PROCESS SOLUTIONS OF ZINC-CONTAINING WASTE DISPOSAL IN STEEL INDUSTRY

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ABSTRACT

Steel industry can be characterized by a significant amount of by-products including fine dust (up to 1.5% of heat size). Dust of gas cleaners, containing above 0.5% Zn and 50% Fe, cannot be directly returned to basic melting facilities due to high contents of zinc that destroys its lining. High consumption of reducing agent, furnace lining corrosion, final product of high impurities content made difficult use of hydrometallurgical processing. Use of hydrometallurgy technologies is held back by zinc in dust, primarily, as ferrites that cannot be opened using alkali, while acids make iron transfer into solution. As a result, major part of smelters stockpiles the dust. Secondary deposits of zinc-containing steelmaking dust can be involved into processing thus expand the feedstock of zinc industry, increase efficiency of steel making and reduce negative impact on environment.

The paper contains chemical and mineralogical analysis of steel dust sample from PAO Severstal and study results on hydrometallurgical extraction of zinc from dust using salt solution. It has been established that ammonium chloride leaching of zinc
from electric arc furnace dust takes place within external diffusion region; optimum parameters of ammonium chloride leaching can result in almost complete and selective extraction of zinc into solution and producing ferrous cake that is applicable for blast-furnace processing. It was revealed that higher level of zinc ferritization in leach has minor negative impact on zinc extraction into solution and keeps minimum iron transfer into solution. Zinc can be extracted from leach solution by zinc hydroxide deposition using ammonia stripping, followed by drying and deposit calcination to produce saleable zinc oxide.

Keywords: secondary deposits; waste reuse; iron and steel industry wastes; zinc-containing dust; zinc ferrite; ammonium chloride leaching of zinc.


1. INTRODUCTION

A huge number of slag and dust dumps were heaped up for many years of smelter operations. It has been well known that old dumps, taken out of operation, have negative impact on air, hydrosphere and soil cover of environment and thus on state of flora, fauna and human health. Therefore, today, slag and dust waste disposal is one of the top priority challenges of environmental protection.

Significant part of accumulated steelmaking wastes is finely-dispersed dust of gas cleaner systems containing up to 20% of zinc and more than 50% of iron, yield is up to 1.5% of heat size. 1-2% of crude in steelmaking going through melting unit is turned into dust. Some technologies may show up to 10%. The pie chart (Figure 1) [1] shows volumes of zinc-containing dust of steel making industry worldwide.

![Figure 1 – Dust volumes of electric arc furnace steelmaking worldwide, million tons per year](image-url)
Dust composition relates directly to chemical composition of charge used. As steel making processes take place under temperatures exceeding 1600 °C, zinc, lead and cadmium that present in charge, are almost fully transferred into gaseous phase and then it is accumulated in gas cleaner apparatus.

Volumes of wastes to be involved into processing are not high. Only 2% of wastes can be used as fuel and mineral fertilizers, and only 18% can be used as secondary materials including 10% for construction industry.

Existing secondary deposits of zinc-containing products can be divided into 3 groups: high zinc (above 20%), medium zinc (5-20%) and low zinc (below 5%).

At present final sludge and dust of steel making industry of high and medium zinc practically are not subjected to disposal. Use of such zinc-containing iron ore materials in blast-furnace charge without preliminary zinc extraction can lead to undesired effects as high zinc in pig iron; incrustation that destroys normal running of smelting process. Zinc, by penetrating into lining, participates in line deformation and its breaking. In order to reduce large amount of zinc, being accumulated in the working chamber of blast furnace, additional coke is consumed of about 2 to 12 kg of coke per 1 kg of zinc. So, steelmaking dust today is primarily stored in sludge dumps and sedimentation ponds, thus it inevitably contaminates environment by disseminating valuable components, primarily, zinc.

