# The Use of Plasma-arc for Extraction of Zinc and Lead from the Steelmaking Dust

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*Abstract*-Steelmaking dust is a by-product of steel production. It consists of metal oxides (iron, zinc, lead, etc.) and can be returned to the production cycle, or can be used in industries where its dispersion and magnetic properties are claimed. It is often impossible because the dust contains zinc and lead. Plasma processes of extraction non-ferrous metals from the dust were studied. Laboratory findings have shown that at high temperatures of plasma process extraction of zinc and lead can pass with high speed. The thermodynamic characteristics of zinc extraction degree were estimated. The research results allow to conclude about the future prospects of plasma recycling steelmaking dust.

Keywords- Plasma-arc; Extraction; Zinc; Lead; Steelmaking Dust

### I. INTRODUCTION

In the process of recycling scrap in electric arc furnace (EAF) dust is formed, which contains vapor of easy flying zinc and lead. At the present time in the world for more than 50 % of the dust is dispatched in the dumps, resulting in lost about 750 thousand tons of zinc per year.

Processing of electrosteel-making dust is necessary to extract ferrous metals in order to return them to the technological cycle; to extract non-ferrous metals in order to reduce the share of their production using traditional technologies non-ferrous metallurgy; to reduce the negative impact on the environment.

## II. THE MAIN WAYS OF USING THE STEELMAKING DUST

Steel-making dust is a by-product of steel production. It consists of metal oxides (iron, zinc, lead, etc.) and can be returned to the production cycle, or can be used in industries where disperse and magnetic properties are claimed. It is often impossible because the dust contains zinc and lead.

The iron oxides content can reach 60 % of the total mass in an electric steelmaking furnace and 80 % of the total mass in a basic oxygen converter. Thus, this type of waste can be considered as a secondary technogenic raw material and can be a source of iron oxides when subjected to some simple treatments. Iron compounds can be efficiently separated from the other components the dust by magnetic separation as long as the compounds are the oxides  $Fe_3O_4$  and  $\gamma$ - $Fe_2O_3$ .

The use of sludge in the sinter machine is problematic due to the high dispersed particles and the high zinc content. Finely the addition of dispersed materials has adverse influence on the gas permeability of the charge and thus reduces the productivity of the sintering machine.

The use of collected dust is an especially important issue due to an increase in the world demand for iron oxides in powder form. Powdered magnetite has greater demand than powdered hematite. The range of applications for iron oxide powders is now very broad [1-5].

The ability of ferromagnetic iron oxides to absorb electromagnetic waves may find application in the fabrication of protective shields and structures while the magnetic properties of ultrafine powders can be used to detoxify biological fluids and remove heavy metals from waste water. One interesting area of application could be the creation of magnetic fluids that can be used for cleaning oil spills on the water surface. The use of magnetic fine powders (nm) in the special gels to restoring (cleaning) works of art allows easy remove dirt from the surface after drying with a magnet.

Depending on the size, particles structure, granulometric and chemical compositions of iron oxides can be used as catalysts and pigments (dyes), in the production of paints for shipbuilding (especially for submarines), in medicine, in the production of lacquers, and in the food industry. Iron-containing pigments are widely used in the rubber and paper industries and other sectors of the national economy. More than 40 % of all synthetic iron oxides for the pigments production are used mainly by the automobile and shipbuilding industries and factories that make metal structures and materials [6]. Such pigments are in a deficit and almost no plants in Russia for their production.

Methods are being developed to use iron oxides in the production of catalysts for the CO conversion by water vapor as part of the ammonia production [7].

Industrial development creates a demand for the powder of iron compounds in general and, in particular, the highly pure iron oxides in which the content of impurity elements is less than 5–10 ppm [8]. These oxides are used to make batteries that are the main component of the memories for magnetic recording equipment. They are also being used as the initial material for making high-quality iron powders, high-purity ferromagnetic powders, high-coercivity ferroelectric magnets, and unique polycrystalline materials for electronics – ferrites. Using dust and sludge from steelmaking operations to obtain iron-containing oxides is more efficient than recycling dust and sludge at metallurgical plants [9].

The widespread use of the metallurgical dust is not possible, as zinc and lead are often contained in the dust.

## III. THE PROBLEM OF EXTRACTING NONFERROUS METALS FROM THE DUST

There are many ways to recover the zinc and lead from dust. Recycle dust containing over 12 % zinc is economically more advantageous. There are pyrometallurgical and hydrometallurgical methods of zinc extraction]. In ferrous metallurgy, where non-ferrous metals can be only by-products, as a rule, are used pyrometallurgical methods. Moreover, although iron and zinc in the dust can be a part of a complex combination, whose properties have been little studied, non-ferrous metals are recovered and extracted with high-temperature processing. However, zinc is oxidized again, and the product processing of dust, often is a crude zinc oxide. Then non-ferrous metals from their oxides can be obtained at the enterprises of non-ferrous metallurgy.

