

# Zinc extraction during recycling of electric arc furnace dust by chlorine-containing polymer wastes

**D. I. Bludova**, Assistant of the Department of Non-Ferrous Metals Metallurgy, Institute of New Materials and Technologies<sup>1</sup>, e-mail: dana.bludova@urfu.ru

**S. V. Mamyachenkov**, Professor, Head of the Department of Nonferrous Metals Metallurgy, Institute of New Materials and Technologies<sup>1</sup>, e-mail: s.v.mamiachenkov@urfu.ru

<sup>1</sup>Ural Federal University named after the First President of Russia B.N. Yeltsin, Ekaterinburg, Russia.

From an environmental point of view, dust from the melting of galvanized steel scrap in electric arc furnaces is a problematic waste stream. In particular, it is impossible to store dust in open areas due to high content of toxic components (lead, zinc, cadmium, etc.). At the same time, the extraction of non-ferrous metals from electric-arc melting dust can make it a valuable source of secondary raw materials and reduce the impact on the environment. In a laboratory study, zinc was extracted from electric arc smelting dust by a chlorination method with a waste halogen-containing polymer. Roasting of galvanized scrap melting dust together with polyvinyl chloride (PVC) waste as a chlorination agent at 950 °C resulted in the evaporation of about 80 wt.% zinc in an oxidizing atmosphere and more than 95 wt.% zinc in a neutral atmosphere. The use of PVC waste in the firing process provides the release of gaseous HCl, which is an effective reagent for the chlorination of zinc compounds in dusts. The presence of solid carbon from polymer pyrolysis in the mixture accelerates the course of chlorination reactions, which is confirmed by the thermodynamic calculations given above. Energy dispersive X-ray spectroscopy of the cinder obtained by roasting at 950 °C in a neutral atmosphere showed that the dry residue of the material in the proposed process does not contain zinc.

**Key words:** electric-arc furnace dust, chlorination, zinc extraction, zinc distillation, neutral atmosphere.

**DOI:** 10.17580/nfm.2023.02.05

## Introduction

The increasing use of galvanized steel in the production of automotive bodies and coatings is leading to an increase in zinc content in electric arc furnace (EAF) dust during the processing of zinc-containing scrap. Electric-arc furnace dust is a complex material that mainly contains zinc, iron and calcium. Other metals such as lead, silicon, aluminum, manganese, magnesium, chromium, nickel, copper, and cadmium occur in lower concentrations. Most of these elements are found in combination with oxygen, but they can also be in the form of chlorides, fluorides, sulfates, and sulfides [1]. The elevated level of zinc in the dust makes its normal recirculation path through the sinter plant or furnace problematic due to the harmful effects of zinc on the technological components of the unit. In addition, the direct turnover of EDF dust results in zinc enrichment of the material in a continuous cycle.

In recent years, researchers have tried to use various chlorinating agents to solve this problem; to effectively chlorinate and ignite the volatile components, additional chlorine, in the form of a solid or gaseous reagent, is added to the metal-containing material, and the metal chlorides with low ignition temperatures are separated from the non-volatile substances when the mixture is roasted [2]. If gaseous chlorinating agents (mainly Cl<sub>2</sub>) are used, they are introduced into the atmosphere directly during roasting, and if the process is based on the interaction of the material with solid chlorinating agents (MgCl<sub>2</sub>, NaCl, KCl, CaCl<sub>2</sub>, NH<sub>4</sub>Cl, etc.), they are mixed with non-ferrous metal containing waste before loading [3].

Such a process has been successfully applied to the treatment of different types of waste, for example, to remove

lead, zinc, cadmium and other metals which, under these conditions, form volatile chlorides from municipal solid waste incineration ash [4–5], from mineral raw materials [6–7], from molten slag [8] and from electronic scrap [9]. However, many of these processes utilize reagents that are relatively high in cost and require strict flow control. In order to achieve the technical performance of an economically viable process, it is first of all necessary to reduce the cost of consumables.

The presented study aims to extract zinc from a complex in composition and difficult to process type of waste – metallurgical dust from the melting of galvanized steel scrap, by means of chlorination and distillation process. We propose polyvinyl chloride (PVC) waste, a chlorinated plastic, as a chlorinating agent, which is a cheap alternative to CaCl<sub>2</sub>, MgCl<sub>2</sub>, Al<sub>2</sub>Cl<sub>3</sub> or FeCl<sub>2</sub>. In the process of heating the polymer, the gaseous hydrochloric acid generated by the decomposition of PVC acts as a chlorination agent. In the proposed process, the joint treatment of the two types of waste avoids the consumption of natural materials and reduces the cost of recycling secondary raw materials.

