Studies on the regularities of the steelmaking zinc-bearing dusts leaching in ammonium chloride solutions

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Dust from steelmaking production, in particular electric arc furnace dust (EAFD), is a rich secondary source of zinc. Different approaches to the EAFDs processing with the production of zinc oxide and metal phases as a final product have been studied.

Ammonium chloride leaching is selective for zinc, does not require special acid-resistant equipment, and is relatively cheap. The advantages of this method are the possibility of obtaining metallic zinc as a commercial product and the absence of the need for additional solution purification from iron and chlorine ions.

Chemical and mineral characterization of Waelz-oxide after the first stage of calcination are presented, the main identified phase is zinc oxide (ZnO), a small amount of Zn associated with iron ($Zn_2Fe_2O_4$) in the ferrites form and lead in the oxide phase (PbO) are also determined.

The thermodynamic analysis of the $Zn(II) - NH_4Cl - NH_3 - H_2O$ system in the HYDRA software medium was carried out, the main zinc compounds were determined under leaching conditions. A matrix of changing conditions is compiled with using the full three-factor experiment method. Based on the obtained results, in the Statistica-10 program, three-dimensional dependences of zinc extraction on varied parameters were constructed and equations describing these dependencies were obtained. The optimal leaching parameters were determined: the concentration of ammonium chloride 4 mol/dm^3, the concentration of ammonia 4 mol/dm^3, the ratio L:S = 15.

Key words: electric arc furnace dust, Waelz process, zinc oxide, zinc ferrite, ammoniacal leaching, ammoniac complexes of zinc, metallic zinc.

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Introduction

The electric arc furnace dust (EAFD) of recycled steelmaking contains large amount of iron, but high content of non-ferrous metals in them, in particular zinc, and makes it impossible to return them into the ferrous metallurgy process stages [1]. The EAFDs have rather compound and diverse chemical composition, which varies depending on the technology used and the feedstock composition. The range of zinc content in dusts is quite wide; ranging from 2 to 25%, in some cases the zinc content reaches 40% [2—3]. As a rule, dust contains iron, zinc, cadmium, lead, chlorine, alkaline and alkaline-earth metals.

Numerous pyro- and hydrometallurgical processes have been developed for the EAFD processing, but only a limited number of technologies have become commercial, most of them are the pyrometallurgical ones [4—5].

Such choice is conditioned by the partial zinc content in the dusts in the form of stable ferrite [6], for the zinc extraction from which either high dissolvent concentrations or elevated temperatures are required. Waelz processing is one of the most-used pyrometallurgical methods of the steelmaking wastage treatment. At present, more than 80% of the ferrous metallurgy dusts are treated by Waelz processing.

The authors of [7] have proposed a technology that allows to destroy stable zinc ferrite by sintering EAFDs with calcium oxide. However, the sintering process is costly, since it requires high consumption of expensive calcium oxide and is energy-consuming. Contaminated zinc oxide and calcium-ferriferous cake, unsuitable for further processing, are the final Waelz processing products; whereas hydrometallurgical method allows to obtain compact metallic zinc [8].

Hydrometallurgical methods are based on dissolving the initial middlings and transferring valuable components into a solution in the form of various compounds [9—12]. At that, the remaining mass of raw materials (in this case, iron and gob) remains in the form of a separated cake.

Sulfuric acid is one of the most common solvents in hydrometallurgy [13]. Hydrometallurgical processes with

sulfuric acid usage are well developed and studied, they proceed strongly and efficiently. However, the ferrous metallurgy dust is mainly represented by oxidized compounds of iron and zinc, and the iron content in the dust is most often much higher than amount of zinc, which makes further processing difficult without introducing additional stages of purification from iron.

Ammoniacal leaching is quite widely used [14−23]. This solvent can be applied to metals capable of forming the copper, nickel and zinc ammonia complexes. One of the advantages of the ammonia system is a possibility of selective zinc transfer into solution, with almost complete conservation of iron in the cake. If EAFD contains other non-ferrous metals, they will also pass into the solution; however, as practice shows, their content in the dust is negligible.

