SILVER IN POLAND. ACHIEVEMENTS IN RESEARCH AND PRODUCTION

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STRIEBRO V POĽSKU – VÝSKUM A VÝROBA

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Abstrakt

Poľsko je jedným z najvýznamnejších svetových producentov striebra, deviatym v celosvetovom meradle a prvým v Eúrope. V roku 2001 sa v Poľsku vyrobilo okolo 1200 ton striebra, hlavne ako vedľajší produkt pri výrobe medi a zinku a pri spracovaní odpadov. V príspevku sú prezentované technológie výroby striebra ako vedľajšieho produktu pri spracovaní medených koncentrátov v KGHM „POLSKA MIEDŹ" a pri spracovaní zinkových koncentrátov v HC „MIASTECZKO ŚLĄSKIE" SA.

V príspevku sú diskutované technológie, vyvinuté pre získavanie striebra z druhotných surovín ako sú: strieborné katalyzátory, elektronický šrot, znehodnotené tranzistory, postriebrené sklenené platne a vyčerpané roztoky zo svetlocitlivých materiálov.
Sú popísané aktivity firmy „INNOVATOR" Ltd. z Inštitútu neželezných kovov v Gliwiciach, ktorá je "spin-off company" inštitútu. Tento podnik sa špecializuje na získavanie striebra a ďalších vzácnych kovov z odpadov a ich prepracovanie do rôznych produktov najvyššej kvality. INNOVATOR sa snaží získať významné postavenie na domácom trhu v marketingu vzácnych kovov a produktov z nich. Podnik vyrába vysoko kvalitné kovy ako sú: strieborný a zlatý prášok a granulát a platinovú, paládiovú a ródiovú hubku. Získané vzácne kovy sú buď predávané priamo ako komerčné produkty alebo využívané ako materiál na prípravu ďalších produktov ako sú: klenotnícke zliatiny, klenotnícke produkty a poloprodukty – rúrky, tyče, drôty a pásky; zlato a platinové kovy sú používané na elektropokovovanie a na prípravu katalyzátorov; na produkty vyrábané práškovou metalurgiou a elektrolyticky postriebrené drôty a pásky z neželezných kovov.

Abstract

Poland is one of the leading world silver manufactures, holding the ninth place in the world and the first place in Europe. In 2001 about 1200 tons of silver was manufactures in Poland, mainly as a by-product of copper metallurgy, zinc metallurgy and from secondary materials.

The technologies for silver production as a by-product in copper concentrates treatment in KGHM "POLSKA MIEDŹ" SA and in zinc-lead concentrates treatment in HC "MIASTECZKO ŚLĄSKIE" SA are presented.

The developed technologies for recovery of silver from secondary materials such as: used silver catalysts, electronic scrap, rejected transistors, silver plated glass scrap, spent solution from light sensitive materials treatment are discussed.

The activity of "INNOVATOR" Ltd., a company of the Institute of Non-Ferrous Metals in Gliwice is described. Innovation Plant INNOVATOR Co. Ltd is a spin-off company of the Institute. The plant specialises in recovery of silver and other precious metals from waste materials and in processing these metals into various highest quality products. INNOVATOR strives to reach a high position on the domestic market in the trade of precious metals and products manufactured from those metals. The plant produces high quality precious metals, such as: silver and gold powder and granulate, platinum, palladium and rhodium sponge. The recovered precious metals are sold directly as commercial products or are used at the Company as a material for further processing into such products as: jewellery alloys, jewellery, jewellery semi-products -tubes, rods, wires, strips; gold and platinum metals compounds used in electroplating and for manufacture of catalysts; products made by powder metallurgy methods; wires and strips from non ferrous metals electrolytically silver plated.

Key words: silver, secondary resources, precious metals

Introduction

Silver is a precious metal of exceptionally various range of applications [1÷7]. The metal and its alloys are used in electronics, electrotechnics, in production of light sensitive materials, for production of catalysts and musical instruments, in medicine (silver has bactericidal properties), for chemical silver plating (mirrors, Christmas tree decorations), in decorative arts, jewellery, for production of coins, as an alloying component in e.g. AgCu, AgCd, AgCuCd, PbAg as well as a component of binders and powder products. Silver coatings are widely used as decorative and protection coatings, mainly in jewellery products and tableware as well as in technical coatings in electronics and electrotechnics. High reflection properties of silver surfaces were used in production of special reflectors and mirrors, and chemical resistance – in construction of equipment (equipment resistant to action of melted alkali metals hydroxides, among others). Figure 1 presents the structure of world silver consumption by A. Brumby [1].

According to the data of the year 1999, the world silver consumption was 27625 ton [8]. Year after year a growing demand in that precious metal can be observed. Poland is one of the leading world silver manufacturers, holding the 9th place in the world and the 1st place in Europe [8, 9]. In 2001 about 1 200 tons of silver was manufactured in Poland, mainly as a by-product of copper metallurgy and zinc metallurgy and from secondary materials.