Since zinc chloride has a higher volatility than zinc metal, this allows it to be extracted at lower temperatures and atmospheric pressure. The special feature and advantage of the proposed chlorination method is that one type of waste is used to treat another type of waste.

An important condition of the waste chlorination process is the atmosphere inside the furnace space. If the oxidizing environment is created by roasting the charge in an air stream, with chlorine gas feed or with oxygen purging, a specially prepared mixture of neutral gas (argon or nitrogen) is required to obtain a neutral environment.

The next determining factor in chlorination is the temperature at which the interaction reactions between the components take place. Chlorination-evaporation processes can take place at temperatures below or above the melting point, which depends on the proportion of the main components of the material [10]. Metallurgical dusts consisting of oxides, ferrites and silicates of metals are characterized by rather high melting points, remain in solid state during roasting, while zinc chlorides of lead and other metals volatilize away [11].

When treating a waste mixture, the interaction between the two types of material during chlorination should also be ensured. The developed contact surface of the material with the chlorine-containing agent simplifies the formation of metal chlorides in the heterogeneous material, the transfer of metal chlorides to the surface and their evaporation. In our case, dense contact was achieved, firstly, by the dispersity of EDF dust itself, and secondly, by creating a homogeneous mixture of dust with powdered PVC.

We used PVC as a chlorinating agent for zinc volatilization, which has a low melting point, thus contributing to a more complete reaction when heated. PVC plastic waste is an organic polymer, which in solid state has low density and high chlorine content (about 56.7%), so at temperatures above 170 °C it decomposes rapidly, with the release of gaseous HCl and organic pyrolysis products. One of such products is the residue of plastic combustion — solid carbon, present in the initial material in the amount of 10 wt.%.

To verify the interaction of the polymer pyrolysis products — gaseous hydrochloric acid in the presence of ash residue, with zinc compounds in the dust, thermodynamic calculations for zinc oxide and zinc ferrite in the presence and in the absence of oxygen were previously performed. This allowed to construct different dependences of the

thermodynamic character of the process of zinc chlorination in EDF dust by means of PVC.

### Initial materials

In laboratory studies fine dust from remelting of OJSC “Severstal” galvanized steel scrap with zinc content of 36.0 wt.% was used. Dust humidity was 1.5%.

Chemical composition of dust, %: Zn — 20–43; Fe — 34–36; Pb — 4.0–5.0; C — 2.4–4.2; S — 1.8–2.0; Na — 2.6–3.0; K — 2.2–2.5; F — 0.2–0.8; Cl — 4.0–6.0.

Phase analysis of electrometallurgical dust was carried out with the integrated use of X-ray and Mössbauer spectrometry methods complementing each other, as well as with the use of electron microscopy.

The spectrum of OJSC “Severstal” electric furnace sludge is shown in Fig. 1.

Fig. 2 shows an image of a dust sample from an electric steelmaking furnace of OJSC “Severstal”. As can be seen from the image, the material consists of a collection of small particles, a small number of larger spherical shaped particles with sharp boundaries, and large aggregated particles of spherical or indeterminate shape. The size of fine particles is in the range of 100–300 nm. The size of melted particles with clear boundaries reaches 1 µm, aggregated particles, which are conglomerates of small particles, reach a size of 10 µm. Fine particles are mainly represented by  $ZnFe_2O_4$  and  $Fe_3O_4$ , which represent about 80–90% of the total dust. Medium-sized particles are oxides or silicates of metals.

EAF dust is characterized as technogenic powdery multi-component micro-sized oxidic materials based on iron oxides, containing zinc. Zinc in dust is represented in the form of zincite, franklinite, that is, it is present in the spinel structure of magnetite, replacing iron atoms. It is possible to reduce zinc from zincite by carbon in the solid state at temperatures above 600–700 °C.

Initial dust, cinder after roasting and cake, obtained after cinder washing, were subjected to qualitative analysis by energy-dispersive X-ray fluorescence spectrometer SHIMADZU EDX-7000 (Japan).

After qualitative analysis of the cinder, it was subjected to leaching with deionized water to remove soluble chlorides. Energy dispersive spectroscopy of the cake obtained after filtration and drying at 105 °C was performed to obtain information on the zinc content of the dry residue.

Quantitative analysis of the cold solution obtained in the trap was performed by atomic absorption spectrometry on an “Analytik jena nova A 300” instrument.

Thermodynamic calculations were performed using the application program package HCS Chemistry ver. 6.1 (Outocumpu, Finland).