According to general requirements specified for waste quality, when using it for agglomeration, zinc content in sintering mix of 10-15% weight – it is up to 0.3%, in agglomerate it is up to 0.05%. The pie chart (Figure 2) [1] presents processing volumes of zinc-containing steelmaking dust worldwide.

Figure 2 – Processing of electric arc furnace steelmaking dust worldwide

Due to increasing production of zinc-coated items and improved rolled metal consumption with coatings, world producers are optimistic about prospects of zinc market providing for strategic planning on zinc production growth. Herewith it seems timely to study possible involving of zinc-containing wastes of iron and steel making into processing including dust and gas cleaner wastes of agglomeration, blast furnace and steel-making. Based on data analysis taken from the literature, in case of high zinc in steel-making dust, zinc can be
extracted using pyrometallurgy and hydrometallurgy. Among assumed pyrometallurgical methods, primarily, this is a large group of methods based on zinc oxide reduction using different reagents to metal and its further stripping, the difference between them is minor and can be related mainly to the type of equipment applied. The most developed technologies here are Waelz, FASTMET and FASTMELT, OXYCUP, Primus [2-5]. However, pyrometallurgy methods have some general drawbacks: product is zinc as oxides with high impurities, that in fact, is a secondary dust; reduction requires high coal, coke breeze or other reducing agents’ consumption; zinc extracted has negative impact on service life of furnace lining. Processing of zinc-containing products at zinc operations requires extra considerable material and energy costs thus having negative impact on high-grade zinc cost.

Hydrometallurgical methods, mainly, oxidized or alkaline leaching, have unmatched advantages such as providing comprehensive processing with high recovery of all valued components, economic efficiency, reduction of air pollution by harmful effluents, better working conditions [5-9]. But these methods are held in as zinc found as ferrites that practically cannot be opened by alkaline and acids make iron transfer into solution.

Solution to development of efficient hydrometallurgical processing of zinc-containing dust can be application of other type of solvents, like salt solutions, e.g. ammonium chloride which use will provide for maximum high zinc extraction into solution while keeping iron amount in insoluble residue [10, 11, 12, and 13].

2. RESEARCH METHODS

Studies were performed using zinc-containing steelmaking dust sample of JSC Severstal (see Table 1).

<table>
<thead>
<tr>
<th>Table 1 – Dust sample chemical composition</th>
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<tbody>
<tr>
<td>Content, %</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>32.1</td>
</tr>
</tbody>
</table>

Dust sample is represented mainly by fine material, 76% of -20 µm grain size. Chemical analysis of individual mineral phases suggests that, in sample, iron is presented both within the oxygen-bearing phases and metallized (Table 2).

<table>
<thead>
<tr>
<th>Table 2 – Chemical composition of dust sample basic phases</th>
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<tr>
<td>Phase</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Iron metallic</td>
</tr>
<tr>
<td>Spinel 1</td>
</tr>
<tr>
<td>Spinel 2</td>
</tr>
<tr>
<td>Zn ferrites</td>
</tr>
<tr>
<td>Pb-Zn ferrites</td>
</tr>
<tr>
<td>Magnetite</td>
</tr>
<tr>
<td>Total</td>
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</table>

Significant part of zinc (up to 80%) is represented by ferrite phase ZnFe2O4 Figure 3.
Figure 3 – Dust grain size -45+20 µm. Zinc basic phases. A – spinel with zinc ferrite, B – zinc oxide grain with ferrite impregnations. Reflection electron images

Aggregate coefficient of environmental hazard of electric furnace dust of JSC Severstal is amounted 1 081.4. The most hazardous component of dust, besides carbon, is zinc. By considering a large volume of dust accumulated and high zinc content in it (16.1%), it can be reasonably treated as a secondary zinc deposit.

