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PRECIOUS METALS IN COPPER SMELTING PRODUCTS

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Mineralogical and geochemical research was carried out on shaft slags, converter slags, suspension slags and copper matte from the Legnica-Glogow Copper Region. Silver appears as small metallic inclusions in metallic Cu, metallic Pb is found in both in copper matte as well as metallic and sulphide droplets in slags. Silver occurs also as solid solution in metallic Cu and as Pb-Ag alloys. The main gold carriers are metallic phases: silver, lead and copper. The main carriers of Pd and Pt is metallic silver and metallic copper.

Key words: mineralogy, geochemistry, copper matte, slag, precious metals

INTRODUCTION

The copper ore-deposit located in the Legnica-Glogow Copper Region is a polimetallic deposit. Copper is associated with following elements: Fe, Pb, Zn, Ni, Co, Mo, Ag, Au, Bi, Ga, Ge, Hg, In, Re, Sb, Se, Sn, Te, Tl, V and platinum group metals (Kucha 1981, 1983, Banaś et al. 1976). In the whole process of metal production they do not have significant importance, but many of them are enriched, mainly during the flotation, metallurgical and refining processes (Rapacz 1998).

Precious metals, which occurs in copper concentrates sometimes form their own minerals or substitutions in others. For example: silver occurs as native silver, Ag-Cu sulphides or substitutions in bornite & chalcocite (Salamon 1979). Gold forms its own minerals or substitutions in arsenides, antimonides, sulphides, organic matter, arsenates and oxysulphides (Kucha 1982, 1990), behave in similar way to the platinum group metals (Kucha 1976, 1982, 1984).

Copper metals is produced in copper smelters, which use two different technologies: multistage smelting - copper smelter in Legnica (HML) and Glogow I (HMG I) (Fig.1); single stage smelting – copper smelter in Glogow II (HMG II) (Fig.2).

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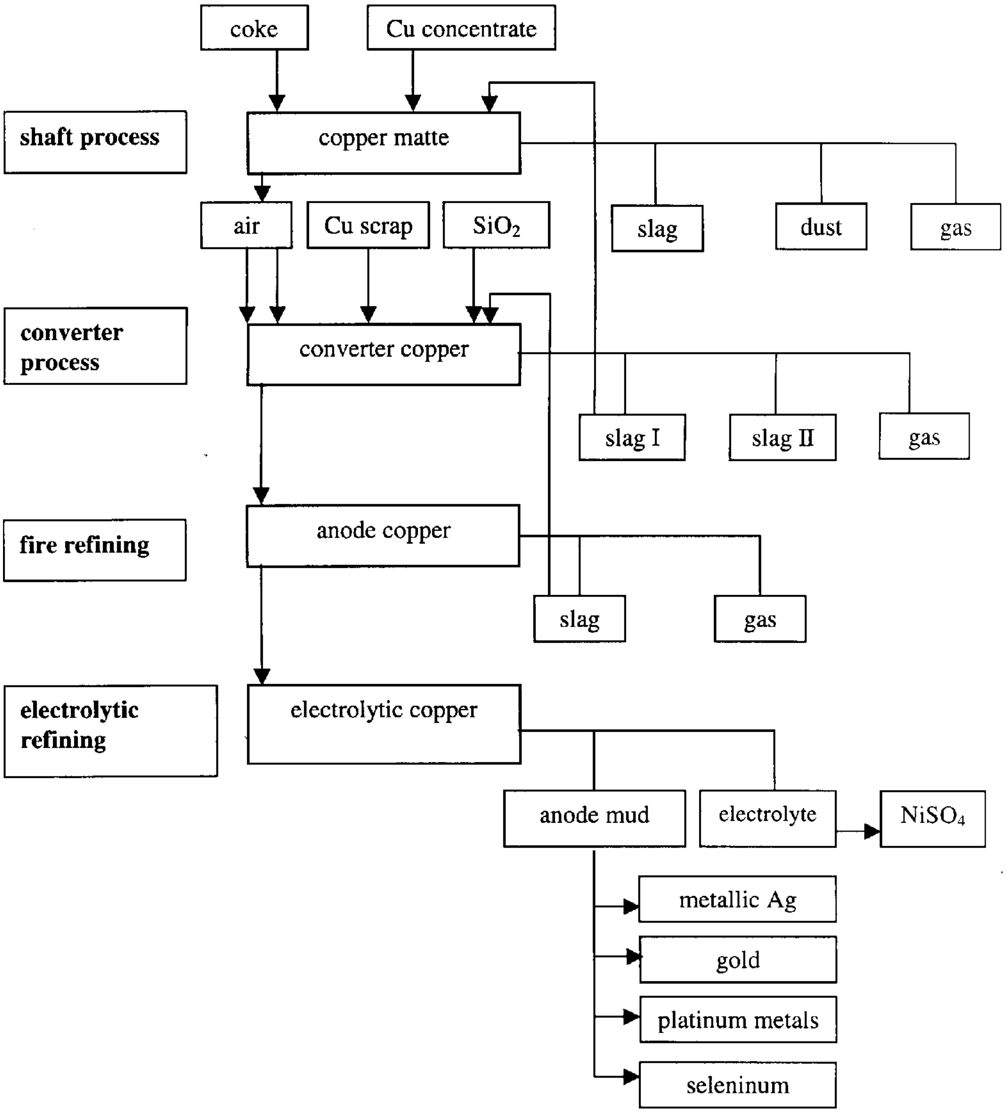