The zinc oxide contained in the dust passes into solution by the following reaction:

$$ZnO + 2NH_4Cl = [Zn(NH_3)_4]Cl_2 + H_2O. \qquad (1)$$

However, zinc ferrite presented in EAFD will be stable in such environments, and therefore the recovery would not exceed 30−40%.

Intensity

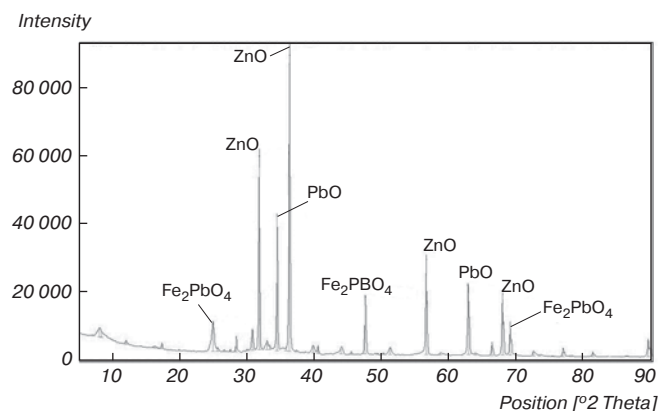**Fig. 1.** Diffractogram of sublimates of the first stage of EAFD calcination
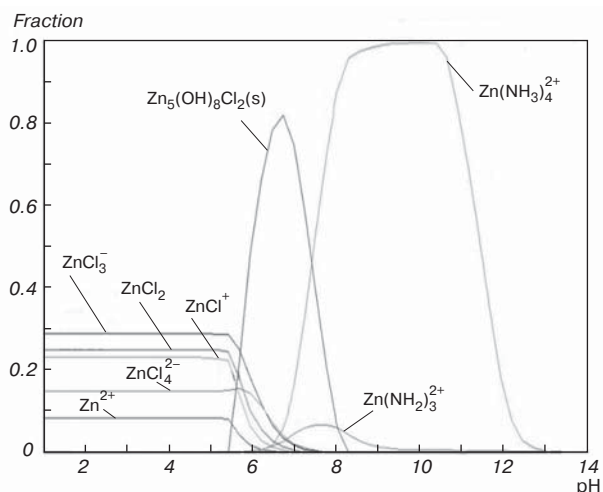

Fraction

Fig. 2. Distribution diagram of zinc compounds in the pH range 1−14

Ammonium chloride leaching of sublimates after high-temperature preparation (Waelz process) is considered as the most promising direction of EAFDs processing. The Waelz stage availability allows to transfer the hardly soluble ferrite phase to the oxide one, which easily dissolves in ammonia-chloride media [7]. The solutions after leaching are suitable as an electrolyte for the final stage of electro-extraction with obtaining metal zinc as a marketable product.

Object of research

In this paper, studied were the sublimates after the first stage of the EAFD Waelz processing with the following chemical composition, %: 61Zn, 10Cl, 6Pb, 4 Ca, 4K, 2Fe.

Semiquantitative mineralogical analysis of the obtained EAFD sublimates was carried out on a PANalytical X'Pert Powder (Netherlands) powder X-ray diffractometer with a vertically positioned goniometer (Fig. 1).

According to the results of X-ray diffraction analysis, the main phase of sublimations, zinc oxide, is identified, and there also is a small amount of lead oxide and iron plumbate. The unidentified phases are presumably the oxides of impurity compounds.

Theoretical data

During leaching with ammonia-chloride solutions, zinc and lead are transferred to a solution from which they can be further isolated as final products. At that, the iron present in the dusts will remain in the form of a solid undissolved residue (cake), which can be returned to the melting stage. Such a method does not require an introduction of additional stages of purification from chlorine and fluorine ions, which complicate processing, as their accumulation negatively affects the passing of electrochemical processes. Chlorine in ammoniacal leaching is directly involved in regeneration of the solvent, ammonium chloride.

In the EAFD ammoniacal leaching process, complex chemical reactions take place with formation of complex zinc compounds resulting from the interaction between Zn^{2+}, Cl^- ions and и NH_3 ligands depending on pH value.

