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Analysis of selected technologies of precious metal recovery processes

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INTRODUCTION

Technology analysis requires a set of internal and external information. Technology has its lifecycle. Knowledge of technology helps an enterprise build its competitive strategy. In the period of the 4th industrial revolution, knowledge is the most important resource of the enterprise. Enterprises are changing technologies in an evolutionary or revolutionary way. (Brodny, J. & Tutak, M. 2016). An example of revolutionary changes in production technology was the restructuring of the steel sector in Poland. Enterprises include technological aspects in quality management systems (Gajdzik, Sitko, 2014), to obtain the market position according to World Class Manufacturing (Gajdzik, 2013).

Silver is a noble metal with exceptionally diverse applications (Babiński 1986; Biały, Wiedzicha Nordin 2018; Brumby 1995; Brydziak, Mizera Piątkowski 2000; Gmelin Handbuch der Anorganishen Chemie Sliber 1975; Górniak, Midor, Kaźmierczak, Kaniak 2018). This metal and its alloys are used in electrical engineering, electronics, in the production of photosensitive materials, for the manufacture of catalysts and musical instruments in medicine (silver has bactericidal properties), for chemical silvering (mirrors, Christmas decorations), in ornamentation, jewelery, for making coins as an alloying component for example AgCu, AgCd, AgCuCd, PbAg and as a component of binders and powder products. Silver coatings have found a wide application as decorative and protective coatings, mainly for jewelery and tableware, as well as technical coatings in electronics and electrical engineering. The high reflectivity of light rays from the silver surface was used in the production of special reflectors and mirrors, and chemical resistance – in the construction of apparatus (among others, apparatus resistant to molten alkali metal hydroxides).

In 2001, about 1,200 tons of silver were produced in our country, mainly as a by-product of copper metallurgy and zinc smelting and from secondary raw materials.

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PREPARATION OF SILVER AS A BY-PRODUCT IN THE PROCESSING OF COPPER CONCENTRATESIN KGHM "POLSKA MIEDŹ" SA

The largest producer of silver in Poland is KGHM POLSKA MIEDŹ SA (Grabowski 2002, Krupka 1988, Krupka 2000, Tutak. M, & Brodny, J. 2019, Krupka 1996, Mining Journal Ltd. 2000, Pluciński, Koźmiński 1994). This combination receives silver from copper ore mined in the Legnicko-Głogowski Copper Mine mines ("Lublin", "Polkowice-Sieroszowice", "Rudna") and processed in the "Legnica" and "Głogów" smelters with an annual production capacity of about 500,000 t of electrolytic copper and about 1100 t of silver. The content of silver in ores mined by Kombinat is 0.0034-0.0067%, in the obtained flotation concentrates 0.0477-0.0961%.

Processing of copper concentrates is carried out using a shaft process and the OKTOKUMPU process involving the direct melting of copper from copper concentrates in a slurry furnace.

Silver and other precious metals contained in copper raw materials are concentrated in the main products of individual technological operations used in copper mills of metallurgical processes. The high recovery rate of silver in subsequent operations leads to the production of anodic copper containing about 0.2-0.3% Ag, which is subjected to electrolytic refining. During copper electrorefining, silver concentrates in the anode slime, which is the starting material for obtaining precious metals. In the initial period of the development of copper metallurgy in Poland, the anode slime was processed in Zink Plant "SZOPIENICE", renamed in 1972 to HMN "SZOPIENICE", where dore's metal was smelted in the baking ovens, which was then refined electrolytically at the TRZEBINIA Metallurgical Plant.

In 1999, it was launched in HM "GŁOGÓW" based on the license of the Swedish company "BOLIDEN". The Noble Metals Department, providing for the processing of all anode slimes coming from copper refining with the assumed annual production capacity of refined silver 1044 t. The produced silver meets the highest requirements of world standards.

