

UTILIZATION OF ZINC IN POWDERS FROM ELECTRIC ARC FURNACES IN STEEL PRODUCTION

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Abstract

The processing of waste powders from steel production in electric arc furnaces is a world problem. The presence of Fe, Zn, Cd, Pb, etc. in the powders makes them a valuable source for these metals. Zinc is the metal that is most often utilized, which leads to reduction of environmental pollution.

The greatest problem in this connection is the presence of chlorine and fluorine in the powders, which influences the electroextraction of zinc in a significantly negative way.

The presented paper shows the results from the study of the possibilities for zinc leaching from powders obtained in the steel production in Bulgaria. A detailed characterization of the powders was made using chemical analysis, XRD, DTA and TGA and Mössbauer spectroscopy. The results from the powder leaching with different solvents give the reason to recommend a technological scheme for the complete and total processing of the waste powders from steel production.

Keywords: Waste powders; EAF; Steel production; Zinc; Utilization

1. Introduction

Each year about 30 million tons of waste materials from the steel production industry in the world are recycled. These waste products are powders from blast-furnace and electric arc furnaces (EAF), fine and coarse fractions from oxygen convertors, sediments

from the water treatment of large ground fractions, etc. [1].

About 20 kg of powder is released from 1 t of produced steel. In this connection different methods are developed (hydrometallurgical and pyrometallurgical) to process these powders with the aim of leaching the valuable metals in them such as

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Zn, Cd, Pb, etc. One of the main problems connected with the processing of the EAF powder is the high halogen content. Halogens are especially harmful in the electroextraction of zinc from zinc-sulphate solutions [2].

The hydrometallurgical process for processing of EAF powders was studied on a laboratory scale by T.Havlik [3-5], J.Sloop [6], J.Alguacil [7]. N.Leclerc [8,9] researches the hydrometallurgical methods for leaching of zinc from zinc ferrites using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. A.Zunkel [10,11] proposes technologies and processes for treatment of powders and maximum leaching of zinc and lead from waste products.

At low concentrations of the useful components or the presence of radioactivity it is necessary for the powders to be stabilized and safely stored [12-14]. R.Sekula [15] tests physical separation methods, and C.Solisio [16] discusses the solubility of zinc and aluminium using *Thiobacillus ferrooxidans*. Selective dissolution of zinc before iron is carried out using ultrasound. With their research G.Ye [2,17] present alternative treatments for leaching of halogens. In laboratory conditions [18-20] experiments were carried with EAF powders using a wealz process to produce zinc oxide.

Regardless of the numerous investigations done, currently there is no universal method to apply in order to utilize the zinc from steel production powders. Depending on the content and quantity of the powders, investments are made in new installations and technologies or existing ones are used.

The high Fe, Cl and F content in the powders leads to significant difficulties in

leaching according to the classic hydrometallurgical scheme for zinc leaching, because it leads to an increase of Cl and F in the solution, and there are strict requirements concerning their content in the zinc sulphate solution for the electroextraction of zinc.

In this connection the aim of the present study is to carry out as complete as possible a characterization of EAF powders obtained in Bulgaria and to study the possibilities of recycling the zinc in them.

2. Experimental

The studies are carried out with a powder-like sample obtained when the outlet granules are ground, and sifting the whole quantity through a 0.2 mm sieve. A study of the influence of temperature and time upon the degree of removing of Cl and F from the powder is carried out in a tube furnace. A sample of 5 g is thermally treated at different temperatures and durations.

DTA and TGA (a Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 0.5 mV; DTG, 1 mV; TG, 100 mg; heating rate, $10^{\circ} \text{ min}^{-1}$; sample mass 100 mg. A ceramic crucible was used. All the studies were performed in air medium.

The X-ray phase analysis of the samples was carried out with an apparatus "TUR-M62" (Dresden, Germany) equipped with a computer-controlled HZG-4 goniometer with Co-K_{α} radiation and Bragg-Brentano geometry. Data base (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase identification.

The Mössbauer spectra were taken with

an electromechanical spectrometer (Wissenschaftliche Elektronik GMBN - Germany) functioning at a constant acceleration mode and at room temperature.

A 70 mCi $^{57}\text{Co}(\text{Cr})$ source and an $\alpha\text{-Fe}$ standard were used. The experimentally obtained spectra were computer fitted to a series of Lorentzian lines by the least squares method. The parameters of hyperfine interactions such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H_{eff}) were determined. The relative weights (G) of the partial components of the spectra were found from the intensities of the corresponding lines.

