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METALLURGY OF NON-FERROUS METALS IN POLAND

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ABSTRACT

The paper presents a review of methods for production of non-ferrous metals used in Poland. Technologies for production of copper and by-product metals applied in KGHM Polska Miedź S.A., for zinc and lead in ZGH Bolesław and HC „Miasteczko Śląskie" Smelters, as well as processes for production of lead from the used lead-acid batteries performed at Baterpol S.A., Orzeł Biały S.A., are described.

Keywords: Non-ferrous Metals Metallurgy, copper, lead, zinc.

INTRODUCTION

Currently, nine industrial plants specialized in production of copper, lead, zinc and by-product metals, i.e. silver, selenium, rhenium, nickel, gold and platinum group elements, are operating in Poland. Production of copper is realized in three plants which use pyrometallurgical technologies (HM Głogów I, HM Głogów II and HM Legnica) and belong to the KGHM Polska Miedź S.A., which is at the moment one of the leading producers of electrolytic copper and refined silver in the world. Zinc is produced by ZGH „Bolesław" Smelter and „Miasteczko Śląskie" S.A. Zinc Smelter. Lead is manufactured by ISP processing of battery scraps and lead-bearing dusts from copper metallurgy. The volume of production of non-ferrous metals in Poland is presented in Table 1.

Institute of Non-Ferrous Metals in Gliwice

Institute of Non-Ferrous Metals is one of the largest public research institutions in Poland and the main scientific-research centre, operating in the non-ferrous metals industry, mainly in the field of such metals as Cu, Al, Zn and Pb. The research is carried out by fourteen IMN Departments, which cover laboratory-, through pilot- and industrial scale tests, to the complete implementation. IMN is operating in the following areas:

- processing of ores and other minerals,
- pyrometallurgy,
- hydrometallurgy,
- environmental protection,
- analytical chemistry,
- processing of metals,
- material engineering especially in the field of new materials,
- recycling,
- batteries and accumulators.

Institute of Non-Ferrous Metals has a staff of about 500 employees. Besides the headquarter in Gliwice, IMN has also three divisions located in:

- Legnica - IMN Legnica Division,
- Poznań - CLAiO, Central Laboratory of Batteries and Cells,
- Skawina - Light Metals Division.

Institute of Non-Ferrous Metals is the owner of the INNOVATOR Company which provides products and services, based on technologies developed by IMN.

Apart from the core scientific activity, IMN conducts also production based on technologies, developed by its research teams. The main offered products are:

Table 1. Production of basic metals and products in 2015.

No.	Products	Production [Mg]
1.	Electrolytic copper	574 310
2.	Zinc	161 497
3.	Refined lead	153 322
4.	Refined silver	1 283
5.	Products of Cu and Cu alloys Cu rod Rolled Cu Extruded and drawn Others	294 018 246 642 2 949 38 908 5 519
6.	Products of Al and Al alloys Al rod Extruded and drawn	38 356 38 300 56
7.	Products of Zn and Zn casting alloys	14 545
8.	Products of Pb	695
9.	Cu and brass casting alloys	4 561
10.	Zn oxide and Pb oxide	24 891

● amorphous alloys,

● bimetallic clad wires,

● processing of waste materials containing non-ferrous metals,

● flotation cells and others,

● hydrocyclones for beneficiation of ores and waste materials,

● reference materials.

Institute of Non-Ferrous Metals is widely cooperating with the Polish and international industrial and scientific organizations.

Since the launch of the EU Framework Programmes, IMN has been actively involved in submitting project proposals in response to the announced calls related to raw materials, societal challenges, new materials issues, including the SPIRE initiative, as well as coordination and support actions. Currently, IMN takes part in 5 projects performed under HORIZON 2020.

Institute of Non-Ferrous Metals is also a Core Partner of EIT-KIC Raw Materials – a Consortium which connects stakeholders from different parts of the raw materials value chain or from different fields of application. EIT-KIC Raw Materials consists of more than 100 partners from leading businesses, universities and research institutes. IMN belongs to one of 6 Co-location Centres, e.g., the Eastern Co-locatio Centres situated in Wrocław, Poland.

Copper metallurgy at KGHM Polska Miedź S.A.

Production of copper at KGHM Polska Miedź S.A. Smelters is conducted with application of two technologies: a shaft furnace process at HM Glogów I and HM Legnica, as well as a flash smelting process at HM Głogów II, where blister copper is produced directly from the concentrates. The domestic and imported chalcosite-bornite concentrates (Cu_2S, Cu_5FeS_4) are the charge materials for the processes. The domestic copper concentrates are produced by three mining plants, i.e. „Lubin", „Polkowice-Sieroszowice" and „Rudna" located in Lower Silesia in the south-western part of Poland. The concentrates differ from typical concentrates in terms of lower content of iron (2.8 - 5.7 %) and sulphur (9.8 - 11.3 %), and high concentration of organic carbon (about 8 %). The main impurities in these concentrates are lead (1.5 - 3.8 %) and arsenic (0.05 - 0.40 %). Table 2 presents compares the composition of the domestic concentrates and the concentrates, processed in the world [1, 3].

Table 2. Composition of copper concentrates processed in Poland and in the world [3].

Type of concentrate (country)		Chemical composition (wt. %)					
		Cu	Fe	S	Zn	Pb	As
KGHM (Poland)	ZG Lubin	18.95	5.61	11.04	0.42	1.77	0.29
	ZG Polkowice	26.94	2.79	9.87	0.34	1.14	0.26
	ZG Rudna	28.38	3.52	11.21	0.62	2.27	0.083
Harjavalta	(Finland)	23-25	24-29	27-32	1.5-2.5	0.2-0.4	-
Saganoseki	(Japan)	30	23	28	-	-	0.14
Norddeutsche	(Germany)	26-32	18-28	23-33	0.5-2.0	0.1-0.5	0.1
Huelva	(Spain)	25	27	37	1	0.1	-
Caraiba	(Brasil)	32.8	20.2	26.3	0.2	-	0.2

Shaft process

The technology for production of copper performed at HM Głogów I and HM Legnica, employs smelting of the briquetted copper concentrates in shaft furnaces, which consists of the following technological stages:

● preparation of a charge, averaging of copper concentrates and dusty return materials, mixing with binder (black liqour) in amount of 10 - 11 % and briquetting of the mixture dried to about 4 % of H_2O,

● smelting of briquettes, with addition of converter slag and coke in the shaft furnace, into the so-called “copper matte”. The produced slag, due to low content of copper (0.3 - 0.5 %) is a waste material,

● converting of copper matte, aimed at oxidation of iron and sulphur, and production of blister copper (about 98 % of Cu),

● fire refining of blister copper in the anode furnaces,

● casting of copper anodes on the carousel-type casting machine,

● electrorefining of anode copper.

The advantage of the shaft process is a high degree of elimination of Pb and As in the first stage of the pyrometallurgical operation, and their accumulation in the gaseous-dust phase.

