Extraction of Zinc and Iron from Electrosmelting Dust

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Abstract—The extraction of zinc and iron from dusty electrosmelting wastes is discussed. The chemical composition of the dust is investigated. Methods of obtaining zinc- and iron-bearing products by reduction are identified. The optimal conditions for the generation and capture of zinc sublimates are determined. A system for processing steel-smelting dust to obtain iron is proposed. Simultaneously, this technology extracts zinc from the dust in the form of zinc-oxide concentrate.

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Steel plants are major sources of atmospheric pollution. The volume of toxic emissions depends on the steel output, the structure of the enterprise, the efficiency of the gas-purification system, technological factors, and so on. With the growing environmental impact of steel plants, renewed attention must be paid to energy efficiency, the comprehensive use of raw materials, environmental protection, and reduction in production costs. Experience shows that the processing of many production wastes is technically feasible and economically beneficial [1, 2].

Recently, global demand for zinc has been rising. Zinc ranks third in terms of output and is widely used in industry [3]. Accordingly, there is a shortage of zinc on the world market. At the same time, the electrosmelting of steel produces large quantities of dust containing metals such as zinc and metal that are environmentally harmful but valuable in metallurgical terms [4]. In terms of raw materials, the environment, and economic considerations, there is a pressing need to process zinc-bearing dust from steel plants so as to obtain two valuable products: zinc-oxide concentrate and granulated iron.

Few methods of processing electrosmelting dust obtained when steel is produced from zinc-bearing metal scrap have been industrially adopted. Pyrometallurgical processes are mainly employed. The only hydrometallurgical process that is operative on an industrial scale is EZINEX (Engitec Technologies, Italy), in which the dust is leached by NH_4Cl solution, with subsequent electrolysis of the liquor containing oxides of zinc and other nonferrous metals [5]. Despite the quality of the products obtained, hydrometallurgical methods have not been widely used on account of the high operating costs, the complexity of the technology, the shortage of reagents (acids and alkalis), environmental pollution, and the difficult working conditions [6].

A common approach to the pyrometallurgical processing of dusty wastes is their utilization in sintering batch. When used for the processing of zinc-rich dust, this method has the following deficiencies.

(1) Certain thermodynamic conditions must be created in the sintered bed. That requires increased solid-fuel combustion, increased basicity, redistribution of the zinc-bearing materials in the lower layers of sintering batch, and the addition of $CaCl₂$ and ground magnesite powder.

(2) Complete removal of zinc in ordinary sintering is impossible because of the presence of oxygen in the gas phase and the presence of iron and silicon oxides in the final sinter.

(3) The use of zinc-bearing iron ore in the batch without preliminary removal of the zinc increases the zinc content in the hot metal, the formation of buildup in the furnace, and the destruction of the furnace lining under the action of zinc.

The CONTOP process developed in Germany calls for the melting of dust, solid fuel, oxygen, and natural gas in a vertical water-cooled reactor at 1800–2000°C [6]. Considerable power is consumed, and all the iron present in the processed wastes is irreversibly converted to slag. The SKF, Steel, and Scan Dust systems for plasma processing of dust are characterized by high productivity but require considerable capital investments.

The Romelt (Russia, 1979), Hismelt (Germany, 1984), DIOS (Japan, 1988), and AusIron (Austria, 1994) processes are based on the reduction of elements from molten wastes in a liquid bath. They effectively extract metallic iron, but the iron oxides remaining in the slag prevent the complete extraction of zinc. The technology developed by OAO Akont (Chelyabinsk) is based on the physical heat of liquid slags from steel smelting. These methods may effectively be used to remove iron from slags and other iron-bearing wastes but are unsatisfactory in terms of the extraction of zinc.

The rotary-kiln process is most widely used around the world for the processing of steel-smelting dust. In this process, the zinc-bearing dust is mixed and pelletized with a solid reducing agent (coke breeze). The pellets are charged in a rotary tubular furnace and heated to 1200^oC in a counterflow of exhaust gases. The zinc and lead are reduced from the dust. Sublimating, they are removed from the furnace with the exhaust gases and then deposited on filters. The product from the filter contains 50–60% Zn, with a small content of impurities (Pb, Cd, etc.). The main deficiencies of this method are the considerable fuel consumption and the contamination of the zinc concentrate with iron oxides [8].

Steel-smelting dust may also be processed in rotary hearth furnaces. The batch loaded in the furnace consists of briquets or pellets of dust, coke breeze, and binder. It is heated by the combustion of fuel supplied through the tuyeres and the combustion of carbon monoxide in the furnace space and the counterflow of exhaust gases. Heating to 1350°C results in rapid reduction of the iron and sublimation of the nonferrous metals, which are subsequently deposited on filters. Various firms use such technologies. The best known are the Fastmet process [9, 10], the Fastmelt process (Midrex, United State), and the Itmk3 process (Kobe Steel, Japan). The products are zinc oxide, reduced iron, and slag. However, these processes also have a number of problems. In particular, the temperature must be optimized, some design elements must be changed (including the discharge mechanism for the final product), the gas-exhaust system must be improved, and the wasteheat boiler must be modified [6, 11].