3. Results and Discussion

The powders obtained in electric arc steel production are granulated and transported to a zinc plant for processing. Their average chemical content is the following (in mass %): Zn–20.15; Fe–32.5; Pb–3.53; Cl–2.13; F–0.35; Sb–0.2; humidity–8.68.

Based on the chemical content the following conclusions can be made:

1. The zinc content in the separate batches is within 18.8–23.1 % and remains within this range during the study. The low zinc content renders the powder unsuitable for independent hydrometallurgical processing.

2. The high content of Cl and F is especially unfavorable in comparison with the requirements for initial raw materials (Cl<0.05 % and F<0.02 %), used with the hydrometallurgical method for zinc production. The Sb content also exceeds the requirements for initial raw materials (Sb<0.005 %).

3. In all samples the Fe content falls

within the range of 28–35 %.

The steel production powder is studied with DTA and TGA analysis. The obtained DTA and TGA curves are presented in Fig. 1.

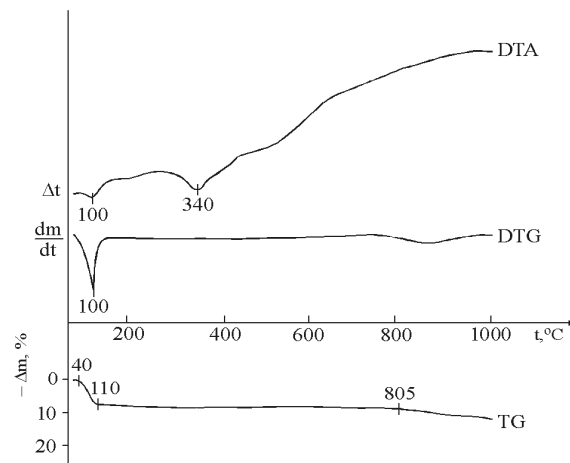


Fig.1. DTA and TGA analysis of EAF powder

The DTA curve shows that in the temperature interval up to 110 °C a slight endothermic effect is observed, which is due to moisture released from the sample. This is confirmed by the TGA curve, according to which the reported mass loss is of the order of 8 %. The second endothermic effect of the DTA curve (340 °C) is not accompanied with mass loss and is probably due to some phase transition. According to the TGA curve up to 805 °C no mass change of the sample is observed, and after the indicated temperature there is a small mass decrease up to 1000 °C. The obtained results show that the powder from steel production is stable, inert and is only slightly influenced by heating in the studied temperature interval.

The measured X-ray pattern (Fig.2) is characterized with comparatively narrow and intensive lines, which is indicative of crystallized phases. On the other hand, the base line registers certain deviations from a straight line, which shows that the presence

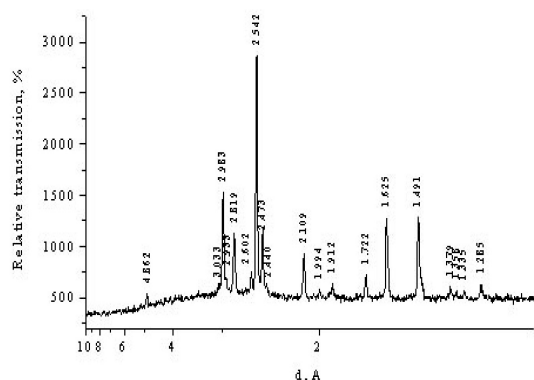


Fig.2. X-ray pattern of EAF powder

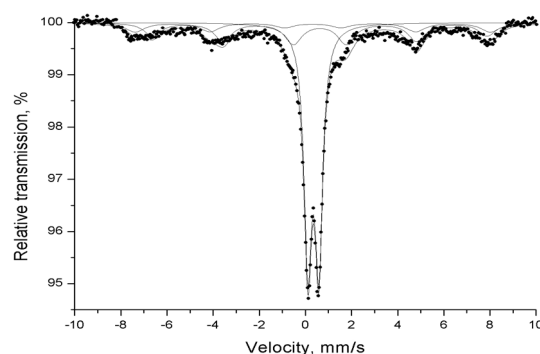


Fig.3. Mössbauer spectrum of EAF powder

of small quantities of an X-ray amorphous ingredient cannot be completely ruled out. The phase content is determined after computer processing of the experimental X-ray patterns. With the aim of mathematically distinguishing between the two phases with spinel structure ZnFe_2O_4 and Fe_3O_4 , the data for the elementary cell parameters was introduced from the relevant PDFs, namely 8,441 Å for the zinc ferrite and 8,394 Å for the magnetite.

