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METHODS OF UTLIZING STEELMAKING WASTE DUSTS WITH ELEVATED ZINC CONTENTS

Metallurgy produces steelmaking dusts with elevated zinc contents as waste. Presented in this paper are various methods of zinc recovery from these waste materials, put to use in different regions of the world. The paper concludes with presenting EU promoted best available technology (BREF): technology of zinc recovery from steelmaking dusts

Key words: steelmaking dusts with elevated zinc contents, hydrometallurgical methods, pyrometallurgical methods, zinc recovery from waste materials, downrolling process

Metallurgy produces substantial amounts of dust. Due to environmental reasons, there are attempts to utilize the whole volume of metallurgical waste dusts, particularly that they are classified as hazardous waste taking into account their contents of such heavy metals as Pb, Zn, Cd, Cr, Ni. Therefore, the emissions of such dusts into the environment are limited by collecting them [1]:

- on dry fabric filters,
- in wet (water) scrubbers.

The choice of the de-dusting method depends on one hand on technological requirements, on the other on the relevant experience. It can be assessed that almost 70% of gasses emitted by Polish plants is cleaned using fabric filters. The dusts immobilized represent the waste that, according to legal regulations compulsory in Poland and the European Union, must be either utilized or made harmless.

The dusts generated in steelmaking processes contain a substantial amount of zinc. The presence of zinc results from producing more and more steel with anticorrosion properties and melting steel in electric furnaces from Zn-bearing scrap metal. Currently, about 40% of zinc in Poland is utilized in anticorrosion protection of steel products, whereas the contribution of steel produced in electric furnaces reaches almost 30%. The steelmaking dusts used to be disposed of on industrial dumps giving rise to secondary dust emissions and, due to leaching of steel-contained metals, to contamination of soil, water and living nature.

The methods of preventing contamination of the environment with zinc involve converting steelmaking dusts containing this element into Zn-bearing, usable concentrates. The requirements of the Law of Waste, growing environmental awareness and economic reasons represent three factors that have contributed to wider utilization of dusts containing elevated amounts of zinc. Steelmaking dusts may be treated using two groups of methods, i.e., pyrometallurgical and hydrometallurgical ones.

HYDROMETALURGICAL PROCESSES

Hydrometallurgical processes are of minor significance in recovering zinc from zinc-bearing waste. They are based on leaching zinc and the process is followed by zinc electrowinning. Sulphuric acid and solutions containing ions with complexing properties (acetates, chlorides) are most often applied as leaching agents. Leaching metallurgical dust in the form of oxides in diluted sulphuric acid results in passing zinc and cadmium into a solution, leaving insoluble sulphates of lead, bismuth and silver as solids. Further recovery of these three metals from the insoluble residue may be carried out applying either recirculating them into pyrometallurgical treatment or converting the sulphates into carbonates with Na_2CO_3 and further processing. Leaching dusts containing metal oxides with acid solution of acetates results in formation of soluble acetate complexes of lead, zinc and cadmium, which pass into the solution [2].

Economy is the main factor making this group of methods less popular than pyrometallurgical ones: production of electrolytic zinc is profitable only in plants whose annual output exceeds 100,000 Mg zinc. It must be remembered that the hydrometallurgical methods additionally generate sludge that is classified within the group of hazardous waste and as such must be made harmless [3].

PYROMETALLURGICAL PROCESSES

Pyrometallurgical processes are carried out at high temperatures. Heat that drives the process is generated by combustion of fuels or in other exothermic industrial reactions. The material (charge) treated in furnaces undergoes various physical and chemical transformations. Two types of the furnaces, i.e., shaft and rotary kilns, are used in pyrometallurgical treating of steelmaking dust. In such high-temperature processes zinc oxide is volatized, then reduced and metallic zinc recovered from its gaseous form. The most common of these processes is downrolling, utilized in more than 30 countries.

Processes of zinc recovery from steelmaking dusts applied in the UK [2]

The most profitable method of utilization of Zn-bearing dusts is based on their processing in a briquetted form (Imperial Smelting Process — ISP) with simultaneous recovering both zinc and lead. ISP is a pyrometallurgical method of producing zinc and its technology was developed and started for the first time in the UK in 1950 by the Imperial Smelting Process Limited company. The most extensive use of the method falls on the years 1960-1975. The ISP technology consists in reducing smelting of agglomerates and briquettes in the IS shaft kiln into raw lead and slag containing around 2% Pb and 3-10% Zn, whereas zinc is recovered from the gaseous phase in a splash lead condenser, and then separated in a special system. The ISP process is currently used also by several plants outside UK: in Germany, France, Italy, Japan, China, Australia, Rumania and Poland.