The technology of obtaining silver from anode slimes covers the following basic operations:

- Preparation of the batch,
- Dore metal melting in the Kaldo furnace,
- Casting anodes,
- Electrolytic silver refining,

Huta "MIASTECZKO ŚLĄSKIE" produces zinc and lead in shaft kilns (ISP) (Imperial Smelting Process). In this plant, zinc and lead concentrates are processed both domestic and imported, with a silver content of 0.01-0.05%. The raw lead obtained from the shaft furnace is a "collector" of accompanying metals such as copper, silver, gold, platinum, arsenic, tin, antimony, bismuth, tellurium, germanium and indium. Of the crude lead containing 0.04-0.18% Ag, silver is recovered (Fig. 1). Lead from the shaft furnace undergoes several-step refining. In the first place copper, arsenic, tin and antimony are removed from the lead, followed by the Parkes method of silver-plating. Silver-plating using this method consists in introducing into the molten lead zinc, which forms with silver intermetallic compounds such as: Ag_2Zn_3 and Ag_2Zn_5 affecting the surface

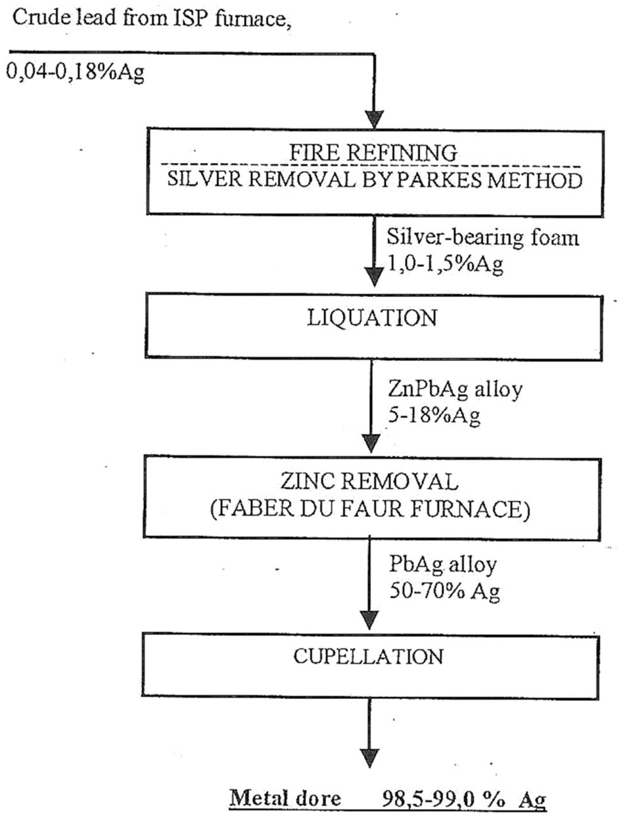

Fig. 1 Flow-sheet of silver production in HC "Miasteczko Śląskie"

The silver-bonded foam is melted in the liquefaction muffle using the changes in the solubility of zinc and silver in lead depending on the temperature. Maintaining a temperature of 920-970°K in the upper part of the muffle, and in the lower part around 600°K you are able to segregate the components. The ZnPbAg alloy with a content of 5-18% Ag is discharged from the upper part of the muffle, from the bottom – lead containing less than 0.01% Ag. The ZnPbAg alloy is deacidated in a Faber du Faura furnace by distillation, resulting in an AgPb alloy with a content of 50-70% Ag, which is directed to the caking oven. In the cafeteria process, contaminants such as zinc, lead and copper are sequentially removed to give dore metal with the following composition: 98.5-99.0% Ag; <1.5% Cu; <0.1% Pb. Dore's metal is cast in the form of anodes weighing 12 kg, which is a commercial product.

DEVELOPED TECHNOLOGIES FOR RECOVERING SILVER FROM SECONDARY RAW MATERIALS

Silver-plated secondary raw materials are characterized by a large diversity in terms of silver content and physical form. Most often, these secondary raw materials are combined with other metals, with glass, ceramics or with plastic masses. Due to this diversity and the relatively high silver content (several dozen or even several hundred times higher than the content of silver from copper concentrates) technologies for recovering silver from them should be precisely adapted to the type of raw material, guarantee a high (close to 100%) silver recovery rate and anticipate the disposal of semi-finished products and waste. Subsequently, the technologies of obtaining silver from various raw materials developed at the Silesian University of Technology were discussed.