Fig. 1. Schematic diagram of technology in Copper Smelter Legnica and Glogow I (modified after Karwan et al. 1996)

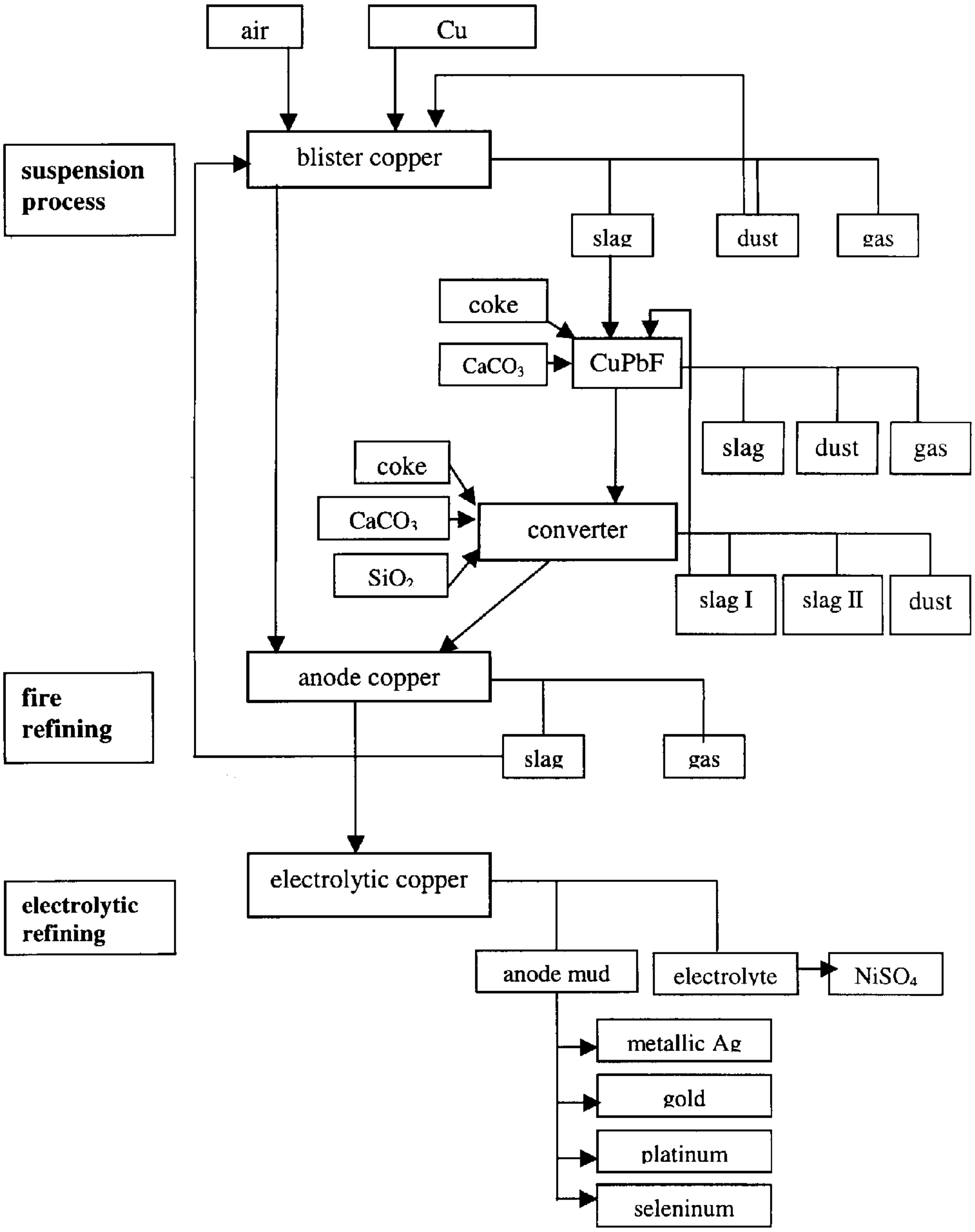

Fig. 2. Schematic diagram of technology in Copper Smelter Glogow II
(modified after Karwan et al. 1996)

During the process of copper concentrate smelting, copper accumulates in the shaft process as a copper matte and converter copper, and in the suspension process as blister and converter copper. Research has shown that part of the copper and other precious elements are lost in the slag by mechanical and physico - chemical ways during these processes (Acuna 2000, Imriś et al. 2000, Sridhar et al. 1997, Simeonov et al. 1996). This causes a loss of precious metals during metallurgical production.

The aim of the study was the mineralogical and geochemical characterisation of the metallurgical slags and copper matte from the Legnica-Glogow Copper Region. Phases hosting precious metals, such as: Ag, Au, Pt and Pd were located and identified, and their chemical composition has been examined.

MATERIALS AND METHODS

Samples of shaft slag from Legnica, converter slag from Legnica and Glogow, suspension slag from Glogow and copper matte from Legnica were studied by reflected light microscopy, scanning electron microscope (SEM), proton induced X-ray emission (PIXE), electron microbe and bulk chemical analysis. Areas for scanning electron microscope (SEM) were selected based on the reflected microscope. The SEM analyses were carried out at AGH using a JEOL ISM 5400 scanning electron microscope. Electron microprobe analyses were carried out at the Institute of Non-ferrous Metals in