INVESTIGATION OF THE ZINC AND LEAD SELECTIVE EXTRACTION PROCESSES FROM ELECTRIC ARC FURNACE DUST [1/2]

Podusovskaia N.V.*, Komolova O.A., Grigorovich K.V.

Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences (IMET RAS)

*npodusovskaya@imet.ac.ru

КИТАЙ 2023 РОССИЯ

1938 ИМЕТ РАН

Relevance

* The order of Rosprirodnadzor from 18.07.2014 № 445

EAF DUST

contains **15–25 %** Zn

and up to **3 %** Pb

In accordance with the order of Rosprirodnadzor*:

«metallurgical dust containing non-ferrous metals» refers to waste II - IV danger class.

The study object

Components content, wt. %: **Fe – 40,0**; **Zn – 13,7**; Ca – 6; Na – 2,8; Mn – 2,6; Cl – 1,8 (1,3); C – 1,74; Mg – 1,5; Si – 1,3; K – 1,0; **Pb – 0,80**; S – 0,47; Al – 0,2; Cr – 0,2; Cu – 0,2; P – 0,1; Ti – 0,05; W (moisture) – 0,25; remainder – oxygen.

Phase content, wt. %: $(Zn,Mn,Fe)_3O_4$ – 82,6; ZnO – 6,0; $Ca_2Fe_2O_5$ – 4,5; MnO_2 – 3,0; Pb_2O_3 – 2,7; SiO_2 – 1,2.

The need to process toxic man-made waste and the need to organize a closed production cycle acutely raise the question of developing technologies for the non-ferrous metals selective extraction from EAF dust.

Theoretical justification

CO content < 60 %	CO content > 60 %
$2Pb_2O_3 + 3C = 4\{Pb\} + 3\{CO_2\}$ $Pb_2O_3 + 3\{CO\} = 2\{Pb\} + 3\{CO_2\}$ $ZnO = \{Zn\} + 0{,}5\{O_2\}$ T > 1975 °C	$Pb_2O_3 + 3C = 2\{Pb\} + 3\{CO\}$ $Pb_2O_3 + 3\{CO\} = 2\{Pb\} + 3\{CO_2\}$ $ZnO + C = \{Zn\} + \{CO\}$ $ZnO + \{CO\} = \{Zn\} + \{CO_2\}$ $Fe_3O_4 + C = 3FeO + \{CO\}$ $Fe_3O_4 + \{CO\} = 3FeO + \{CO_2\}$

60 CO content, %

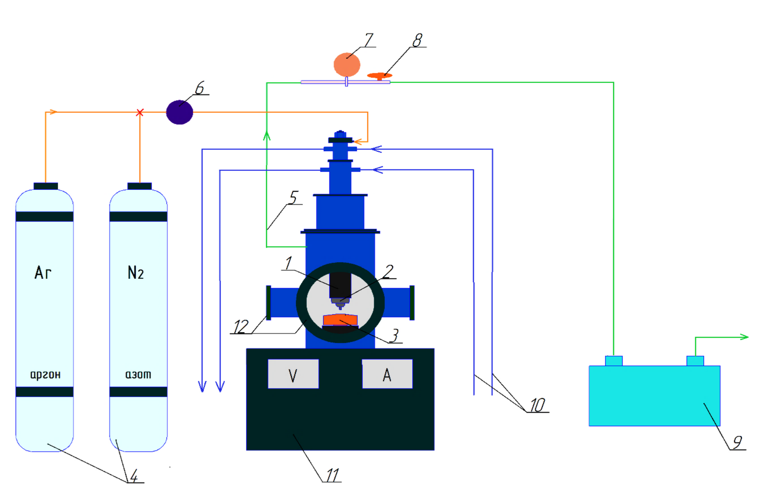
According to the data*, lead is an easily recoverable element, and zinc is restored only under highly reducing conditions. In this regard , the selective extraction of lead and zinc can be implemented in two ways:

- sequential recovery with atmosphere control;
- reduction of the lead-containing phase followed by thermal dissociation of the zinc-containing phase.

Essential detail: during the heating process, solid-phase recovery of iron-containing phases is possible in the temperature range 500–750 °C.