Analysis of literature and industrial practice shows that development of hydrometallurgical technology should be considered prospecting to produce rich zinc concentrate and iron-bearing residue that meets the requirements of blast-furnace ironmaking. Ammonium chloride leaching was selected as a hydrometallurgy processing method of metallurgical waste using salt solutions. Based on literature, basic interactions that take place in zinc-containing dust decomposition by ammonium chloride solution are the following:

\[ \text{ZnO} + 4\text{NH}_4\text{Cl} \rightarrow [\text{Zn(NH}_3)_4\text{]}_2\text{Cl}_2 + \text{H}_2\text{O} + 2\text{HCl} \]  

High thermodynamic probability of ferrite and zinc oxide decomposition in ammonium-chloride medium within the temperature interval of 273-473 K is caused by formation of stable zinc tetrammine which presence within the system NH$_3$ – NH$_4$Cl - H$_2$O provides for decreasing of ammonium partial pressure in gaseous phase due to additional Zn (NH$_3$)$_4^{2+}$ ionic hydration.

Study of impact of the basic parameters of ammonium chloride leaching of zinc was carried out using HEL Poly-Block autoclave unit. Ammonium chloride consumption was varied from 50 to 400%, from theoretical amount for reaction (1), L:S=3-5. Leaching time was 30-240 minutes within the temperature interval 20-100°C. Solution was agitated using autoclave stirrer with rotation speed (up to 900 rpm).

3. RESEARCH RESULTS

It has been established that ammonium chloride leaching held under optimum parameters (ammonium chloride consumption is 300% of theoretical amount, 80°C, 2 hours) provides for high (no less than 95%) zinc extraction into solution at quantitative concentration (at least 98%) of iron and silicate components in solid residue thus making possible one-stage process of zinc selective leaching. Ferrous cake containing up to 40% of iron, 12-13% of calcium and less than 0.6% zinc, can be returned into blast furnace as a flux addition. Estimated value of apparent activation energy is 22.4 kJ/mol thus, jointly, by considering the first stage reaction on zinc...
and expressed process velocity dependence on agitation rate, makes it possible to state that the process of ammonium chloride leaching of zinc from steelmaking dust runs in external diffusion region.

It has been revealed that increasing content of ferrite zinc up to 75% has minor negative impact on zinc transfer into solution (by 8-10%) that can be a determining factor when making selection of ammonium chloride leaching as a processing method of waste zinc-containing materials of different types that can be characterized by high ferritization.

Ammonia stripping at 80 °C from ammonium-chloride solutions up to pH 6.6 is accompanied by decomposition of zinc tetrammines thus providing for selective deposition of more than 90% of zinc as hydroxide to its residual concentration in recycled liquor of less than 5 g/l.

Process flow diagram was developed of hydrometallurgical processing of zinc-containing dust of steelmaking including autoclave ammonium chloride leaching, zinc deposition by ammonium stripping from mother liquor, zinc hydroxide calcination to produce saleable oxide and ammonium regeneration (Figure 4).

![Figure 4](http://www.iaeme.com/IJCIET/index.asp)

**Figure 4** – Process flow diagram of ammonium-chloride processing of steel-making dust
(1 – Autoclave, 2 – pump, 3, 5 – drum filter, 4 – reactor for ammonium stripping, 6 – scrubber, 7 – heat exchanger)

4. CONCLUSIONS
Ammonium chloride leaching of steelmaking dust is an efficient and selective process that allows zinc to transfer into solution almost in full at temperature of 80 °C, ammonium chloride consumption of 300%, L:S=3, process duration of 120 minutes, by concentrating iron in solid residue of leaching applicable for return into blast-furnace process. Zinc can be extracted from liquor due to zinc hydroxide deposition, drying and calcination of the latter to produce zinc
oxide. Presence of ferrites in zinc in dust does not mean its refractory character for ammonium chloride leaching thus providing processing of dust with high ferrite content that cannot be treated by any other technologies.

Process solutions proposed can significantly boost production of zinc due to involving of large volumes of zinc-containing waste products into processing, reduce footprint area for its stockpiling and decrease man-made burden on environment.

REFERENCES