Gliwice using a JEOL JCXA 733 at 20 kV. The following spectral lines and synthetic standards were used: S K_{α}, Fe K_{α}, Co K_{α}, Cu K_{α}, Zn K_{α}, MgO K_{α}, Ni K_{α}, Ag L_{α}, As L_{α}, Mo L_{α}, PbF_2 M_{α}, Au M_{α}. All analyses were ZAF corrected. The PIXE analyses were carried out at the Institute of Nuclear Physics in Cracow. The proton energy was 2,5 MeV and beam intensity was up to 5μA, time counting was 20 to 30 min. The beam diameter on the target was about 0,5 mm. Analyses were corrected by "Maestro" software package. Bulk chemical analyses were done at Omac Laboratories Ltd., Loughrea, Ireland by inductively coupled plasma (ICP).

SLAGS

The main component of slag is a glass phase that contains abundant small, oval aggregates of metallic copper, sulphides, Fe-Co alloys, Pb-Ag alloys, spinels, sphalerite, arsenate phases and sometimes olivine and pyroxene or amphibole crystals. The proportion of glass phase to crystalline phase changes widely in different slags. Porosity changes from a single pore to structures similar to pumice (Muszer 1996, Kucha et al. 1998).

METALLIC COPPER

Metallic copper from slag creates small, oval aggregates (Fig.3). Analyses in microarea showed that its chemical composition is as follow (%wt): Al 0,05-0,08, V 0,04-0,08, S 0,07-0,21, Mn $\leq$ 0,02, Fe 0,11-0,67, Co 0,03-0,17, Ni 0,03-0,16, As up to

0,06, Ag 0,05-0,41, Zn 0,05-0,2, Pb 0,09-0,33 (Tab.1). Sometimes metallic Cu from suspension and converter slags (HMG II) contains detectable gold. Gold concentration in suspension slag are from 0,225±0,04 to 0,304±0,03 and in converter slag from 0,016± 0,009 to 0,024±0,009 (Tab.2).