* Marchenko N.V. et al. Metallurgy of heavy non-ferrous metals, 2009

Experiments in the laboratory plasma arc furnace

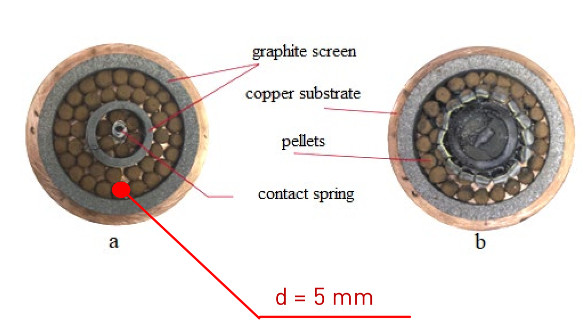


1 – plasmatron; 2 – cathode node; 3 – anode node; 4 – gas cylinders; 5 – gas removal system; 6 – flow meter; 7 – pressure gauge; 8 – vacuum system valve; 9 – vacuum pump; 10 – water cooling system; 11 – control panel; 12 – viewing window

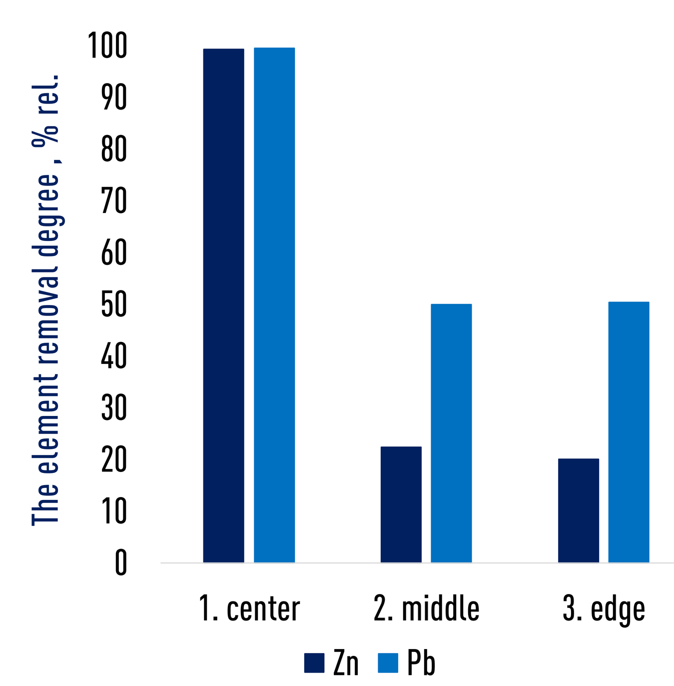
Scheme of the laboratory plasma arc furnace

Experiment parameters

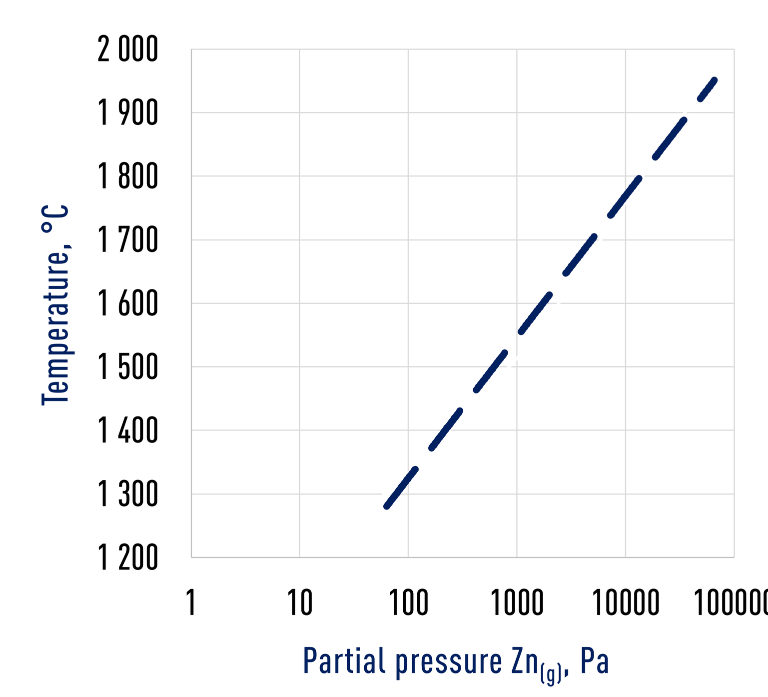
Zone	The zone radius, mm	Average the zone temperature, °C	
		arc	at the surface
1. center	4–10	5248	2474
2. middle	13–19	3683	1692
3. edge	19–25	2466	1083



Scheme of samples placement on a substrate before (a) and after (b) plasma treatment



The dependence of Zn and Pb removal degrees from EAF dust during plasma treatment from the location



Dependence* of the reaction temperature $ZnO = Zn_{(g)} + O_{2(g)}$ on the partial pressure $Zn_{(g)}$

* Thermodynamic modeling in the Terra program

To confirm the possibility of removing zinc and lead from EAF dust into the gas phase at high temperature without introducing a reducing agent and to assess the effect of the process temperature on the lead and zinc removal degree the EAF dust, it was heated in a laboratory plasma arc furnace. Since the arc temperature decreases when moving away from its axis, an attempt has been made to create several temperature zones in the furnace due to the samples axisymmetric laying.