The distribution diagram of ion forms for the $Zn(II) - NH_4Cl - NH_3 - H_2O$ system is performed in HYDRA software and is shown in Fig. 2. The diagram demonstrates the proportion of $Zn(II)$ involved in formation of a complex compound with a certain number of ligands, depending on pH. In the low pH range (<5.5), four chlorocomplexes coexist and interact with $Zn(II)$ ions in the solution; $[ZnCl_3]^-$ is a predominant form. In the pH range from 5.7 to 7.5, $Zn(II)$ mainly exists in the form of a marginally soluble $[Zn_5(OH)_8]Cl_2$ hydroxocomplex; $[Zn(NH_3)_3]^{2+}$ ammine complex is being formed in modest amounts.

It might be well to point out that Cl^- ions may be substituted by H_2O и NH_3 molecules in the neutral pH range, which explains the beginning of formation of hydroxo- and ammine complexes in different pH ranges. An alkaline

area is characterized by formation of ammine complexes with different composition. At pH values from 8.0 to 11.0, $[Zn(NH_3)_4]^{2+}$ ammine complex is predominant and binds 98% of Zn (II) ions. At high OH^- (pH > 12) concentrations, zinc becomes soluble due to formation of stable zincate ions.

Technique of experiment

Leaching has been carried out in a reaction beaker at constant stirring and room temperature. The varied parameters are as follows: L:S (X_1) ratio 10−20, initial concentration of ammonium chloride (X_2) 2−4 mol/dm^3 and free ammonia (X_3) 2−4 mol/dm^3. The influence of these factors on the studied process has been evaluated by mathematical planning of the experiment. Zinc extraction into solution (Y) was chosen as a response. The complete three-factor experiment matrix is presented in the Table 1.

During leaching, pH of the solution has been maintained at 8−9, which corresponds to the area of maximum

Table 1.
Matrix of a complete three-factor experiment

X_1	L:S	X_2	C_{NH_4Cl}, mol/dm^3	X_3	C_{NH_3}, mol/dm^3	(Y) Zinc extraction, %
−1	20:1	−1	2	−1	2	93.3
−1	20:1	−1	2	0	3	93.4
−1	20:1	−1	2	+1	4	95.6
−1	20:1	0	3	−1	2	93.4
−1	20:1	0	3	0	3	95.2
−1	20:1	0	3	+1	4	96.2
−1	20:1	+1	4	−1	2	94.8
−1	20:1	+1	4	0	3	94.4
−1	20:1	+1	4	+1	4	95.4
0	15:1	−1	2	−1	2	89.9
0	15:1	−1	2	0	3	91.1
0	15:1	−1	2	+1	4	93.2
0	15:1	0	3	−1	2	93.1
0	15:1	0	3	0	3	95.3
0	15:1	0	3	+1	4	96.1
0	15:1	+1	4	−1	2	95.0
0	15:1	+1	4	0	3	95.5
0	15:1	+1	4	+1	4	96.4
+1	10:1	−1	2	−1	2	79.2
+1	10:1	−1	2	0	3	89.5
+1	10:1	−1	2	+1	4	92.7
+1	10:1	0	3	−1	2	90.6
+1	10:1	0	3	0	3	93.7
+1	10:1	0	3	+1	4	93.9
+1	10:1	+1	4	−1	2	88.4
+1	10:1	+1	4	0	3	95.2
+1	10:1	+1	4	+1	4	96.2

stability of zinc ammine complexes (Fig. 2). Further, the solid and liquid phases have been separated by filtration on a nutsch filter. The solution has been analyzed for zinc and lead content by atomic absorptive method using an Analitik Jena novAA 300 spectrometer.

Cake has been analyzed on a Shimadzu XRD-7000C X-ray diffractometer.

Results and discussion

The results of X-ray phase analysis of cake after leaching are presented in Fig. 3.

It follows from the X-ray photograph that lead is concentrated in the cake, as well as there is a small amount of iron. It is possible to observe the residual zinc content in the cake, which is confirmed by the results of analysis of solutions, according to which the extraction of zinc reached a maximum of 97%.

According to the data obtained in STATISTICA software, the surfaces which characterize the dependences of zinc extraction on two factors at the fixed third one has been drawn up.