SILVER RECOVERY FROM SPENT SILVER CATALYST

The silver catalyst is used in the synthesis of ethylene oxide. The catalyst is in the form of Raschig balls or rings with a mass of about 0.5 g, of silver oxide coated aluminum. The silver content in the used catalyst is 7-15%. The essence of the developed technology for recovering silver from the used Al_2O_3-Ag catalyst is the dissolution of a silver layer located on the surface of a ceramic carrier in a dilute solution of sulfuric acid (1-2.5% H_2SO_4) at a temperature of 350-370°K in the presence of an oxidant – $KMnO_4$ or MnO_2 with the subsequent inclusion of silver from the pickling solutions using the cementation method. The silver deposit precipitated from the solution may be directed to the melting or converted into silver salts (Sitko, Mikuś, Bożek 2018).

Both in the process of silver pulping and its separation from the solution, yields close to 100% are achieved. Technological wastes in the form of diluted sulphate solutions and silver-ceramic shapes have a practical application.

Technology is characterized by the simplicity of technological operations, during which no toxic gases or dust are released. Full utilization of technological waste allows to recognize the developed technology as waste-free. It should be noted, however, that not all types of silver catalysts are suitable for processing by the developed method (Bołoz Ł., Midor K. 2018).

RECOVERING SILVER FROM SCRAP OF SILVER-PLATED GLASSES

Scrap silver-plated glasses from the Christmas tree decorations factory and thermos contain 0.02 to 0.2% Ag.

The developed technology for recovering silver from this waste consists in dissolving a silver layer in a dilute solution of sulfuric acid (1-5% H_2SO_4) and an oxidizing agent, for example 0.1-0.5% $KMnO_4$. The dissolution process carried out at about 290°K (without heating) takes 5 to 20 minutes (the dissolution time depends on the type of glass cullet). The following can be used as oxidizing substances: $KMnO_4$, $K_2Cr_2O_7$, H_2O_2, KNO_3, $NaNO_3$ and others. Bearing in mind the course of subsequent technological processes of silver recovery and the necessity to utilize waste solutions, $KMnO_4$ was considered the most suitable oxidant. During the digestion of silver-coated glass cullet a reaction occurs:

$$10Ag+2KMnO_4+8H_2SO_4 = 5Ag_2SO_4+2MnSO_4+K_2SO_4+8H_2O$$

Silver chloride is released from the pickling solution, which after rinsing with water is reduced with formaldehyde in an alkaline environment:

$$Ag_2SO_4+2NaCl=2AgCl+Na_2SO_4$$

$$2AgCl+HCHO+2NaOH=2Ag+HCOOH+2NaCl+H_2O$$

The reduction product is silver powder, which after drying is melted and cast into bars. The silver obtained in this way has a purity of > 99.95% (Krupka 1996).

SILVER RECOVERY FROM SCRAPPED ELECTRONIC DEVICES

The starting material is separated from scrapped electronic and electrotechnical devices with silver-plated electrical contacts and other elements made of silver-plated copper. These elements in the form of shapes of different mass contain 2-8% Ag; 92-98% Cu. The recovery of silver from this material consists in the selective dissolution of the silver coating and the secretion of silver from the crystallizing sludge in the saturated pickling solution. The technological scheme is shown in Fig. 2.