The PVC was construction waste powdered to a coarseness of 100 microns. In laboratory studies, the materials were mixed in 1:1 ratio, that is, based on the elemental zinc content in EAF dust to the chlorine content in terms of the hydrochloric acid amount released from given amount of polymer (58.3%), in the mixture “EAF dust:

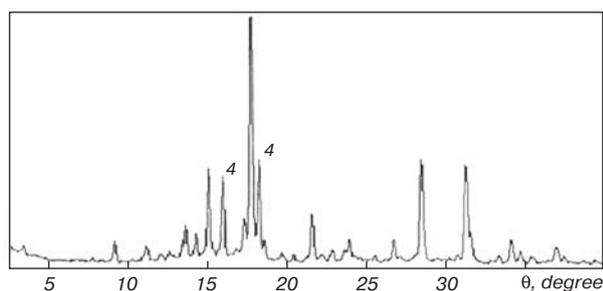


Fig. 1. X-ray phase spectrum of electric furnace dust of Severstal plant (the positions of zinc oxide lines are indicated (4))

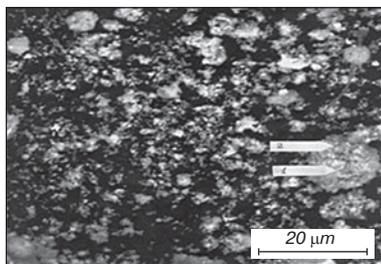


Fig. 2. EDS image of OJSC “Severstal” dust

chloride agent (PVC)", a ratio of Zn/HCl equal to 0.62 was obtained. Since it is known that zinc chloride, compared to chlorides of other metals, has a particularly high vapor pressure and volatilizes, including during chlorination [12], there are publications where the influence of the content of zinc compounds on the pyrolysis of chlorine-containing plastic has been determined. Thus it was found that at the joint pyrolysis of these components about 2/3 of chlorine is consumed for the formation of  $ZnCl_2$  [13], and the ratio of 1:1 was taken as optimal.

### Chlorination experiments

The experiments were performed in a horizontal quartz glass tube (500 mm long, 28 mm inner diameter) heated by an electric furnace (Fig. 3). The use of quartz glass as reactor materials limited the maximum temperature to 1000 °C. Since PVC decomposition starts at temperatures above 170 °C [14], the operating temperatures of the process were chosen to be between 300 °C and 950 °C.

Before the experiment, 4.0 g of steelmaking dust was mixed with a chlorinating agent (PVC) at a Zn/HCl mass ratio of 0.62 using a mortar and pestle. The prepared sample was then placed in an aluminum oxide boat, which was placed in the center of a tubular reactor. The sample was then heated to the desired temperature (from 300 to 950 °C in 50 °C increments) at a heating rate of about 0.6 °C·s<sup>-1</sup> in a stream of air or neutral gas using a variable flow rate compressor, at a rate of 2–3 dm<sup>3</sup>/min. The overpressure was 10 mmHg, the flue gas discharge was from the other end of the quartz tube, and the exhaust gas was sanitized by barbotage in a volatile product trap filled with sulfuric acid (1 mol·l<sup>-1</sup>) to prevent hydrolysis reaction and to capture zinc chloride vapor. The sample in the furnace was held at the operating temperature for 60 min.

After the experiment, the reactor tube was washed with 1 mol·l<sup>-1</sup> sulfuric acid to collect products ( $ZnCl_2$ ) that had condensed on the cold sections. The resulting solution was combined with sulfuric acid trap solution and diluted for quantitative analysis by atomic absorption spectrometry.

### Thermodynamic basis

To determine the direction of the interaction reactions between the EAF dust sample and the chlorination reagent used, a thermodynamic analysis of the chlorination of the mixture components should be carried out [15]. The formation of intermediates, particularly ferric chloride, can be both a driving and inhibiting force in this process. Calculation of the Gibbs free energy change of the hydrochloric acid chlorination reactions of zinc oxide and zinc ferrite in dust in the presence and absence of oxygen access was performed using HCS Chemistry ver. 6.1. The calculation was performed assuming that all compounds are in a stable state.

This calculation did not include the organic phase consisting of  $C_2H_3Cl$ . Although the degradation of polyvinyl chloride is accompanied by the formation of thermodynamically favored gases HCl, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub>, as well as an ash residue, it was conventionally assumed that zinc compounds react with the main degradation products of PVC – HCl and solid carbon.