The presence of the two zinc phases (ZnFe_2O_4 and ZnO) with a close content shows that the hydrometallurgical leaching of zinc will be rendered difficult. This is due to the fact that ZnFe_2O_4 is slightly soluble in diluted solutions of H_2SO_4 .

This gives the reason to search for other methods to utilize the zinc from this waste product.

The calculated ratios between the crystal phases (in %) is the following: ZnFe_2O_4 –21; ZnO –19; Fe_3O_4 –56; Pb_2O_3 –4.

The obtained experimental Mössbauer spectrum (Fig.3) has a complex profile and includes components with doublet and sextet characteristics. The mathematical processing

is initially made according to a model including 1 sextet and 1 doublet. The doublet component has parameters that can determine it as belonging to ZnFe_2O_4 . For the component with extra fine magnetic structure 1 sextet is initially introduced. The isomeric shift determined in this way is 0.42 mm/s. This value is situated between the values characteristic of the iron ions, included in the two sub-lattices of the magnetite. Because of this a second treatment was carried out with a model including 2 sextets having parameters similar to those of the magnetite. In the inclusion of this component the ferromagnetic characteristics of the sample were taken into consideration, as well as the data from the X-ray diffraction. The obtained values of the line width (about 3 times larger than the standard) are indicative of the presence of iron ions, which are included in a number of components with similar parameters. The possibility that other ions except iron ions (for example Zn) may be included in the magnetite structure cannot be ruled out too.

The results from the Mössbauer spectroscopy confirm the presence of two main iron-containing phases (Fe_3O_4 and

ZnFe₂O₄). The ratio of the two components – paramagnetic and ferromagnetic is 57:43 (Table 1).

time for heating and the temperature (Fig.4). More significant is the influence of the temperature factor. From the obtained results

Table 1. Results from the Mössbauer analysis of the powder

| Components | IS, mm/s | QS, mm/s | Heff, T | FWHM, mm/s | G, % |
|---|----------|----------|---------|------------|------|
| Sx1 – Fe ³⁺ _{tetra} , Fe _{3-x} O ₄ | 0.3 | 0 | 47.9 | 1.01 | 14 |
| Sx2 – Fe ^{2.5+} _{octa} , Fe _{3-x} O ₄ | 0.63 | 0 | 45.1 | 0.9 | 29 |
| Db-ZnFe ₂ O ₄ | 0.34 | 0.47 | - | 0.4 | 57 |

It can be presupposed that in a solution of H₂SO₄ the whole quantity of ZnO will dissolve, while ZnFe₂O₄ will remain in the cake. A part of the iron linked as Fe₃O₄ will also pass into the solution together with the ions of Cl and F. This confirms once again that it is impossible to begin directly with powder leaching in the zinc production.

The EAF powder subjected to study contains 2.05 % chlorine that contaminates the electrolyte. During the electroextraction of zinc the chlorine ions corrode the lead anodes, lead lining of the baths, lead or aluminium coils for cooling water. The lead ions passed into the solution and after that in the cathodic zinc. The concentration of chlorine in the electrolyte sometimes reaches 500-600 mg/dm³ at an admissible content of 100-150 mg/dm³.

The behavior of chlorine at the thermal treatment of EAF powder is studied at different temperatures and durations. The intervals in which these factors change are chosen on the basis of the data from the DTA and the operation practice of the wealz furnaces.

The obtained results show that the degree of chlorine removal is influenced by both the

it is clear that the influence of the time is manifested more strongly up to 30 – 40 min, after which there is hardly any change of the graphic dependencies.