Processes of zinc recovery from steelmaking dusts applied in Italy

The biggest Italian plant Ponte Nossa (a scheme of the production line at the Ponte Nossa plant is presented in [4]) produces raw zinc oxide from steelmaking dusts. Zinc oxide is manufactured in a single rolldown furnace with a length of 60 m and a diameter of 3.6 m. The plants treats annually 89,000 tons of dusts from electric steel-melting shop which are the main component of the furnace charge. The dusts contain 26–27% Zn and 3-5% Pb. Calcium oxide CaO is the other charge component, added in the amount 30 Mg/24 hrs. The furnace is fired with gas. The downrolling process is based on expelling zinc and lead from oxidized waste materials roasted in rotary kilns. The annual output includes 34,000 Mg raw zinc oxide containing 68% Zn and 6-7% Pb. Slags with the content <1% Zn, 2.5–3.5% Pb and 5–7% C represent tailings that are disposed of on dumps after cooling with water. Recoveries of metals in the downrolling process are 98% for zinc and 60% for lead.

Processes of zinc recovery from steelmaking dusts applied in Germany [4]

The plant in Duisburg (a scheme of the production line at the B.U.S. plant in Duisburg is presented in [4]) produces raw zinc oxide in downrolling processing of steelmaking dusts. The furnace charge is composed of 40-50% steelmaking dusts (they contain 25–28% Zn), 30–40% fine coke and around 20% sand. The sand is added to bind iron present in the charge into weakly soluble compounds free of lead. Due to that, slag produced is ecologically not deleterious and can be subject to further utilization. The charge is treated in a rotary kiln around 41m long with a diameter of 3.6 m. The chemical character of the charge and its physical parameters combined with high rotational speed of the kiln (1.3 revolution/min.) secure a fast rolling movement of the charge down the kiln. Consequently, the annual production capacity of the furnace is 22,000 Mg raw zinc oxide.

The raw zinc oxide produced in Duisburg is not subjected to cleaning processes. The average contents of essential elements in the zinc oxide produced are as follows: Zn — 56.02%, Pb — 8.20%, Cd — 0.06%, Fe — 3.95%, S_{tot} — 0.87%, $Si0_2$ — 2.58%, As — 0.013%, Ge — 0.002%, C — 4.00%, Cl — 2.62%, F — 0.11%. Considerable amounts of fluorine and chlorine are characteristic of raw zinc oxides obtained in downrolling processing of steelmaking dusts.

Another technology of recovering zinc and lead applied in Germany (Frankfurt) [4] involves processing steelmaking dusts in a fluidal-bed furnace. The Lurgi AG company has developed a furnace with a circulating fluidal bed (CFB furnace). The dusts containing usually above 15% zinc oxide and 55% iron oxides are combined with coke or bituminous (hard) coal in the CFB furnace fired with coke-oven gas. Good mixing of reagents and working temperatures about l000°C secure selective reduction of zinc oxide without simultaneous reducing iron oxides. The system of dry gas scrubbing concentrates zinc- and lead-bearing dust (around 30% Zn and Pb). Both metals are next recovered in refining plants.

Processes of zinc recovery from steelmaking dusts applied in Japan and Russia

In Japan, e.g. in the Nisso Smelting plant, metallurgical dusts are processed in rolldown furnaces with diameters of 2 m and lengths 30 m and 38 m with an output 35 and 65 Mg/24 hrs, respectively. The furnaces are fired with fuel oil. Furnace off-gas is cleaned in cyclones and on electrofilters in one furnace unit, and in the other unit the dusts are recovered in a dust chamber and on double flue-flow electrofilters. The furnace charge has an addition of 30% fine coke [3].

The technology used in Russia [2] involves rolldown furnaces with a length of 41 m and diameter of 2.5 m; the charge has an addition of sand.