According to the data of Table 1, the most probable mechanism of zinc oxide chlorination by reactions (3), (4) and (9), i.e. in an air current (3–4) or with simultaneous decomposition of zinc ferrite in the presence of excess hydrochloric acid and solid carbon (9), when there is chlorination of zinc and iron at once. Since the reaction (9) depends on the content of both zinc oxide and zinc ferrite, it is realized until all  $ZnFe_2O_4$  is consumed. The addition of solid carbon to the system has a strong effect on the chemical equilibrium; in its presence as an ash residue of PVC degradation, the chlorination process proceeds more intensively by reactions (3–4) at almost any operating temperature, and by reactions (1) and (5) when the roasting temperature rises above 600 °C. The use of hydrochloric acid alone has a limitation, according to thermodynamic calculations reactions (6–7) become less likely when heated to 900 °C. At temperatures from 0 to 950 °C there can also occur chlorination of zinc oxide

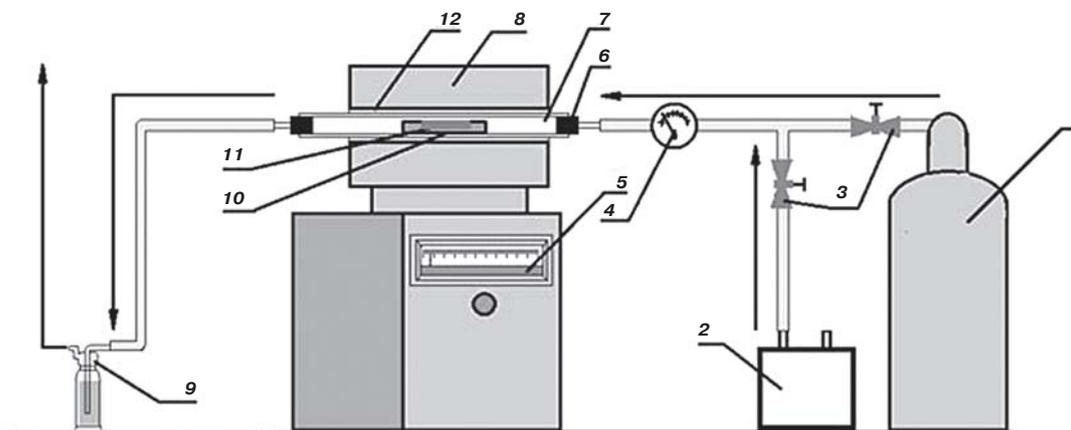


Fig. 3. Apparatus scheme of laboratory research on chlorinating roasting of steelmaking dust:

1 – argon tank, 2 – air compressor, 3 – stop valve, 4 – pressure regulator, 5 – temperature controller, 6 – plug, 7 – quartz tube, 8 – horizontal tube furnace, 9 – gas trap, 10 – alumund boat, 11 – mixture weight, 12 – furnace lining

by iron chloride, according to reaction (10), and in the presence of oxygen the probability of interaction between chlorides is much higher (reaction (11), **Table 1**).

The behavior of zinc ferrite in the presence of PVC is more complicated and is not determined unambiguously. The interaction of  $\text{ZnFe}_2\text{O}_4$  with  $\text{HCl}$  is possible in the presence of carbon by a series of parallel reactions (**Table 2**), their course is determined by obtaining zinc chloride, iron chloride, iron (II) oxide or iron (III) oxide as products. Thus, chlorination of zinc ferrite with  $\text{HCl}$  does not proceed directly (reactions (12), (19), (22), (25) in **Table 2**), but it is possible indirectly, through interaction with previously formed iron chloride, in the presence of

hydrochloric acid and oxygen at temperatures from 0 to 600–700 °C in reaction (29), or chlorination directly with  $\text{FeCl}_2$ , when roasting is carried out at temperatures of about 900 °C (reaction (28), **Table 2**). Since, when the system of metal oxides with  $\text{HCl}$  is heated, a phase containing metal chlorides is gradually formed in it.

Overall, the analysis shows that  $\text{HCl}$  is a thermodynamically efficient chlorinating agent. The water produced during acid neutralization is removed from the system either by volatilization or by reaction with residual organic matter and carbon after PVC decomposition. The resulting  $\text{CO}$  is a potential reducing agent, which, remaining in the furnace space, can lead to the formation of

Table 1  
Values of Gibbs free energy change of zinc oxide chlorination reactions at different temperatures