It is indicative that at 1100–1200 °C and

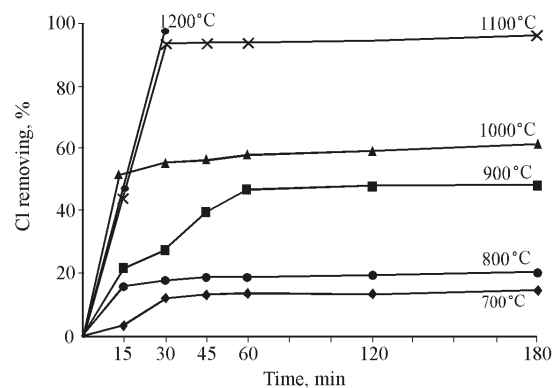


Fig.4. Degree of chlorine removal depending on the temperature and the duration of thermal treatment

duration of 30 min a degree of chlorine removal of over 95 % is achieved. These results show that at the processing of steel production powder in wealz furnaces a considerable part of the chlorine will pass into the wealz oxides, which will render them unusable for direct leaching with H₂SO₄.

It is imperative in such cases to take

precautions for preliminary removal of the Cl and F from wealz oxides before zinc leaching.

The obtained results for the removal of fluorine at tempering of up to 1200 °C in air medium are shown in Fig.5.

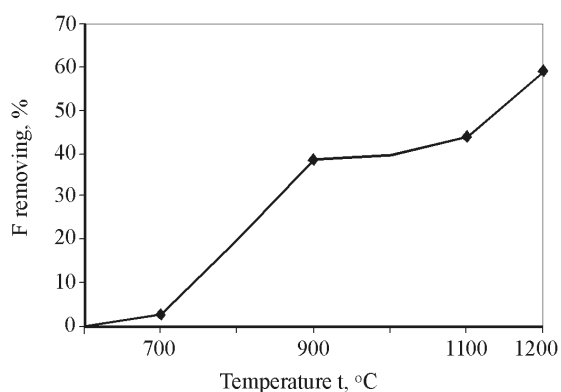


Fig.5. Degree of removal of F at thermal treatment ($\tau = 30$ min)

The results unambiguously show the positive influence of the increase of temperature on the degree of fluorine removal. A maximum degree was obtained at 1200 °C (59.0 %).

In comparison with the Cl removal in the same condition it is obvious that the degree of removal of F is considerably lower. This shows that a smaller part of F will pass in the wealz oxides compared to Cl, but yet its concentration will be high and will hinder the direct leaching of the wealz oxides. It is known from literature and the practical implementation of the processing of such powders that Cl can be leached with the help of H₂O, and for the leaching of F a favorable influence is the addition of Na₂CO₃.

In this connection an investigation was carried out about the behavior of Cl leached at different temperatures with and without

the utilization of Na₂CO₃ (Fig.6).

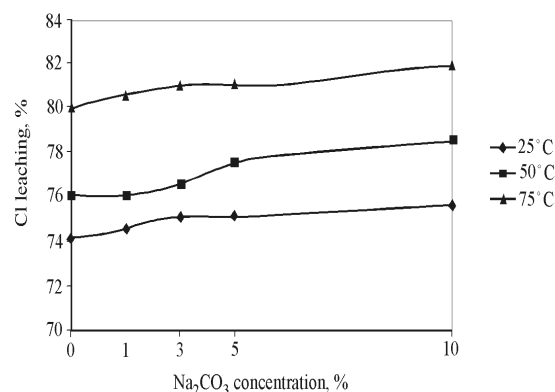


Fig.6. Degree of chlorine leaching depending on the concentration of Na₂CO₃ and the temperature ($\tau = 30$ min)

The presented results disclose that a considerable part of the chlorine passes into a solution even without the addition of Na₂CO₃ (over 75 %). The addition of Na₂CO₃ does not influence the degree of leaching of Cl. The influence of the temperature increase factor is of far greater significance.

Based on literature data, the practice of water-alkaline washing and the experiments carried out by us, it was established that the addition of Na₂CO₃ influences mainly the passing of F into a solution, but the degree of leaching of F does not exceed 20 %.

In recent years work on zinc electrolysis from a chloride solution has been more and more active. This process has a few advantages, especially when leaching raw materials or semi-finished products that have significant quantities of admixtures. Some of the most widely used reagents for zinc leaching are NaOH and NH₄Cl. In this connection an initial investigation was carried out on zinc leaching from EAF

powder using these two reagents.

The factor temperature of leaching was mainly studied at all other parameters constant (Figs. 7 and 8). The concentration of the NaOH and NH_4Cl solutions used is chosen on the basis of literature data.