The main disadvantage of this technology is the complicated and expensive process for preparation of briquettes, and the application of a binder in the form of black liqour, which is mainly imported to Poland. Another problem is the generation of large quantities of gases, which are de-dusted by the wet method and combusted in the power boilers with additional fuel (natural gas, coal dust). These gases contain about 0.5 % of SO_2, which is neutralized in the Solinox installation for desulphurization of gases. Lower energy efficiency and high costs of the shaft furnace process were the basis for the decision to replace the existing technology, used at HM Głogów I, by an one stage flash smelting process. The second flash smelting furnace at HM Głogów I will start to operate in 2016. The flash smelting process for production of Cu blister has a number of advantages in comparison to the shaft furnace process:

● lower costs,

● complete recovery of S,

● recovery of heat from off-gases.

The flash smelting technology, which is planned to be introduced at HM Głogów I, is similar to the one currently used at HM Głogów II, which has been modified.

One stage flash smelting process

The possibility for application of one stage flash smelting process is determined by the composition of the Polish copper concentrates, characterized by low content of iron and sulphur. In the flash smelting process, in addition to copper of composition similar to converter copper, technological gases of high SO_2 concentration, directed to utilization in the sulphuric acid plant, are formed. This process has been applied for the first time in 1978 at HM Głogów II. The process flow sheet is presented in Fig. 1.

The flash smelting process consists of the following technological operations:

● preparation of a charge of proper grain size and moisture content below 0.3 % of H_2O,

● smelting of copper concentrate in the flash smelting furnace, aimed at production of blister copper,

● copper removal from the flash slag, containing 12 - 16 % of Cu in the electric furnace. The products of the copper removal process are: waste slag containing

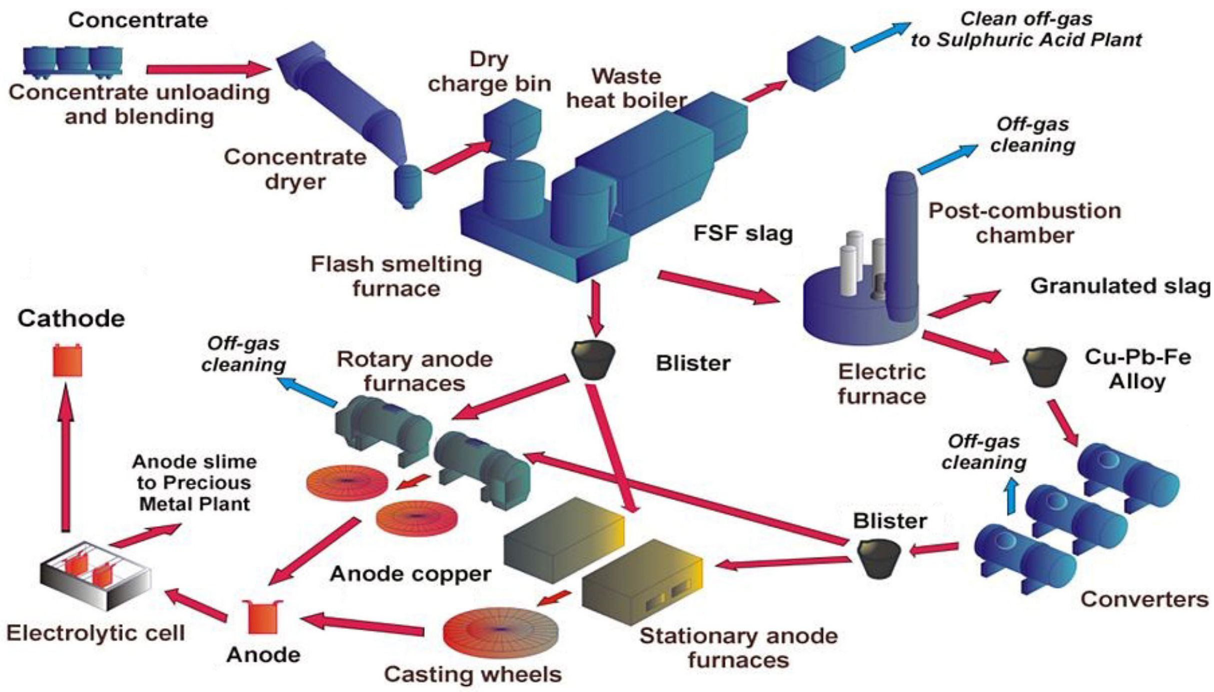

Fig.1. HM Głogów II one stage flash smelting process flow sheet.

from 0.4 to 0.6 % of Cu, process gases, dusts containing Pb and Cu-Pb-Fe alloy, subjected to further processing aimed at recovery of copper,

- Cu-Pb-Fe alloy converting,
- fire refining of blister copper and converter copper, performed in the rotary and stationary anode furnaces,
- casting of anode copper on carousel-type rotary machines,
- electrorefining of anode copper.

One of the main advantages of the one stage flash smelting process is related to method for charge preparation, which is three times less expensive than briquetting, and elimination of one technological stage i.e. copper matte converting, for about 2/3 of the produced copper. A positive aspect of this technology is also the achievement of one steady, in terms of time and chemical composition, stream of off-gases containing SO_2, which are transferred to a sulphuric acid plant. The application of the process enables also complete use of organic carbon and metal sulphides, included in the concentrate, as additional sources of energy.

Smelting of copper concentrates (Table 3) in the flash smelting furnace takes place at high oxygen potential, which is aimed at production of blister copper of low Pb content (below 0.3 %, Table 4).

One of the consequences of the high oxidation level of the copper concentrate components is the high Cu content in the flash slag. Recovery of copper from the flash slag is conducted by reduction in the electric furnace, which leads to production of Cu-Pb-Fe alloy and waste slag. The produced Cu-Pb-Fe alloy is then subjected to a two-stage converting process. In the first stage, oxidation of iron bound to application of SiO_2 in the form of fayalite slag returned to the electric furnace, takes place. The second stage is oxidation of the lead with addition of limestone, which leads to production of converter copper, directed to fire refining in the anode furnaces and slag, which is subjected to reduction due

Table 3. Average composition of copper concentrates, processed in a flash smelting furnace.

Component	Cu	As	SiO_2	Fe	Pb	S	Zn	MgO	CaO	Al_2O_3	C_{og}	C_{org}
wt. %	27.5 - 30.5	0.1 - 0.2	13.5 -15.5	5.5 - 7.0	1.5 - 2.5	12.0 - 13.5	0.6 - 0.8	2.8 - 3.4	4.5 - 5.5	4.2 - 5.0	8.5 - 9.3	6.5 - 8.0

Table 4. Chemical composition of products from smelting of the concentrates in a flash smelting furnace.

Flash slag							
Cu	Fe	Pb	Zn	SiO2	MgO	CaO	Al_2O_3
11,5-16,5	9-12	3-3.8	1-1.5	28-31.5	3.7-4.5	11.3-15.5	7.2-8.5

Blister copper					
Cu	Fe	Ni	O_2	Pb	S
> 98.5	<0.1	<0.1	0.2-0.5	0.2-0.3	<0.1

Dusts									
Al_2O_3	Fe	MgO	Pb	S	SiO_2	Zn	CaO	Cu	S_{SO4}
2.65 ÷ 3.13	4.4 ÷ 4.5	2.4 ÷ 3.1	4.16 ÷ 4.86	15.1 ÷ 15.6	5.79 ÷ 8.32	0.86 ÷ 0.96	6.57 ÷ 7.88	16.3 ÷ 17.6	14.8 ÷ 15.0

to the high level of copper content (15 - 20 %).