1. Obtaining of silver as a by-products in copper concentrate treatment at KGHM „POLSKA MIEDZ" SA

KGHM POLSKA MIEDZ SA is the biggest manufacturer of silver in Poland [9÷14]. The silver comes from copper ores excavated in the mines of Legnica-Glogow Copper District („Lublin", „Polkowice - Sieroszowice", „Rudna") and processed in smelters „Legnica" and „Głogow", of capacity about 500,000 t of electrolytic copper and over 1,150 t of silver per year. Silver content in the excavated ores is 0,0034-0,0067%, and in the received flotation concentrates is 0,0477-0,0961%. The treatment of copper concentrates is conducted by shaft process and by OUTOKUMPU process, in which copper is directly smelted from copper concentrates in a flash-smelting furnace.

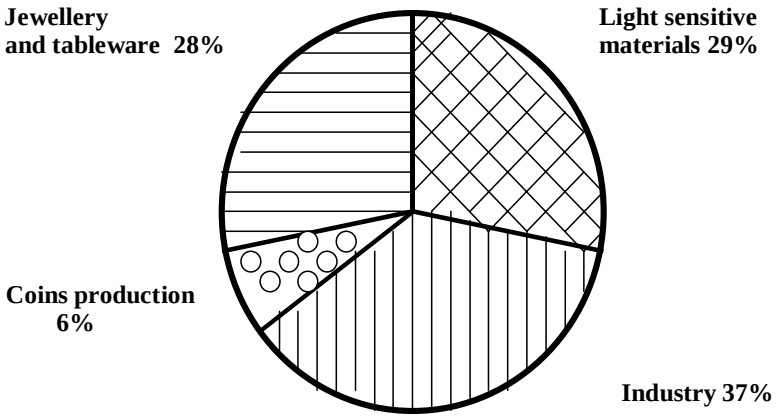

Fig.1 Structure of world silver consumption

Both silver and other precious metals, contained in copper materials, concentrate in main products of individual technological operations used in metallurgical processes in copper smelters. The high level of silver recovery in subsequent operations leads to production of anode copper containing 0,2 - 0,3% Ag, which then undergoes electrolytic refining. During copper electrorefining, silver concentrates in anode slime, which is a source material for obtaining precious metals. In the early stage of copper metallurgy development in Poland, the anode slime was processed in HMN „SZOPIENICE", where in cupellation furnaces doré metal was smelted, then electrorefined in ZM „TRZEBINIA". In 1993 in HM „GŁOGOW" the Precious Metals Department was launched, basing on a licence of Swedish company „BOLIDEN", expected to treat the whole anode slime resulting from copper refining with assumed capacity for refined silver production at 1 044 t per year. The full capacity was reached in 1994, and at the same time a quality success was achieved. The produced silver meets the highest world standards.

The technology for obtaining silver from anode slime (Fig. 2) consists of the following basic operations:

- charge preparation,
- smelting of doré metal in Kaldo furnace,
- casting of anodes,
- electrolytic silver refining,
- smelting of cathode silver, casting of ingots and granulated material.

The tables 1 to 3 present composition of materials for production of precious metals as well as composition of semi-products and the final product – refined silver.

2. Obtaining of silver as a by-product in production of zinc and lead at HC „MIASTECZKO SLASKIE"

HC „MIASTECZKO SLASKIE" produces zinc and lead in ISP (Imperial Smelting Process) furnaces. The smelter processes zinc and lead concentrates, of both domestic origin and from import, of silver content 0,01-0,05%. Crude lead received from the shaft furnace is a „collector" of accompanying metals, such as copper, silver, gold, platinum metals, arsenic, tin, antimony, bismuth, tellurium, germanium and indium. Silver is recovered from the crude lead

which contains 0,04-0,18% of Ag (Fig. 3). The lead from the shaft furnace undergoes multistage refining. In the first place copper, arsenic, tin and antimony are removed from the lead, and then silver removal is conducted by Parkes method.