No.	Chlorination reaction	$\Delta G$ , kJ/mol at $t$ , °C		
		300	600	950
1	$\text{ZnO}_{(l)} + 2\text{HCl}_{(g)} \rightarrow \text{ZnCl}_{2(l)} + \text{H}_2\text{O}_{(g)}$	-1.53	-13.43	-25.80
2	$2\text{ZnO}_{(l)} + 2\text{HCl}_{(g)} + \text{C}_{(s)} = \text{ZnCl}_{2(g)} + \text{Zn}_{(l)} + \text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	75.53	43.20	2.45
3	$\text{ZnO}_{(s)} + 2\text{HCl}_{(g)} + \text{C}_{(s)} + 0.5\text{O}_{2(g)} = \text{ZnCl}_{2(g)} + \text{CO}_{(g)} + \text{H}_2\text{O}_{(g)}$	-163.60	-202.48	-245.65
4	$\text{ZnO}_{(s)} + 2\text{HCl}_{(g)} + \text{C}_{(s)} + \text{O}_{2(g)} = \text{ZnCl}_{2(g)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(g)}$	-296.62	-409.11	-421.89
5	$2\text{ZnO}_{(s)} + 4\text{HCl}_{(g)} + \text{C}_{(s)} = 2\text{ZnCl}_{2(g)} + \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$	32.65	-23.24	-87.06
6	$\text{ZnO}_{(s)} + \text{FeO}_{(s)} + 4\text{HCl}_{(g)} = \text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$	-116.74	-53.29	3.15
7	$\text{ZnO}_{(s)} + \text{ZnFe}_2\text{O}_{4(s)} + 4\text{HCl}_{(g)} = 2\text{ZnCl}_{2(g)} + \text{Fe}_2\text{O}_{3(s)} + 2\text{H}_2\text{O}_{(g)}$	-94.80	-34.86	24.81
8	$\text{ZnO}_{(s)} + \text{ZnFe}_2\text{O}_{4(s)} + 8\text{HCl}_{(g)} = 2\text{ZnCl}_{2(g)} + 2\text{FeCl}_{2(g)} + 4\text{H}_2\text{O}_{(g)} + 0.5\text{O}_{2(g)}$	-1.66	93.06	169.07
9	$\text{ZnO}_{(s)} + \text{ZnFe}_2\text{O}_{4(s)} + 8\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = 2\text{ZnCl}_{2(g)} + 2\text{FeCl}_{2(g)} + 4\text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-199.20	-104.78	-29.97
10	$\text{ZnO}_{(s)} + \text{FeCl}_{2(g)} = \text{ZnCl}_{2(g)} + \text{FeO}_{(s)}$	-39.33	-37.44	-35.98
11	$\text{ZnO}_{(s)} + \text{FeCl}_{2(g)} + \text{C}_{(s)} + 0.5\text{O}_{2(g)} = \text{ZnCl}_{2(g)} + \text{FeO}_{(s)} + \text{CO}_{(g)}$	-103.34	-178.37	-250.15

Table 2  
Values of Gibbs free energy changes of zinc ferrite chlorination reactions at different temperatures

No.	Chlorination reaction	$\Delta G$ , kJ/mol at $t$ , °C		
		300	600	950
12	$\text{ZnFe}_2\text{O}_{4(s)} + 8\text{HCl}_{(g)} \rightarrow \text{ZnCl}_{2(g)} + 2\text{FeCl}_{3(g)} + 4\text{H}_2\text{O}_{(l,g)}$	72.62	121.78	172.21
13	$\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + \text{C}_{(s)} = \text{ZnCl}_{2(g)} + 2\text{FeCl}_{2(g)} + 3\text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	-107.25	-66.80	-49.43
14	$\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = \text{ZnCl}_{2(s)} + 2\text{FeCl}_{2(s)} + 3\text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-142.72	-75.60	-27.62
15	$\text{ZnFe}_2\text{O}_{4(s)} + 4\text{HCl}_{(g)} + \text{C}_{(s)} = \text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + \text{FeO}_{(s)} + 2\text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	-46.99	-42.70	-53.93
16	$\text{ZnFe}_2\text{O}_{4(s)} + 4\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = \text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + \text{FeO}_{(s)} + 2\text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-82.47	-51.49	-32.12
17	$\text{ZnFe}_2\text{O}_{4(s)} + 2\text{HCl}_{(g)} + \text{C}_{(s)} = \text{ZnCl}_{2(g)} + 2\text{FeO}_{(s)} + \text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	13.27	-18.59	-58.42
18	$\text{ZnFe}_2\text{O}_{4(s)} + 2\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = \text{ZnCl}_{2(g)} + 2\text{FeO}_{(s)} + \text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-22.21	-27.39	-36.61
19	$2\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} = 2\text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + \text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + 0.5\text{O}_{2(g)}$	50.49	111.47	157.12
20	$2\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + \text{C}_{(s)} = 2\text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + \text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	-111.58	-77.58	-62.73
21	$2\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = 2\text{ZnCl}_{2(g)} + \text{FeCl}_{2(g)} + \text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-147.05	-86.37	-40.92
22	$\text{ZnFe}_2\text{O}_{4(s)} + 2\text{HCl}_{(g)} \rightarrow \text{ZnCl}_{2(g)} + \text{Fe}_2\text{O}_{3(s)} + \text{H}_2\text{O}_{(g)}$	16.63	10.07	1.70
23	$\text{ZnFe}_2\text{O}_{4(s)} + 2\text{HCl}_{(g)} + \text{C}_{(s)} = \text{ZnCl}_{2(g)} + \text{Fe}_2\text{O}_{3(s)} + \text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	15.01	4.93	-13.38
24	$\text{ZnFe}_2\text{O}_{4(s)} + 2\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = \text{ZnCl}_{2(g)} + \text{Fe}_2\text{O}_{3(s)} + \text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-20.46	-3.87	8.43
25	$3\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} = 3\text{ZnCl}_{2(g)} + 2\text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + 0.5\text{O}_{2(g)}$	46.16	100.69	143.83
26	$3\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + \text{C}_{(s)} = 3\text{ZnCl}_{2(g)} + 2\text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$	-115.91	-88.35	-76.02
27	$3\text{ZnFe}_2\text{O}_{4(s)} + 6\text{HCl}_{(g)} + 0.5\text{C}_{(s)} = 3\text{ZnCl}_{2(g)} + 2\text{Fe}_3\text{O}_{4(s)} + 3\text{H}_2\text{O}_{(g)} + 0.5\text{CO}_{2(g)}$	-151.39	-97.14	-54.21
28	$\text{ZnFe}_2\text{O}_{4(s)} + \text{FeCl}_{2(s)} \rightarrow \text{ZnCl}_{2(l)} + \text{Fe}_3\text{O}_{4(s)}$	50.62	4.98	-37.75
29	$\text{ZnFe}_2\text{O}_{4(s)} + \text{FeCl}_{2(s)} + 4\text{HCl}_{(g)} + \text{O}_{2(g)} = \text{ZnCl}_{2(g)} + \text{Fe}_3\text{O}_{4(s)} + 2\text{H}_2\text{O}_{(g)} + 2\text{Cl}_{2(g)}$	-44.03	-10.05	35.11

