Master's thesis

Extraction of Zn from dust generated during steel production

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Date(17/07/2023)

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DECLARATION OF AUTHORSHIP

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PREFACE, DEDICATION, ACKNOWLEDGEMENT

I dedicate this thesis to amity of three universities: Saint-Petersburg Mining University, Montanuniversität Leoben and TU Bergakademie Freiberg. I am sincerely grateful that this synergy made the thesis happen.

ABSTRACT

In this master's thesis, the technologies of zinc extraction from steelmaking dust have been analysed. On the basis of the analysis the technological scheme for ferrous metallurgy waste processing of "‘Severstal’" company was developed, which includes two-stage dust leaching with hydrochloric acid, extraction, re-extraction, carbonization, HCl regeneration in "Ruthner" furnace and electrolysis. A number of experiments were conducted to identify the optimum parameters (temperature and duration) for the leaching operation. The option of providing hydrochloric acid regeneration in order to ensure the closure of the technology was also proposed. Factors that can affect the economic efficiency of the technology in case of implementation in the production scale were considered. Aspects affecting industrial safety have also been evaluated and measures to maintain a safe production environment have been proposed.

The paper consists of pages and includes 16 figures and 20 tables.

Keywords: zinc, electric-arc furnace dust, leaching, hydrochloric acid, hydrometallurgy, extraction, waste, ferrous metallurgy waste, processing of industrial raw materials.

ZUSAMMENFASSUNG

In dieser Masterarbeit wurden die Technologien zur Zinkextraktion aus Stahlwerksstaub analysiert. Auf der Grundlage der Analyse wurde ein technologisches Schema für die Verarbeitung von Abfällen aus der Eisenmetallurgie des Unternehmens "‘Severstal’" entwickelt, das eine zweistufige Auslaugung des Staubs mit Salzsäure, eine Extraktion, eine erneute Extraktion, eine Karbonisierung, eine HCl-Regeneration im "Ruthner"-Ofen und eine Elektrolyse umfasst. Es wurde eine Reihe von Versuchen durchgeführt, um die optimalen Parameter (Temperatur und Dauer) für die Laugung zu ermitteln. Es wurde auch die Möglichkeit einer Salzsäureregeneration vorgeschlagen, um den Abschluss der Technologie zu gewährleisten. Faktoren, die die wirtschaftliche Effizienz der Technologie im Falle einer Umsetzung im Produktionsmaßstab beeinflussen können, wurden berücksichtigt. Aspekte, die sich auf die Arbeitssicherheit auswirken, wurden ebenfalls bewertet, und es wurden Maßnahmen zur Aufrechterhaltung einer sicheren Produktionsumgebung vorgeschlagen.

Das Papier umfasst 16 Seiten mit 16 Abbildungen und 20 Tabellen.

Schlüsselwörter: Zink, Lichtbogenofenstaub, Auslaugung, Salzsäure, Hydrometallurgie, Extraktion, Abfälle, Abfälle aus der Eisenmetallurgie, Verarbeitung von Industrierohstoffen.

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1 INTRODUCTION

Metallurgy is one of the leading industrial sectors in terms of air emissions. In the cast iron and steel industry, for every tonne of product produced, a large number of different wastes and by-products are generated. These secondary materials are either used directly in production operations (domestic scrap, dry dross, etc.) or require additional treatment before practical use (oil-containing dross, sludge and dust from gas treatment plants, etc.).

During steelmaking in electric arc furnaces (EAF) 10 to 15 kg of dust per tonne of metal products are generated (Barcza et al., 1995, p.25). This electric arc furnace dust (EAFD) is normally collected as fine dust in a bag filter or as sludge in a scrubber system. Traditionally, the EAF dust has been deposited or dumped in landfills. Recently the use of galvanised scrap in steel production has increased rapidly, resulting in higher zinc, lead and cadmium content in the dust (Machado et al., 2006). In many countries the disposal of EAFD is environmentally hazardous at present and only allowed to be stored at approved sites because toxic metals (Pb, Cr and Zn) can leach into drinking water. Hexavalent chromium (Cr^{6+}) and lead (Pb) are carcinogens, and zinc makes it impossible to process EAF dust directly: the zinc in the recycled scrap can interfere with the electric furnace refractories and cause damage. The presence of Zn also blocks the absorption of gas, which can cause the whole process to stop.