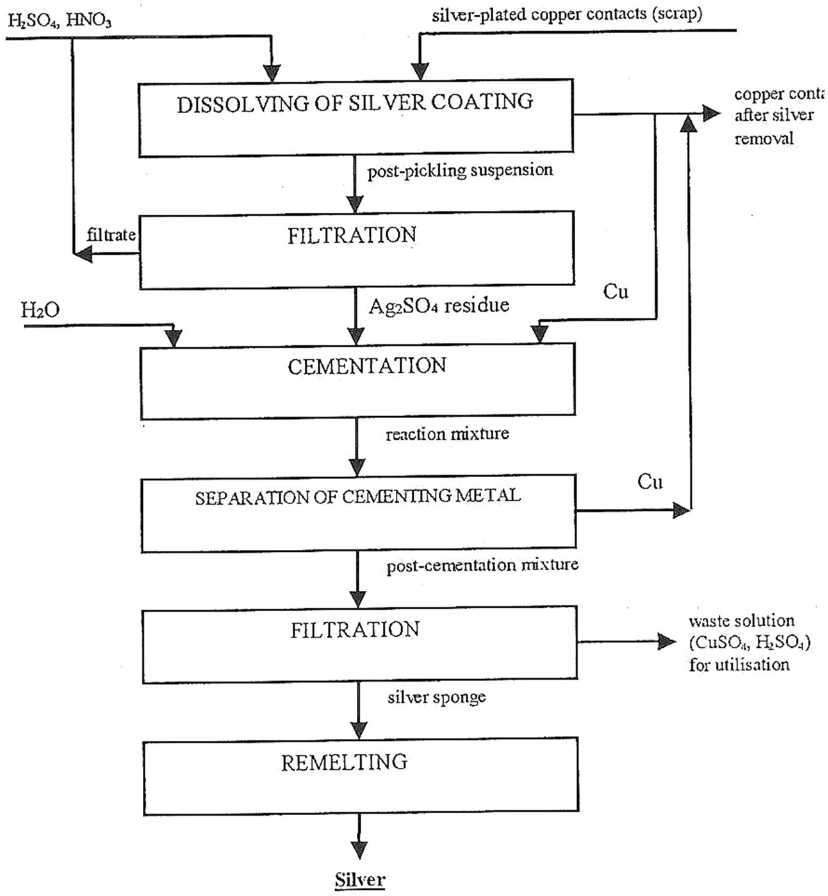

Fig. 2. Flow-sheet of silver revocery from silver-plated copper contacts

The first technological operation is the dissolution of a silver coating in a solution of concentrated H_2SO_4 and HNO_3 acids. The best results of the selective removal of the silver coating were achieved using a solution made up of 18-19 parts by volume of a steak. H_2SO_4 and 1 part by volume of ste. HNO_3 at a temperature of 350-365°K. To the heated etching solution are introduced silver-plated contacts located in the perforated Teflon container and etched to complete dissolution of silver, within 5 to 30 minutes (depending on the thickness of the silver coating). After the silver has been dissolved, the container along with the silver-coated fittings is removed from the solution and rinsed with water. The pickling solution is used several times to refilify subsequent batches of material. During the silver-plating operation, the etching solution is impregnated with silver compounds and silver sulphate is crystallized. After filtering the pickling slurry, a precipitate is formed, the main component of which is Ag_2SO_4. The filtrate (after the addition of H_2SO_4 and HNO_3) is recycled for re-digesting, silver is released from the precipitate. The silver separation is carried out by cementing the Ag_2SO_4 suspension in an aqueous solution with copper. A suitable material cementing silver turned out to be silver-plated in the previous technological operation of copper fittings. After the cementation process is completed and after the excess of the cementing metal has been separated (on the sieve), the post-cementation suspension is filtered to obtain a silver sponge and a diluted post-cementation solution containing $CuSO_4$ and H_4SO_4. This solution does not contain silver and is directed to utilization. The sponge is melted to obtain metallic silver with a purity of 98-99% Ag.

SILVER RECOVERY FROM SCRAPPED COMPOSITE TRANSISTORS WITH SILICONE MASS

The starting material is scrapped and scrapped silver-bonded composite transistors with silicone mass. An exemplary chemical composition of such transistors: 52% Cu; 3.93%Ag, 0.025% Au and silicone mass. In order to be able to recover metal from them, it is first necessary to remove silicone covers that shield metal parts. These enclosures can be removed by mechanical or chemical means. Due to the gold loss occurring in the mechanical removal of silicone, a chemical method was chosen consisting in the dissolution of silicone in a caustic soda solution. Satisfactory results in silicone mass removal were achieved using a 50-55% NaOH solution at 433°K for about 50 minutes. After the dissolution of the silicone, metallic shapes with an exemplary composition of 92-93% Cu, 7.0% Ag, 0.043% Au were obtained. The fittings made of silver-plated copper can be directly used for the production of Cu-Ag alloys. This method is suitable for processing non-gold fittings. The developed technology allows the recovery of silver, gold and copper. The first technological operation is the removal of silicone mass by dissolving it in a caustic soda solution. The gold elements separated from this mass are recovered, using a mechanical method of removing golden wires from silver-plated fittings using a vibratory ball mill and 2 mm sieves. The < 2 mm fraction is made of gold wires. The recovery rate of gold is 75-80%. Metallic fused metal bodies are pickled in a mixture of sulfuric and nitric acids to selectively dissolve the silver coating. Satisfactory silver pulping results were achieved when using a mixture of concentrated H_2SO_4 and HNO_3 in a volume ratio of 20:1, at a temperature of 310-320°K, in about 10 minutes. Silver is separated from the pickling solution in the form of AgCl. After rinsing and drying, the silver chloride melts with the canteen method together with other silver concentrates the product is dore's metal containing about 99% Ag (Pluciński, Koźmiński, 1994).