The Cu-Pb alloy containing less than 5 wt. % of Pb, and a slag (2 - 4 % Cu; 40 - 50 % Pb; 6 - 10 % Fe), which is a raw material for lead production (Fig. 2), are produced during the slag reduction process.

The method for processing of the slag, produced during the converting of the Cu-Pb-Fe alloy enables the removal of lead (Figs. 3, 4) and arsenic (Figs. 5, 6) from the copper production cycle.

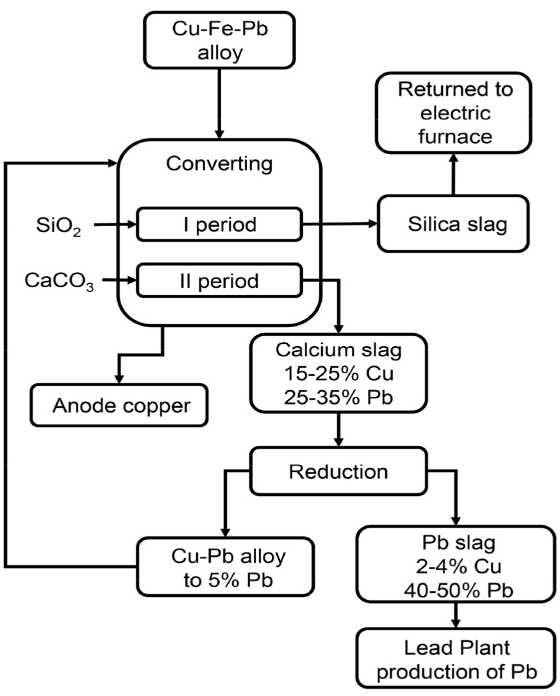

Fig. 2. Flow sheet of Cu-Fe-Pb alloy converting.

Apart from the processed copper concentrates Cu scraps in amount of about 110,000 Mg/year are also smelted at HM Głogów and HM Legnica. The scraps, characterized by Cu content above 80 %, are smelted in the converters during the operations of copper matte converting. The scraps of higher quality (above 98 wt. % Cu) are processed in the anode furnaces [2].

The annual production of copper at KGHM Polska Miedź S.A. Smelters is presented in Fig. 7.

KGHM Polska Miedź S.A., in addition to copper, is also specialized in recovery of by-product metals, i.e. silver, gold and platinum group elements, lead, selenium, rhenium and nickel. These metals occur in the Polish concentrates in the following quantities: silver (400 - 1000 ppm), gold (0.03 - 0.69 ppm), platinum (0.01 - 0.03 ppm), lead (1.5 - 3.8 wt. %), selenium (52 - 74 ppm), rhenium (4 - 12 ppm), nickel (310 - 620 ppm). The technologies for recovery of the above-mentioned metals have been mainly developed by Instytut Metali Nieżalnych.

Nickel in the form of nickel sulphate is recovered from the electrolyte, coming from copper electrorefining. The quantity of the produced nickel sulphate is at the level of about 2,750 Mg/year.

The important element produced at KGHM is rhenium. This metal is obtained from the weak sulphuric acid, generated in the HM Głogówi HM Legnica sulphuric acid plants. Rhenium is recovered in the form of ammonium perrhenate and metallic rhenium [3].The volume of production of rhenium in Poland is presented in Fig. 8.

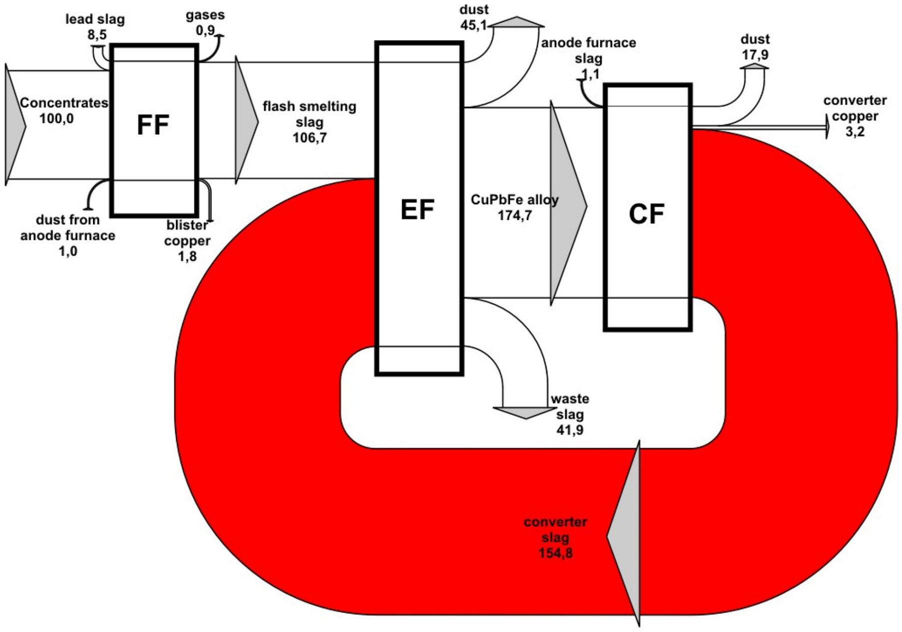

Fig. 3. Lead balance in the flash smelting process (fully completed copper production cycle) [10].

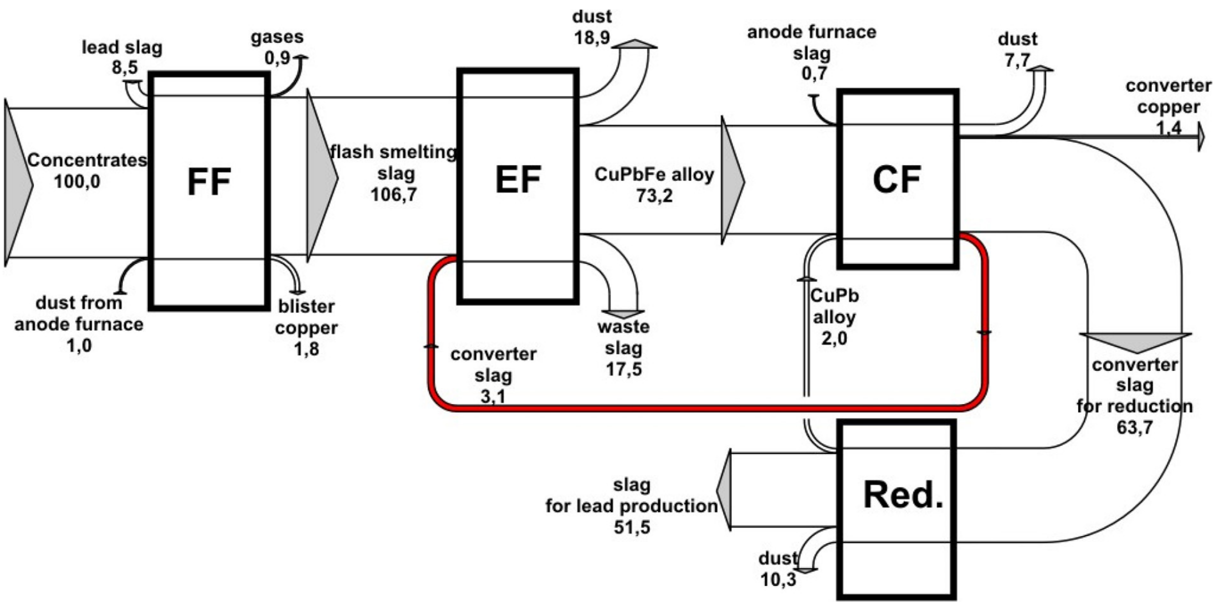

Fig. 4. Lead balance in the flash smelting process (directing of converter slag to separate treatment, i.e. lead production) [10].

