

ENVIRONMENTAL IMPACT OF THE USE OF AUTOMOTIVE SCRAP AS CHARGE MATERIAL IN METALLURGICAL PROCESSES

Received - Primljeno: 2002-10-24
Accepted - Prihvaćeno: 2003-04-30
Review Paper - Pregledni rad

Increased content of automotive scrap in metallurgical charge raises the content of zinc and lead in the dust from melting installations. Every year 1.2 mln tons of zinc-coated scrap comes to the market to be recycled. The cost of the waste dumping will be systematically growing, this comes refers to both the dumping fee and costs of transport from the plant to the dumping ground. The dust collected in the process of melting is, on one hand, a valuable raw material while, on the other, special processes are required for its effective management. Zinc-containing dust can be processed by two methods: hydrometallurgical refining and pyrometallurgical refining.

Key words: *dust, zinc, metallurgical process, cupola, recycling*

Automobilski otpad rabljen kao materijal za taline u metalurškim procesima. Povećana količina automobilskog otpada u metalurškim talinama podiže sadržaj cinka i olova u prašini metalurških postrojenja. Svake godine 1.2 mln tona otpada presvučenog cinkom dolazi na tržište radi recikliranja. Troškovi prikupljanja otpada rasti će sustavno. To se odnosi i na troškove spremanja i troškove prijevoza od pogona do mjesta odlaganja. Prašina sakupljena tijekom procesa taljenja, s jedne strane, vrijedan sirovinski materijal, s druge strane, potrebni su posebni postupci za uspješno upravljanje tim otpadom. Prašina koja sadrži cink, može se obraditi na dva načina: hidrometalurškim rafiniranjem i pirometalurškim rafiniranjem.

Ključne riječi: *prašina, cink, metalurški proces, kupolna peć, recikliranje*

INTRODUCTION

The use of zinc-coated sheet has considerably increased over the past few years, specially in automotive industry and household appliances. Consequently, the volume of scrap containing zinc has also increased and along with it the zinc content in recirculated waste and in secondary raw materials used by metallurgical plants. The content of zinc is also increasing due to the changed proportion in purchased/own scrap used as metallurgical charge. Continuous casting of steel, enjoying nowadays a wide-spread popularity all over the world, has contributed to a decreased volume of process scrap used by steelworks. The reduced use of process scrap is also due to some improvements in the technology of steel making. Less of process scrap used by the plants means more of the scrap purchased from various out-of-plant sources, and this, in turn, means that the volume of the zinc-coated scrap will increase as well [1]. Similar problems occur when the automotive scrap is

used by foundries in melting of cast iron and steel. The increasing volume of zinc-coated scrap has brought considerable increase of Zn content in dust coming from the melting installations (electric arc furnaces, cupolas), quite often to a level above 16 % [2]. This is an important obstacle in safe dumping of this dust.

Unfortunately, it is expected that the next years will see further increase in the volume of zinc-coated scrap, both purchased outside the plants as well as produced by the plants themselves. The producers of vehicles are using more and more of the electro-galvanized zinc-coated plates. Out of 6.5 mln tons of steel used annually by the European automotive industry, about 85% have an anti-corrosive protection. Due to this, 1.2 mln tons of zinc-coated scrap comes every year to the market to be recycled. The scarcity and high prices of the plain sheet, often amounting to about 192 euro/ton, compel the metallurgists to use zinc-coated sheets which are half price only [3]. However, this being the case, some problems emerge when the scrap is remelted because of impurities escaping to the atmosphere and problems of metallurgical nature resulting from deterioration of metal quality due to the presence

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of residual zinc. Another problem, quite important in terms of the environmental protection, is the possibility of zinc penetrating into, e.g., moulding sands with later elution of this element to environment [4].

For example, the thickness of Zn coating on a car body sheet is 7-10 μm , which is corresponding to about 110 g/m². With 0.8 mm thickness of this sheet, the amount of Zn introduced together with charge will be 20 kg Zn/t of scrap. If the content of zinc-coated scrap in the charge is, e.g., 40 %, this will give 8 kg Zn/t of scrap introduced to the furnace [5].

The dust collected in the extraction units operating at the melting installations can be regarded as a very valuable raw material because of zinc and iron compounds present there and the possibility of their recovery (Table 1.).