RECOVERY OF SILVER FROM USED SOLUTIONS USED FOR PROCESSING PHOTOSENSITIVE MATERIALS

Studies on the structure of silver consumption in the world have shown that about 30% of this metal falls on the production of photosensitive materials (Babiński, 1986). Silver is used to obtain photosensitive emulsions that cover film and photographic films as well as X-ray films and photographic papers. The recovery of silver from used photographic materials, including the used solutions used to process photosensitive materials, is of great economic and ecological importance. A technology for recovering silver from used thiosulphate solutions from photographic plants with a silver concentration of 2-3 g/dm^3 and from solutions after treatment of X-ray films with a silver content of 5-20 g/dm^3 was developed. The diagram of the developed technology is shown in Fig. 3.

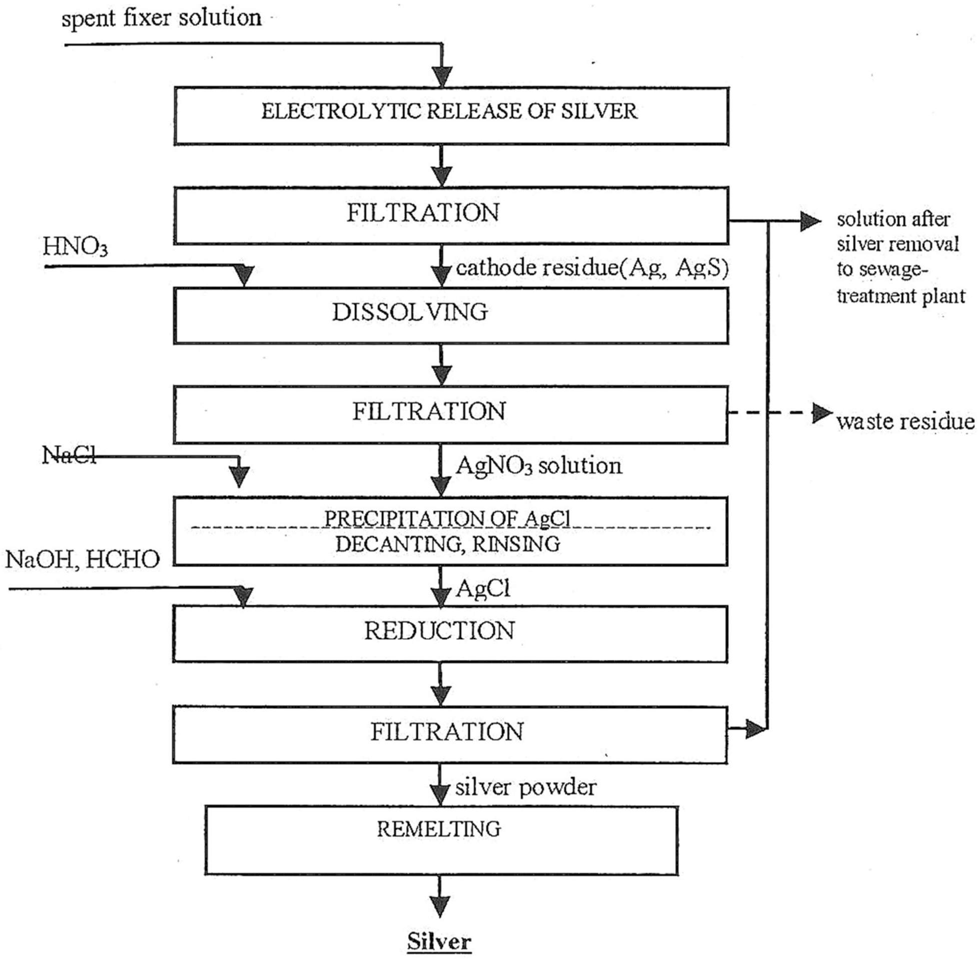

Fig. 3 Flow-sheet of silver recovery from spent solutions for light sensitive materials treatment

The first technological operation, being the "key" to solve the problem of silver recovery from thiosulphate solutions is the electrolytic secretion of silver. Electrolysis product – a silver concentrate with an 80-90% Ag content (which can be a commercial product) is processed to obtain pure silver. For this purpose, the post-electrolytic precipitate is reconstituted in nitric acid (V) at a concentration of approx. 30% at the boiling temperature to obtain a silver nitrate solution:

$$6Ag+8HNO_3=6AgNO_3+2NO+4H_2O$$

$$Ag_2S+4HNO_3=2AgNO_3+S+2NO_2+2H_2O$$

The post-reaction slurry consisting of silver (I) nitrate solution (I) and elemental sulfur is filtered. The solution of silver (I) nitrate (I) precipitates hardly soluble silver chloride:

$$AgNO_3+NaCl=AgCl\downarrow+NaNO_3$$

ACTIVITY OF THE "INNOVATOR" PLANT AT THE INSTITUTE OF NON-FERROUS METALS IN GLIWICE

INNOVATOR The company is an organizational unit at the Institute of Non-Ferrous Metals in Gliwice (Brodny, J. and Tutak, M. 2016b). This plant specializes in the recovery of silver and other precious metals from waste materials and in the processing of these metals in the highest quality of various products. INNOVATOR also strives to take a high position on the domestic market in the trade in precious