Precious Metals Plant

The anode slimes, coming from the electrolytic refining of copper, are the raw material for production of precious metals. The content of silver in the anode slimes is at the level of about 40 %. The Boliden technology is applied (Kaldo furnace). Production of silver consists of the following major technological stages:

- preparation of a charge, i.e. crushing and drying (below 2 % of H_2O) of the anode slime with return materials (slimes from wet de-dusting of the off-gases, dusts from the bag filter, slag from silver converting),
- melting of Dore metal in the Kaldo rotary furnace (decomposition of $PbSO_4$ into PbO and formation of the slag), its reduction (decrease of silver content in the slag and reduction of copper and selenium oxides to the metallic phase), converting (removal of selenium, cop-

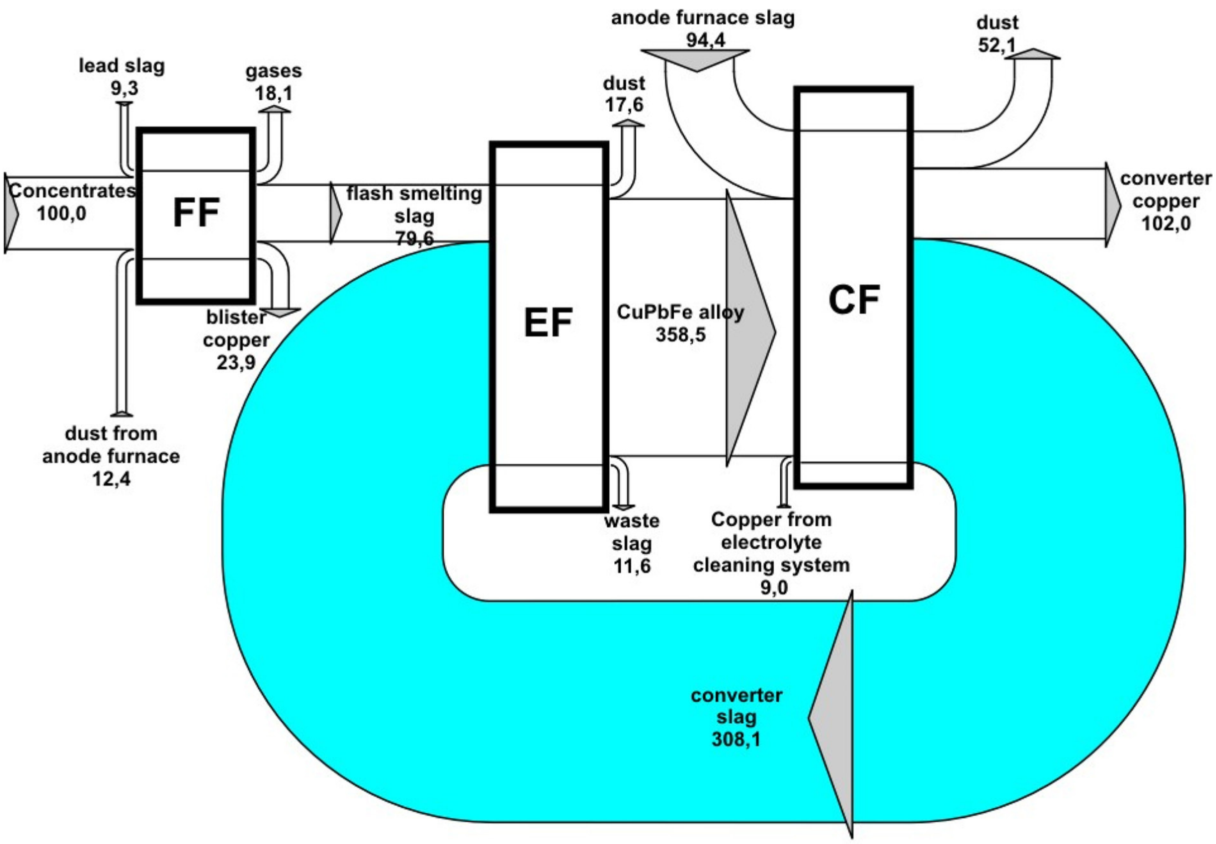

Fig. 5. Arsenic balance in the flash smelting process (fully completed copper production cycle) [10].

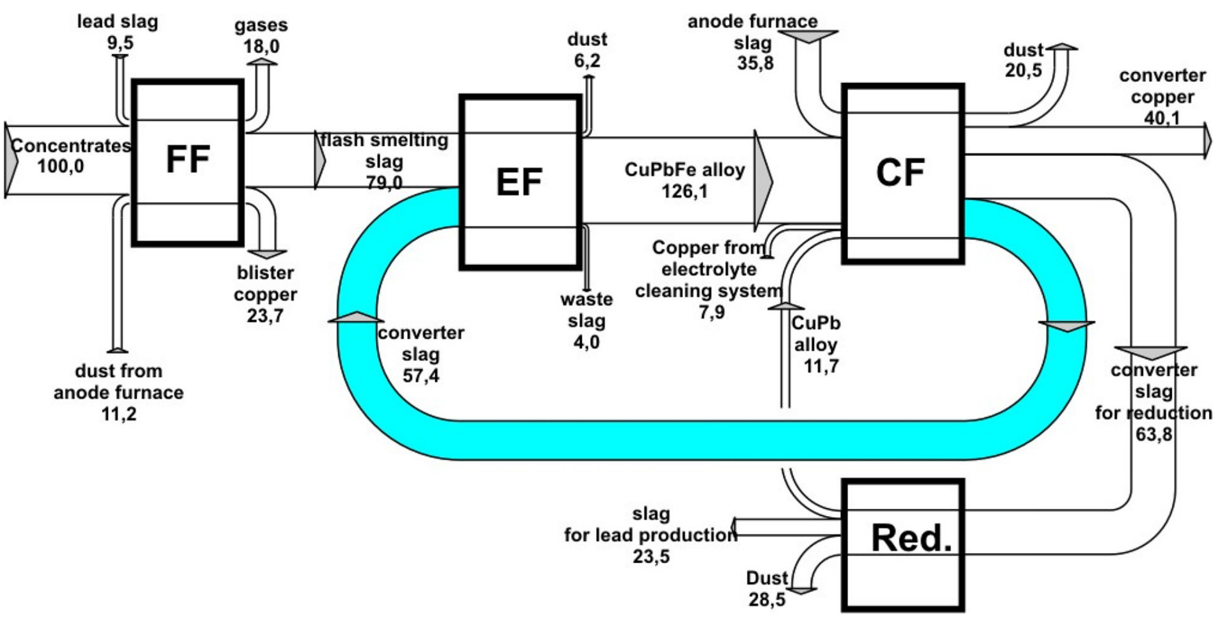

Fig. 6. Arsenic balance in the flash smelting process (directing of converter slag to separate treatment, i.e. lead production) [10].

per and lead from crude silver) and refining, aimed at production of silver with Pb and Se content below 0.02 wt. %, and Cu content below 0.8 wt. %,

- casting of anodes,
- electrorefining of silver, to refined silver (above 99.99 % of Ag) and slime containing metals, which are more precious than silver (gold, platinum, palladium).

