THE BOLESLAW ELECTROLYTIC ZINC PLANT

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ELEKTROLYTICKÁ VÝROBA ZINKU V ZÁVODE BOLESLAW

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Abstrakt

Prevádzka na výrobu zinku elektrolýzou s kapacitou 75 000ton za rok, je súčasťou závodu Základy Gorniczo-Hutnicze BOLESLAW. Tento závod je najväčším výrobcom zinku v Poľsku.

Výroba v tomto závode začala v roku 1955 s kapacitou 15 000 ton za rok a do dnes sa znásobila 5-násobne. Na začiatku závod spracovával len výpražky z oxidov zinku (60% Zn%, 3-4% Pb, 0,03 % Cd), ktoré boli produkované z pár vo Waeltz peci pri kalcinácii v rotačných peciach. Podiel výpražkov vo vsádzke pochádzajúcej zo koncentrátov sulfidu zinku rástol počas rozmachu závodu BOLESLAW. V súčasnosti sú pražené len sulfidické koncentráty a sú spracovávané výpražky z praženia vo fluidnej peci. Príspevok prezentuje obecný popis závodu ZGH BOLESLAW a diskutuje procesy praženia, lúhovania, čistenia a elektrolýzy. Udáva tiež chemické zloženie rôznych materiálov vyskytujúcich sa v procese.

ABSTRACT

The electrolytic zinc plant, with a capacity 75 000 tonnes per year, is a part of Zaklady Gorniczo-Hutnicze BOLESLAW. It is the biggest zinc producer in Poland. The electrolytic zinc plant started up in 1955 with a capacity 15 000 tonnes per year, and multiplied its production by 5 till nowadays. At the beginning, the plant processed only calcine from zinc oxides (60% Zn, 3-4% Pb, 0,03 % Cd) which were produced from Waeltz fumes by calcination in a rotary kiln. Participation of calcine from zinc sulfide concentrtes in the feed grew during the BOLESLAW plant expansion. Currently, only roasted sulphide concentrates, calcine from fluid-bed roasters, is processed. This paper presents a general description of the ZGH BOLESLAW plant and discusses the processes of roasting, leaching, purification and electrolysis.Also shown are the chemical analyses of the various process materials.

Key words: zinc production, electrolytic plant, hydrometallurgy

INTRODUCTION

The electrolytic zinc plant started up in 1955 as a part of the mining and metallurgical complex Zaklady Gorniczo - Hutnicze "BOLESŁAW" which had a mining and metallurgy tradition rooted in the XIII century.

Currently existing as a government enterprise, ZGH BOLESŁAW owns two Zn-Pb mines OLKUSZ and POMORZANY, a concentration and flotation plant OLKUSZ - POMORZANY, a pyrometallurgical wastes treatment plant - RECYCLING S.A. a subsidiary company, a roasting plant with a sulfuric acid plant, en electrolytic zinc plant and auxiliary plants.

The Zn-Pb ores from local deposits are poor in comparison to world deposits. Their global zinc and lead contents are to 6 - 7%. Sphalerite and galena are the main minerals.The ores are concentrated by selective flotation with prior concentration in heavy liquids. This prior concentration allows the separation of coarse, dolomite in quantity about 40 % of the total mine output. The whole production of dolomite in quantities exceeding 1 000 000 tonnes per year is sold as a valuable commercial product. Zinc sulphide concentrates from the concentration plant contain about 53 - 55 % Zn and 1.5 % Pb, and the galena concentrate contains about 50 % Pb and 1.5 % Zn.

ZGH BOLESLAW produces:

Electrolytic zinc

Sulfuric acid

Zinc concentrates

Lead concentrates

Dolomite

Zinc oxides (as fume and as calcine)

Zinc alloys

Magnesium sulfate

Zinc sulfate

Cadmium sponge

ZGH BOLESLAW is the biggest zinc producer in Poland. It recently undertook many development and modernization works. These activities aimed at a zinc production of over 75 000 tonnes annually, about 5 times more than starting production of 15 000 tonnes per year.