metals as well as products manufactured on the basis of these metals.
The recovery of precious metals is carried out on the basis of modern technologies that are constantly improved. The plant obtains high quality precious metals, such as:

- Silver powder and granulate in the AgO, Ag1, Ag2 grade
- Gold sponge and granules in Au grade 99.9,
- Pt 99.9 platinum sponge,
- Pdadium sponge grade Pd 99.9,
- Rhodium sponge in grade Rh 99.9.

Recovered noble metals are a direct commercial product or are used in the Company as raw materials for further processing into such products as:

- Jewelery alloys,
- Jewelery,
- Semi-finished products used in jewelery – tubes, rods, wires, tapes,
- Gold and platinum compounds used in electroplating and catalyst production,
- Products made by powder metallurgy,
- Non-ferrous metal wires and bands galvanically plated, tinned, nickel plated.

In the recent period, the commercial activity carried out by the Wholesale of Jewelery Products "INNOVATOR" has become more and more important in the Company.

CONCLUSION

Against the background of silver properties and structure, the technologies of obtaining silver in our country as a by-product in the processing of copper concentrates in KGHM POLSKA MIEDŹ S.A. and with the processing of zinc and lead concentrates in Huta Cynku "MIASTECZKO ŚLĄSKIE". Discussed technology for recovering silver from secondary raw materials such as: used silver catalysts, scrapped electronic devices, defective transistors, scrap of silver-plated glasses, used solutions used to process photosensitive materials.
Poland is at the forefront of global silver producers, taking ninth place in the world and first place in Europe.

ACKNOWLEDGEMENT

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REFEENCES

Babiński, W. (1986). Srebro i jego zastosowanie. Gliwice: Skrypt Pol. Śl.

Biały, W., Wedzicha J. and Nordin V. (2018). Masurement of Weldings Incompatibility in Constructions. Multidisciplinary Aspects of Production Engineering, 1, pp. 117-128.

Bołoz, Ł. and Midor, K. (2018). Process innovations in mining industry and effects of their implementation presented on example of longwall milling heads. Acta Montanistica Slovaca, 23(3), pp. 282-292.