In the recent years, production of silver at KGHM

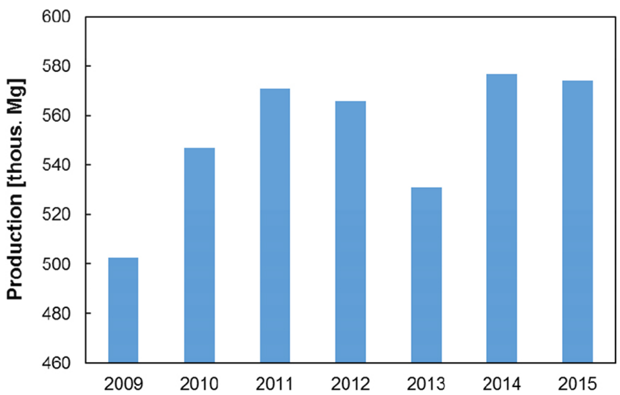

Fig. 7. Production of electrolytic copper at KGHM Polska Miedź S.A. in 2009-2015.

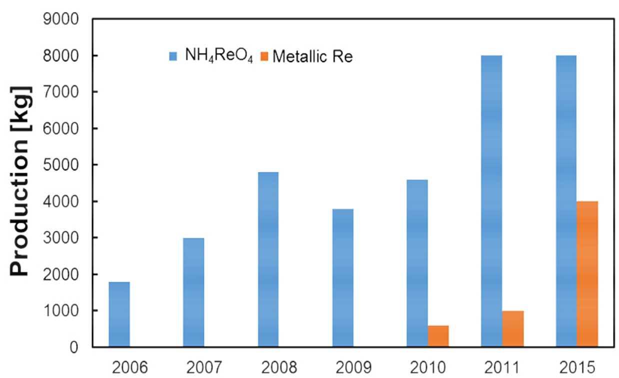

Fig. 8. Production of rhenium in Poland.

was at the level of about 1,200 Mg/year, and the company is the first Ag producer in the world. Proceeds from the sale of silver represent 15 % of KGHM total revenues.

At HM Głogów Precious Metals Plant gold and platinum-palladium concentrates are also produced.

Selenium, contained in the slime, is removed with the dusty off-gases during the smelting process, conducted in the Kaldo furnace. As a result of the wet de-dusting a suspension is produced. Together with NaOH addition it is directed to the leaching process, aimed mainly at precipitation of lead. The solution, after leaching, is subjected to precipitation of selenium with the application of SO_2. The final product of the process is technical selenium containing 99.65 % Se. The production volume of technical selenium varies from 80 to 90 Mg/year.

Zinc and lead metallurgy in Poland

Zinc in Poland is produced by ZGH „Bolesław" Capital Group, which consists of the following Plants:

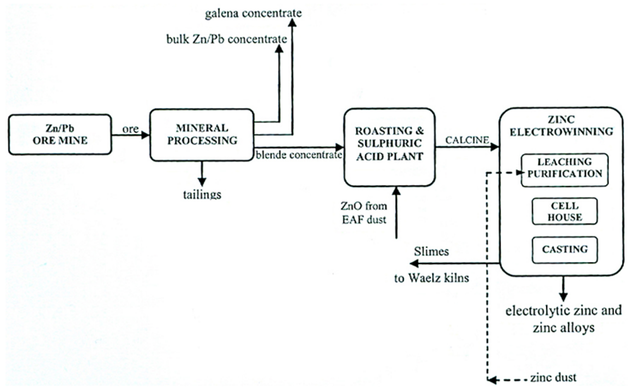

Fig. 9. ZGH „Bolesław" electrolytic zinc production flow sheet [5].

- ZGH „Bolesław" in Bukowno - Zinc Mine and Smelter,
- „Bolesław Recycling" - Recycling Smelter, which uses Waelz kiln technology,
- HC „Miasteczko Śląskie" - Smelter, which uses ISP technology for processing of primary and secondary materials.

The total production volume of zinc by the „Bolesław" Group in 2015 was at the level of 161,000 Mg.

ZGH „Bolesław" in Bukowno

The production of electrolytic zinc in ZGH Bolesław is mainly based on processing of the company's own concentrates with the average content of (wt. %): 55 - 57 of Zn; 1.6 - 4.2 of Pb; 4.3 - 5.5 of Fe, 0.1 - 0.3 of Mg, in the amount of 125,000 - 130,000 Mg/year. The general flow sheet of zinc production is presented in Fig. 9.

The concentrate is subjected to fluidized-bed roasting in two furnaces of production capacity from 400 to 450 Mg/day. Crude zinc oxide, which comes from the „Bolesław-Recycling" Waelz kiln process, is also added to the roasting process in the amount of about 10 %. The process is carried out at temperature of 950^{o}C.

The obtined zinc calcine is then subjected to a two-stage leaching process (Fig. 10).

The first neutral leaching is carried out in the leaching tanks of 80 m^3 volume. Then hydroseparation takes place. The suspended matter, with fine particles of zinc calcine, goes to a settler. The underflow from the settler, with slimes after the separation in the hydrocyclones is subjected to a second acidic-neutral leaching. The slurry after the second leaching is separated from the solution by sedimentation and pressure filtration. The

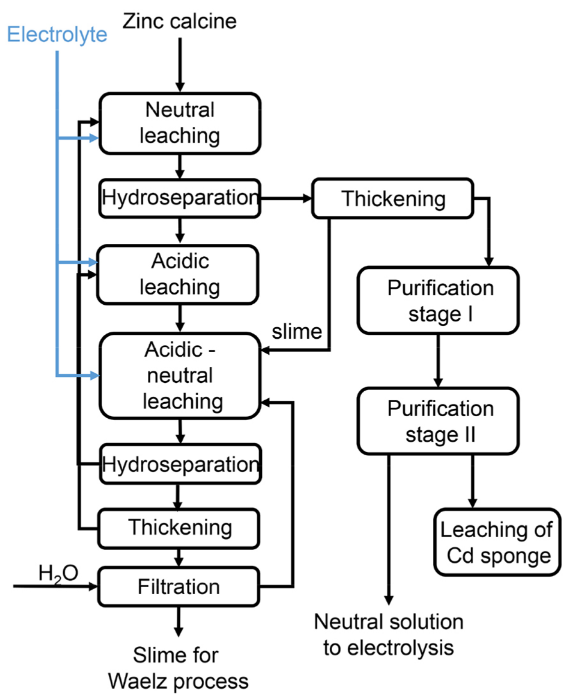

Fig.10. Flow sheet of zinc calcine leaching at ZGH „Bolesław".

solution is returned to the second stage of leaching. The filtration cake, which is a final by-product and contain (wt. %) 17.5 - 19.5 of Zn; 8 - 10.5 of Pb and 20 - 23 of Fe, is directed to the Waelz kiln process. The mass of the slimes, sent to the Waelz kiln process, is at the level of 20 - 25 % of the zinc calcine mass. The recovery rate of the zinc leaching reaches the level of about 90 %.