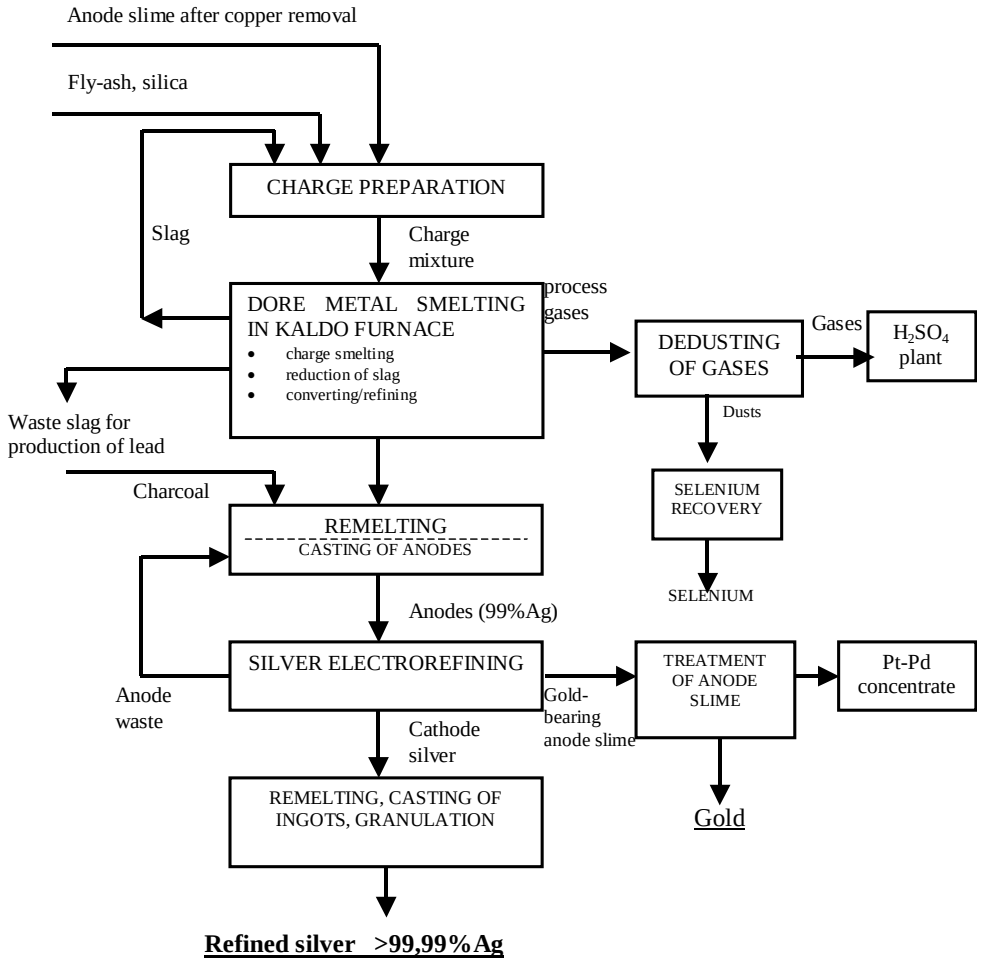

Fig.2 Flow-sheet of silver production in HM „GLOGOW"

The extraction of silver is conducted by introduction of zinc to the melted lead, which forms intermetallic compounds with silver, such as: Ag_2Zn_3 and Ag_2Zn_5, floating onto the surface of the melted metal in a form of silver-bearing foam. The desilverization takes place in the following way: into the lead, melted in the pot at the temperature of 730-740 K, zinc is introduced in the volume of 12-15kg per ton of lead and the content of the pot is mixed for 12-14 hours. After reducing the temperature to 660-670 K and removing the mixer, the silver-bearing foam is collected from the surface of the melted metal, of Ag content 1,0-1,5%.

The silver-bearing foam is remelted in a liquation muffle with a use of temperature dependant variations in solubility of zinc and silver in lead. By maintaining the temperature of upper part of the muffle at 920-970 K and in the lower part at about 600K the segregation of

components is achieved. From the upper part ZnPbAg alloy is removed, of Ag content 5-18%, and from the lower part – lead which contains below 0,01% of Ag. Zinc is removed from ZnPbAg alloy in Faber du Faur furnace, by distillation method and in the result AgPb alloy is obtained, of Ag content 50-70%, which is directed to a cupellation furnace. During the cupellation process following impurities are subsequently removed: zinc, lead and copper, and the doré metal is obtained of composition: 98,5-99,0% of Ag; <1,5% of Cu; <0,1% of Pb. Doré metal is cast into plates, weighting 12 kg, which can be sold as a commercial product. In 2001 HC „MIASTECZKO SLASKIE" produced 27 tons of silver.

Table 1Chemical composition of anode slime used for production of precious metals

Anode slime origin	Ag %	Pb %	S %	Cu %	Se %	Sb %	Au ppm
HM GŁOGÓW	35-45	25-35	5-7	0,5-1	1,5-3	1,5-4	120-300
HM LEGNICA	35	25-35	4-6	1,25	1,5-3	1,5-3	20-30

Table 2 Chemical composition of silver alloys after reduction and after converting and refining in Kaldo furnace

Material	Ag %	Pb %	Se %	Cu %	Bi %	Te %	Au %
Alloy after reduction	83-90	2-9	4-6	1,5-3	0,2-0,4	0,2-0,5	0,02-0,1
Alloy after converting and refining – dore metal	99,1-99,5	0,01-0,02	<0,01	0,3-0,8	0,004-0,006	0,01-0,015	0,02-0,1

Table 3 Impurities content in electrolytically refined silver

Pb ppm	Cu ppm	Bi ppm	Te ppm	Au ppm	As ppm	Sb ppm	Se ppm	Zn ppm	Fe ppm	Ni ppm	Impurities in total ppm
2-4	10-30	1-4	1-2	1-3	0,5-1	0,5-1	<2	0,5-1	1-4	<2	<100

3. Technologies developed for recovery of silver from secondary materials

Silver-bearing secondary materials vary greatly in silver content and in physical form. Most often, these secondary materials are coupled to some other metals, to glass, ceramics or some plastics. Because of that variety and because of relatively high silver content (several dozens and sometimes even some hundreds times higher than in copper concentrates) technologies for recovery of silver from those materials should be precisely adjusted to the type of the material, should guarantee a high (close to 100%) degree of silver recovery and take into consideration utilisation of semi-products and waste. Following is description of technologies for silver recovery from various materials, developed at the Silesian University of Technology.