Zinc is the third most used non-ferrous metal[1]. In steelmaking dusts the zinc content varies from 2 to 46%, which forms a demand for the processing of the intermediate product in order to further extract the useful component (Pereskoka et al., 2010, p.11).

Zinc in domestic production is extracted from pyrite-polymetallic ores. Russia is a traditional zinc producer (250 thousand t/a of refined metal), but poor ore quality limits the growth of metal production. In this connection, expansion and modification of the mineral resource base of zinc may allow solving problems on modernization of processes and technologies of extraction of the valuable component. One of the

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[1] STATE REPORT ON THE STATE AND USE OF MINERAL RESOURCES OF THE RUSSIAN FEDERATION IN 2019, Moscow, 2020

options for modifying the mineral raw material base is the involvement of technogenic zinc-containing raw materials into processing.

Zinc extraction can be carried out using both pyro- and hydro-technologies. Both variants are expensive and require different additional raw materials. However, the extraction of useful components is economically viable with the right parameters and the right processes.

The purpose of this study is to develop a suitable technological scheme, selection of optimum parameters and reagents of the leaching process to achieve high zinc recovery in the solution for further processing.

Research objectives:

- To analyse existing methods of steelmaking dust processing;
- To develop the technology most suitable for providing high zinc recovery from a specified raw material;
- To determine the most optimal leaching process parameters;
- To evaluate the theoretically developed technological process.

The object of the study is the process of zinc leaching from dust generated during steel production.

The subject of the study is the behaviour of zinc and some other impurities in the process at the selected parameters.

2 TECHNOLOGICAL PART

2.1 General characteristics of the object of study

The object of the study in this paper is the EAFD, which was provided by ‘Severstal’ PJSC, metallurgical plant of Cherepovets. The dust is odourless, powdery, finely dispersed and brown in colour.

The chemical composition (Table 1) was provided by Gipronickel Institute LLC after analysis by atomic emission and infrared spectrometry.

Elements	Content (wt, %)
Fe	39.00
Zn_{OA}	13.30
Zn_{ox}	5.60
Zn_f	7.70
Cu	0.13
Ni	0.03
Cr	0.21
Mn	2.80
Mg	0.98
Al	0.37
Pb	0.76
Ca	5.43
SiO_2	3.32
S	0.37
C	2.74
Cl^-	3.59
F^-	0.44

Table 1: Chemical composition of the dust from electric steelmaking furnace.

The data obtained by X-ray phase and optical analyses of the mineralogical composition are shown in Figure 1. The X-ray diffraction diffractogram reveals that the dust consists of phases such as iron, graphite, zinc ferrite, spinels, Fe-oxides, which are typical forms of the main mineral phases (Figure 2).

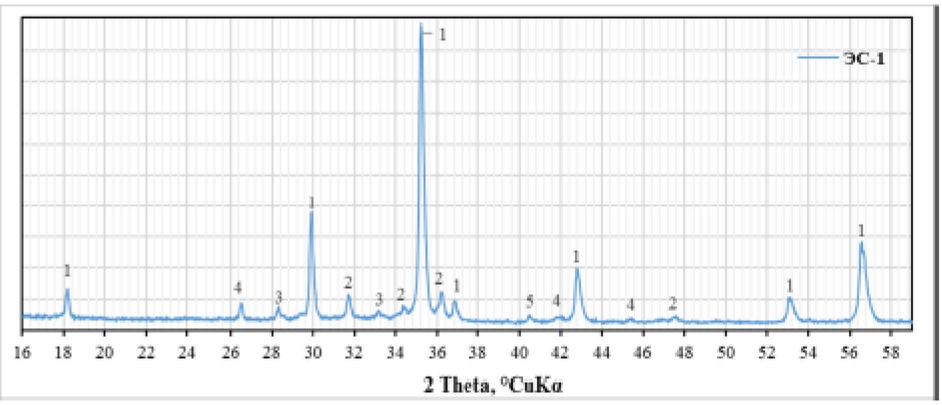

Figure 1: Fragment of a diffractogram of the EAFD sample
1 - zinc ferrite; 2 - zinc oxide; 3 - garnets; 4 - graphites; 5 - manganese oxide.