Having analyzed the obtained surfaces, one can conclude that significant increase in zinc extraction at all studied L:S ratios takes place as concentration of NH_4Cl in the solution rises; the same may be applied to the free ammonia concentration increase. The surface describing an effect of ammonia and ammonium chloride concentration at L:S = 10 is shown in Fig. 4. It can be noted that at L:S = 10, maximum extraction of zinc into the solution (more than 90%) is being achieved for almost all values of ammonia and ammonium chloride concentrations. This is probably connected with the high total concentration of ammonium ions (NH_4^+), sufficient to bind Zn(II) ions and to form stable ammine complexes, which become more stable in the pH range 8−9.

High zinc recovery requires elevated (at least 4 mol) ammonium chloride and ammonia contents in the initial leaching solution. Zinc recovery reaches a maximum value of 96.4% at L:S = 15 and the starting ammonium chloride and ammonia concentration of 4 mol/dm^3.
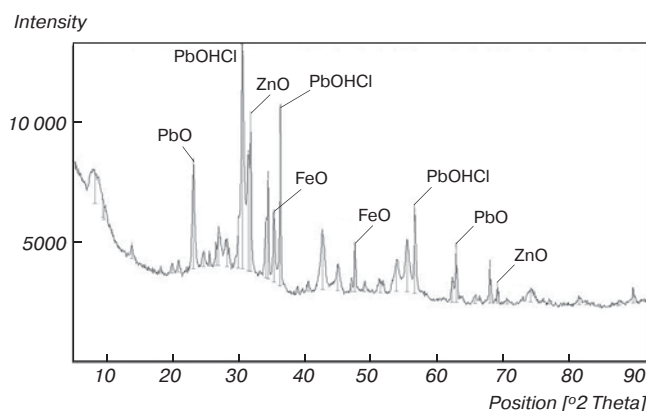

Fig. 3. X-ray photograph of the cake after leaching of EAFD sublimates

The response surface equation at the fixed L:S = 15 (Fig. 5) is as follows:

$$Y = 67.658 + 11.108 \cdot X_2 + 3.608 \cdot X_3 - - 0.475 \cdot X_2 \cdot X_3 - 0.150 \cdot X_3^2 - 1.25 \cdot X_2^2. \qquad (2)$$

Positive coefficients at X_2 and X_3 in Equation (2) indicate the influence of these factors on zinc extraction into solution. A higher coefficient at X_2 reports a slightly greater effect of ammonium chloride concentration in comparison with the ammonia one:

$$Y = 13.664 + 22.542 \cdot X_2 + 24.175 \cdot X_3 - -1.425 \cdot X_2 \cdot X_3 - 2.533 \cdot X_2^2 - 2.633 \cdot X_3^2, \qquad (3)$$
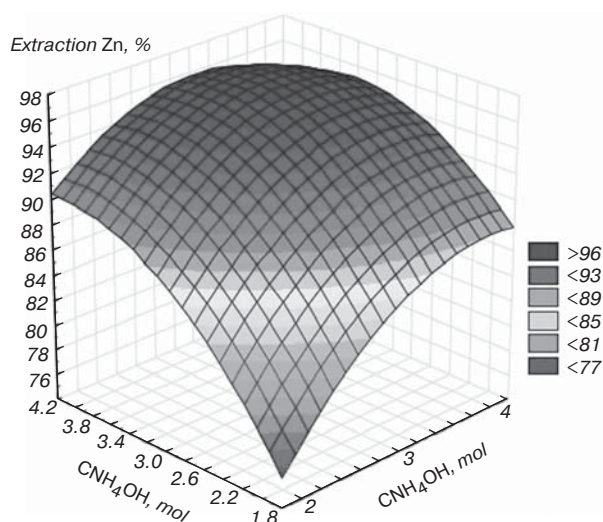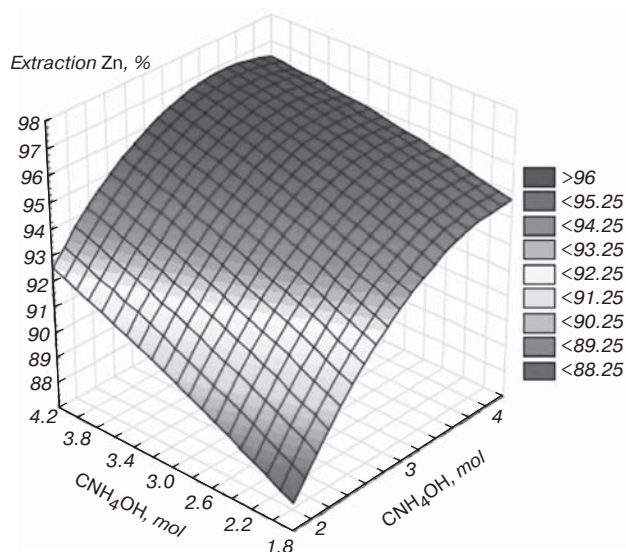