4. Recovery of silver from used silver-plated catalyst

Silver-plated catalysts are used, among others, in synthesis of ethylene oxide. The catalyst is in a form of balls or Raschig rings weighting about 0,5 g, composed of aluminium oxide covered with silver. Silver content in the used catalysts is about 7-15%. The idea of the developed technology for recovery of silver from the used catalyst Al_2O_3-Ag (Fig. 4) lies in

dissolving the silver layer on the surface of the ceramic medium in a dilute sulphuric acid solution (1-2,5% H_2SO_4) at the temperature of 350-370 K, in a presence of oxidizer - $KMnO_4$ or MnO_2, with subsequent precipitation of silver from the spent pickling liquors by cementation methods. The silver residue precipitated from the solution can be directed to remelting or processed into silver salts [15]. Both in the process of silver dissolving and in its release from the solution the efficiency is close to 100%. Technological waste in a form of dilute sulphate solutions and ceramic profiles after silver removal can find practical application. Characteristic feature of that technology is simplicity of the technological operations, during which no toxic gases or dusts are emitted. The complete utilisation of the technological waste allows for treating that technology as a wasteless. It has to be noted, however, that not all types of silver catalysts can be treated by the developed method.

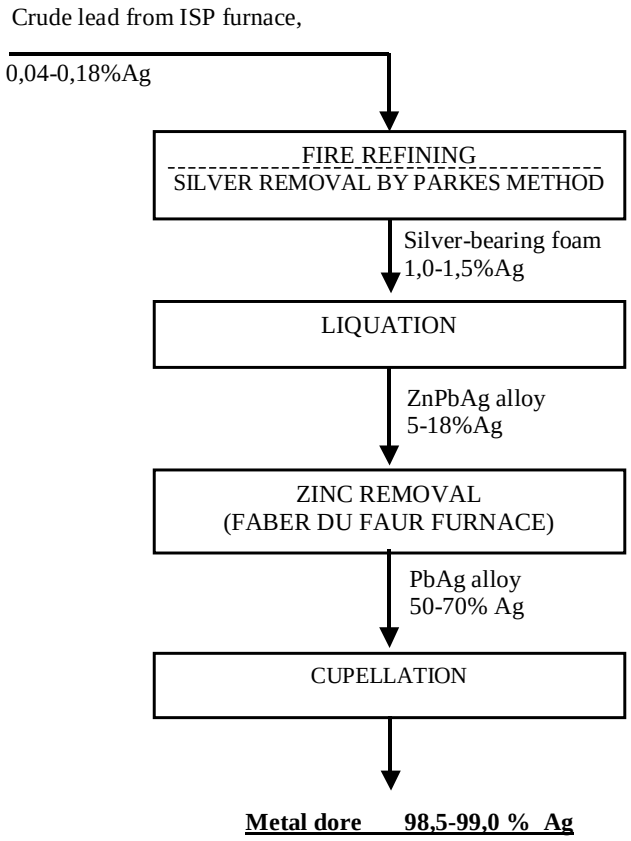

Fig.3 Flow-sheet of silver production in HC „MIASTECZKO SLASKIE"

5. Recovery of silver from silver plated glass scrap

Silver plated glass scrap from production of Christmas tree decorations and vacuum bottles contains 0,02 to 0,2% of Ag. The developed technology for recovery of silver from that scrap (Fig. 5) is based on dissolving silver layer in a dilute sulphuric acid solution (1-5% H_2SO_4) and in an oxidizing agent, e.g. 0,1-0,5% $KMnO_4$.

Process of dissolving, conducted at the temperature of about 290 K (without heating) takes 5 to 20 minutes (the time of dissolving depends on the type of the cullet). As oxidizing

agents can be used: $KMnO_4$, $K_2Cr_2O_7$, H_2O_2, KNO_3, $NaNO_3$ and others. Considering the subsequent technological processes of silver recovery and necessity for utilisation of waste solutions, $KMnO_4$ was assumed to be the most appropriate oxidizer. During pickling of the silver-plated cullet the following reaction takes place:

$$10Ag + 2KMnO_4 + 8H_2SO_4 = 5Ag_2SO_4 + 2MnSO_4 + K_2SO_4 + 8H_2O \quad (1)$$

From the spent pickling liquor silver chloride is released which, after rinsing with water, is reduced by formaldehyde in the alkali conditions:

$$Ag_2SO_4 + 2NaCl = 2AgCl + Na_2SO_4 \quad (2)$$

$$2AgCl + HCHO + 2NaOH = 2Ag + HCOOH + 2NaCl + H_2O \quad (3)$$

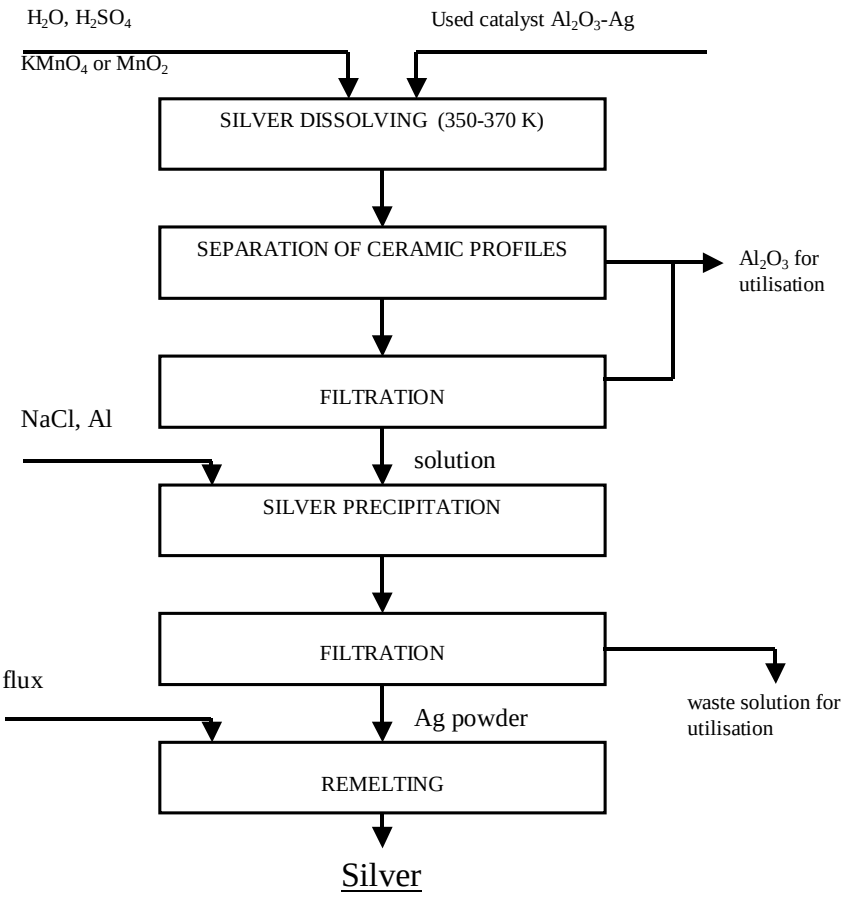

Fig.4 Flow-sheet of silver recovery from used catalyst Al_2O_3-Ag

The product of the reduction is silver powder which, after drying, is remelted and cast into bars. Purity of the resulting silver is > 99,95% [16].

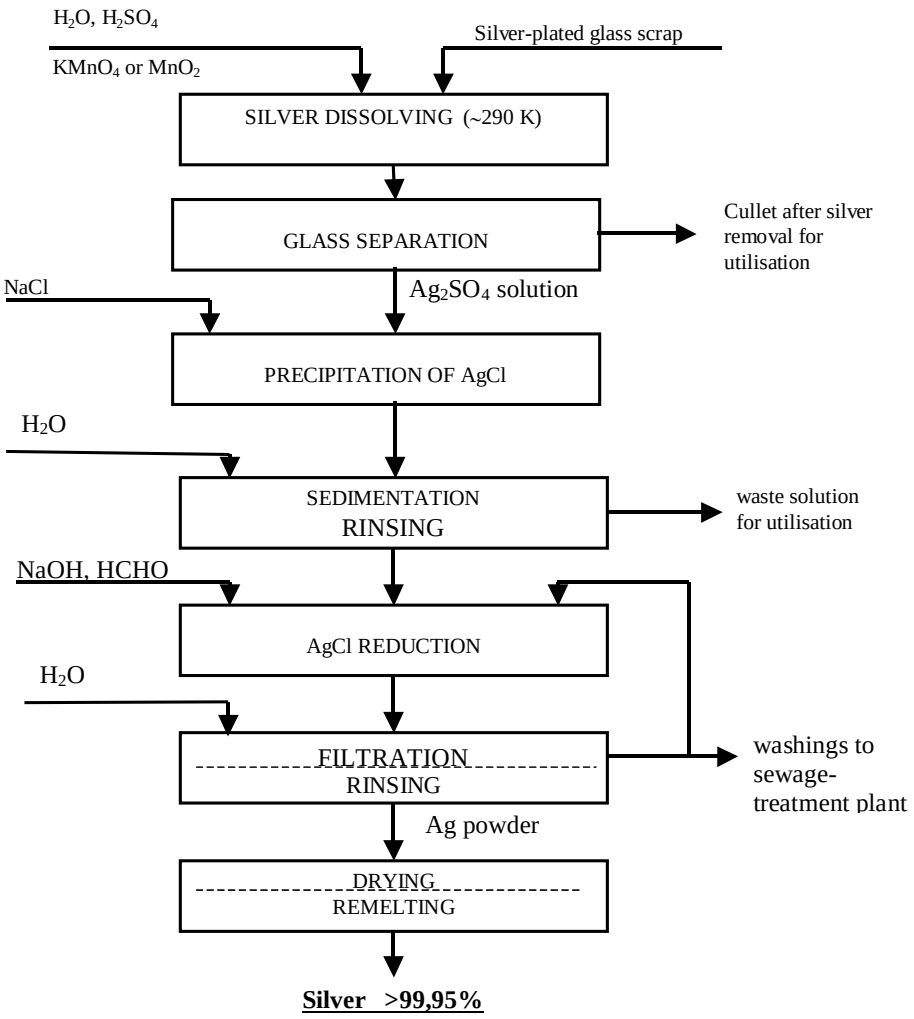

Fig.5 Flow-sheet of silver recovery from silver-plated glass scrap

6. Recovery of silver from electronic scrap

The source materials are silver plated electric contacts and other components made of silver-plated copper, isolated from electronic and electrotechnic scrap. The components in a form of profiles of various weight contain 2-8% of Ag; 92-98% of Cu. Recovery of silver from that material lies in the selective dissolving of the silver coating and isolating the silver from the residue, which crystallizes in a saturated spent pickling liquor [17]. Figure 6 shows the flow-sheet of that process. The first operation is dissolving of the silver coating in a solution of concentrated acids H_2SO_4 and HNO_3. The best results of selective removal of the silver coating have been reached with a use of a solution composed of 18-19 volume parts of concentrated H_2SO_4 and 1 part of concentrated HNO_3, at the temperature of 350-365K. Silver coated contacts, placed in a perforated teflon container, are introduced into the heated pickling solution and pickled until the complete dissolving of silver is reached, during 5 to 30 minutes (depending on

thickness of the silver coating). After dissolution of the silver, the container with profiles is removed from the solution and rinsed with water.