RAW MATERIALS

Over the period 1955-1961, the electrolytic plant processed only calcined zinc oxide having a composition of 60% Zn, 3-4% Pb, 0.03% Cd .The zinc oxide was produced by calcination of the fumes from Waelz process at temperatures from 1420 to 1470 K. Zinc carbonate ores, Zn-Fe residues and other zinc-bearing materials were used as raw materials in the Waelz process. After enhancement of the electrolytic zinc plant in 1962, the importance of roasted sulphide concentrates was continuously growing in the feed. Currently, only the calcine from fluid-bed roasters is processed. Table 1 shows the analysis of the raw material processed over the period 1998-1999.

Table I Chemical analysis of zinc raw materials at ZGH BOLESLAW (1997 - 1998), %

ROASTING AND GAS TREATMENT

The roasting and sulfuric acid plant was commissioned in 1969 as a facilty equipped with two fluid-bed roasters having a hearth surface 15 m^2 each and single contact acid facilities. During the following years the plant was modernized and expanded. Currently, two fluid-bed roasters, each of a hearth area of 27 m^2, with waste heat boilers are in use. Gases are processed in converters with four shelves of MONSANTO vanadium pentoxide catalyst. A double conversion system increases the conversion of SO_2 to SO_3 and to reduces SO_2 emission. A ROSEMOUNT System was introduced to control roasting and flue gas processing in 1994. The system provides precise, remote, and central control of the whole process including: the furnace with its waste-heat boiler, the scrubber, the electro-precipitators, conversion apparatus, sorption towers, blowers, acid drains treatment and sulfuric acid storage.

The application of the Rosemount System results in a good quality of roasted concentrates for subsequent processing and ensures the compliance of the stack gasses and waste waters with the new environmental regulations (SO_2 content in stack gasses is kept below 120 mg/Nm^3). The wastewater from the sulfuric acid plant is processed in the acid waste waters plant (commissioned in 1996) in connection with the acid drains from other plants.

WAELZ PLANT

The Waelz Plant was commissioned in 1952 and was equipped with thirteen Waelz kilns and two rotary kilns for calcination of the Waelz fumes. The specifications of both kilns were as follows:

Length	40 m
Outer diameter	3.0 m
Lining thickness	250 mm
Inclination	2°/4°
Rotational speed	0.67 rpm

The Waelz plant processed 400 000 tonnes per year of zinc carbonate ore typically containing 10 % Zn and 2 % Pb and Zn-Fe residues with zinc contents of about 16-18 %. After running out of zinc carbonate ore deposits and because of environmental reasons, nine kilns were liquidated in 1989. Currently, six kilns are operated: 4 as Waelz kilns and 2 for calcination of Waelz fumes.

At the same time, changes were introduced in feed: residues from the electrolytic zinc plant are processed with some addition of zinc-bearing materials from waste water treatment plant, and other secondaries like EAF dusts coming from steel mills (electric arc furnace dusts). Table II shows the typical analysis of residues from the electrolytic zinc plant.

Table II Chemical analysis of Fe-Zn residues, %

About 50 000 tonnes per year of different zinc-bearing raw materials are processed with typical contents of 19 % Zn and 4 % Pb . This allows the production of about 13 000 tonnes of calcinated ZnO (55-62 %Zn and 12 % Pb) as well as 2 600 tonnes of Pb-Zn-Cd concentrate per year. Coke in feed approximately equals 35 %. Waelz fumes contain 47-55 % Zn, 15-20% Pb, 0.5-1 % Cd. Slag is formed in quantities of about 38 000 tonnes per year with a typical analysis of about 2 % Zn and 0.4 % Pb. Addition of silica to the feed results in the formation of a glassy slag allowing its utilization in mining (for excavation filling) and road building. Table III shows the chemical analysis of Waelz slag.

Table III Chemical analysis of Waelz slag, %

LEACHING

After commissioning of the electrolitytic zinc plant, the leaching process was adopted to treat only the calcine of the zinc oxides (60% Zn, 3-4% Pb and 0,03% Cd) produced from the Waelz fumes by calcination in a rotary kiln. This material is very difficult for zinc extraction by hydrometallurgical methods. Leaching was carried out by reverse leaching at low acidity. Because of the high level of colloids in the slurries, solid/liquid separation created many problems. Slurries with high viscosity were practically impossible to clarify and the filtration rate was rather low. The high specific volume of the residues resulted in a great amount of occluded zinc. For these reasons, reverse leaching was recognized as correct, but resulted in low zinc yields. Participation of calcine from zinc sulphide concentrates grew during the BOLESLAW plant expansion. Currently only roasted sulphide concentrates, calcine from the fluid-bed roasters, are processed.