The solution after neutral leaching is subjected to the process of purification by cementation. The purified electrolyte containing about 150 g/l of zinc is directed to the electrolytic process.

The produced zinc cathodes are smelted in the induction furnace of capacity up to 30 t. The Z1 grade electrolytic zinc and its alloys are the products of this process. The production volume of zinc at ZGH „Bolesław" in 2015 was about 80000 Mg.

The second Plant, i.e. „Bolesław Recycling", which belongs to the same Capital Group, is also situated at the ZGH „Bolesław" Smelter site. This plant uses Waelz kilns for production of zinc oxide [6].

The basic charge materials for the Waelz process

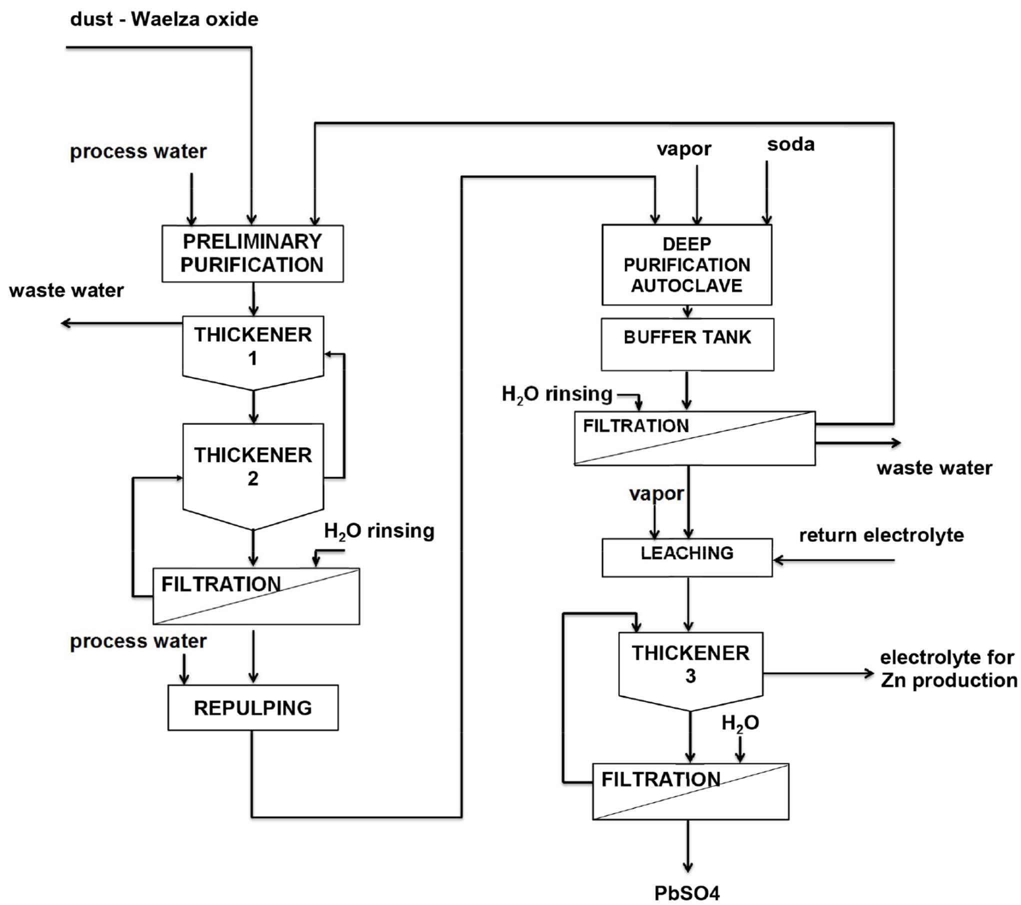

Fig. 11. Flow sheet of chlorine and fluorine removal from crude zinc oxide.

are dusts from electric arc furnace, containing (wt. %) 15 - 35 of Zn; 20 - 38 of Fe; 2 - 6 of Pb, and the slimes from zinc calcine leaching, which are processed separately. In addition, limestone and a reducing agent (coke or anthracite in the amount of 30 - 35 %, relative to the zinc-bearing material dry mass) are introduced. The materials are processed in furnaces with a diameter of 2.6 m and length of 40 m, with production capacity at the level of 80 Mg/day. The charge is dosed continuously and the furnaces are fired with gas burners.

The de-dusted off-gases, in the case of processing of slimes, are directed to desulphurization. The suspension of water and ground calcium carbonate is used as a sorbent of SO_2, and as a result synthetic gypsum is obtained. The efficiency of the installation for off-gases desulphurization exceeds 98 %. The product of steel dusts processing is the so-called "crude zinc oxide". It contains (wt. %): 57 – 63 of Zn, 4.5 - 5.8 of Pb, 5.5 - 7.5 of Cl, 0.15 - 0.25 of F, 4.8 - 5.8 of K_2O, 1 - 2.5 of Fe, 0.5 - 2 of SiO_2 and is purified from chlorine and fluorine in the new industrial installation [8].

The processes for chlorine and fluorine removal (Fig. 11) are carried out with application of hydrometallurgical methods in a two-stage dechlorination process, i.e. initial and deep dechlorination, with application of autoclaves.

The purified zinc oxide containing (wt. %): around 65 of Zn; < 0.02 of Cl and < 0.02 of F, after leaching in the circulating electrolyte is introduced into the zinc electrolysis process.

HC„Miasteczko Śląskie" Imperial Smelting Process (ISP)

The process, used at HC „Miasteczko Śląskie" enables processing of raw materials of very different chemical compositions. Currently, this is the only plant in Europe where ISP process is still used with one shaft furnace operating. This technology is applied for processing of Zn-Pb sulphide and oxide type concentrates. The technology, which is shown in Fig. 12, enables simultaneous recovery of zinc and lead [5, 7].