metallic zinc. This transformation (reaction (2), **Table 1**) is possible when the mixture is heated above 950 °C.

The above thermodynamic justifications prove that PVC has the ability to chlorinate metal compounds during the firing of steelmaking dusts. The change in Gibbs energy has negative values for the overwhelming number of reactions in the whole temperature range investigated. This once again emphasizes the fact that the evaporation of zinc in the form of its chloride is realized in the presence of gaseous hydrochloric acid. By reactions (13–16) the chlorination of zinc ferrite immediately to  $ZnCl_2$  and  $FeCl_2$  is realized.

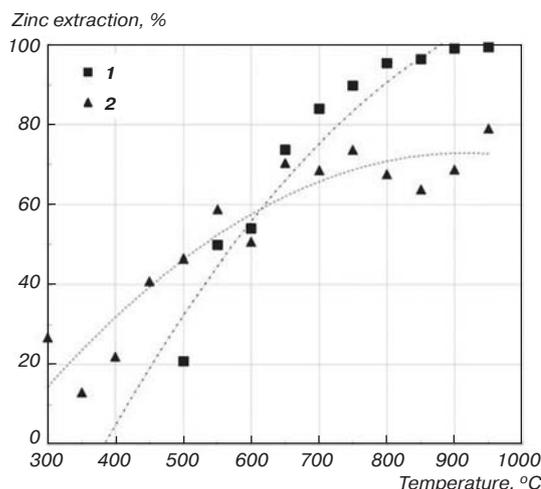
### Discussion of the experimental results

The regularities of the process of zinc chloride volatilization from dust from remelting of galvanized steel scrap using PVC as a chlorine agent in different atmospheres in the range of operating temperatures from 300 °C to 950 °C with a step of 50 °C were studied in laboratory conditions. Graphical dependence of zinc extraction from dust in the form of  $ZnCl_2$  on the mixture roasting temperature in air and in an inert gas current is shown in **Fig. 4**.

It was demonstrated that in case of roasting in oxidizing atmosphere zinc volatilization started more intensively and did not have an unambiguous direct correlation with temperature. Since PVC dehydrochlorination occurs at relatively low temperatures around 250 °C, HCl and other gaseous reaction products are formed in this process within a short time interval [16]. Thus, zinc evaporation in the presence of carbon in the polymer composition occurred already at 300 °C and reached 80% at the maximum temperature of 950 °C, which is consistent with thermodynamic calculations.

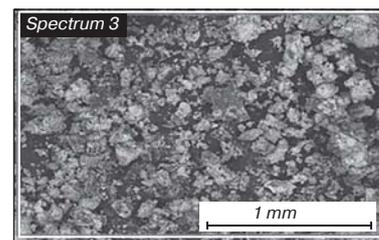
The highest degree of zinc recovery was achieved by roasting in an inert environment, although the reaction of dust components with PVC in air started more rapidly. If in the presence of oxygen this value changed stepwise and decreased in the range from 50 to 80 wt.%, in neutral gas atmosphere a constant decrease of zinc content in the solid residue to 5 wt.% was observed. As can be observed, the critical point was the roasting temperature of 600 °C, because at conditions of 600 °C, carbon combustion occurs, which has an intensifying effect on the metal chlorination process.