It was found that in zone 1 (t=2200–2700 °C), the zinc and lead removal degree is more than 99%, which confirms the possibility of selective Zn extraction with preliminary lead-containing phases removal. At the same time, thermodynamic modeling shows the possibility of reducing the thermal dissociation reaction temperature with a decrease in the partial pressure of zinc in the gas phase (from t=1970 °C to t=1300 °C). In the other two zones (t=800–2000 °C), lead is removed more intensively than zinc. The metals removal degrees from EAF dust are 50% and 20%, respectively. It was revealed that plasma heating is not suitable for holding EAF dust in a temperature zone of 600–1300 °C.

Experiments in the laboratory muffle furnace

Experiment parameters

Parameters	Meaning
Processing temperature, °C	300, 600, 900, 1150
Heating speed, °C/min	5
Initial temperature, °C	25
Exposure duration, min	60
Atmosphere	air
Total weight of the examples, g	150
Sample weight in 1 crucible, g	25
Layer height, mm	25–30
Crucible material	alund
Crucible dimensions, mm	D = 52 mm, d = 26 mm, H = 38 mm

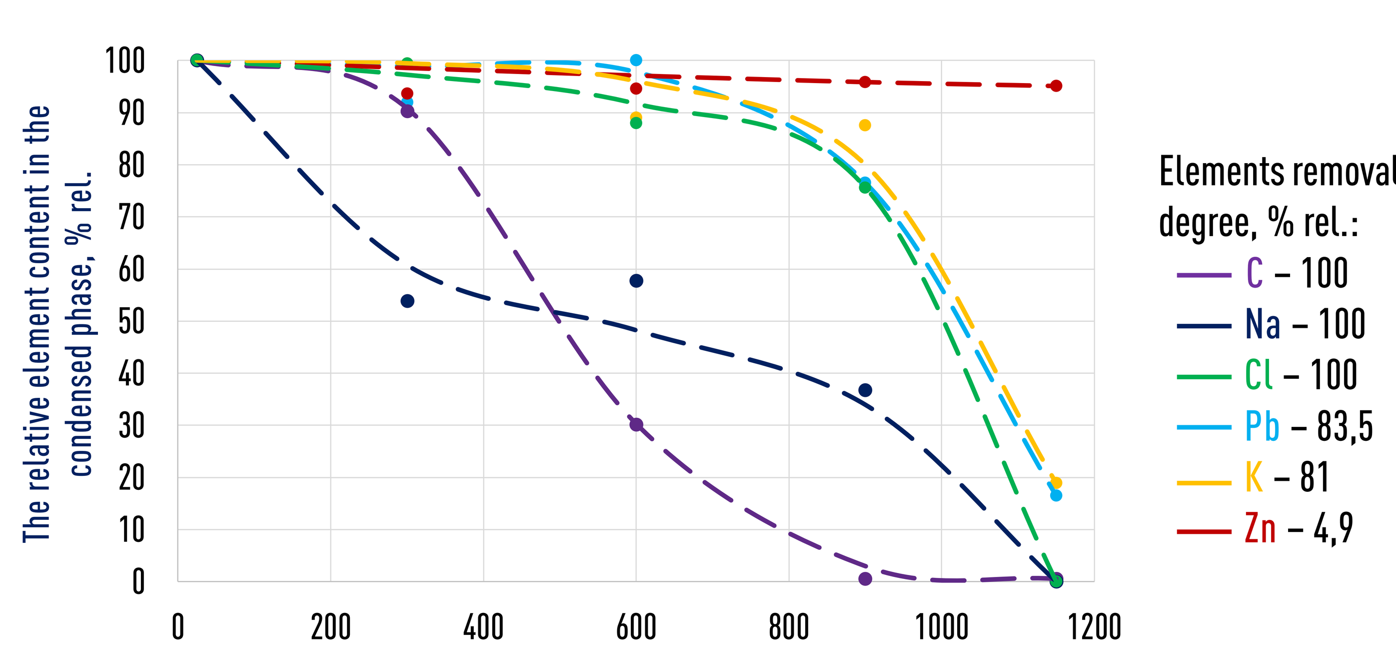
Actual mass loss, wt. %:

300 °C – 0,544

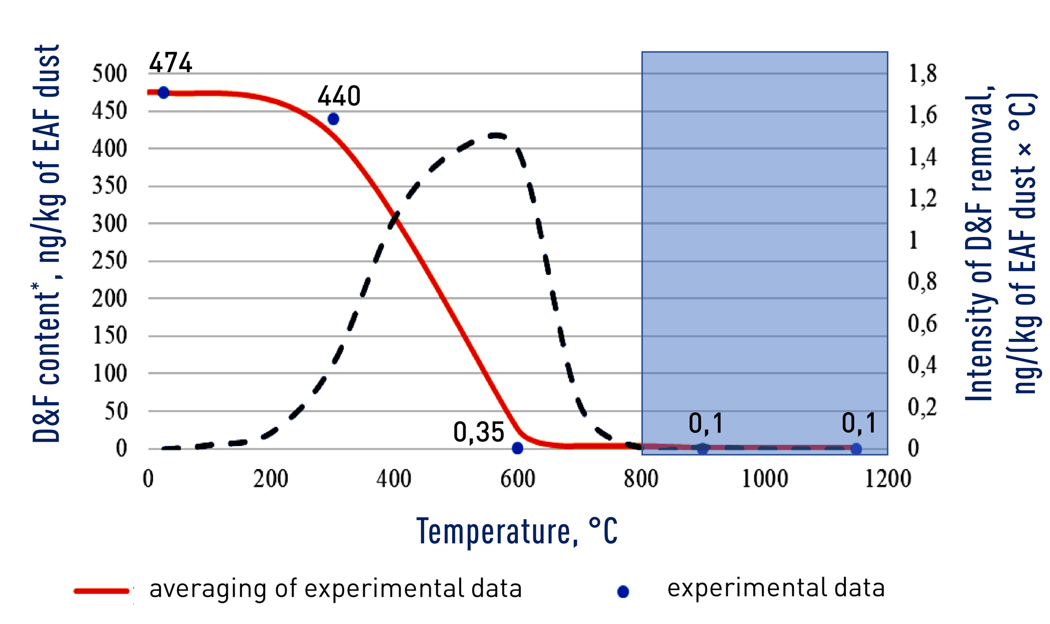
600 °C – 1,060

900 °C – 2,753

1150 °C – 5,613



Pb, C, Na, Cl, K, Zn content change during heating of EAF dust in the air atmosphere



Change of dioxins and furans (D&F) content during EAF dust heating in the air atmosphere

* Analytical Ecotoxicology Laboratory, IPEE RAS named after A.N. Severtsov

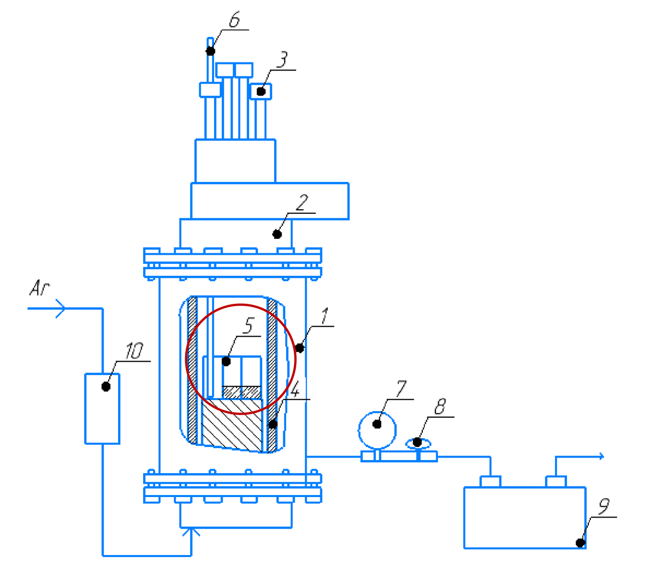
It was found that when the EAF dust was heated in the air atmosphere to 1150 ° C, the content of C, Na, Cl in it decreased to traces; the K content decreased by 81%; Pb by 83.5%; the decrease in the Zn content did not exceed 5%.

Heating the samples to 300 °C doesn`t led to a significant change in the D&F content. When heated to 600 °C, the D&F content is significantly reduced to 0.35 ng/kg of EAF dust. This corresponds to 99.9% reduction in D&F content. Since the D&F destruction in an oxidizing atmosphere occurs at a temperature above 800 °C, the most likely D&F desorption from the surface of EAF dust without their destruction. This factor should be taken into when creating EAF dust recycling technologies.