The particle size varies from 0.100 to 0.045 mm. Based on the analysis of the particle size distribution, which is presented in Table 2, it can be seen that the size of the main fraction (37.63%) is -0.020 mm.

Fraction, mm	Content (wt, %)
+0,100	10,75
-0,100+0,045	19,35
-0,045+0,020	32,26
-0,020	37,63
Итого	100,00

Table 2: Granulometric composition of electric steelmaking dust.

From the analysis of the chemical composition of the main mineral phases of the dust samples examined, it is clear that Zn is mainly represented by oxide and ferrite forms (Table 3).

Mineral	Mg	Al	Si	Ca	Mn	Fe	Zn	O	Other	Total
Ca silicate	4.1	3.59	11.37	24.17	0.75	9.85	8.38	36.01	1.78	100
Zn ferrite				3.77	1.07	57.14	8.21	28.79	1.02	100
Zn ferrite				0.37		58.04	13.26	28.33		
Fe oxide				0.26		69.09	0.69	29.96		
Zn ferrite				5.56		44.97	22.43	27.04		100
Fe oxide				1.49	1.49	64.87	1.62	29.96		100
Zn oxide				0.44		2.47	74.53	20.8	1.75	100
Zn oxide				0.48	0.93	3.32	71.41	21.28	2.58	100
Zn oxide				0.72		2.65	73.68	20.98	1.97	100

Table 3: The composition of dust minerals.

The zinc ferrite in the sample is represented by spherical and irregular shapes (Figure 3) and is associated with Fe oxides (Figure 4). The spinel aggregates consist of silicate inclusions and Ca-Fe oxides (Figure 5). The predominant forms of iron are zinc ferrite, oxide and spinel minerals of variable composition. The latter two contain rounded iron phenocrysts in metallic form. The graphitic phase occurs as rare tabular aggregates up to 0.5 mm in size.

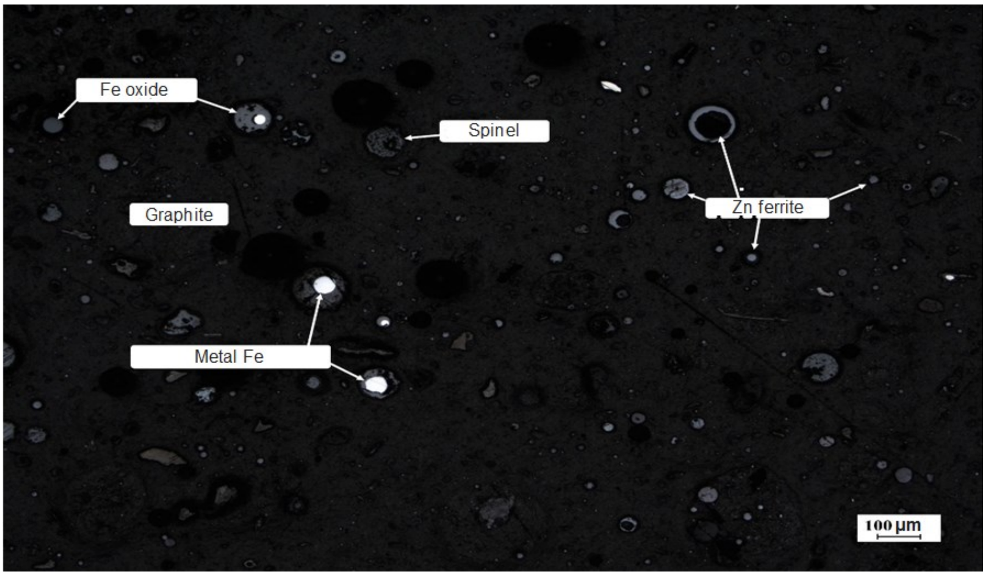

Figure 2: Characteristic forms of the main mineral phase extraction of EAFD sample.

