual Meeting in Denver, Colorado, February 24-26

[10] KUXMANN, U. et al. (1990): Experiments for studing the behaviour of Sn, Ni, Sb, and Pb in electrolytic refining of copper. – In: GDMB-Schriftenreihe, Heft 28: 57.

[11] GANA, R. & FIGUEROA, M. (1993): Direct electrorefining of copper scrap using an anode-support system in a bipolar cell. – Journal of applied electrochemistry, **23**: 813-818.

[12] FIGUEROA, M. & GANA, R. (1994): Direct electrorefining of copper scrap using a titanium anode-support system in a monopolar cell. – Journal of applied electrochemistry, **24**: 206-211.