SULPHIDES

Copper sulphides from slags are similar in composition to chalcocite and half-bornite (Kucha et al.1998). Sulphides similar to Cu_2S very often contain inclusions of metallic silver, metallic copper, Fe-Co alloys, and Pb-Ag alloys (Fig.4, 5). Metallic silver from converter slag (HL) contains (%wt.): up to 0,75 S; 1,42-2,44 Fe; up to 0,64 As; 3,66-4,73 Pd; up to 0,41 Sb; up to 0,73 Te; up to 1,01 Au; up to 0,74 Hg and up to 1,88 Bi (Cichowska & Kucha 2000). Fe-Co alloys are reach in Ni, Cu and As. Pb-Ag alloys are very small and difficulty to examine.

ARSENATES

Their chemical composition is close to $CaAsO_4$. They create big crystals and contain from 3,01 to 3,88 %wt. of S; from 28,36 to 29,76 %wt. Ca; from 0,10 to 0,27 % wt. Fe; 0,23 to 0,65 % wt. Cu; from 31,05 to 33,68 %wt. As; from 2,68 to 3,29 %wt Pb; from 30,05 to 34,03 %wt.O. They have sometimes small admixture of Co, Ni, Ag, Sn and La.

The other phases, such as: spinels, pyroxenes, amphiboles and sphalerite do not contain detectable admixtures of precious metals.

Bulk chemical analyses showed that there is 6 ppm Ag, 9 ppb Au, ≤ 2 ppb Pt and Pd in shaft slag from Legnica and about 40 ppm Ag, 8 ppb Au, ≤2 ppb Pt and Pd in converter slag from Legnica.

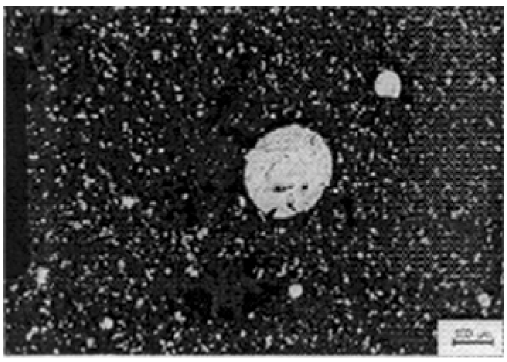

Fig. 3. Microphotograph of suspension slag from HMG II – metallic copper (oval bright) with Fe-Co alloys. Reflected light. Scale bar 100 μm

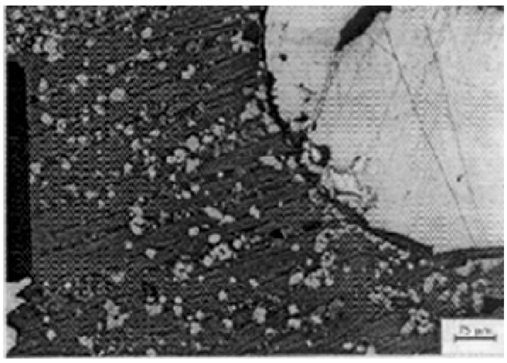

Fig.4. Microphotograph of converter slag from HMG II – chalcocite (oval light-grey) with light metallic copper inclusions. Reflected light. Scale bar 75 μm

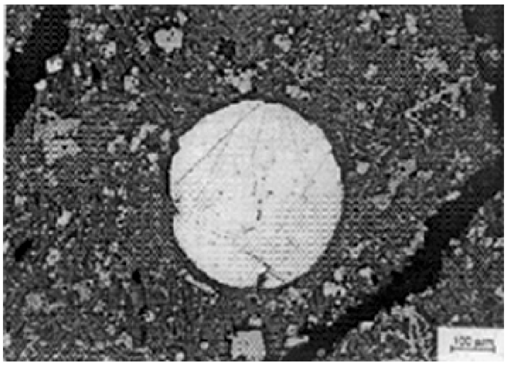

Fig.5. Microphotograph of converter slag from HL – chalcocite (oval light) with light metallic silver inclusions. Reflected light. Scale bar 100 μm

Table 1. Chemical composition of metallic copper from slags (%wt.), electron microprobe analyses (Not detected: Mn ≤0,02)