The basis of the zinc pyrometallurgical extraction process is removing it from oxides in recovery burning:

$$ZnO + C = Zn_{(v)} + CO;$$

$$2ZnO + C = 2Zn_{(v)} + CO_2.$$

The lead starts to recover to the metallic state at the temperature of 650  $^{0}$ C, and at the temperature of 900  $^{0}$ C begin to evaporate and converted into a gas phase. Zinc oxide is also partially restored; however, a significant amount of gaseous zinc is formed at temperatures above 1000  $^{0}$ C. The effective removal of zinc from EAF dust is possible already at a temperature of 1000-1100  $^{0}$ C, including when used as a reducing agent substandard carbon materials [9].

In the process of recovery burning at high temperatures zinc ferrite decomposes on the reaction:

$$ZnFe_2O_4 + 2 C = Zn_{(v)} + 2Fe + 2CO_2.$$

The reaction is going fuller with increasing temperature.

All existing processes for recycling have the peculiarity that the dust residues are returned to the metallurgical production for further extraction of iron after the extraction of zinc and lead. However none of the existing processes does allow to get along with the non-ferrous metal oxides, high-technological powders of iron oxides. Powders of pure oxides of metals can be obtained by plasma processing.

Plasma process (for example 'Tetronics') provides more effective recovery of zinc and iron, in compared with other (for example 'Waelz-process'). This process has several advantages: can be used on the large and the small enterprises thanks to the compactness of the equipment, high efficiency, environmental friendliness, and flexibility. At the same time, many questions remain unresolved. In particular, the decision the questions associated with determining the optimum parameters of a reactionary zone and velocity of process for the purpose of the maximum extraction of zinc and lead. It is also important for use of different types of waste for receiving high-disperse powders of oxides of iron and other metals.

## $\ensuremath{\text{IV}}\xspace$ . The formation mechanism and properties of the dust from EAF

The properties of the steel-making dust from EAF depend on the mechanism of its formation and are determined by the influence of electric arcs on the furnace charge (bath). High concentration of energy, local overheating of the metal up to the temperature of 3000-3500 <sup>0</sup>C leads to intensive evaporation of iron and other elements, especially easy volatile. Intensive dust generation is also the result electric erosion of the surface a charge and the electric- and gas-dynamic forces that lead to the spattering of a metal and dispersion of droplets in an arc.

Oxygen blowing metal bath is another factor in the dust formation, which due to the intensive oxidation of the mixture components (melt) and local overheating of a metal up to the temperature of 2700–2800 <sup>o</sup>C takes place its intensive evaporation. The pneumatic dispersing, fragmentation of the liquid metal drops in the oxygen jet is as well as the metal scattering as a result of the burst CO bubbles on the surface contributes to the dust formation too.

Finely dispersed dust is produced mainly by evaporation in the areas of electric arcs and further condensation of particles. The nature of these processes has a significant influence on the properties of the dust particles, their size, shape, composition. The chemical and mineralogical composition of dust can be very different.

Assessment of the elemental composition of steel-making dust from EAF (dust out of the bag filter) was carried out with the help of x-ray fluorescent analyzer 'Magnesium-1', it was used to calculate the oxide composition (Table 1).

	T.	ABLE I O	XIDE CON	APOSITIO	N OF DU	ST (% M	ASS)	
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Al <sub>2</sub> O <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	CuO	Fe <sub>3</sub> O <sub>4</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Ni <sub>2</sub> O	$P_2O_5$	PbO	SiO <sub>2</sub>	TiO <sub>2</sub>	MgO	MnO	$V_2O_5$	ZnO	S	С
1.25	8.1	0.33	0.2	36.2	2.4	1.5	0.03	0.22	2.4	17.7	0.01	2.6	3.1	0.03	14.1	1.6	8.2

The given data show that the concentration of lead in dust reaches 7 %, zinc -30 %, iron content -46 %, which testifies to the fact that this dust is a valuable product and may be subject to recycling with the extraction of nonferrous metals and to returning the remaining dust back into production.