Brodny, J. and Tutak, M. (2016). Determination of the zone endangered by methane explosion in goaf with caving of operating longwalls. 16th International Multidisciplinary Scientific SGEM Conference Proceedings, 1(2), pp. 299-306. DOI:10.5593/SGEM2016/B12/S03.039

Brodny, J. & Tutak, M. (2018a). Determination of the Zone with a Particularly High Risk of Endogenous Fires in the Goaves of a Longwall with Caving. Journal of Applied Fluid Mechanics, 1(3), pp. 545-553. DOI:10.18869/acadpub.jafm.73.246.27240

Brodny, J. and Tutak, M. (2016b). Analysis of gases emitted into the atmosphere during an endogenous fire. Proceedings of 16th International Multidisciplinary Scientific GeoConference SGEM 2016, pp. 75-82. DOI: 10.5593/SGEM2016/HB43/S06.011.

Brumby, A. (1995). Recycling of precious metals – an old business with new challenges, International Conference – Precious Metals, Kosice, pp. 162-165.

Byrdziak, H., Mizera, A. and Piątkowski J. (2000). KGHM Polska Miedź SA – Biuletyn.

Gajdzik, B. and Sitko, J. (2014). An analysis of the causes of complaints about steel sheets in metallurgical product quality management systems. Metalurgija,53(1), pp. 135-138.

Gajdzik, B. (2013). World class manufacturing in metallurgical enterprise. Metalurgija,52(1), pp. 131-134.

Gmelin Handbuch der Anorganishen Chemie-Silber (1975), Springer-Verlag, Heidelberg, 61.

Górniak, A., Midor, K., Kaźmierczak, J. and Kaniak, W. (2018). Advantages and disatvantages of using methane from CNG in motor vehicles in polish engine. Masurement of Weldings Incompatibility in Constructions. Multidisciplinary Aspects of Production Engineering,1, pp. 241-247.

Grabowski, T. (2002). Zakład Działalności Innowacyjnej – INNOVATOR Sp. z o.o., Rudy i Metale Nieżelazne, 5, pp. 234.

Krupka, D. (1988). Odzyskiwanie srebra ze złomu posrebrzanego szkła, Pol. Śl., UL. 12/88, (niepubl.).

Krupka, D. (2000). Odzyskiwanie srebra ze zużytych roztworów stosowanych do obróbki materiałów światłoczułych. Katowice: Sprawozdanie Pol. Śl, (niepubl.)

Krupka, D. (1996). Prace dyplomowe uczestników II Amerykańsko-Polskiego Studium Podyplomowego, 27. Katowice: Politechnika Śląska.

Mining Journal Ltd. (2000). Mining Annual Review 2000, SILVER.

Pluciński, S., Koźmiński W. (1994). A new precious metals plant in Poland. IPMI Conference, Vancouver.

Praca zbiorowa (1996). Monografia KGHM. Lubin: Polska Miedź SA.

Sitko, J., Mikuś, R. and Bożek, P. (2018). Analysis of device failure in the mechanical production plant. Masurement of Weldings Incompatibility in Constructions. Multidisciplinary Aspects of Production Engineering,1. pp. 93-99.

Tutak. M, & Brodny, J. (2019). Predicting Methane Concentration in Longwall Regions Using Artificial Neural Networks. Inernational Journal Environmental Research Public Health 16, 1406; pp. 1-22. DOI:10.3390/ijerph16081406.

Abstract: The article presents the technologies of obtaining precious metals as a by-product in the processing of copper concentrates in KGHM POLSKA MIEDŹ SA and in the processing of zinc and lead concentrates in Huta Cynku "MIASTECZKO ŚLĄSKIE". Discussed technologies for recovery of silver from secondary raw materials such as: used silver catalysts, scrapped electronic devices, defective transistors, scrap of silver-plated glasses, used solutions used for processing photosensitive materials are discussed. Jewellery and tableware and technical coatings in electronics and electrical engineering. The high reflectivity of the light rays from the silver surface was used in the production of special reflectors and mirrors, and chemical resistance in the construction of apparatus (such as equipment resistant to molten hydroxide alkali metals).

Keywords: plant, recovery, analysis, quality