Table 1. Iron and zinc content in metallurgical waste
Tablica 1. Sadržaj željeza i cinka u metalurškom otpadu

Material	Fe content [%]		Zn content [%]	
Dust from blast furnace	18.71	39.71	0.06	2.77
Blast furnace slag	8.51	24.05	3.69	33.30
Dust from electro filters of sintering plant	38.82	52.52	0.04	0.18
Converter slag	57.21	60.98	3.03	5.20

RECYCLING OF USED CARS

One of the most important sources of zinc-coated sheet is the automotive industry, and strictly speaking the dumped old cars. In Poland, for example, over the past few years, the number of vehicles has reached about 13 mln pieces, including about 9 mln pieces of motor cars. Among the latter ones, over 40 % are the cars ten years old and more. By rough estimates, over 2 mln motor cars are 15 years old and more, and in the nearest future they should be withdrawn from running and subjected to the recycling process [6].

Recycling of the used cars is one of the preventive measures taken in order to protect the environment and the natural resources in our Globe by reducing to minimum the volume of the waste, specially of the hazardous waste from the discarded cars. In 1991 the European Commission regarded the used cars that need to be recycled as one of the top priority streams of the waste and initiated a program of strategy for their recycling. As a main trend in the actions taken, the urgent need of having permanently reduced the volume of the, so called, post-automotive waste, entirely useless, has been indicated. The Directives prepared by the European Union recommend the following:

- by year 2006 the re-use and recovery of parts and materials from cars withdrawn from running should equal

minimum 85 %, wherein the re-use and recycling should reach minimum 80 % of the vehicle total weight,

- by year 2015 the re-use and recovery of parts and materials from cars withdrawn from running should equal 95 %, wherein the re-use and recycling should reach minimum 85 % of the vehicle total weight.

Correct dismantling of cars requires large financial outlays. The European companies producing cars are forced to allocate miliard sums of money to satisfy the regulations for disposal of the used cars. For example, Volkswagen will have to allocate 1.3 mld euro, Renault and Fiat 800 mln euro each, Daimler Chrysler - 380 mln euro. Each year in Europe 12 mln of the used cars are disposed, and an average cost of recycling falling to one single car is 189 euro. Quite often this is more than the total value of the disposed car.

What can be recovered in the disposed car? Many very precious raw materials. They include alloys of ferrous and non-ferrous metals, some plastics, recovered parts and assemblies of the drive system, oils and some performance fluids. The automotive waste is used mainly by steelworks and foundries. From a used car, parts made from ferrous alloys can be recovered in almost 100 % and those made from non-ferrous alloys - in 90 % [7]. From the data published in [8] it follows that from a ten-year running disposed car weighing 1010 kg, which holds 535 kg of steel, 126 kg of cast iron, 53 kg of non-ferrous metals, 51 kg of rubber, 91 kg of plastics, 40 kg of glass, and 114 kg of other materials, the following can be recovered for economic reuse: 99 - 100 % steel, 98 - 100% cast iron, up to 95 % aluminium and lead, up to 60 % copper, 5 - 10 % plastics. Altogether this makes 75% of the total recovery of these materials.

THEORETICAL BACKGROUNDS

Table 2. sums up the most important physical and thermodynamic properties of pure zinc and iron. Much lower

Table 2. Physical and thermodynamic properties of Zn and Fe
Tablica 2. Fizička i termodinamička svojstva cinka i željeza

Parameter	Zn	Fe
Atomic number	30	26
Atomic weight	65.38	55.85
Group / Period	2b/4	8/4
Density [g/cm ³]	7.18	7.87
Melting point	420	1536
Boiling point	907	2862
Heat of fusion [kcal/kg]	26.8	59.1
Heat of evaporation [kcal/kg]	421.6	1496.0
Melting point of bivalent oxides	1975	1377

heat of evaporation and lower melting point of zinc as compared with iron make the pressure of zinc vapours at the temperature of molten steel very high.