INVESTIGATION OF THE ZINC AND LEAD SELECTIVE EXTRACTION PROCESSES FROM ELECTRIC ARC FURNACE DUST [2/2]

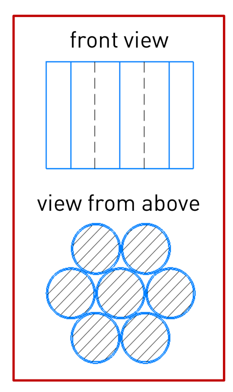
Podusovskaia N.V.*, Komolova O.A., Grigorovich K.V.
Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences (IMET RAS)
*npodusovskaya@imet.ac.ru

Experiments in the laboratory vacuum resistance furnace



1 – furnace body; 2 – furnace lid; 3 – viewing window; 4 – graphite heater; 5 – working alund crucibles; 6 – thermocouple; 7 – pressure gauge; 8 – vacuum system valve; 9 – vacuum pump; 10 – rotameter

Scheme of the vacuum resistance furnace



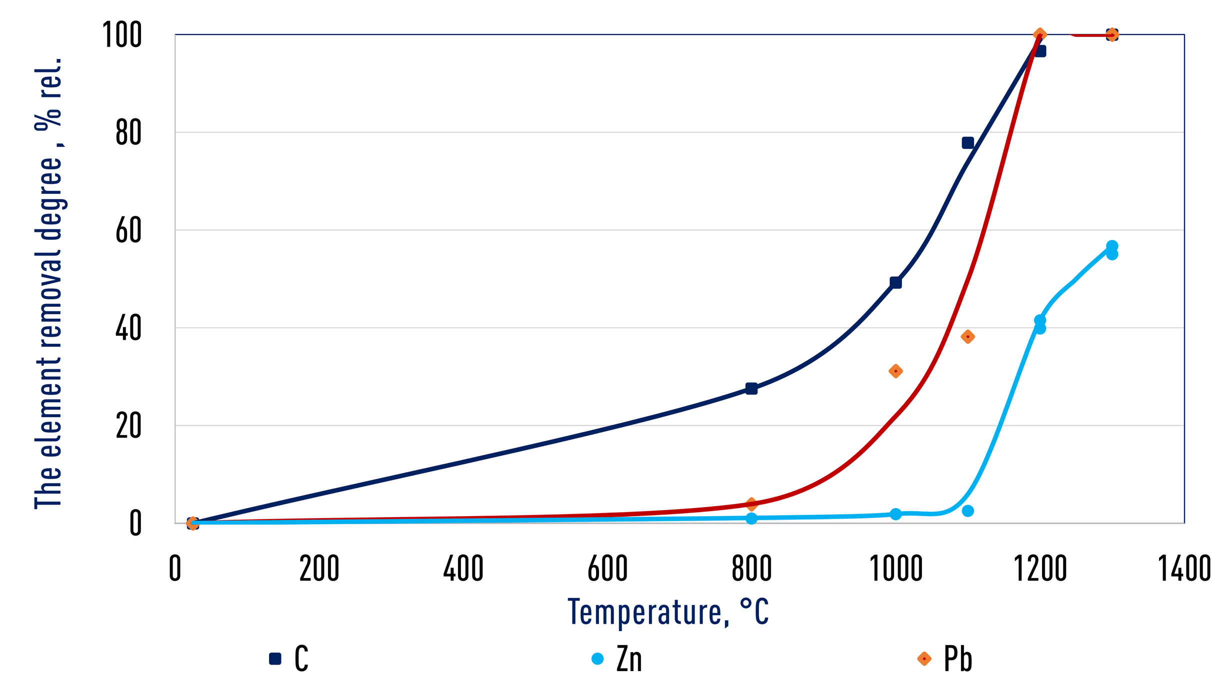
the crucibles layout scheme

Experiment parameters

Parameters	Meaning
Processing temperature, °C	20–1300
Heating speed, °C/min	15
Atmosphere	argon
Argon consumption, l/min	0,5
Total weight of the examples, g	21
Sample weight in 1 crucible, g	3
Layer height, mm	12–15
Crucible material	alund
Crucible dimensions, mm	D = 19 мм, d = 18 мм, H = 40 мм, h = 38,5 мм

Actual mass loss, wt. %:

800 °C – 2,32 | 1000 °C – 3,64 | 1100 °C – 4,28
1200 °C – 10,04 | 1200 °C – 21,49

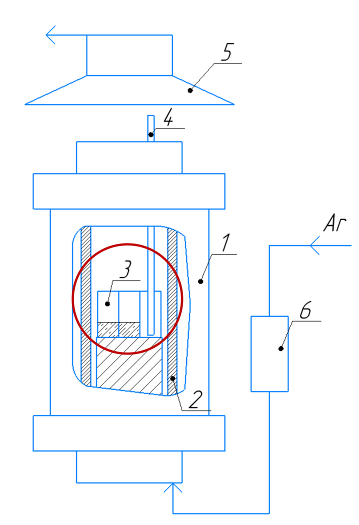


Dependence of the element extraction degree on the temperature during heating in the vacuum resistance furnace in the argon current

It was found that when the EAF dust was heated to 1200 °C, the lead content in it decreased to traces; the carbon content by 96%; the zinc content decreased by 60%.