The leaching process has been modernized. Primarily, the new leaching flowsheet was prepared on a basis of our own research and development work connected with the experiences of the world's zinc electrolysis plants which apply iron precipitation in the form of goethite. This allows zinc yields at the level of 95 to 98 %. The high zinc yield is the main advantage of the goethite method. From the other side, the main problems at the erection of the plant and its operation are connected with the severe requirements for the leaching and precipitation equipment, heating to 360-370K, and especially with difficulties in the utilization/storage of goethite residues. It was found that the goethite method would probably be the best, but only for new plants that are processing local concentrates. An additional limitation was caused by fact that chosen method has to be applied in an old, existing plant in rather difficult technical and economical conditions. It was necessary to consider the presence of existing buildings and facilities, local resources, and the possibility of residue treatment in the Waelz plant, which was situated in the neighborhood. Accordingly, it was decided to modernize the process in the way shown on the flowsheet in Figure 1.

The first stage of leaching, the so-called acid-neutral leach, is operated continuously. About 90 % of the zinc is leached from the calcine. The slurry is prepared for further processing by solution purification and zinc electrolysis. Neutral slurry is classified in hydrocyclones for zinc-bearing sands recovery. The main objective of this stage is to recover the surplus of calcine that was used for neutral leaching . This stage has to be prepared and operated in a very precise and careful way. The overflow from the hydrocyclones is transported by gravity to Dorr thickeners. The overflow from the thickeners is pumped to a solution purification plant and the underflow is pumped to low acid leaching tanks. After classification, the pulp is washed and filtered at Larox filters. The Fe-Zn cake from the filters is transported by conveyors to the Waelz Plant.

Fig.1 Flowsheet of ZnS concentrate processing at ZGH Boleslaw

Fig.2 Flowsheet of the leaching and purification section

Underflow from the hydrocyclones is pumped to next stage of leaching. Zinc-bearing sands from the hydrocyclone underflow are processed using REDOX acid leaching for recovery of all zinc compounds from the sands (including zinc ferrites), as well as for the preparation of manganese sulfate and ferric sulfate solutions having the concentrations required at the first stage of calcine leaching. Sands leaching is carried out in two stages. In the first stage, the sands are leached with spent electrolyte and sulfuric acid (initial acidity: 20-25 % of H_2SO_4) in the presence of a reducing agent. As reduction agents can be used ZnS concentrates, Waelz fumes or crystalline ferrous sulfate. Same MnO_2 is added to the leaching tank in the second stage of leaching (oxidation stage), for the oxidation of iron compounds according to the following reactions:

$$Fe_2(SO_4)_3 + ZnS = 2FeSO_4 + ZnSO_4 + S \qquad (1)$$

$$2FeSO_4 + MnO_2 + H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O \qquad (2)$$

$$ZnS + 4MnO_2 + 4H_2SO_4 = ZnSO_4 + 4\,MnSO_4 + 4H_2O \qquad (3)$$

The leaching process requires temperature of about 360 K and a reaction time of 4 hours (2 hours in the reduction stage and 2 hours in the oxidation stage). When sands with an analysis of 39.9 % Zn, 8.94 % Fe, 2.32 % Pb and 1.76 % Mn, were leached, the best results were obtained with some addition of Waelz fume as a reductant. The zinc yield from the zinc-bearing sands was obtained at the level 93 % with a solution analysis: 157 g/dm^3 Zn, 24 g/dm^3 Fe, 20 g/dm^3 Mn, 40g/dm^3 H_2SO_4 for an addition of 10 % fume. Both the research works and industrial practice made it clear that there is no need of sands grinding before leaching to obtain a good yield of zinc and to produce a solution with ferric contents at the level required in the first stage of calcine leaching. The leaching plant flowsheet is shown in Figure 2.

Calcine is transported from the roasting section to the leaching plant by railway cars for a distance of about 200 meters and next is unloaded either in six silos with a total capacity 3200 tonnes of calcine or directly to a mixer. Unloading directly to mixer is the most common practice. Spent electrolyte (free acid content 10-15 % H_2SO_4) is added to the mixer in the proportions from 1:3 to 1:4. The outlet is pumped to the leaching tanks. Spent electrolyte from a launder situated above the leaching tanks continuously feeds the mixer and three in-line leaching tanks , each with a capacity 80 m^3. The first leaching tank is fed with: slurry from the mixer, solution from sands leaching, manganese dioxide, and spent electrolyte to produce a slurry of 3.0 pH. The outlet from the first leaching tank is pumped to the second tank and subsequently to the third leaching tank. The slurry pH from the second tank is 4.8, and from third one is 5.1.