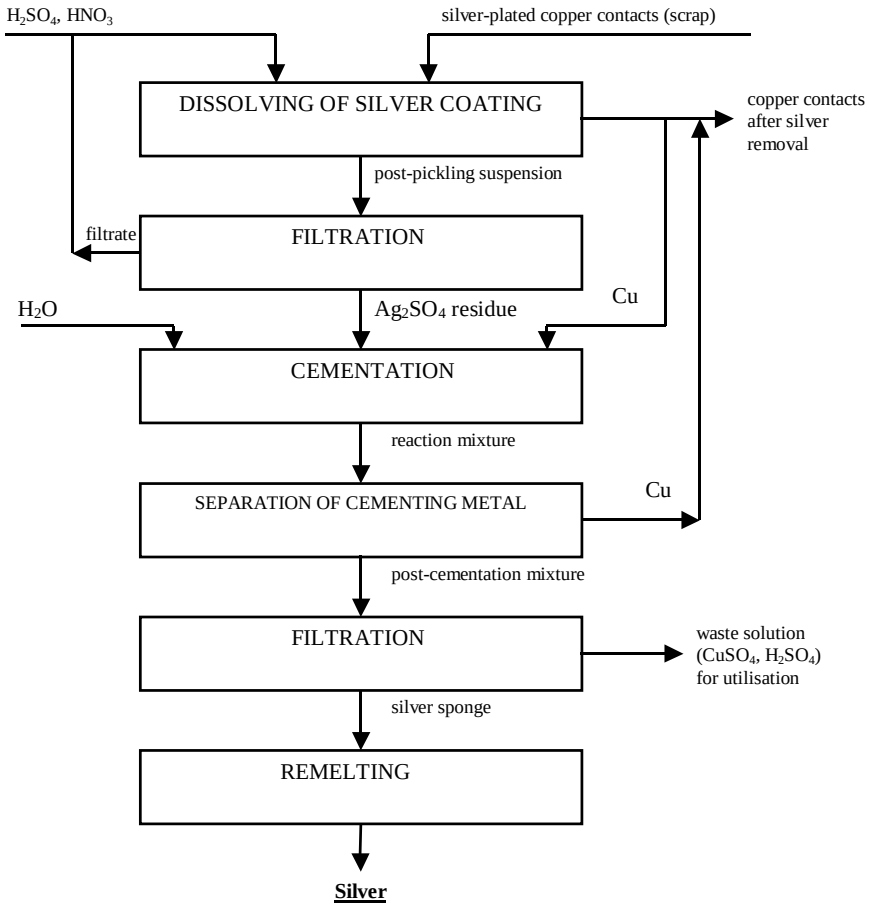

Fig.6 Flow-sheet of silver recovery from silver-plated copper contacts

The pickling liquor is used several times, for silver removal from subsequent batches of the material. During process of silver extraction, the pickling liquor becomes saturated with silver compounds and crystallization of silver sulphate takes place. After filtration of the spent pickling suspended matter a residue is received, of which the main component is Ag_2SO_4. The filtrate (after adding H_2SO_4 and HNO_3) is recycled to the next pickling, and from the residue silver becomes released. The release of the silver is conducted from suspended Ag_2SO_4 by cementation method in a water solution with a use of copper. The copper profiles, from which silver was removed in the previous technological operation, proved to be an adequate material for cementation of silver. After finishing cementation process and after separation (on sieve) of surplus of cementating material, post-cementation suspended matter is filtered, which leads to receiving a silver sponge and dilute post-cementation solution which contains $CuSO_4$ and H_4SO_4. The solution does not contain silver and is directed to utilisation. The sponge is remelted and metallic silver is received of purity 98-99 % of Ag.

7. Recovery of silver from scrap of transistors coupled with silicone mass

The source materials are rejected and scrap silver-bearing transistors coupled with silicone mass. An example of composition of such transistors can be: 52 % Cu; 3,93 % Ag, 0,025 % Au and silicone mass. To make recovery of metals possible, in the first place a silicone casing, which shield metallic parts, has to be removed. The casing can be removed by mechanical or chemical methods. Because of the gold loss which occurs when mechanical removal of silicone is applied, chemical method has been chosen, based on dissolving silicone in a caustic soda solution. Satisfactory results in removal of silicone mass were achieved with application of 50-55 % NaOH solution, at the temperature of 433 K, during about 50 minutes. After dissolution of the silicone, metallic profiles were obtained of exemplary composition 92-93 % of Cu, 7,0 % of Ag, 0,043 % of Au. Profiles made of silver-plated copper can be used directly for production of Cu-Ag alloys. Such a method is suitable for processing profiles with no gold content. The developed technology (Fig. 7) gives possibility of recovery of silver, gold and copper. The first technological operation is removal of silicone mass by its dissolving in a caustic soda solution. From the profiles, separated from that mass, gold is recovered by mechanical method consisting in detachment of gold wires from silver-plated profiles with a use of vibrating ball mill and sieves of 2 mm mesh. Fraction < 2mm is composed of gold wires. The degree of recovery is 75-80 %. The metallic profiles after gold removal are subjected to pickling in a mixture of sulphuric and nitric acids, for selective dissolution of the silver coating. Satisfactory results of silver dissolving have been reached when a mixture of concentrated acids H_2SO_4 and HNO_3 in volume proportion of 20:1 was used, at the temperature of 310-320 K for about 10 minutes. From the spent pickling solution silver is released in a form of AgCl. After rinsing and drying up the silver chloride is remelted together with other silver concentrates by cupellation method. The product is dore metal which contains about 99% of Ag [18].