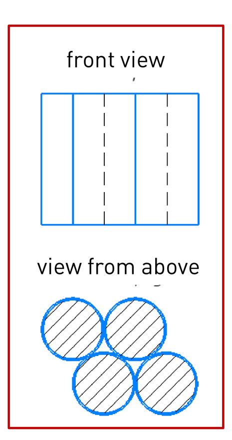
Intensive lead removal took place at temperatures above 1000 °C, and intensive zinc removal began at temperatures of 1200 °C and above. To investigate the possibility of lead and zinc selective removal from EAF dust, a detailed study of their behavior in the temperature range of 800-1200 °C under isothermal conditions is necessary.

Experiments in the laboratory Tamman furnace



1 – furnace body; 2 – graphite heater; 3 – working alund crucibles; 4 – thermocouple; 5 – gas removal system; 6 – rotameter

Scheme of the laboratory Tamman furnace



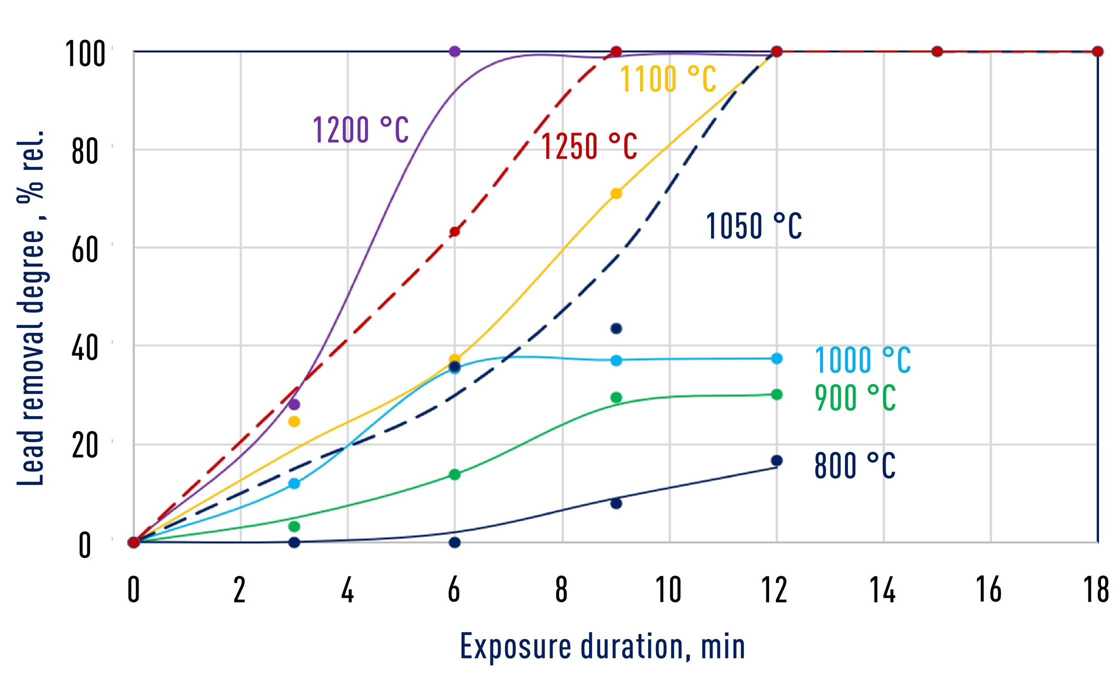
the crucibles layout scheme

Experiment parameters

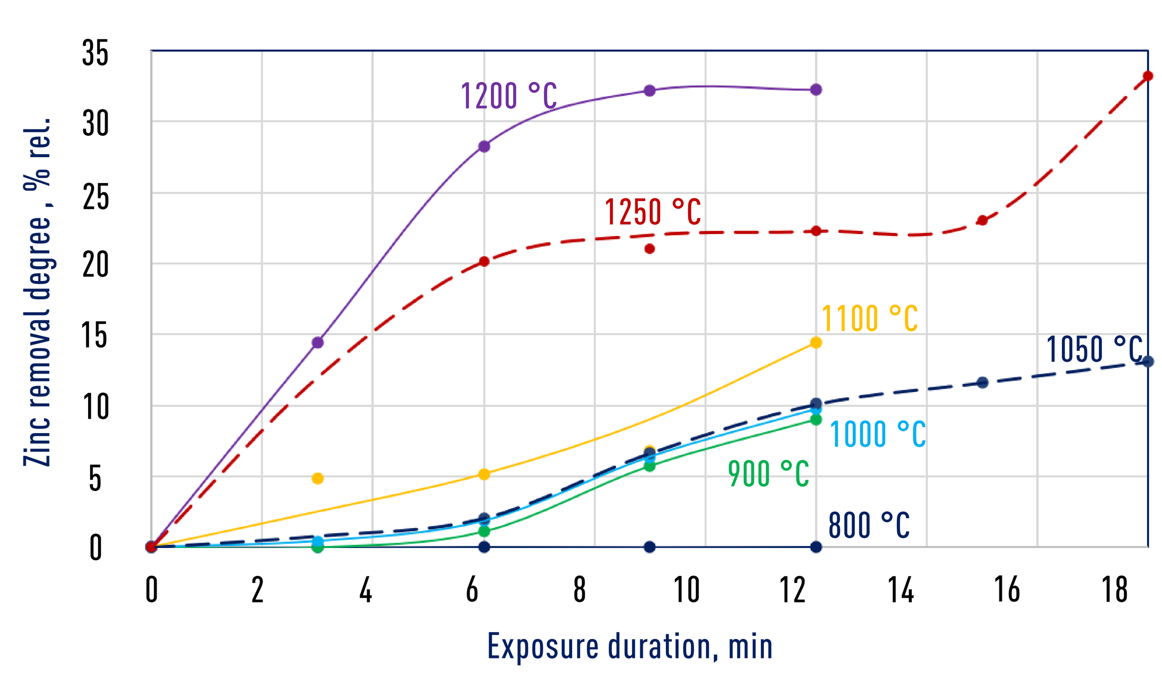
Parameters	Meaning
Processing temperature, °C	800, 900, 1000, 1200 1050, 1250
Exposure duration, min	3, 6, 9, 12 6, 9, 12, 15, 18
Atmosphere	argon
Argon consumption, l/min	1
Total weight of the examples, g	21
Sample weight in 1 crucible, g	3
Layer height, mm	12–15
Crucible material	alund
Crucible dimensions, mm	D = 19 мм, d = 18 мм, H = 40 мм, h = 38,5 мм