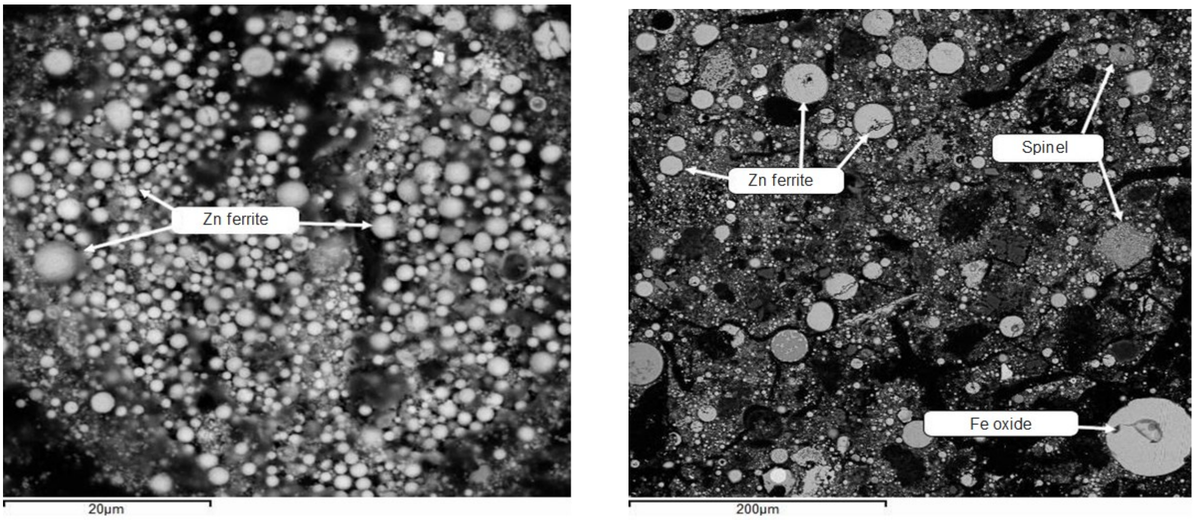

Figure 3: The spheroidal allocations of the main mineral phases.

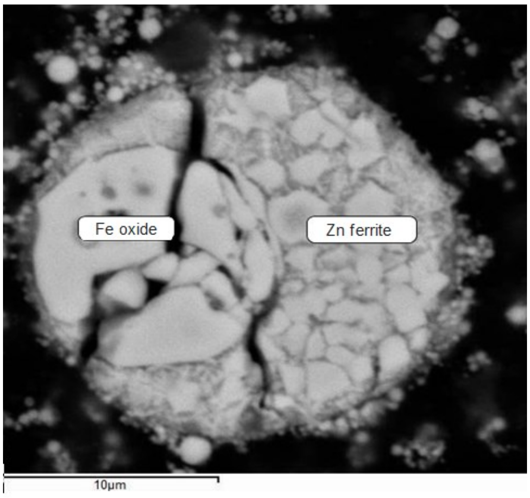

Figure 4: Rounded bonding of iron oxide with zinc ferrite.

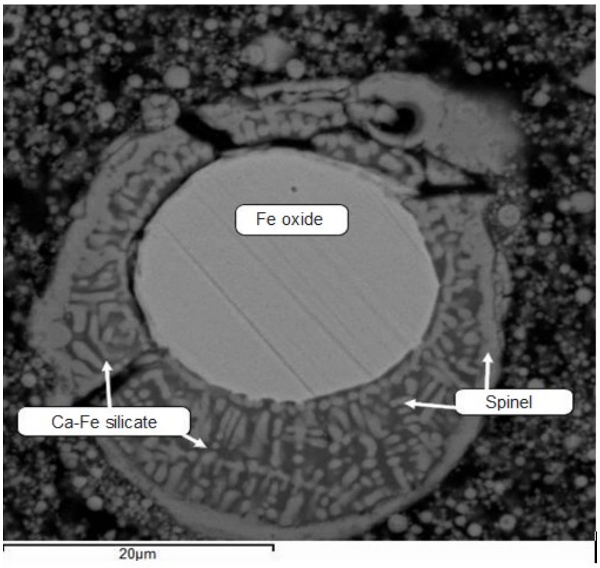

Figure 5: Spinel grain with zinc impurities and inclusion of rounded iron oxide grain.

Zinc ferrite, spinel, calcium and iron silicates, iron, zinc and manganese oxides in EAF dust are mainly in the form of spherical and irregularly shaped particles.