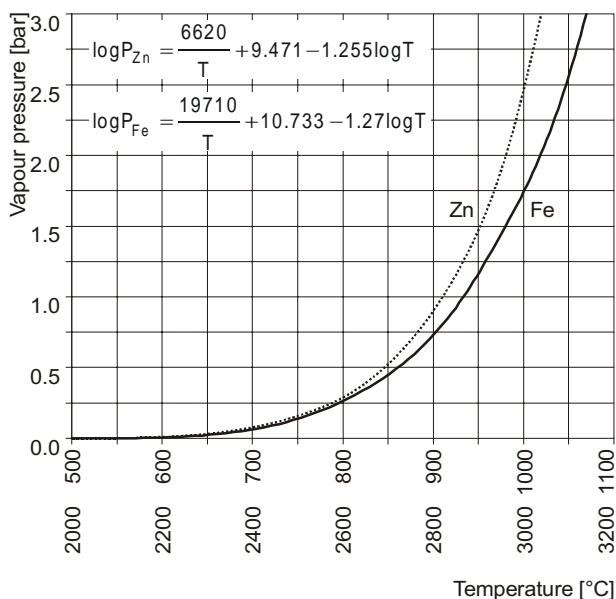


Figure 1. Vapour pressure of Zn and Fe versus temperature
Slika 1. Tlak pare cinka i željeza u usporedbi s temperaturama

Figure 1. draws a relationship between the temperature and pressure of zinc and iron vapours. The isobaric lines for both elements are running almost parallel to the pressure of 3 bars but iron temperature is by about 2000 degrees higher than that of zinc (at the same pressure). Figure 2. shows plotted zinc pressure - temperature relationship up to

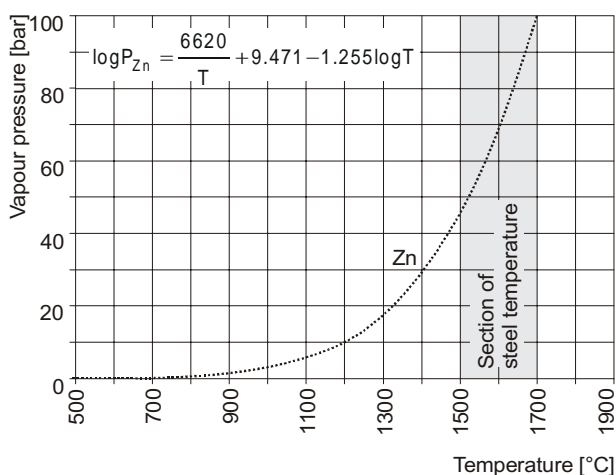


Figure 2. Vapour pressure of Zn at steelmaking temperatures
Slika 2. Tlak pare cinka na temperaturi proizvodnje čelika

the temperature range of molten steel, i.e. up to 1700 °C. In the range of 1500 - 1700 °C the pressure of pure zinc is from 50 to 1006 bars. In a system of Fe - Zn the pressure of vapours is proportional to Zn activity in the bath, and hence it is clear that the pressure of Zn vapours on the side of iron

will be much lower. As follows from the Fe - Zn phase equilibrium diagram, the removal of Zn through boiling can occur when an adequate partial pressure of Zn has been reached. According to the evaporation curves, at a normal pressure and solidification temperature, the content of about 15 % is necessary for Zn removal.

The stability of oxides increases in the system of ZnO, FeO, CO. According to this rule, zinc evaporating from liquid iron can be oxidized to ZnO only when it gets in contact with oxygen present in the atmosphere (white fumes are formed). The dust is carried away together with waste gas, and it contains a high volume of iron, specially in the form of oxides.

RECYCLING OF ZINC FROM THE SCRAP USED IN ELECTRIC ARC FURNACES

Purchased scrap containing metallic zinc includes waste zinc-coated sheet, profiles, grids, pipes and other elements. The content of zinc in steel samples taken at the initial stage of melting from an arc furnace can reach 0.16 % (Table 3.). Drastic drop of Zn content in steel has been noted in samples taken from the ladle. This fact can be

Table 3. Changes of Zn content in steel melted in electric furnace and assigned for continuous casting

Tablica 3. Promjena sadržaja cinka u čeliku taljenom u električnoj peći i namijenjenom kontinuiranom lijevanju

Place where sample was taken	Zn content [%]			
	Melt 1	Melt 2	Melt 3	Melt 4
Sample from furnace	0.160	0.022	0.130	0.006
Sample from furnace	0.140	0.020	0.120	0.005
Sample from ladle	0.056	0.008	0.063	0.003
Sample from ladle	0.053	0.007	0.061	0.002
Sample from ladle	0.052	0.007		
Sample after sec. treatment	0.048	0.006	0.055	0.002

explained by zinc evaporation when the steel is tapped. No significant reduction in zinc content during the secondary ladle treatment has been recorded. The distribution of zinc content in billets is practically homogeneous. Tracing the values of Zn content in molten steel from electric arc furnace up to an installation for continuous casting one can see some melts which can contain more of this element. With higher zinc content in steel (> 120 ppm), during continuous casting of billets with small cross-sections, the phenomenon of "zinc boiling" in moulds for continuous casting may occur. This phenomenon resembles very much the effect of steel boiling when it starts solidifying and has been insufficiently deoxidized. The high pressure of zinc vapours at the temperature of molten steel results in small steel droplets being thrown out from the bath. Zinc solubility in steel drops with temperature drop

which makes zinc evaporate and causes the above mentioned phenomenon. The phenomenon of "zinc boiling" is efficiently reduced with increasing degree of steel deoxidizing [2]. Stirring of the bath by, e.g., oxygen blowing promotes evaporation of the dissolved zinc.