Analysis of the dust mineralogical composition on the x-ray diffract meter DRN "FARAD" showed the presence in the dust  $Fe_3O_4$ , ZnO, and other oxides –  $Mn_2O_3$ ,  $Cr_2O_3$ , CaO. Further research is needed for a more detailed determination of the dust mineralogical composition. According to the data of the work [9], the main mineralogical components of EAF-dust are magnetite  $Fe_3O_4$ , oxide of zinc ZnO, oxide of lead PbO, ferrite of zinc ZnO·Fe<sub>2</sub>O<sub>3</sub> (ZnFe<sub>3</sub>O<sub>4</sub>). This is confirmed by the results of foreign publications [10]. Different authors on the basis of x-ray analysis and Mossbauer spectroscopy are obtained the following compound – ZnFe<sub>2</sub>O<sub>4</sub>,  $Fe_3O_4$ ,  $MgFe_2O_4$ ,  $FeCr_2O_4$ , MgO,  $Mn_3O_4$ ,  $SiO_2$ , ZnO,  $Fe_2O_3$ ,  $FeF_3$ ,  $ZnF_2$ ,  $ZnCl_2$ ,  $PbCl_2$ ,  $PbF_2$ ,  $MnO_2$ . Perhaps there are the presence of franklinite with isomorphic-replaced metals ( $Zn_xMe_y$ )Fe<sub>2</sub>O<sub>4</sub> in the dust, where Me is the Mn, Co, Ni, Cr, Cs, etc. The dust may contain small amounts of sulfates, sulfides and chlorides, however more than 90 % of the dust contains oxides.

The simultaneous presence in the dust of ferrite, chloride, fluoride and zinc oxide requires the study of their thermodynamic characteristics and mechanism their formation. They can significantly affect the quality of dust, as a product for further use or recycling.

The modeling of the process of evaporation in the EAF revealed, that to such composition of elements of the dust it can contain complicated compounds:  $FeSiO_3$ ,  $Ba(CrO_2)_2$ ,  $Ca_3SiO_5$ ,  $CaFe_2O_4$ , which was not found in instrumental analysis [11]. Iron oxide is been mainly in the form of magnetite and hematite, manganese is represented by three oxides, barium, calcium is included in the composition of complex compounds.

In Fig. 1 are shown differential (1) and integrated (2) distribution curves of particles in the sizes for dust from EAF: a - before aggregation, b - after.



Fig. 1 Differential (1) and integral (2) curves of the particle size distribution for dust from EAF: a - before aggregation; b - after

Distribution curves of particles in the sizes was studied a method of laser diffraction on the analyzer of particles of ANALYSETTE 22 Micro Tec plus (Fritsch firm, Germany) which allows to carry out measurements in a range from 0.08 microns to 2000 microns with very high resolution to 108 channels of measurement.

It may see that particles have the sizes in the range of 0.1-1 microns (m. 0.3 microns) before aggregation and in the range of 20-200 microns (m. 100 microns) after. The volume of one agglomerate can exceed the volume of one particle in hundreds of thousands times.

The number of particles collisions, leading to coagulation is greater, the greater the concentration of aerosol. This is a cause an averaging of the sizes of disperse particles in the stream of gases. On Fig. 1, both in the first and the second case the disorder of particles in the sizes makes 10 times.

Fig. 2 shows examples of micrographs of dispersed particles captured in the filter of the gas-cleaning system of an EAF.

Individual coarse particles of circular form (200–500  $\mu$ m diameter) can be seen in Fig. 2a at low magnification (×230). An increase in magnification to 10000 (Fig. 2b) makes it possible to evaluate the friability and porosity of the surfaces of these particles.

Taking photographs at an even greater magnification ( $\times$ 17000) makes it possible to conclude that the coarse particles often consist of individual spherical structures of submicron size. Analysis of the structure of the particles at  $\times$ 17000 and  $\times$ 35000 reveals the presence of 80–100 nm particles in the conglomerates.



Fig. 2 Electron micrographs at different magnifications showing the dust from electric steelmaking operations

V. STUDY OF THE EVAPORATION PROCESS OF ZINC AND LEAD IN PLASMA FURNACE

## A. Experimental Technique

Fig. 3 shows the laboratory plasma-arc furnace with graphite cathode by the discharge current 130–200 A, voltage – 30 V, the total pressure in the chamber furnace 0.08-0.1 MPa.



Fig. 3 Scheme of laboratory furnace

1 - plasmatron; 2 - window; 3 - cylinder with argon; 4 - vacuum pump; 5 - control panel; 6 - valve vacuum system; 7 - manometer; 8 - gas removal system; 9 - cooling system

The crucible is a graphite tube with an internal diameter of 12 mm and a height of 20-30 mm. Graphite powder has been added to the dust for the recovery of metals, the ready sample with the mass of 9-10 g has been placed in the copper crucible, which was installed in the furnace chamber (Fig. 4).

Plasma treatment takes 0.5–5 min. The sample was left to cool down after switching off the electric power supply in the furnace chamber, and then was taken out from the furnace and secondary dust was collected from the walls of the furnace chamber for further analysis (Fig. 5). The sinter remained in the crucible with small metal drops, which is easily crumbled.