Processes of zinc recovery from steelmaking dusts applied in USA and Sweden

To more important pyrometallurgical methods of treating steelmaking dusts in the USA and Scandinavian countries belong the Tetronies Plasma Process and the Flame Reactor Process. The plasma process takes place at high temperatures (around 1600°C) in strongly reducing atmosphere. Zinc vapours are directed into a condenser of the construction similar to that used in the Imperial Smelting process. Two plasma installations (electric furnaces) were operational for some years in the USA but both have been shut down. The reasons of abandoning this technology involved problems with running the condenser, mainly because of aggregating buildups, and also manufacturing of considerable amounts of hard zinc. However, the plasma shaft furnace installation (Plasmadust) processing annually around 60,000 Mg dusts and developed by the ScanArc Plasma Technologies has been still operational in Sweden. The main element of this installation consists of the shaft furnace fired with three plasma burners. The charge composed mainly of steelmaking dusts is totally reduced to pig iron containing Ni, Cr, Mo, etc. Reduced Zn, Pb and Cd in the form of vapours are directed into a splash condenser of the Imperial Smelting type.

Focusing particularly on processing of steelmaking dust, the Horsehead Resource Development Company has developed its Flame Reactor Process, based on reducing the dust components in a special reactor, from which zinc vapours are directed into an oxidizing chamber. Final effects of the process, i.e., the yields and the quality of the product, are comparable to those obtained in rolldown furnaces. The technology is currently used in a plant in Monaca (USA) that processes annually 20,000 Mg of dusts.

Another method used in the USA is called the Horsehead St. Joe Flame Reactor Process. The process proceeds in a special reactor, in which zinc oxide is reduced. Zinc vapours with process gases are then directed into a combustion chamber, where they undergo secondary oxidation. The final product in the form of zinc oxide goes down the production line to be processed into metallic zinc.

The Tetronics process has been developed in cooperation between Tetronics Research and Development (UK) and International Mill Service (USA) and is based on reduction of zinc oxide in the electric furnace. The process of reduction are kept within the field of stability of iron oxides. Zinc vapours are further carried into the Imperial Smelting splash condenser. The Tetronics process has currently been implemented in the USA.

Processes of zinc recovery from steelmaking dusts applied in Poland

The rolldown technology is used for zinc recovery in Poland as it is done in more than 30 countries. The respective line producing zinc from steelmaking dusts has been installed in "Bolesław Recykling" Ltd. in Bukowno near Krakow and the company manufactures zinc concentrates in the form of powder or granulates (Fig).

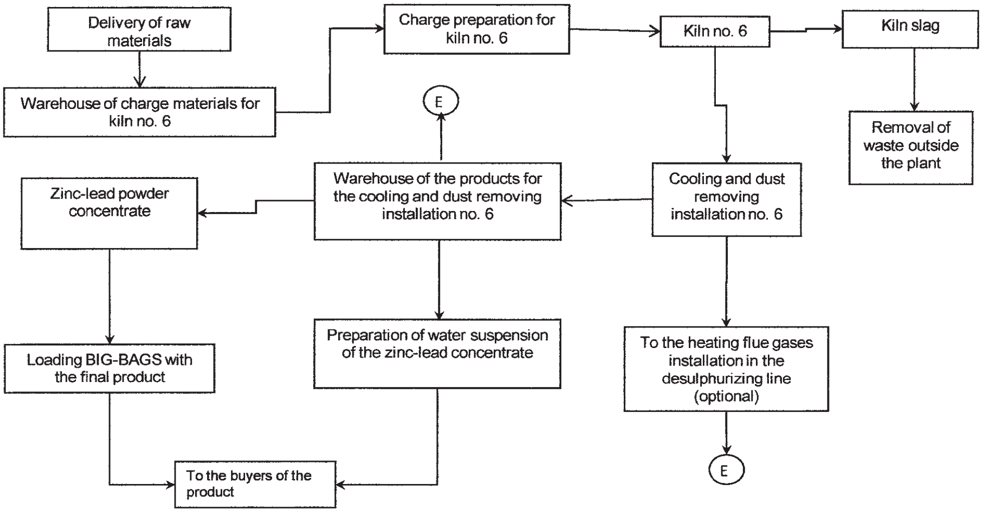

Fig. Flow-chart of the Zn-producing line of the "Bolesław-Recykling" Ltd company (E – emitter)

Essential components of the process charge are zinc-bearing waste materials, among which currently prevail sludge from hydrometallurgical production of zinc and sludge from industrial water treatment plant as well as dusts from an electric steel-melting shop. The charge mixture is prepared in a special plant section, from which it is transported by conveyors to the charge bins of six technological lines and then further *via* charge troughs into rolldown furnaces. Zinc oxide in the form of dust is the product of the rolldown process. The zinc dust is trapped in bag filters and next from the collective hoppers of the filters is directed using pneumatic conveyance into storing bins. Depending on the requirements of buyers, the final product may have the powdery form or be prepared as granulates. Tailings originating along the production line include slags from the rolldown furnaces and synthetic gypsum formed in desulphurization of flue gases.