2.2 Analysis of the basic technology

Leaching is the basic technology of the developed process scheme. Its analysis is based on data obtained from the calculations of Gibbs energy and material balance.

Possibility of spontaneous reactions

To analyse the sequence of metal transfer into solution, it was assumed that the leaching process is described by the following reactions:

$$ZnO+2HCl=ZnCl_2+H_2O \tag{1}$$

$$ZnFe_2O_4+2HCl=ZnCl_2+Fe_2O_3+H_2O \tag{2}$$

$$PbO+2HCl=PbCl_2+H_2O \tag{3}$$

$$CaO+2HCl=CaCl_2+H_2O \tag{4}$$

$$CaSiO_3+HCl=CaCl_2+H_2SiO_3 \tag{5}$$

$$Fe_2O_3+6HCl=2FeCl_3+3H_2O \tag{6}$$

$$CuO+HCl=CuCl_2+H_2O \tag{7}$$

$$MgO+HCl=MgCl_2+H_2O \tag{8}$$

As It is commonly known, the possibility of spontaneous reaction is determined by the Gibbs energy, which is calculated according to formula (9). The reaction is spontaneous if $\Delta G < 0$.

$$\Delta G^0=\Delta H^0-T\cdot\Delta S^0 \tag{9}$$

ΔH - enthalpy of the system, kJ;

ΔS - entropy of the system, kJ;

T - temperature, K.

The enthalpy and entropy values are calculated using formulae 10 and 11 respectively.

$$\Delta H^0=\sum n\,H^0_{\text{конеч.прод.}}-\sum n\,H^0_{\text{нач.прод.}} \tag{10}$$

$$\Delta S^0=\sum n\,S^0_{\text{конеч.прод.}}-\sum n\,S^0_{\text{нач.прод.}} \tag{11}$$

An example calculation for the 1st reaction

1. Calculation of the enthalpy:

$$\Delta H^0 = H^0_{ZnCl2} + H^0_{H2O} - (H^0_{ZnO} + 2H^0_{HCl})$$

$$\Delta H^0 = (-415+(-285,8)) - (-350,6+(2\cdot(-91,8))) = -166,6 \text{ KJ/mol}$$

2. Entropy calculation:

$$\Delta S^0 = S^0_{ZnCl2} + S^0_{H2O} - (S^0_{ZnO} + 2S^0_{HCl})$$

$$\Delta S^0 = (111,5+87,4+70,1) - (43,6+186,8) = -240,7 \text{ KJ/mol}$$

3. Calculation of Gibbs energy at 298 K

$$\Delta G^0 = \Delta H^0 - T\cdot\Delta S^0$$

$$\Delta G^0 = -166\ 600 - 298\cdot(-240,7) = -94\ 871,4 \text{ KJ/mol}$$

4. Calculation of Gibbs energy at 323 K:

$$\Delta G^0 = \Delta H^0 - T\cdot\Delta S^0$$

$$\Delta G^0 = -166\ 600 - 323\cdot(-240,7) = -88\ 853,9 \text{ KJ/mol}$$

In the same way the Gibbs energies for the reactions 2-8 were calculated. The data obtained are presented in Table 4.

Reaction	**Gibbs energy *(∆G°), J/mol***	
	298 K	***323 K***
$ZnO + 2HCl = ZnCl_2 + H_2O$	-94,817.4	-88,853.9
$ZnFe_2O_4 + 2HCl = ZnCl_2 + Fe_2O_3 + H_2O$	-81,296.4	-74,854.2
$PbO + 2HCl = PbCl_2 + H_2O$	-171,484.8	-165,683.9
$CaO + 2HCl = CaCl_2 + H_2O$	-191,352.2	-185,480.7
$CaSiO_3 + HCl = CaCl_2 + H_2SiO_3$	-101,128.0	-95,764.7
$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$	-31,941.1	-23,085.5
$CuO + HCl = CuCl_2 + H_2O$	-80,760.9	-74,842.4
$MgO + HCl = MgCl_2 + H_2O$	-69,517.3	-63,544.9

Table 4: Gibbs energy values of the main reactions.

It is evident from the data obtained that during the leaching process the solution is contaminated with other elements. Zinc ferrite is one of the last to dissolve, which causes the loss of a valuable component. It is also worth paying attention to the fact that iron (III) is dissolved in the last place, which means that it is impossible to contaminate the solution with this element. Hence, the source of iron impurity in the solution is ferrite.