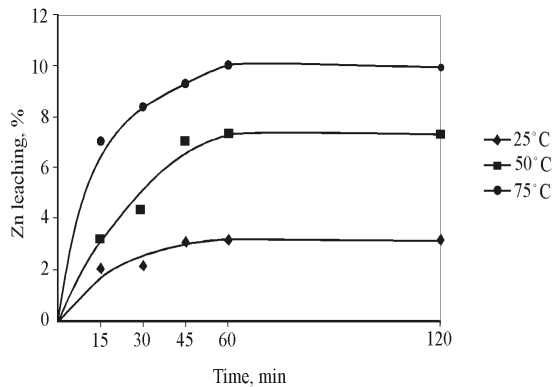


Fig. 7. Degree of zinc leaching with a 5% solution of ammonia chloride for different temperatures and times

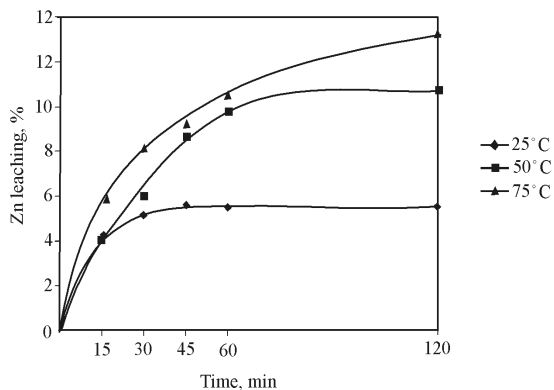


Fig. 8. Degree of zinc leaching with a 5% solution of NaOH

In both cases of leaching it is obvious that the factors temperature and time of leaching influence positively the passing of zinc into a solution.

However, we have to note that the obtained results for the degree of zinc

leaching at these conditions are very low. This is probably due to the high content of the stable and hard to dissolve ZnFe_2O_4 , contained in the EAF powder.

A main part of the iron in the researched powders is in the form of Fe_3O_4 . At the same time the zinc is almost equally distributed between ZnFe_2O_4 and ZnO . Having in mind that the two zinc-containing phases are paramagnetic, and Fe_3O_4 is highly magnetic, it is of a certain interest to check the possibility of magnetic separation of the powder.

The results obtained from the magnetic separation showed that when the process is repeatedly carried out, a magnetic fraction with a very low zinc content, and a non-magnetic fraction with a zinc content exceeding the initial one more than twice can be obtained. This gives the reason to propose a technological scheme for the processing of EAF powders (Fig. 9), including magnetic separation.

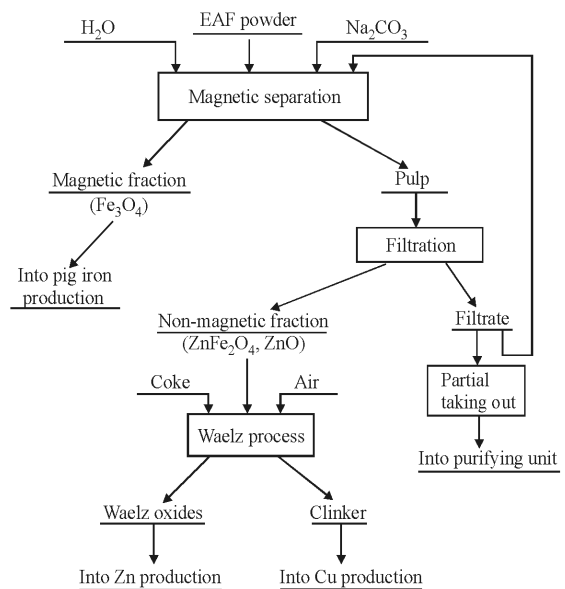


Fig. 9. Technological scheme for processing of EAF powders using magnetic separation

4. Conclusion

1. A detailed characterization of EAF powders was made using chemical analysis, XRD, DTA and TGA and Mössbauer spectroscopy. It was established that main phases in the powder are (in mass %): ZnFe₂O₄–21; ZnO–19; Fe₃O₄–56; Pb₂O₃–4.

2. At the thermal treatment of the powders up to 1200 °C 95 % of the chlorine and 59 % of fluorine are removed from them and pass into the gas phase.

3. The leaching of zinc from the powders with the help of NaOH and NH₄Cl shows a low degree of passing of the zinc into a solution.

4. The washing of the EFA powders with water and Na₂CO₃ leads to the passing of a considerable part of the chlorine into the solution (over 75%), while the degree of leaching of F does not exceed 20 %.

5. A technological scheme was proposed for the processing of EAF powders using preliminary magnetic separation.

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