Fig. 4. Dependence of zinc extraction into solution upon the starting concentration of ammonium chloride and ammonia at L:S = 10

$$Y = 87.431 + 5.292 \cdot X_2 - 2.075 \cdot X_3 - - 0.425 \cdot X_2 \cdot X_3 - 0.583 \cdot X_2^2 + 0.717 \cdot X_3^2. \qquad (4)$$

When L:S = 10, both factors have the same influence on a degree of zinc recovery into solution, as it can be seen from the coefficients in Equation (3); at that, zinc extraction into solution reaches 96%. Equation (4) describes the surface at L:S = 20 (Fig. 6), from which it can be seen that concentration of ammonia has weak influence on a degree of zinc recovery into solution; maximum recovery also reaches 96%. In that case, L:S = 10 is taken as an optimal value.

The following response surfaces were constructed at the fixed concentration values of 2−4 mol/dm^3 for free ammonia and of 2−4 mol/dm^3 for ammonium chloride.

The shape of the response surfaces is almost the same for all fixed values of free ammonia concentration (Fig. 7). Zinc recovery increases dramatically as both ammonium chloride concentration in the solution and L:S ratio rise, reaching values of 96−97 %.

Maximal zinc recovery of 96.2% at the free ammonia concentration of 4 mol is also achieved under the following optimal conditions: NH$_4$Cl concentration of 4 mol/dm^3 and L:S = 15, according to the following equation:

$$Y = 75.331 + 0.982 \cdot X_1 + 6.758 \cdot X_2 - - 0.185 \cdot X_1 \cdot X_2 - 0.483 \cdot X_2^2 - 0.0093 \cdot X_1^2. \qquad (5)$$

In these conditions, favorable influence of ammonium chloride concentration on the leaching result is more pronounced.

Fig. 8 shows a surface describing the dependence of zinc extraction into solution upon the ammonia concentration and L:S ratio at the ammonium chloride concentration of 4 mol/dm^3.
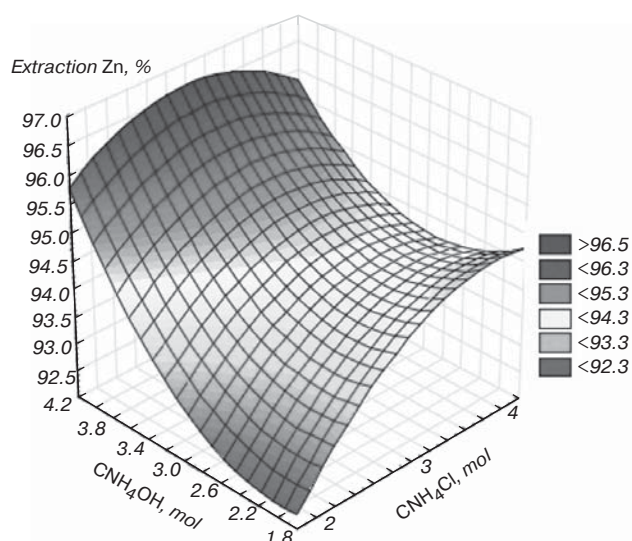

Fig. 5. Dependence of zinc extraction into solution upon the starting concentration of ammonium chloride and ammonia at L:S = 15

Fig. 6. Dependence of zinc extraction into solution upon the starting concentration of ammonium chloride and ammonia at L:S = 20

For the fixed ammonium chloride concentration of 4 mol/dm³, the following response surface equation is obtained:

$$Y = 50.3 + 3.280 \cdot X_1 + 11.833 \cdot X_3 -$$
$$0.360 \cdot X_1 \cdot X_3 - 0.068 \cdot X_1^2 - 0.800 \cdot X_3^2. \quad (6)$$

Maximum zinc extraction into solution of 96.4% can be reached at optimal values of factors as follows: L:S = 15, C_{NH_4OH} = 4 M.