RECYCLING OF ZINC CONTAINED IN CUPOLA DUST

Characteristic of dust collected from cupolas

Dust is one of the main waste materials in cupola process. The severity of dust emissions from cupola depends on the type of cupola and usually amounts to 8-10 kg/t of molten iron. Table 4. gives typical data which characterize dust emissions from cupola [10]. Special attention deserves the fact that the dust contains chemical compounds of non-ferrous metal alloys (lead and zinc mainly).

Table 4. **Chemical composition and physical properties of dust emitted from an acid-lined cupola of 8 t/h melting rate**
Tablica 4. **Kemijski sastav i fizička svojstva prašine emitirane iz 8 t/h peći s kiselinskim obzidom**

Compound	Content [% weight]	Compound	Content [% weight]
Dust content 5 - 13 kg/t of molten cast iron			
Grain size < 10 µm ZGD -20%, ZGD -30% < 100 µm ZGD -50%, ZGD < 70%		Size of ZnO particles 0.01 - 3 µm	
Iron oxides	30 - 60	SiO ₂ (also as Fe ₂ SiO ₄)	about 25
C (from coke)	3 - 15.0	MnO	3 - 10
Al ₂ O ₃	1 - 3.0	MgO	1 - 3
CaO	< 1	ZnO	up to 3 (max 20)
PbO and oxides of other heavy metals	< 1	S	up to 2
Alkaline oxides soluble in water (Na ₂ O i K ₂ O) from coke ashes	0.3 - 5.0	Sulphates soluble in water	0.3 - 5.0
ZGD - cold blast cupola; ZGD- hot blast cupola			

In Germany, 30.000 tons of dust leave cupolas every year. The dust contains, on an average, 20 % zinc, which means that about 6.000 tons Zn have to be processed by the industry. The content of so large amounts of zinc in cupola dust determines its chemical and physical properties as well as the possibilities of recycling.

Methods of utilizing cupola dust

Dumping of cupola waste is a serious problem in terms of the regulations of environmental protection. On one hand, this dust is rich in carbon. On the other, it may con-

tain large amounts of heavy metals (Zn, Pb), which can be leached out to the environment. Yet, on account of the high content of iron (12-16 % Fe), the dust from cupola can make a valuable raw material [11]. If, additionally, the possible high zinc level in this dust is taken into consideration, then looking for some means of utilizing this dust sounds a solution quite reasonable [12].

Cupola dust is usually returned directly to cupola, and the process can be executed by two methods [4]:

- direct blowing of dust into cupola, usually combined with other dust,
- preliminary operation of briquetting and introducing dust in this form together with a charge to cupola.

Blowing of dust

Air Products has developed for Buderus Guss GmbH foundry (Germany) a technology which enables continuous blowing of solid particles, including cupola dust, in oxygen jet to a hot blast cupola [13]. Altogether, during 24 hours of foundry operation 7.5 tons of the solid waste (cupola dust, dust from the fettling shop, used moulding sand, and industrial waste) are produced. All this waste can be introduced jointly to a cupola, but each type will affect in a different way the run of the cupola process. Dust from cupola containing about 15 % carbon can serve as a fuel. A mixture of these substances is introduced to cupola through a fuel-oxygen burner of special design which also serves for blowing of oxygen. The results collected on cupola operation have indicated that the solid waste blown by this method into a furnace neither deteriorates the quality of cast iron melt nor does it reduce the furnace melting rate.

The amount of the introduced cupola dust and industrial waste did not cause any problems in furnace operation. Additionally, recycling of Cu, Zn, and Cr and iron re-use were possible. The slag produced by the technological process was granulated in dry condition to form a vitreous material. The harmful matters were imprisoned in the vitreous matrix and due to this were effectively protected from being eluted.