Fig. 4 The process of processing of dust in the plasma-arc furnace



Fig. 5 General view of the remnant in the crucible (a) and secondary dust (b)

#### B. The Results of the Experiment

The results of the experiment are given in Table 2. The contents of zinc and lead in dust after plasma treatment (without melting) has decreased (from 17.7 % to 1.2 % and from 3.5 % to 0.2 %, respectively), while secondary dust has been enriched with these components (to 60.3 % and 10.87 %, respectively).

TABLE 2 CHEMICAL AI	NALYSIS OF	THE DUST AND	DERIVED PRODUCTS

Sectore and the sector	Composition, % (mass)											
Substances, products	Fe	Pb	Zn	Al	Ca	Cu	Κ	Mg	Mn	Na	Ti	Σ
Sample of dust	40.8	3.5	17.7	17.7	9.0	0.2	3.1	2.4	3.7	1.8	0.1	100
Secondary dust	12.8	10.8	60.3	0.4	2.2	2.0	7.3	0.7	0.9	2.7	0.02	100
The remain in the crucible	61.9	0.2	1.2	2.3	17.6	2.5	0.5	5.8	7.1	0.7	0.3	100

The degree of extraction amounted to: for zinc -93.2 %, for lead -94.3 %. Iron content in the residue rose from 40.8 % to 61.9 %.

The material balance of the process is showed in Table 3.

TABLE 3 THE MATERIAL BALANCE OF THE PROCESS

Given:	Received:							
Dust:	Formed secondary dust:	m <sub>s.d</sub> .=1.26 g.						
m=4.23 g	The remain in the crucible :	$m_{c.}= 1.64 \text{ g}$						
	The resulting gases:	$m_g = 0.91 g$						
	Loss	$m_l = 0.42 \ g$						
	Total:							
4.23 g		4.23 g						

Since the mass the initial sample dust was 4.23 g, and the contents of C and S - 7.9 % and 1.6 %, respectively, then 0.77 g, carbon and 0.14 g, sulfur in the form of oxides moved into gas.

The total mass of secondary dust, formed in the experiment, was determined by the content of zinc in the sample of dust and in the rest after the experiment. When the concentration of zinc in the dust – 17.7 %, it's quantity of zinc will be of 0.74 g. When the content of zinc in the rest – 1.2 % Zn, it's mass will be 0.02 g. Therefore, the mass of vaporized zinc is 0.72 g. Zinc content in the secondary dust received 60.3 %. The amount of the secondary dust has been calculated  $m_{s.dust} = 1.19$  g on the basis of the experimental results. Unrecorded the amount of substances composed of 0.49 g.

C. Theoretical Analysis of the Dust Evaporation

By the Langmuir equation [12]

$$w = \alpha \cdot p^0 \cdot \sqrt{\frac{A}{2\pi \cdot R \cdot T}},\tag{1}$$

where

 $\alpha$  - coefficient of Langmuir;

 $p^0$  - pressure saturated steam element, Pa;

A - the atomic weight of the element, kg;

R - the universal gas constant,  $\frac{J}{mol \cdot K}$ 

#### T - temperature, K.

was calculated theoretical speed of evaporation of zinc, lead and iron. The results of the calculation: at temperature of 1193 K (when  $\alpha$ =1) evaporation rate is for Zn – 118.51 kg/(m<sup>2</sup>·s), for Pb – 0.115 kg/(m<sup>2</sup>·s) and for Fe – 2.40·10<sup>-9</sup> kg/(m<sup>2</sup>·s). This is for pure metals. People can see that the evaporation rate of zinc and lead significantly above the evaporation rate of iron.

Thermodynamic analysis of the oxides evaporation (decomposition) from dust also showed: zinc and lead almost completely is transferred to the gas phase as a result of plasma processing. The calculation was performed using the program 'Terra' [13]. As an example, Fig. 6 shows a diagram for zinc and lead. Calculation results show that the condensed phase  $ZnO_{(c)}$  there is to the temperature of about 1300 K. At temperatures above 1300 K  $ZnO_{(c)}$  decomposes forming vapour of Zn. For the presentation in Table 1, the composition of dust with the carbon content of 8 % the process of evaporation of lead begins with practically the same temperature that zinc, but first there is a recovery lead oxide. Iron is recovered remaining in the condensed phase Fe<sub>(c)</sub> and noticeably evaporates only from the temperature of 2700 K.



Fig. 6 The dependence of the content of the condensed and gas phases of zinc and lead from temperature

In the presence of sulphur in the dust the concentration of gaseous Pb changes depending on the temperatures, in particular at 1500 K, due to the formation of sulphides of lead.

### VI. CONCLUSIONS

These results have showed that zinc and lead can be separated from iron by the plasma heating. Rapid heating of dust to the temperature of 1300...1700 K and rapid cooling of formed vapors in the atmosphere of inert gas will allow to get the pure metals (zinc and lead), and in the atmosphere of oxygen, can get a mixture of their oxides. To separate the zinc, and the lead from each other further researches are needed.

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