Sample	Al.	V	S	Mn	Fe	Co	Ni	Cu	As	Ag	Zn	Pb	Σ
5A/1	0,03	≤0,04	≤0,07	≤0,02	0,39	0,17	0,14	99,41	≤0,06	0,03	≤0,05	0,17	100,34
5A/2	≤0,05	0,05	≤0,07	≤0,02	0,36	0,01	0,08	99,56	≤0,06	0,04	≤0,05	0,24	100,34
5A/3	0,08	0,08	≤0,07	≤0,02	0,67	0,02	0,08	96,82	≤0,06	0,26	≤0,05	0,19	98,2
5A/4	0,06	≤0,04	≤0,07	≤0,02	0,57	≤0,03	0,16	97,03	≤0,06	0,12	≤0,05	0,22	98,16
7B/1b	≤0,05	≤0,04	≤0,07	≤0,02	0,06	0,03	0,07	98,51	≤0,06	0,33	≤0,05	0,33	99,35
7B/2b	≤0,05	≤0,04	≤0,07	≤0,02	0,11	0,04	≤0,03	99,71	≤0,06	0,05	≤0,05	0,11	100,02
6A/3b	≤0,05	≤0,04	0,16	≤0,02	0,36	≤0,03	≤0,03	98,71	0,06	0,41	0,3	≤0,09	100
6A/4b	≤0,05	≤0,04	0,21	≤0,02	0,41	≤0,03	≤0,03	99,11	≤0,06	0,24	0,02	≤0,09	99,99

Table 2. Chemical composition of metallic copper. Suspension slag (X26037G/3**,** X26037H/3, X26037I/3) and converter slag (X26A37P/5, X26037L/7) from HMG II. PIXE analyses [%wt.]

Elements	X26037G/3	X26037H/3	X26037I/3	X26A37P/5	X26037L/7
Ca	0,054 ±0,004	0,078 ±0,007	0,108 ±0,006	0,005 ±0,002	0,012 ±0,003
Cr	0,119 ±0,008	0,053 ±0,010	0,111 ±0,010	0,027 ±0,008	0,026 ±0,005
Fe	12,718 ±0,060	16,368 ±0,081	17,853 ±0,074	6,130 ±0,050	2,713 ±0,030
Ni	≤0,005	≤0,005	≤0,005	0,583 ±0,050	0,120 ±0,020
Cu	32,324 ±0,120	36,294 ±0,152	41,692 ±0,140	60,604 ±0,215	28,236 ±0,080
Br	0,033 ±0,005	0,214 ±0,006	0,304 ±0,031	0,959 ±0,180	0,838 ±0,081
La	≤0,005	≤0,005	≤0,005	0,066 ±0,020	0,023 ±0,009
Au	0,250 ±0,020	0,225 ±0,040	0,304 ±0,031	0,024 ±0,009	0,016 ±0,009
Pb	2,604 ±0,062	3,485 ±0,070	3,519 ±0,083	33,348 ±0,221	6,935 ±0,090

COPPER MATTE

The main component of copper matte are copper sulphides, which constitute 80 – 95 %, metallic copper 5 – 17 % and Fe-Co alloys, metallic silver, galena, Pb-Ag alloys, Pb-Ni alloys, Pb-Cu alloys and arsenides.

COPPER SULPHIDES

Copper sulphides are the main component of copper matte. There are two different sulphides, one is similar in chemical composition to $Cu_{5,75}Fe_{0,25}S_4$ and other to $Cu_{5,5}Fe_{0,5}S_4$ (Kucha et al. 1998).These sulphides contain (%wt.) Al from 0,10 to 2,86; As from 0,10 to 0,83; Ag from 0,10 to 0,20 and Pb from 0,15 to 2,45.

METALLIC COPPER

Metallic Cu forms veins, oval and irregular droplets of variable sizes (Fig.6). Copper aggregates are from single µm to several cm. Metallic copper contains inclusion of Fe-Co alloys, Pb-Ag alloys, metallic silver, metallic lead and copper oxides. Chemical composition of metallic Cu is shown in table 3. Metallic copper contains admixture of gold, which is associated with lead (Fig.7). The Au content is from 0,08 to 0,39 % wt. Tab.3, 4). There is also platinum in amount of up to 0,113±0,004 %wt.