The first stage is sintering of the materials, which is conducted in a Dwight-Lloyd sintering machine. The charge for sintering is zinc-lead sulphide concentrate or waste materials of oxide type with return sinter, and a fluxing agent (sand and limestone). The sintering process is carried out in two variations:

● for sulphide concentrates with sulphur content at the level of 20 %, the produced gases contain 5 - 7 % of SO_2 and are used for production of sulphuric acid,

● for sulphur content in the charge up to 2 % (during processing of secondary materials of oxide type),

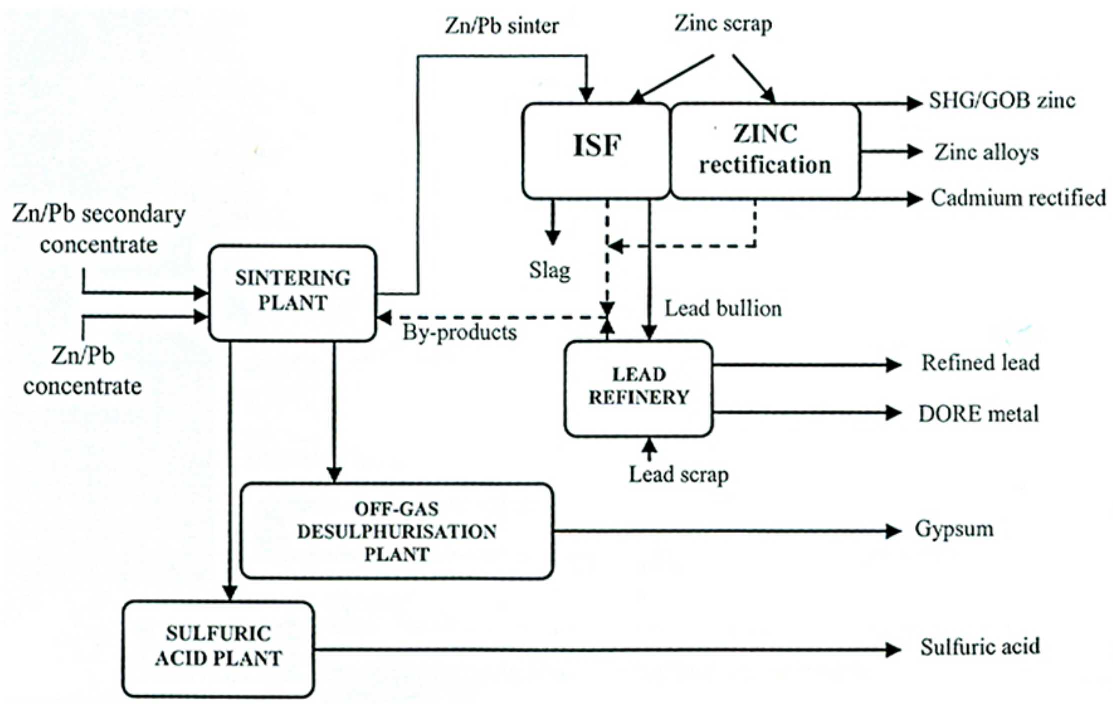

Fig. 12. HC „Miasteczko Śląskie" ISP technology flow sheet [5].

addition of coke or anthracite as a fuel to the charge, is needed. The produced gases contain 0.3 - 0.5 % of SO_2 and are subjected to desulphurization by the wet limestone method with production of synthetic gypsum.

The imported zinc-bearing materials of oxide type contain such impurities as chlorine and fluorine, which are unfavourable for the whole process. In order to remove these impurities, the hydrometallurgical method for removal of these elements by leaching in a solution of sodium carbonate is used.

The aim of sintering is the production of the sinter of possibly high strength properties, low sulphur content and high porosity. The sinter is directed to reduction smelting in the shaft furnace. The basic processes of smelting and reduction are conducted at temperature of about 1200°C. Lead, liquid slag, technological gases containing CO_2, CO, N_2 and zinc vapors are produced. The liquid products of the process are tapped off periodically to a settler, where their separation takes place. The separated liquid slag is subjected to granulation. The gases are sent to a condenser, where lead splashing condensation of Zn vapors occurs. Liquid lead, containing dissolved zinc, is directed to the separation system, where as the result of temperature reduction to 450°C, zinc is separated from the liquid lead. The off-gases after de-dusting are used for: heating Cowper stoves, coke heaters, firing of lead refining kettles and heating up of water in the power plant.

Zinc is directed to a refining process by the New Jersey method in rectifying columns. The installation consists of seven columns: three lead columns, two cadmium columns, one re-distillation and one „baby" column. Crude zinc from the shaft furnace, containing around 2 % of impurities like Pb, Fe, Cu, Sn and Cd, is directed to the three lead columns, where the whole amount of cadmium and about half of the amount of zinc, are evaporated. The remaining part of Zn, with the impurities, flow to the lower part of the column and through a valley are transferred to a liquation furnace. As the result of the temperature reduction, the impurities in the form of dross and hard zinc, are precipitated from the metal bath. Purified zinc of Z5 grade, characterized by purity at the level of min. 98.5 % and no cadmium content, of which lead is the main impurity, is cast into ingots and blocks. A part of metal from the liquation furnace is directed to the re-distillation column, where from the evaporated part after condensation, the refined zinc of Z1 grade is produced.

The Zn-Cd alloy, condensed in the lead columns condensers, is directed to two cadmium columns. The metal vapors, moving to the upper part of the column, raise up the whole amount of cadmium and small amount of zinc, and the flowing metal is the highest purity zinc of Z1 grade.

The condensated metal vapors from the cadmium columns, which contain above 50 % of Cd, are sent to the „baby" column, where as the result of the separation, cadmium containing about 1 % of Zn is produced.

Lead is subjected to refining in the kettles for production of refined lead and its alloys. As the result of the lead refining, silver froth is produced, from which Dore metal is obtained after its processing in the liquation muffle, the distillation furnace and the cuppelation furnace.

Lead Processing Plant at HM Głogów (KHGM Polska Miedź S.A.)

Processing of lead-bearing materials coming from copper metallurgy is conducted at HM Głogów I. The charge materials for the process are:

- slimes from wet de-dusting of the gases from the shaft furnaces,
- converter dusts from process of copper matte converting,
- dusts from electric furnace,
- converter slimes from wet de-dusting of the gases from Cu-Pb-Fe alloy converting process,
- dross from lead refining.

The chemical composition of the lead-bearing materials coming from copper metallurgy is shown in Table 5.

Crude lead is smelted from the mixture of lead-bearing materials, using an installation, which consists of the following technological systems:

- charge preparation centre,
- system for charging a rotary furnace with materials,
- 4 rotary furnaces, each of capacity of 30 Mg of the charge,
- installation for conditioning and de-dusting of the process gases,
- installation for slag crushing and Fe-As speiss separation.

The products of the lead-bearing materials smelting in the rotary-rocking furnaces are: crude lead, Fe-As

Table 5. Chemical composition of lead-bearing materials [4].

	Shaft slime HMG I	Shaft slime HML	Converter dusts HMG I	Pb-Zn dusts (Electric Furnace)	Converter slime HMG II	Slag (Precious Metals Plant)	Dross Pb Refinery
	wt. %						
Pb	38.9	44.4	52	35.4	58.6	71.7	69
Cu	1.75	0.78	0.61	2.32	0.95	1.36	8
Ag	0.0093	0.016	0.028	0.008	0.008	0.23	0.11
Zn	6	6.07	6.66	23.41	4.22	23.41	6
As	3	5	1.81	0.46	4.58	1.06	5
Fe	0.8	0.7	0.089	0.3	0.21	1.4	1

speiss and slag. Table 6 presents the chemical composition of the products.

Crude lead is directed to the lead refinery, located at HM Legnica. The production of crude lead at HM Głogów is at the level of 27,000 Mg/year.