The output of the rolldown furnaces calculated into the dry mass of zinc-bearing charge is:

— 80 Mg/24 hrs in the furnace treating high-sulphur charge,
— 140 Mg /24 hrs in the furnace treating sulphur-free charge, which after recalculation into normal (wet) charge gives:
— 121.2 Mg/24 hrs in the furnace treating high-sulphur charge,
— 155.5 Mg/24 hrs in the furnace treating sulphur-free charge.

Shrinking of primary resources and environmental reasons are the factors that have altered steelmaking waste dusts with elevated zinc contents into a valuable secondary material. Among the methods of utilization of such zinc-bearing waste that have been discussed above, the most rational and cost-effective is the method based on rolldown zinc processing. It is the method metallurgically proved worldwide, also in the Polish plant run by the „Bolesław Recykling" Ltd company.

Steelmaking dust disposed of on dumps have negative impact on the environment, mainly due to uncontrolled emission of dusts containing heavy metals, particularly zinc, lead and cadmium. These emissions contaminate the atmosphere, surface and underground waters, and soils as well. Therefore, the existing methods of utilization of the steelmaking dusts containing elevated amounts of zinc described above should urgently be improved and adapted to the best available technologies (BREF), advised by the European Union. According to them, the raw materials to the process (steelmaking dusts, scrap metal, fine coke) are stored in the bins. They must be mixed, sometimes pelletized, weighted and sent directly or *via* the charge bin into the rolldown furnace (Waelz kiln). The working temperature of the kiln is usually 1200°C. The charge is dried going down the kiln and then heated to the required temperature by a stream of counter-current flowing combustion gases and in the contact with the hot kiln lining. Depending on the inclination angle of the kiln, its length and rotation speed, the time of the charge residence in the kiln ranges from 4 to 6 hours. In the strongly reducing atmosphere of the kiln, zinc oxide is reduced to metallic zinc that is vaporized, and next oxidized with excess air. Zinc oxide is carried away from the kiln with flue gases and separated out in filtering installations. The system of flue gas cleaning is usually composed of the dust settling chamber, cooling section and electrofilters, and if further cooling is applied of bag filters as well. Slags formed in the kiln are continuously removed from the down end of the furnace and transfered to cooling. After cooling, sieving and crushing, the slag may be utilized in construction works, for instance as the road sub-crust. Besides, the slag may be an addition in cement manufacturing processes, and considering its high Fe content also in iron metallurgy.

According to BREF, steelmaking dusts are the essential component of the rolldown charge, but the Waelz kilns may also treat final waste sludge from hydrometallurgical production of zinc (as it is done in the Polish plant in Bolesław — see above). Zinc oxide — the final product of the rolldown process — may be processed in several ways. One of them is its briquetting or pelletizing and further processing in shaft furnaces.

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МЕТОДЫ УТИЛИЗАЦИИ СТАЛЕЛИТЕЙНЫХ ПЫЛЕВЫХ ОТХОДОВ С ПОВЫШЕННЫМ СОДЕРЖАНИЕМ ЦИНКА

Резюме
В металлургическом производстве вырабатывается значительное количество сталелитейной пыли с повышенным содержанием цинка, которая считается отходом производства. В статье представлены различные методики восстановления цинка из отходов, которые используются в различных странах мира. В статье представлена методика BREF, признанная в ЕС как одна из лучших — технология восстановления цинка из сталелитейных пылевых отходов.

Ключевые слова: сталелитейные пылевые отходы с повышенным содержанием цинка, гидрометаллургические методы, пирометаллургические методы, восстановление цинка из отходов, процесс обкатки.

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МЕТОДИ УТИЛІЗАЦІЇ СТАЛИВАРНИХ ПИЛОВИХ ВІДХОДІВ З ПІДВИЩЕНИМ ВМІСТОМ ЦИНКУ

Резюме
У металургійному виробництві виробляється значна кількість сталеливарного пилу з підвищеним вмістом цинку, яка вважається відходом виробництва. У статті представлені різні методики відновлення цинку з відходів, які використовуються в різних країнах світу. У статті представлена методика BREF, визнана в ЄС як одна з кращих, — технологія відновлення цинку із сталеливарних пилових відходів.

Ключові слова: сталеливарні пилові відходи з підвищеним вмістом цинку, гідрометалургійні методи, пірометалургічні методи, відновлення цинку з відходів, процес обкатки.