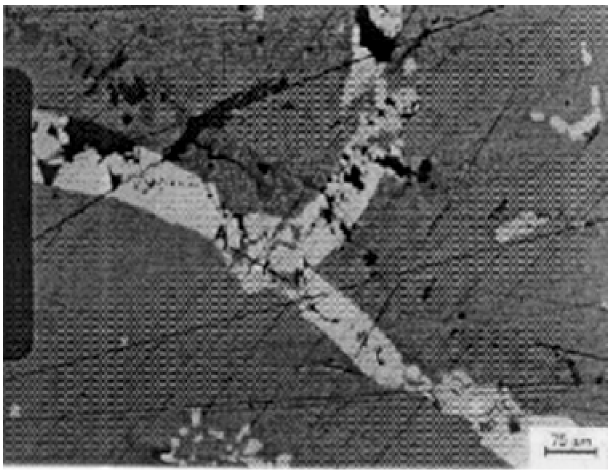

Fig.6. Microphotograph of copper matte from HL –metallic copper. Reflected light. Scale bar 75µm

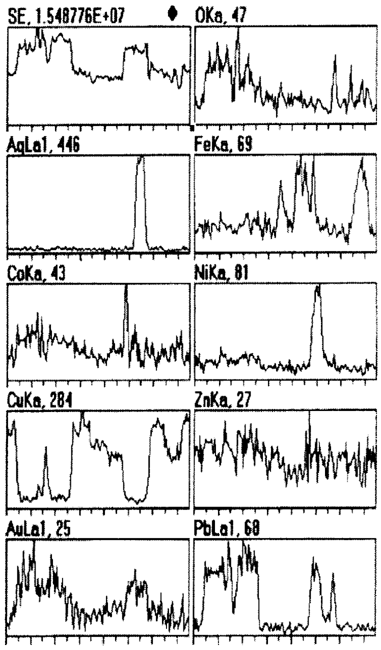

Fig.7. Distribution of O, Ag, Fe, Co, Ni, Cu, Zn, Au, Pb in the copper matte alongside profile A-B marked in fig. 6

METALLIC SILVER

Metallic Ag forms small inclusions in metallic copper. It contains (%wt): Fe 0,26 to 0,57, Co 0,03 to 0,19; Ni 0,03 to 0,15; Cu 2,27 to 5,07, As 0,06 to 0,08 and Pb 0,06 to 6,99 (Tab.5). Metallic silver sometimes has an admixture of gold of up to 0,94 % wt. (Kucha et al. 1998).

ALLOYS

Various metals alloys occur mainly in metallic copper as small droplets. They have small sizes and different chemical composition.
Fe-Co alloys, beside Fe and Co, consist of Ni, Cu, Mo, As and Ag changing from 0,01 to 0,18 % wt.

Pb-Ag alloys have admixtures of Cu, Ni, Co, Fe and sometimes up to 0,48 % wt. Au (Kucha et al. 1998). Pb-Ag alloys like Pb-Ag alloys from slags are very small and difficulty to analyse.

Pb-Cu alloys consist of (%wt.): Pb 26,85 to 72,59; Cu 14,78 to 64,67; Fe 0,91 to 2,29; Co 0,09 to 10,95; Ni 0,15 to 0,81 and Ag up to 0,22. These alloys contain also up to 0,52 %wt. Au, but this problem requires further research.

Pb-Ni alloys consist of (%wt.): Pb 53,61 to 69,79; Ni 21,16 to 26,62; Cu 4,15 to 7,01; Co 0,29 to 2,58; Fe 1,43 to 6,26 and sometimes of up to 7,75 Ag.

METALLIC Pb

Metallic lead creates inclusions in metallic copper. It has small admixtures of Cu, Fe, Cr, Co and up to 0,33 % wt. Ag and up to 0,48 % wt. Au.

Bulk chemical analyses of copper matte showed significant content of: >1000 ppm Ag, 72 ppb Au, 13 ppb Pt and 18 ppb Pd.

Table 3. Chemical composition of metallic copper from copper matte (%wt.), electron microprobe analyses

Sample	O	Cr	Fe	Co	Ni	Cu	Mo	Ag	Au	Pb	Σ
19A/4	≤0,05	≤0,02	0,30	0,06	1,50	96,28	≤0,06	0,38	≤0,08	≤0,06	98,52
19C/1	≤0,05	≤0,02	0,56	≤0,03	≤0,03	97,14	≤0,06	0,47	≤0,08	≤0,06	98,17
19C/5	≤0,05	≤0,02	1,54	0,45	1,42	94,23	≤0,06	0,54	≤0,08	1,31	99,49
19C/2A	≤0,05	≤0,02	2,12	0,39	0,36	95,87	≤0,06	0,17	≤0,08	≤0,06	98,91
19D/2	2,24	0,91	0,24	≤0,03	≤0,03	96,67	0,23	0,66	≤0,08	≤0,06	100,95
19D/3	1,02	0,22	0,08	≤0,03	≤0,03	94,82	0,16	0,94	≤0,08	≤0,06	97,24
20/4b	≤0,05	≤0,02	0,41	0,08	0,01	98,08	≤0,06	0,30	0,39	0,31	99,58
20/4'b	≤0,05	≤0,02	0,44	0,03	≤0,03	98,03	≤0,06	0,35	0,30	0,20	99,35

Table 4. Chemical composition of metallic copper from copper matte. PIXE analyses [%wt.]