In Russia, there is practically no processing of steel-smelting wastes. However, since Russia is a large steel producer, which inevitably involves the generation of dust and other wastes, waste processing is essential to permit stable development and the efficient use of resources and production facilities.

EXPERIMENTAL METHOD

We consider an averaged sample of zinc-bearing dust from eleven steel plants, in the form of a reddish brown powder (particle size ≤ 0.06 mm). In Fig. 1, we show the results of granulometric analysis of the dust sample on an Analizette-22 NanoTecPlus Instrument (Fritsch, Germany). According to analysis on an S8 Tiger X-ray spectrometer with wave dispersion (Brucker, Germany), the dust mainly consists of iron and zinc oxides,

Fig. 1. Size distribution of particles in the sample of zincbearing dust.

Fig. 2. X-ray diffraction diagram of the sample of zincbearing dust.

with small quantities of oxides of alkali metals, silicon, manganese, and so on. The composition of the zincbearing dust is as follows: 26.02 wt % ZnO, 36.90 wt % Fe₂O₃, 5.975 wt % Na₂O, 2.98 wt % K₂O, 10.43 wt % CaO, 3.75 wt % Cl, 0.34 wt % P₂O₅, 1.04 wt % SO₃, 4.79 wt % SiO₂, 0.66 wt % Al₂O₃, 1.31 wt % MgO₃ 2.88 wt % MnO, 2.11 wt % PbO; the content of other materials is 0.80 wt %.

The modification of the iron in the dust is investigated by X-ray phase analysis on a DRON-3 instrument (Russia). As we see in Fig. 2, many of the iron atoms in the sample are bound with oxygen in magnetite, with marked replacement of the iron atoms by zinc atoms to form zinc ferrite ZnFe_2O_4 . However, most of the zinc is present in the form of the oxide ZnO.

The presence of chlorine hinders the extraction of zinc oxide from the dust [6]. The mean chlorine content in the dust sample is 3.75%. In the initial material, chlorine forms chlorides with the alkali metals also present.

In the experiment on the direct reduction of iron from iron- and zinc-bearing dust by Rapid Cast Iron (RCI) technology, the slag-forming fluxes employed are oxides of calcium and silicon with particles smaller than 0.1 mm. In calculating the quantity of fluxing additives introduced in the batch, the formation of fusible slag with $(CaO + MgO)/SiO₂ = 0.15-0.32$ is taken into account [4]. In the presence of silicon dioxide, silicates (of type $xFeO \cdot ySiO_2$) are formed and facilitate the transfer of the batch components to slag.

In the experiments, we use pelletized batch. To establish the optimal conditions for the production of zinc sublimates, we conduct experiments with different reducing agents: coal and coke with solid-carbon content 54.1 and 97.0%, respectively. The binder is carboxyl–methyl cellulose with added distilled water to obtain a thick paste [12]. Round pellets of mass 15– 30 g are formed from the paste. The batch composition is as follows: $60-85\%$ dust; $7-20\%$ reducing agent; up to 10% SiO₂; up to 5% CaO; 1% binder; 2–5% moisture. To remove moisture, the pelletized batch is dried for 0.5 h in an EKPS10 laboratory electrofurnace at 250° C [13].

The pelletized batch is smelted in a system consisting of an LHT08/17 high-temperature furnace (Nabertherm, Germany) and a water-cooled gas line with forced exhaust of the gaseous reaction products. For more complete zinc capture, the waste gases are passed through a distilled-water solution.

To improve the conversion of iron to carbide, crushed coke is placed in a corundum crucible and the prepared pellets are added. The crucible with the batch is charged in a furnace at 1150°C and the temperature is raised at \sim 11°C/min to 1380–1450°C. After 10-min holding of the pellets in the furnace, the temperature is reduced to 1150°C, the crucible with the products is extracted, and the sublimates captured in the cooled section of the apparatus are collected. The products are weighed and sent for determination of the quantitative and qualitative composition by X-ray fluorescent and X-ray phase analysis. The batch composition and the melt temperature are corrected on the basis of data regarding the effectiveness of slag separation from the valuable product (iron) and its degree of extraction.

RESULTS AND DISCUSSION

In the initial stages of the research, the goal is to determine the possibility of producing granulated iron and optimal conditions of the process. To that end, experiments are conducted with different composition and quantities of the reducing agents and fluxes.