Introducing dust in the form of briquettes

Jointly with RUF (Germany), LINDE developed a technology to re-use foundry dust in the form of briquettes, this also including the dust from cupola [14]. The technology was used by a foundry operating the cupola with oxygen-enriched blast. The briquettes were introduced into a metallic charge together with other charge components (scrap and pig iron), to be next transferred to a cupola shaft. Oxides undergoing the process of reduction are passing to cast iron, other oxides pass to the slag. The slag is transferred to a granulating device and is later re-used as a

valuable raw material, very demanded in road building. The developed technology, besides some strictly economic advantages resulting from an effective use of the waste, also offers some benefits as regards the protection of environment. A solution of this type seems to be much more recommended for practical use than blowing of loose dust into a cupola, although from the economic point of view it can be less advantageous (additional process of drying and briquetting, an addition of binding agents necessary).

RECYCLING OF ZINC IN BLAST FURNACE PROCESS

Quite often, the dust contained in waste gas from the steelmaking plants, i.e. from electric furnaces, and specially from oxygen converters, contains large amounts of iron, and as such can serve as a raw material in the process of ore reduction. Therefore this dust is processed by ore sintering plants and the sintered product is used in blast furnaces [1]. The sintering plants also use own dust collected in the operation of cleaning the waste gas from a sintering plant and from the blast furnace. All these types of dust introduce zinc to the blast furnace charge. The more the dust circulates in a metallurgical plant in a closed loop, the more rapidly increases the content of zinc in the blast furnace gas. Zinc in blast furnace disturbs the run of the metallurgical process and reduces life of the furnace lining. Most of zinc introduced to a blast furnace together with the charge escapes from this furnace in the form of dust carried away by the waste gas. A small amount of zinc only is transferred to the pig iron and slag. Inside the blast furnace, zinc is circulating in a sort of closed loop. The circulation consists in zinc oxide (possibly sulphide) reduction in lower part of the blast furnace, a convection of zinc vapours up the furnace, followed by condensation of these vapours on the still cold lumps of charge and on the masonry envelope of the furnace. The zinc that has condensed on the lumps of charge is again lowered with this charge to the hot zone of the furnace and there evaporates, while the zinc that has condensed on the masonry envelope of the blast furnace can remain there for quite a long time. The vapours of metallic zinc can condense in the pores of refractory material used for furnace lining. With zinc temperature lower in those pores and the gas reducing potential weaker (higher ratio of CO_2/CO), the metallic zinc is oxidised, which makes its volume increase. This phenomenon has a destructive effect on the structure of the material which happens to be affected by the zinc vapours. The vapours of zinc can act as a "binder" for the small lumps of charge, resulting in the formation of charge build ups on the masonry envelope of the blast furnace. The build ups can be detached from the masonry envelope increasing zinc content in the blast furnace gas or zinc evaporation through a tapping hole on tapping of pig iron

[15]. The build ups can also have some secondary effects, namely cause drop of temperature in the blast furnace and tearing away of the surface layers of the lining with the build ups sticking to it.

MAIN TRENDS IN UTILISATION OF THE ZINC-CONTAINING DUST

Figure 3. shows in a schematic way the theoretical possibilities of processing the zinc-containing dust. Basically speaking, zinc-containing dust can be processed by two methods: hydrometallurgical and pyrometallurgical refining. The difference between these two processes occurs at the stage when zinc compounds are reduced to the form of