Crude lead, containing up to 2 % of impurities (such as: Cu, Ag, Sn, Sb, Bi, Te, As, Tl and Cd), is subjected to the refining process, conducted in the Pb refinery at HM Legnica, in order to produce high grade refined lead of 99.97 - 99.99 % Pb. The fire refining is conducted as a multi-stage process in separate kettles and covers [4]:

- drossing and liquation of copper,
- copper removal with sulphur and galena mixture,
- Sn, Sb and As removal with oxygen,
- silver removal with zinc,
- vacuum zinc removal,
- bismuth removal with Mg-Ca alloy,
- removal of Mg, Ca and the rest of zinc with NaOH and $NaNO_3$,
- Tl removal with zinc chloride,
- final refining with NaOH and $NaNO_3$.

Production of refined lead at the HM Legnica refinery reaches about 30,000 Mg/year.

Orzeł Biały S.A. and Baterpol Sp. z o.o.

In Poland four plants, including Orzeł Biały S.A. and Baterpol Sp. z o.o., are specialized in recycling of lead. In both smelters spent car batteries are processed. Their technologies differ in the method for preparation of the charge for the pyrometallurgical stage.

The technology for processing of battery scraps, applied by Baterpol Sp.zo.o., includes three main stages:

- Crushing and separation - battery breaking process and electrolyte filtration. The solid fraction is subjected to separation by a hydrodynamic method and as the result the metallic fraction, polypropylene from the casings/bodies, and lead paste, containing sulphur compounds are obtained.
- Desulphurization of lead paste - paste containing about 8 % of sulphur with electrolyte is directed to desulphurization by the sodium method, which consists of the reaction of lead sulphate with sodium carbonate, in order to obtain lead carbonate. Then a filtration process takes place. The product of the process is a desulphurized paste (sulphur content up to 1 %), directed to the pyrometallurgical stage, and a solution of sodium sulphate (VI).
- Crystallization of sodium sulphate (VI) - the solu-

Table 6. Chemical composition of the lead-bearing materials smelting products.

	Pb	Cu	Fe	Zn	As	Sb	Sn	Bi	Ag	Tl	S
	wt. %										
Pb (crude)	98.9	0.35	-	-	0.28	0.15	0.15	0.07	0.036	0.025	-
Fe-As speiss	3	2	65	-	23	-	-	-	-	-	2
Slag	8.5	2.2	25.1	14.1	0.5	-	-	-	-	-	19.4

tion of sodium sulphate is sent to a process of crystallization and drying. As the result of these operations, anhydrous sodium sulphate (VI) is produced, the level of its purity enabling its application in the household chemistry.

As the one of the first process stages (Orzeł Biały S.A), crushing of the batteries and their separation are carried out. As the result, solid fraction and electrolyte are obtained.

From the electrolyte the solid components are separated and the solution of H_2SO_4 is directed to filter press. The purified electrolyte is a commercial product. In the case of lack of potential market outlets, the acid is neutralized with a lime suspension. The gypsum, produced after neutralization of the solution, is transferred to the dump. The solid fraction is subjected to a multi-stage process of crushing and separation. In consequence the following fractions are produced:

- plastic fraction (ebonite, PCV and polypropylene),
- fraction, where lead occurs in metallic and sulphate forms (up to 70 % Pb), directed to the furnaces.

In both companies processing of the used batteries with technological additives (coke breeze, ferrous scrap, soda) is conducted in the Dörschel and BJ short rotary furnaces. The furnace is characterized by a drum form of diameter of 2.6 m and length of 7 m. In the front wall there is a hole, where the burner is situated. The gas exhaust outlet is located in the rear wall, in the burner axis. The produced crude lead is sent to a refining process which consists of:

- drossing process (removal of impurities in the form of slag inclusions, sulphides and intermetallic compounds),
- removal of copper (deep removal of copper),
- removal of antimony, tin and arsenic by oxidation with oxygen,
- removal of silver with the application of zinc,
- removal of zinc with the application of NaOH and $NaNO_3$,
- final refining with the application of NaOH and $NaNO_3$.

The process is conducted in refining kettles of capacity of about 10 m^3 (100 Mg), which are fired with a gas burner. Lead, after refining, is pumped into the casting kettle, where at temperature of 420 - 440^{o}C casting of refined lead of P1 and P2 grades and purity of 99.98 %, or casting of lead alloys, are carried out.

CONCLUSIONS

The Polish non-ferrous metals industry is concentrated around three large Capital Groups:

- KGHM Polska Miedź S.A.,
- Bolesław Group,
- Impexmetal,
- and others.

KGHM Polska Miedź S.A. is a leading company, which is the eighth-largest copper producer in the world. The possessed resources of this metal locate the company on the fourth place in the world. KGHM Polska Miedź S.A.is also a world's leading producer of silver and such metals as: lead, rhenium and selenium.

The second is the ZGH „Bolesław"Group, which is focused on zinc and lead production. The three metallurgical plants, which belong to this concern, are specialized in complex processing of the company's own Zn-Pb concentrates, as well as recycling of different Zn-Pb materials, coming from the domestic and world's markets. The ISP process enables processing of zinc-lead waste materials.

Besides the largest producers of non-ferrous metals, smaller companies are also operating in Poland. These include two plants - Orzeł Biały and Baterpol, specialized in recycling of used car batteries.

At present, the Polish metallurgy of non-ferrous metals has a high technological level. It is evidenced by the achieved technological indicators. The products are characterized by high quality, while maintaining high environmental standards.

There are numerous examples of new, innovative technological solutions applied in the Polish non-ferrous metals industry, i.e.:

I Processing of ores

- New type flotation machines.
- New construction hydrocyclones.
- Installation for processing of old flotation tailings aimed at additional recovery of Zn and Pb.

II Metallurgy of copper

The new second flash smelting furnace at HM Głogów I for direct production of copper from the concentrates with application of:

- production of copper concentrates with different contents of C_{org},
- roasting of part of the concentrates before the flash smelting process, aimed at elimination of C_{org},

● new technology for copper removal from the slag in a rectangular-shaped electric furnace,

● new solutions in the field of after burning of gases from an electric furnace for copper removal from the slag,

● new technology for processing of Cu-Fe-Pballoy with concentration of lead in a converter slag, directed to production of lead.

III By-product metals

● Technology for recovery of Re in the form of ammonium perrhenate, and metallic rhenium from the weak sulphuric acid of the copper smelters sulphuric acid plants.

● Development of a new technology for removal of As from the technological cycle of copper smelters and ecologically safe storage of As waste (scorodite).

IV Metallurgy of Zn and Pb

● Application of zinc oxide, coming from processing of EAF dusts in the Waelzkilns, directly for electrolysis (excluding fluidized-bed furnaces) by removal of Cl and F in autoclaves.

● Improvement of economics of the ISP process by processing of oxide waste materials with application of desulphurization of gases by wet limestone method (gypsum).

● A new HCM unit/plant for Zn rectification from ISP process.

● A new technology for production of zinc oxide from hard zinc waste.

● Development of new Zn alloys for galvanizing process.

● A new installation for separation of battery scrap, before smelting in the BJ rotary furnaces.

● New technologies for refining of lead from processing of battery scraps, e.g. - with the application of a technology for removal of Cu from lead with Al.

● Application of oxygen for smelting of lead dusts from copper metallurgy in short rotary furnaces.

● New Pb alloys for batteries.

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