The decomposition of PVC produced large gas bubbles, which gave the mixture of materials a spongy appearance when roasted. The pores where the gaseous hydrochloric acid came to the surface from the thickness of the suspension permeated the sample and promoted uniform



**Fig. 4.** Graphical dependence of zinc extraction into the gas phase during chlorination of EDP dust with polymer in oxidizing and neutral atmosphere as a function of roasting temperature (reaction duration 60 min, Zn/HCl ratio = 0.62): 1 — zinc extraction by argon roasting; 2 — zinc extraction by air roasting

**Fig. 5.** Microphotograph of cake after washing of cinder obtained by roasting at 950 °C in a neutral atmosphere



mixing of the two materials. The large specific surface area created by the expansion of the mixture resulted in efficient evaporation of zinc chloride.

The cinder after thermal degradation of the chlorinated polymer did not contain any carbonaceous residues. Thermodynamic calculations have shown that the presence of HCl and ash residue simultaneously during roasting leads to the formation of zinc and iron chlorides in parallel, in some cases also iron oxides, in addition, the oxidation of carbon to CO and CO<sub>2</sub> is also predicted.

After roasting, the obtained cinder was leached with water to remove soluble metal chlorides and the cake obtained after filtration was sent for energy dispersive spectroscopy. The result is shown in **Table 3**, which shows the absence of zinc compounds, that is, it can be argued that the zinc contained in the steelmaking dust sample during chlorination with PVC waste was successfully converted

Table 3

Result of elemental analysis of the cake sample after washing of cinder obtained by firing at 950 °C in neutral atmosphere, wt. %

Spectrum	O	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Mn	Fe	Total
Spectrum 1	30.81	2.81	0.60	0.29	1.41	0.70	12.30	1.98	5.55	0.30	2.69	40.56	100.00
Spectrum 2	30.50	2.78	0.70	–	1.48	0.74	12.48	1.91	5.57	0.22	2.54	41.09	100.00
Spectrum 3	30.69	2.87	0.52	0.26	1.49	0.64	12.50	1.96	5.56	0.19	2.58	40.75	100.00
Max.	30.81	2.87	0.70	0.29	1.49	0.74	12.50	1.98	5.57	0.30	2.69	41.09	–
Min.	30.50	2.78	0.52	0.26	1.41	0.64	12.30	1.91	5.55	0.19	2.54	40.56	–

to the form of  $ZnCl_2$ , which was evaporated during roasting, and its residues were removed during washing. The image obtained by microphotography of the cake sample (Fig. 5) demonstrates the particle shape characteristic of iron oxides.

### Conclusion

Chlorination of metallurgical dust and evaporation of zinc as  $ZnCl_2$  in the presence of PVC as a chlorinating agent were investigated. The use of PVC waste provides an opportunity to utilize one type of waste to treat another — metallurgical dust. HCl released during PVC decomposition at relatively low temperatures triggers chlorination reactions of zinc compounds. The carbonaceous residue is more stable, it reacts at higher temperatures (above 600 °C), reducing zinc over a longer period of time.

1. In this process, thermodynamically preferable was the treatment in a neutral medium in the presence of carbon, which was provided by the process of thermal degradation of the polymer containing carbon molecules in its composition. Roasting of galvanized scrap remelting dust together with polyvinyl chloride (PVC) waste as a chlorination agent at 950 °C in a neutral gas stream leads to evaporation of more than 95 wt.% of zinc.

2. The cinder obtained by roasting the dust mixture with PVC in air for 1 hour contained about 20 wt.% zinc. Further treatment of the obtained cinder or selection of chlorination conditions is required.

3. It is assumed that when the ratio of zinc to hydrochloric acid content is changed to a lower side, zinc extraction during chlorination will be more active due to the excess of HCl.

4. An advantage of the process may be the ability to extract volatile zinc chloride from toxic steelmaking dust by chlorination with chlorinated polymer waste at relatively low process temperatures.

5. When implementing the technology in production for purification of the obtained product from organic residues of pyrolysis it is proposed to capture zinc chloride vapors using a wet scrubber, at this stage ozonation or UV-irradiation of the solution will be required. In such a case further, zinc chloride, hydroxide or oxide can be obtained from aqueous medium by known methods as a commercial zinc product, depending on the customer's needs.