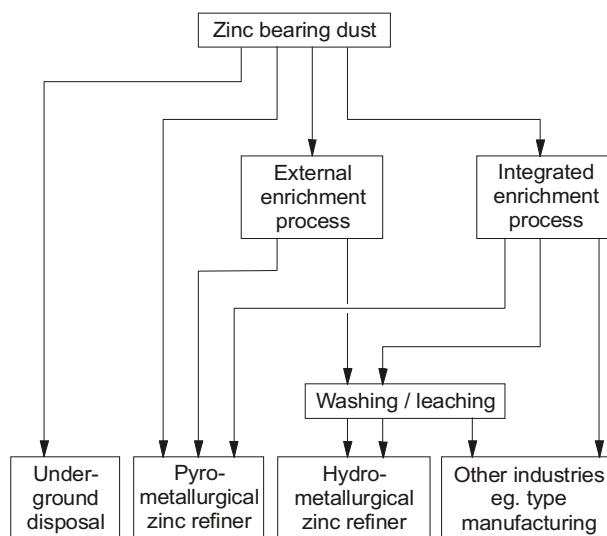


Figure 3. Block diagram for material utilization of zinc bearing dusts

Slika 3. Blok dijagram materijalnog iskorištavanja prašine koja sadrži cink

metallic zinc. In the former case, electrical energy is used (electrolysis); in the latter - coke or hydrogen. In the case when the dust contains zinc compounds of the ferrite or silicate type, which are hardly soluble or insoluble in sulphuric acid, what is indispensable for the process of electrolysis to be effectively carried out is earlier application of the thermal processes to transform zinc compounds into zinc oxide. The basic pyrometallurgical process used in zinc recovery is Imperial Smelting Process, which consists in blowing the zinc-containing dust together with an addition of carbonaceous materials through tuyeres into a shaft furnace (Figure 4.). This process is suitable for processing of dust containing at least 15 % by weight of zinc without any restrictions as regards the upper boundary value. The primary material can contain high volume of lead and cadmium (up to 2 % by weight) The admissible content of alkalies and halogens in dust is up to 10 % by weight.

An interesting method has been elaborated in France. According to this method, zinc is removed from the metal

bath in vacuum during melting and holding of liquid metal in induction furnace [3].

High-temperature reduction of oxides

In the process of reduction made with carbon, zinc is removed in the form of vapours and sponge iron is produced. Yet, containing certain amount of unreacted carbon and ash, this material cannot be returned to arc furnace. Certain amounts of toxic CO are, moreover, produced. Therefore the process of reduction made with hydrogen seems to be much more justified economically and more friendly to the environment. The process is conducted at a temperature of 1000 - 1100 °C, and produces a mixture of zinc, lead and cadmium oxides along with the sponge iron.

In thus produced sponge iron containing 50-58 % Fe, the concentration of heavy metals (Cd and Pb) is low, and the material can be returned to an arc furnace or safely disposed to a dumping ground. From the zinc oxide containing 50 - 56 % Zn it is possible to recover Zn i Pb.

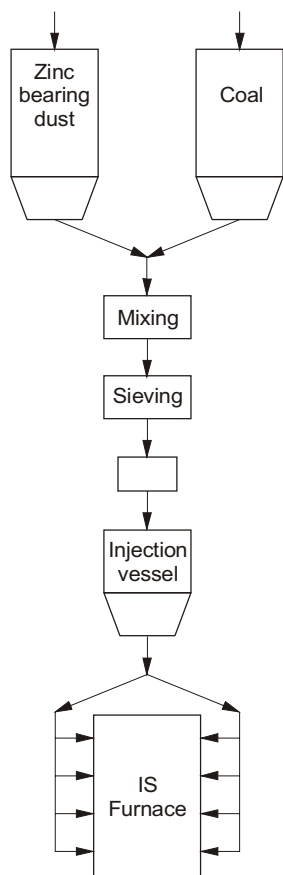
High-temperature dust processing by “Enviroplast” process

This process was developed by Mintek’s from South Africa. It can be used for processing of dust with high content of Cr and Ni. In the “Enviroplast” process the dust is melted in plasma arc furnace operated with direct current of 1 - 1.5 MW.

High-temperature process developed by Glassification International Ltd [17]

The Glassification process is used for utilisation of dust from electric arc furnaces and it consists in processing of this dust into glassy materials.

The fabricated products are neutral to the environment, while the process itself is simple and can be easily carried



8 injection pipes to 16 tuyeres

Figure 4. **Basic flow diagram for direct zinc recovery from dusts in the ISP furnace**
Slika 4. **Osnovni dijagram toka izravnog dobivanja cinka iz prašine u ISP peći**

out in the plant where the dust is created. In this process, besides the dust from arc furnaces, other waste products from the melting process, such as slags, used refractory materials, rolling scale, and grinding waste, can be effectively utilized.

CONCLUSION

Increased content of automotive scrap in metallurgical charge raises the content of zinc and lead in the dust from melting installations.

The dust collected in the process of melting is, on one hand, a valuable raw material while, on the other, special processes are required for its effective management. When the content of zinc compounds is very high, this dust creates certain hazard to the environment.

The cost of the waste dumping will be systematically growing, this referring to both the dumping fee and costs of transport from the plant to the dumping ground. Therefore it is highly advisable that the plants look for such solutions that would reduce the incurred expenses. The, proposed in this study, methods of the waste management directly on the spot where it is formed (steelworks, foundry plant) are expected to bring considerable savings.

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