Thus, processing of the planned experiment results has allowed to determine optimal process parameters of zinc leaching from the sublimates of EAFD Waelz proces-sing as follows: ammonium chloride concentration — 4 mol/dm³, free ammonia concentration — 4 mol/dm³, L:S ratio — 10.

In these conditions, zinc extraction into solution (according to the obtained experimental data) exceeds 96%; the obtained solutions are suitable for further zinc purification and electroextraction.

Conclusion

The possibility of using the ammonium chloride solutions for zinc extraction from EAFDs was studied. The feasibility of the ferrous metallurgy zinc-containing dusts processing in an ammonium chloride system with prelim-inary dust calcination in a Waelz rotary kiln is considered; zinc extraction into solution is up to 97%.

The influence of ammonium chloride and ammonia concentrations as well as the L:S ratio are studied; the three-dimensional extraction dependences upon a set of factors are constructed. It may be deduced that zinc re-covery rate is more affected by the ammonium chloride concentration. However, the ammonium chloride and ammonia concentrations are influencing equally at the lowest L:S ratio.

Optimal parameters of a leaching process were se-lected as follows: L:S = 15, the ammonia concentration 4 mol/dm³ and the ammonium chloride concentration 4 mol/dm³; their combination allows to extract 96−97% of zinc from EAFD.
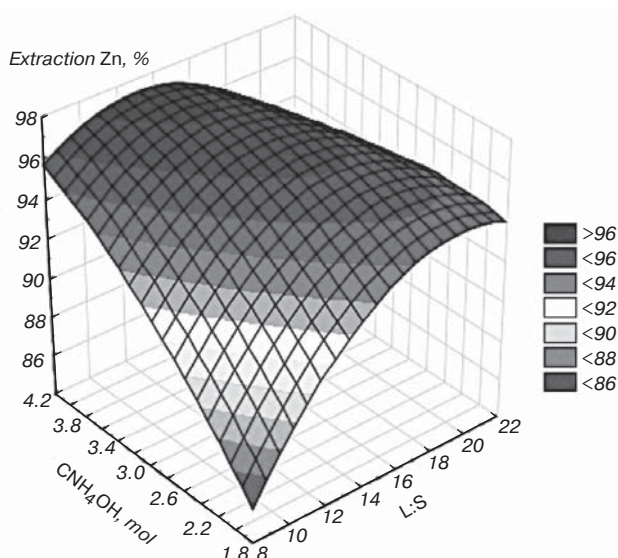

Fig. 7. Dependence of zinc extraction into solution upon the starting concentration of ammonium chloride and L:S at the ammonia concentration of 4 mol/dm³
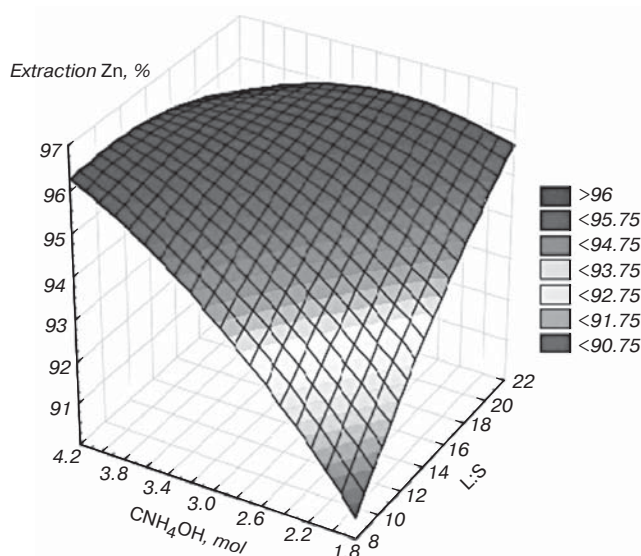

Fig. 8. Dependence of zinc extraction into solution upon the starting concentration of ammonia and L:S at the ammonium chloride concentration of 4 mol/dm³

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