### References

1. Toporkova Yu. I., Bludova D., Mamyachenkov S. V., Anisimova O. S. A Review of Processing Methods for Electric Arc Furnace Dust. *iPolytech Journal*. 2021. Vol. 25, Iss. 5. pp. 643–680.
2. Wang S.-J., He P.-J., Lu W.-T., Shao L.-M., Zhang H. Comparison of Pb, Cd, Zn, and Cu Chlorination During Pyrolysis and Incineration. *Fuel*. 2017. Vol. 194. pp. 257–265.
3. Lu X. L., Wei L., Liu Y. S. Effect of Chlorine-Containing Compounds on Evaporation of Heavy Metals in Secondary Gasification of Fly Ash From Municipal Solid Waste Incinerator. *Acta Scientiarum Naturalium Universitatis Pekinensis*. 2012. Vol. 48, Iss. 1. pp. 133–138.
4. Nowak B., Rocha S. F., Aschenbrenner P. Heavy Metal Removal from MSW Fly Ash by Means of Chlorination and Thermal Treatment: Influence of the Chloride Type. *Chemical Engineering Journal*. 2012. Vol. 179, Iss. 1. pp. 178–185.
5. Wang X.-T., Xu B., Zhao D.-N., Jin B.-S. Experimental Analysis of Heavy Metals Behavior During Melting Process of Fly Ashes from MSWI Under Different Atmospheres. *4<sup>th</sup> International Conference on Bioinformatics and Biomedical Engineering, Chengdu, China, 18–20 June 2010*. pp. 1–4.
6. Giergiczny Z., Król A. Immobilization of Heavy Metals (Pb, Cu, Cr, Zn, Cd, Mn) in the Mineral Additions Containing Concrete Composites. *Journal of Hazardous Materials*. 2008. Vol. 160, Iss. 2-3. pp. 247–255.
7. Kanari N., Gaballah I., Allain E. A Low Temperature Chlorination–Volatilization Process for the Treatment of Chalcopyrite Concentrates. *Thermochimica Acta*. 2001. Vol. 373, Iss. 1. pp. 75–93.
8. Kageyama H., Osada S., Nakata H., Kubota M., Matsuda H. Effect of Coexisting Inorganic Chlorides on Lead Volatilization from  $CaO - SiO_2 - Al_2O_3$  Molten Slag Under Municipal Solid Waste Gasification and Melting Conditions. *Fuel*. 2013. Vol. 103. pp. 94–100.
9. Gustafsson A. M. K., Steenari B.-M., Ekberg C. Recycling of CIGS Solar Cell Waste Materials — Separation of Copper, Indium and Gallium by High-Temperature Chlorination Reaction with Ammonium Chloride. *Separation Science and Technology*. 2015. Vol. 38. pp. 2415–2425.
10. Yu J., Sun L., Ma C., Qiao Y., Xiang J., Hu S., Yao H. Mechanism on Heavy Metals Vaporization from Municipal Solid Waste Fly Ash by  $MgCl_2 \cdot 6H_2O$ . *Waste Management*. 2016. Vol. 49. pp. 124–130.
11. Kurashima K., Matsuda K., Kumagai S., Kameda T., Saito Y., Yoshioka T. A Combined Kinetic and Thermodynamic Approach for Interpreting the Complex Interactions During Chloride Volatilization of Heavy Metals in Municipal Solid Waste Fly Ash. *Waste Management*. 2019. Vol. 87. pp. 204–217.
12. Santos F., Brocchi E., Araújo V., Souza R. Behavior of Zn and Fe Content in Electric Arc Furnace Dust as Submitted to Chlorination Methods. *Metallurgical and Materials Transactions: B*. 2015. Vol. 46. P. 1729–1741.
13. Masuda Y., Uda T., Terakado O., Hirasawa M. Pyrolysis Study of Poly(vinyl chloride)–Metal Oxide Mixtures: Quantitative Product Analysis and the Chlorine Fixing Ability of Metal Oxides. *Journal of Analytical and Applied Pyrolysis*. 2006. Vol. 77, Iss. 2. pp. 159–168.
14. Yoo J.-M., Kim B.-S., Lee J.-C., Kim M.-S., Nam C.-W. Kinetics of the Volatilization Removal of Lead in Electric Arc Furnace Dust. *Materials Transaction*. 2005. Vol. 46, Iss. 2. pp. 323–328.
15. Yuan G., Chen D., Yin L., Wang Z., Zhao L., Wang J. Y. High Efficiency Chlorine Removal from Polyvinyl Chloride (PVC) Pyrolysis with a Gas-Liquid Fluidized Bed Reactor. *Waste Management*. 2014. Vol. 34, Iss. 6. pp. 1045–1050.
16. Yoshioka T., Saitoh N., Okuwaki A. Temperature Dependence on the Activation Energy of Dechlorination in Thermal Degradation of Polyvinylchloride. *Chemical Letters*. 2005. Vol. 34, Iss. 1. pp. 70–71.