8. Recovery of silver from spent solutions used in treatment of light sensitive materials

Studies of world silver consumption have shown that about 30 % of that metal is used in production of light sensitive materials [1]. Silver is used for production of light sensitive emulsion, which in turn is used for coating of film stock and photographic films as well as X-ray films and photographic paper. Recovery of silver from the used photographic materials, including spent solutions for treatment of light sensitive materials, is of very big, both economical and ecological, importance. A technology has been developed for recovery of silver from spent thiosulphate solutions coming from photographic studios, of silver content 2-3 g/dm^3 and from solutions after treatment of X-ray films of silver content 5-20 g/dm^3 [19]. Figure 8 shows the flow sheet of the developed technology.

The first technological operation, which is crucial for solving the problem of silver recovery from thiosulphate solutions, is electrolytical release of silver. The product of the electrolysis – silver concentrate of Ag content 80-90 % (which can be used as a commercial product) is processed for obtaining fine silver. To do that, the post-electrolytical residue is dissolved in nitric acid of concentration ca. 30 % at the temperature of the boiling point, which leads to obtaining silver nitrate solution:

$$6Ag + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O \quad (4)$$

$$Ag_2S + 4HNO_3 = 2AgNO_3 + S + 2NO_2 + 2H_2O \quad (5)$$

The suspended matter resulting from the reaction, composed of silver nitrate solution and sulphur, is filtrated. From the received silver nitrate solution precipitates sparingly soluble silver chloride:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3 \quad (6)$$

After decantation of the solution, silver chloride residue is washed with water. NaOH is added to the suspended in water silver chloride until pH~9 is reached and then, with continuous mixing at the temperature of the boiling point, formaldehyde is added in small batches, which reduces silver chloride into metallic silver. The final product is a silver powder (homogenous, light-grey residue) which after drying is remelted and cast into bars. Such produced silver has purity of > 99,5%Ag.

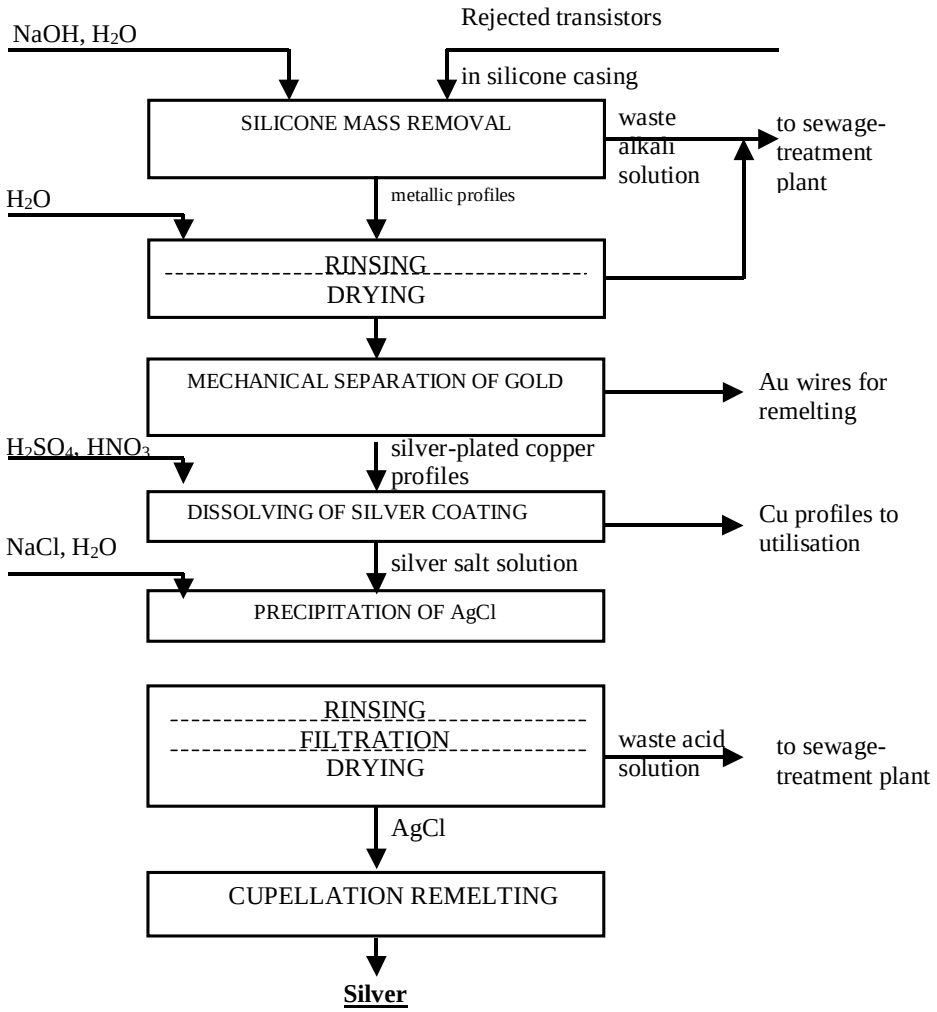

Fig.7 Flow-sheet of silver recovery from rejected transistors coupled with a silicone mass