The extraction of iron and zinc from the dusty steel-production wastes is based on their reduction from materials containing oxygen and carbon [14]. The reduction of iron and zinc from the batch by solid carbon is only partial; this is a secondary process. The main reducing agent is CO. (Solid carbon participates in the decomposition of $CO₂$ to obtain carbon monoxide, which accelerates the production of elementary zinc [14].) Since iron is present as $Fe₂O₃$ in the batch, reduction by CO proceeds in the following sequence [4]

$$
Fe_2O_3 \to Fe_3O_4 \to FeO \to Fe.
$$

Some of the reduced iron is bound with carbon from the coke to form iron carbide $Fe₃C$, in our view. (In other words, the iron is carburized.)

The active reduction of zinc by carbon monoxide begins at 906°C [8, 15]. The zinc enters the vapor phase

$$
ZnO + CO = Zn\hat{I} + CO_2.
$$
 (1)

Most of the zinc is converted to vapor at 1100°C. As already noted, the bulk of the zinc is bound in the dust with iron, in the form of zinc ferrite ZnFe_2O_3 . The ferrite is fairly well reduced by carbon monoxide

$$
ZnO \cdot Fe_2O_3 + 2CO = Zn \uparrow + 2FeO + 2CO_2,
$$

$$
\Delta G_{1273}^\circ = -876.2 \text{ kJ/mole}.
$$
 (2)

Zinc is reduced more rapidly from zinc ferrite than from zinc oxide and also at lower temperatures. The process occurs in stages, but the zinc oxide is only reduced after complete reduction of the iron from the iron oxide. The elementary iron formed may reduce the ZnO [8].

At the given experimental temperatures, oxidized lead compounds are reduced to metallic lead [3]. Some of the lead evaporates and, on condensing, contaminates the zinc formed. Most of the lead remains in the slag, without evaporating.

The metallic phase obtained experimentally consists of individual spheroidal gray particles (granules) of iron (4–6 mm), with characteristic magnetic properties; the carbon content is 2–3%. At that stage, the extraction of iron in the granules is around 50%; the remaining iron is distributed in the slag. As a result of smelting, we obtain glassy black slag with satisfactory separation from the iron granules. The composition of the products is as follows: 20–25% iron granules; 55– 65% slag; $15-20\%$ sublimates.

As already noted, the lowest temperature for the reduction of zinc from the dust is considerably lower than the initial temperature of iron reduction. Therefore, at $t > 1100$ °C, the zinc is reduced and volatilizes; it is mostly deposited on the cooled part of the laboratory apparatus. It follows from X-ray phase analysis that the captured sublimates contain up to $73.3-79.8$ wt $\%$ zinc

Fig. 3. System for processing dusty waste from steel production.

in oxidized form. The zinc extraction in the concentrate is 90%, which is adequate.

The results indicate that the quality of the zincoxide sublimates is higher in the experiments with reduction by coke. When using the different reducing agents, the composition (wt %) of the captured sublimates is as follows:

We see that the chlorine content varies from 6.88 to 9.64 wt % in the samples, and the fluorine content is up to 0.63 wt %. However, the content of zinc oxide is 79.82 wt %. (The customer requirement is at least 75 wt %.) The halogen content in the zinc sublimates may be reduced by additional thermal or hydrometallurgical treatment.

On the basis of our results, we recommend the processing system in Fig. 3 for steelmaking dust.

CONCLUSIONS

Laboratory results regarding the processing of zinc-bearing dust from steel production permit the following conclusions.

(1) The dust from gas-purification systems at smelting furnaces (an averaged sample) contains a relatively high content of zinc (26.02% ZnO) and a relatively low content of iron $(36.9\% \text{ Fe}_{2}\text{O}_{3})$.

(2) The dust must be processed in two stages so as to maximize the separation of the valuable components (zinc and iron) in individual products: granulated iron; and zinc-oxide concentrate.

(3) In the first stage, with heating at 11° C/min to 1380–1450°C, the zinc is reduced from the batch and sublimates. The zinc oxide formed is captured and cooled.

(4) The zinc extraction in the oxide concentrate is 90%, on average.

(5) The zinc sublimates meet the requirements on zinc concentrate in terms of ZnO content. However, the chlorine and fluorine content exceeds customer requirements. Reduction in their concentrations calls for additional roasting and hydrometallurgical treatment.

(6) The type of reducing agent affects the quality of the zinc sublimates formed. The ZnO content is 8.9% more when using coke rather than coal, on average. The chlorine content is 28.6% lower, on average, when using coke.

(7) In the second stage of the process, the temperature must be maintained at 1380–1450°C for 10 min to ensure complete melting of the reduced iron and its coagulation.

(8) Because of the low iron content in the initial material, it is difficult to obtain large iron pieces on processing. The iron granules obtained measure 6 mm or less.

The next step is to optimize the reducing parameters so as to improve the extraction of iron in the granulated product.

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