Elements	X26037S	X26037T	X26037U
Ti	0,014 ±0,005	0,020 ±0,005	0,014 ±0,005
Cr	0,031 ±0,007	0,020 ±0,012	0,012 ±0,008
Mn	0,016 ±0,006	0,017 ±0,007	0,024 ±0,007
Fe	0,030 ±0,009	0,027 ±0,009	0,049 ±0,020
Ni	0,030 ±0,009	0,027 ±0,009	0,049 ±0,020
Cu	87,215 ±0,310	92,586 ±0,320	77,186 ±0,320
Au	≤0,005	0,054 ±0,030	0,112 ±0,020
Pt	0,113 ±0,004	≤0,005	≤0,005
Pb	0,397 ±0,090	0,469 ±0,130	0,498 ±0,061

CONCLUSIONS

The aim of the study was mineralogical and geochemical characterisation of the metallurgical slags and copper matte from the Legnica-Glogow Copper Region. Analyses showed that main carrier of precious metals are metallic copper and metallic lead.

Silver appears as small metallic inclusions in metallic Cu, metallic Pb and in both the copper matte and sulphides droplets in slags. Sometimes metallic Ag contains an increased admixture of gold. In converter slags from Legnica Ag is connected with copper sulphides and contains up to 4,73 %wt. Pd. The presence of Pd in these products suggests that this precious metal escapes to slags. This problem requires father research.

The main carrier of gold is metallic copper, metallic silver, metallic lead and Pb-Ag alloys. The presence of Au is connected with Pb. Gold present in suspension slags is probably entirely recovered. Au-Pb association controls gold behaviour during smelting. Further research on this subject is warranted because the timing and the way of removal of Pb from copper matte may cause significant loss of gold.

Analyses performed so far showed that detectable amounts of Pt occur only in the metallic copper from copper matte. The problem requires further study.

ACKNOWLEDGEMENT

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Celem badań była charakterystyka minralogiczno-geochemiczna żużli i kamienia miedziowego z Legnicko-Głogowskiego Okręgu Miedziowego oraz identyfikacja faz, w których lokują się metale szlachetne.Próbki żużli i kamienia miedziowego były badane przy użyciu mikroskopu do światła odbitego, skaningowego mikroskopu elektronowego (SEM), mikrosondy elektronowej, analizy fluorescencyjnej indukowanej jonami (PIXE) + ICP.

Głównym składnikiem żużli jest faza szklista zawierająca małe, okrągłe wtrącenia miedzi metalicznej, siarczków, stopów Fe-Co, Pb-Ag, spineli, sfalerytu, faz arsenowych, czasem kryształy oliwinu, piroksenów, bądź amfiboli. Głównym składnikiem kamienia miedziowego są siarczki miedzi 80-95%, miedź metaliczna 5-17%, a także stopy Fe-Co, Pb-Ag, Pb-Ni, Pb-Cu i arsenki.

Srebro pojawia się jako małe inkluzje w miedzi i ołowiu metalicznym zarówno w kamieniu miedziowym, jak i w siarczkowych wkropleniach w żużlach. Czasem Ag metaliczne zawiera domieszkę złota. W żużlach konwertorowych z Legnicy srebro związane z siarczkami miedzi zawiera do 4,73 % wag. Pd. Obecność Pd w tych produktach sugeruje ucieczkę tego metalu do żużli. Problem palladu wymaga dalszych badań.

Głównym nośnikiem złota jest miedź metaliczna, srebro metaliczne, ołów metaliczny i stopy Pb-Ag. Obecność Au związana jest z Pb – problem wymaga dalszych badań. Przeprowadzone do tej pory badania wykazały, że Pt związana jest z miedzią metaliczną z kamienia miedziowego. Badania nad obecnością metali szlachetnych w produktach hutniczych miedzi będą kontynuowane.