Lead complete transition into the gas phase during the experiments was achieved at temperatures t=1050 °C and 1100 °C (τ=12 minutes) and at temperatures t=1200 °C and 1250 °C (τ=6 and τ=9 minutes, respectively). A decrease in the lead transition intensity to the gas phase is associated with sample surface melting. At temperatures t =900 °C and t=1000 °C an increase in the exposure duration of the samples from 9 to 12 minutes did not lead to an increase in the lead extraction degree in the carbon presence in the samples, therefore, it can be assumed that several Pb_2O_3 reduction reactions occurred in the temperature range of 800–1200 °C.

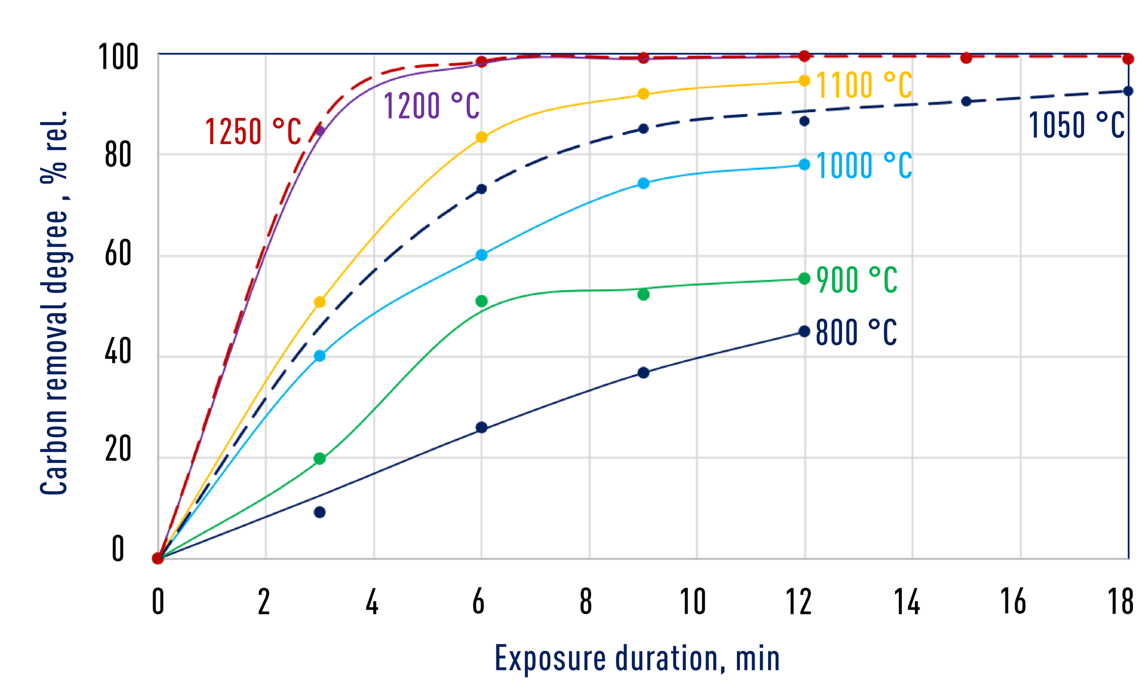
In parallel with the lead complete transition to the gas phase, zinc extraction was observed in an amount from 10.1 to 28.2% rel., which indicates that lead selective extraction was not achieved when heating EAF dust under experimental conditions. At 1200 °C, there is an exit to the plateau of the zinc extraction degree, with a parallel decrease in the carbon content in the EAF dust to zero values, therefore, it can be assumed that the zinc-containing phases reduction reactions will cease due to the lack of a reducing agent. Subsequent exposure of EAF dust at temperatures of 1050–1200 °C, presumably, will lead to the selective zinc extraction, which is associated with the lead complete removal from the EAF dust during the experiment.