Neutral slurry is classified in hydrocyclones (350D/12°). Underflow from hydrocyclones is pumped to acid leaching, and the overflow to five Dorr thickeners, each with a diameter of 9.5 meters. MAGNAFLOC 338 is used for this process (0.017 kg per tonne of cathode zinc). Underflow from each Dorr thickener is pumped to low acid leaching, and after classification and washing to LAROX filters. The filter cake with a maximum moisture content of 17 % is fed to Waelz kilns.

SOLUTION PURIFICATION

Solution clarified in Dorr thickeners is next purified by cementation. Purification is carried out continuously in two stages, at temperature of 323-328K, and with filtration after each stage. First stage equipment consists of five purification tanks, each with a capacity 40 m^3 partly in-line and partly in parallel, equipped with mechanical mixers with a rotary speed 70 rpm. Output from the last purification tank is filtered in four plate filters with a surface area 160 m^2. This filter cake is the raw material for cadmium production. Solution from the first stage, with an analysis varying from 20 to 50 Cd mg/dm^3, is purified with Zn dust in the second stage. The purification is carried out in three tanks in-line. Each of them has capacity 40 m^3. The Zn dust is added in the form of water suspension. Overflow from the purification tanks is filtered at three HOESCH filter presses with a surface 160 m^2. The cake is returned to the first stage of purification, and the purified solution is pumped to HAMON fan cooling towers via a 50 m^3 tank.

Zn dust is consumed in a quantity of 25 to 27 kg per tonne of cathode zinc. The Table IV presents chemical analysis of the zinc sulfate solution before and after purification.

Table IV Chemical analysis of the $ZnSO_4$ processing solution, g/dm^3

The cooled solution is transported by gravity to four 800 m^3 in-line tanks from which it is fed to the cellhouse.

ELECTROLYSIS AND MELTING

The cellhouse is equipped with 528 cells having a capacity of about 2.5 m^3 each in cascade-lines. Each cell is equipped with 30 cathodes and 31 PbAg1 anodes and two water coolers. Inlet water at a temperature 286K is delivered from a local mine. The cells are grouped in two units. Each unit with 22 double cascades of six cells in each cascade-line. Electric current goes to electrodes through copper bus bars. Each cascade is connected in series, and the electrodes in the cells are in parallel. The dimensions of the electrodes are the following: for the Al cathodes 1080 x 620 x 6 mm, and for the PbAg1 anodes 1000 x 580 x 6 mm. Neutral electrolyte is fed to each cell, and the overflow from the upper cell flows through the lower cells of the cascades. From the lowest cell, it finally flows to the spent electrolyte tank through the collecting launder. The temperature of electrolysis is about 310 K. The zinc deposit is removed manually in 24-hours cycles. The current density is variable in the range from 300 to 500 A/m^2 because of power costs optimization. The current efficiency is 91 %.

Zinc plates are transported to the induction melting furnaces by railway cars. Zinc plates in the form of stacks are fed to the furnaces with roller-conveyer. The yield of zinc during melting is 97,6 %. There are produced 25 kg ingots and 1000 and 2000 kg blocks on casting machines. The temperature of zinc during casting is 793-813 K. Zinc ingots are stacked in 9-layers stacks weighing 1 000 kg, strapped with steel tape, and transported to storage by fork lifts.

Zinc alloys are also produced at the zinc foundry. The foundry is equipped with three 20 tonne induction furnaces, one 30 tonne furnace, one 12 tonne furnace (for alloys), and three casting machines (in-line system) for 25 kg ingots (2) and blocks (1).

Metal is separated from the drosses on a drum screen and recycled to furnace. Ashes are utilized in the production of Zn compounds .

The BOLESLAW Electrolytic Zinc Plant produces zinc with the analysis shown in Table V.

Table V Chemical analysis of the electrolytic zinc, %

Currently, modernization of the Plant is continued in direction of solution purification improvement and zinc alloys production.

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