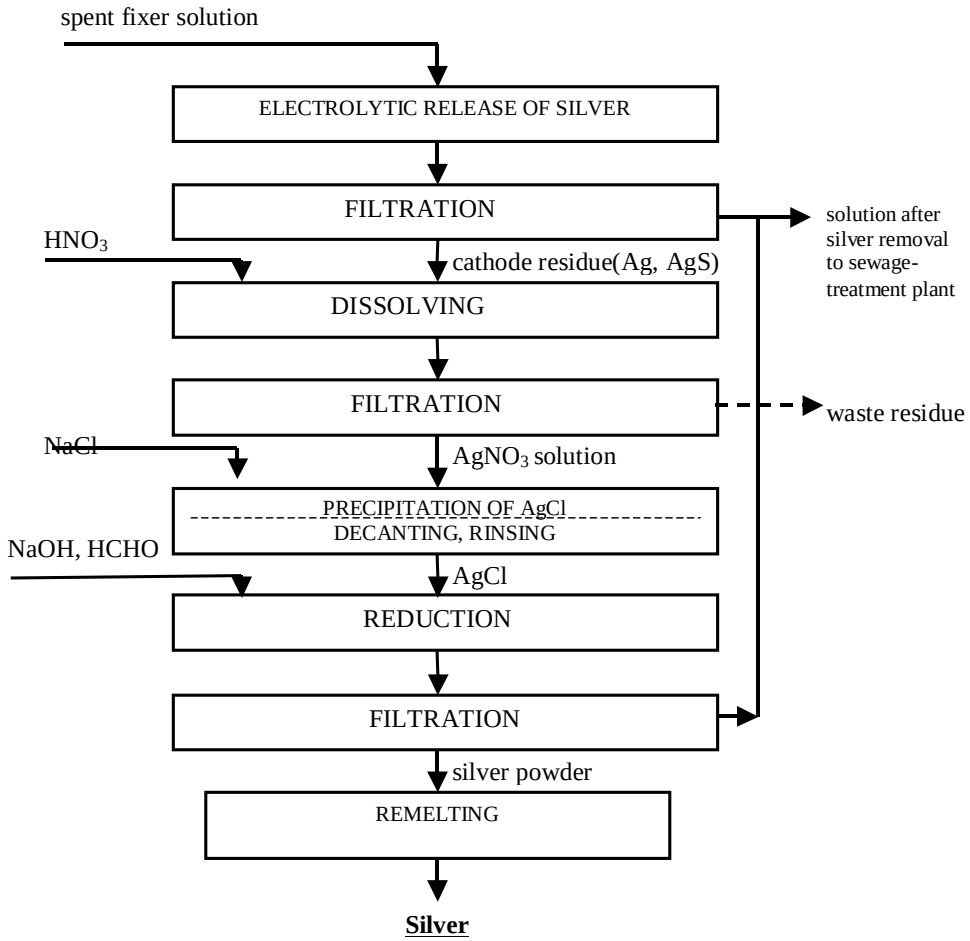

Fig.8 Flow-sheet of silver recovery from spent solutions used for light sensitive materials treatment

9. Activity of „INNOVATOR" Ltd., a company of the Institute of Non-Ferrous Metals in Gliwice

Innovation Plant INNOVATOR Co. Ltd is a spin-off company of the Institute of Non-Ferrous Metals in Gliwice [20]. The plant specialises in recovery of silver and other precious metals from waste materials and in processing these metals into various highest quality products. INNOVATOR strives to reach a high position on the domestic market in the trade of precious metals and products manufactured from those metals. The recovery of precious metals is conducted with a use of modern, continuously improved, technologies. The plant produces high quality precious metals, such as:

- silver powder and granulate of grade Ag0, Ag1, Ag2
- gold powder and granulate of grade Au 99,9,
- platinum sponge Pt 99,9,
- palladium sponge Pd 99,9,
- rhodium sponge Rh 99,9.

The recovered precious metals are sold directly as commercial products or are used at the Company as a material for further processing into such products as:

- jewellery alloys,
- jewellery,
- jewellery semi-products – tubes, rods, wires, strips,
- gold and platinum metals compounds used in electroplating and for manufacture of catalysts,
- products made by powder metallurgy methods,
- wires and strips from non-ferrous metals electrolytically silver-, tin-, nickel plated.

One of the activities of the Company, becoming more important in the last years, is also running a jewellery wholesale business.

Summary

Against a background of features and structure of silver consumption, the technologies for silver production in Poland, as a by-product in copper concentrates treatment in KGHM POLSKA MIEDZ SA and in zinc and lead concentrates treatment in HC „MIASTECZKO SLASKIE", are presented. The developed technologies for recovery of silver from secondary materials such as: used silver catalysts, electronic scrap, rejected transistors, silver plated glass scrap, spent solution from light sensitive materials treatment are described.

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