Dependence of lead removal degree from EAF dust on the temperature and exposure duration when heated in the Taman furnace in the argon current



Dependence of zinc removal degree from EAF dust on the temperature and exposure duration when heated in the Taman furnace in the argon current



Dependence of carbon removal degree from EAF dust on the temperature and exposure duration when heated in the Taman furnace in the argon current

Conclusions

In parallel with the experiments, the temperature intervals of the possible reactions of the transition of zinc- and lead-containing phases to the gas state were determined using the thermodynamic modeling program HSC Chemistry. Considering the initial phase composition, 39 reactions were analyzed, 11 of which were selected, comparable with experimental data.

Reactions	Equation* of Gibbs energy changes	Reaction temperature, °C
$Pb_2O_3 + 3C = 2Pb_{(g)} + 3CO_{(g)}$	ΔG = -0,6895T + 309,83	T>449
$Pb_2O_3 + 1,5C = 2Pb_{(g)} + 1,5CO_{2(g)}$	ΔG = -0,43T + 126,66	T>295
$Pb_2O_3 + 3CO_{(g)} = 2Pb_{(g)} + 3CO_{2(g)}$	ΔG = -0,1705T + 56,507	0–2000
$Pb_2O_3 + C = 2PbO_{(g)} + CO_{(g)}$	ΔG = -0,4356T + 352,5	T>809
$2Pb_2O_3 + C = 4PbO_{(g)} + CO_{2(g)}$	ΔG = -0,6982T + 582,89	T>835
$Pb_2O_3 + CO_{(g)} = 2PbO_{(g)} + CO_{2(g)}$	ΔG = -0,2626T + 230,39	T>877
$ZnO + C = Zn_{(g)} + CO_{(g)}$	ΔG = -0,2917T + 279,51	T>958
$2ZnO + C = 2Zn_{(g)} + CO_{2(g)}$	ΔG = -0,4104T + 436,9	T>1064
$ZnFe_2O_4 + 2C = Zn_{(g)} + 2Fe + 2CO_{2(g)}$	ΔG = -0,4433T + 382,36	T>863
Σ $ZnFe_2O_4 + 2CO_{(g)} = Zn_{(g)} + 2FeO + 2CO_{2(g)}$	ΔG = -0,1538T + 173,25	T>1126
Σ $ZnFe_2O_4 + C = Zn_{(g)} + 2FeO + CO_{2(g)}$	ΔG = -0,3233T + 292,46	T>905

**Thermodynamic modeling program HSC Chemistry 6*

Possible implementation options for the technology of lead and zinc selective removal from EAF dust

	I stage	II stage	III stage
Processes	• D&F desorption • Afterburning of exhaust gases and quenching with lime milk: $2Ca(OH)_2 + 2Cl = CaCl_2 + Ca(OCl)_2 + 2H_2O$ • Solid-phase reduction of spinel Fe_3O_4 / $(Zn,Mn,Fe)_3O_4$ with carbon of EAF dust	Reduction of Pb_2O_3 by carbon or carbon monoxide	A) Reduction of ZnO by carbon or carbon monoxide B) Thermal dissociation of ZnO
Conditions	t = 500–600 °C	t = 1050–1100 °C; adding carbon or CO (< 60%)	A) t = 1200 °C adding carbon or CO (< 60%) B) t = 1975 °C at partial pressure $Zn_{(g)}$ 10^5 Pa; t = 1300 °C at partial pressure $Zn_{(g)}$ 60 Pa

The lead and zinc selective removal process should be carried out in three stages:

- at the first stage, D&F desorption with burning and quenching of waste gases with lime milk should be carried out to prevent the ecotoxicants re-formation;
- at the second stage, the lead oxide reduction by carbon or carbon monoxide is carried out;
- at the third stage, zinc is removal into the gas phase by reduction or thermal dissociation of zincite.