Material balance

On the basis of chemical and mineralogical composition of dust and leaching reactions the material balance has been calculated. Taking into account that the capacity of the electric steelmaking dust was taken as 15 thousand t/a[2], the calculation of the material balance is carried out on the daily capacity, i.e., 41 tons.

In the calculation of the initial composition of raw materials the percentage of iron III in oxide form (56.9%) was taken into account. The data obtained are presented in Table 5.

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[2] Data of the company "SeverStal"

While calculating the balance of the products obtained after the 1st stage of leaching, the following parameters are taken into account:

- Zinc recovery into solution: 45%;
- Iron recovery into the solution: 4.1%;
- Residue yield: 74%;
- Residue moisture after thickening: 20%.

The data are shown in Table 6Table 9.

Content, t											
Element	Cu	Fe	Mg	Zn	Pb	Ca	SiO2	C	O	Other	Σm
Compound											
CuO	0.05								0.01		0.07
ZnO				2.30					0.57		2.86
$ZnFe_2O_4$		3.96		3.16					3.11		10.22
MgO			0.40						0.27		0.67
PbO					0.31				0.02		0.34
CaO						1.32			0.53		1.85
CaSiO3						0.91	1.36		0.36		2.63
Fe2O3		9.10							3.90		13.00
C								1.12			1.12
Fe		2.94									2.94
Other										5.42	5.42
Σm	0.05	15.99	0.40	5.45	0.31	2.23	1.36	1.12	8.77	5.42	41.11

Table 5: Daily composition of the initial solution.

Content, t										
Element	Cu	Fe	Mg	Zn	Ca	SiO2	H_2O	Cl	Other	Σm
Compound										
$CuCl_2$	0.05							0.06		0.11
$FeCl_3$		0.66						2.49		3.15
$MgCl_2$			0.40					1.19		1.59
$ZnCl_2$				2.45				2.68		5.13
$CaCl_2$					2.23			3.95		6.18
H_2SiO_3						1.36	0.41			1.77
Other								10.31	110.94	121.24
Σm	0.05	0.66	0.40	2.45	2.23	1.36	0.41	20.68	110.94	139.18

Table 6: Daily composition of the solution after leaching

Content, t							
Element	Fe	Pb	Zn	Cl	O	Other	Σm
Compound							
Fe_2O_3	10.17				4.36		14.52
$PbCl_2$		0.31		0.11			0.42
$ZnFe_2O_4$	5.17		3.00		2.95		11.12
Other						4.36	4.36
Σm	15.33	0.31	3.00	0.11	7.31	4.36	30.42

Table 7: Daily composition of the residue after leaching

Compound	**Inflow, t**		**Reacted, m**	**Formed, t**	**Outflow, t**	
	S	**L**			**S**	**L**
CuO	0.07					
ZnO	2.86					
$ZnFe_2O_4$	10.22					
MgO	0.67					
PbO	0.34					
CaO	1.85					
$CaSiO_3$	2.63					
Fe_2O_3	13.00					
C	1.12					
Fe	2.94					
Other	5.42					
HCl		10.31	10.10			0.20
$CuCl_2$				0.11		0.11
$FeCl_3$				3.15		3.15
$MgCl_2$				1.59		1.59
$ZnCl_2$				5.13		5.13
$CaCl_2$				6.18		6.18
H_2SiO_3				1.77		1.77
H_2O		110.94		2.45		113.38
Fe_2O_3					14.52	
$PbCl_2$					0.42	
$ZnFe_2O_4$					11.12	
Other					4.36	
Total	41.11	121.24			30.42	131.52
Overall	162.36				161.94	

Table 8: Material balance by the compounds

Inflow, t			***Outflow, t***		
	S	***L***		***S***	***L***
1. Dust	41.11	121.24	3. Slurry	30.42	139.18
Included:			3.1 Solution:		139.18
1.1 CuO	0.07		3.1.1 $CuCl_2$		0.11
1.2 ZnO	2.86		3.1.2 $FeCl_3$		3.15
1.3 $ZnFe_2O_4$	10.22		3.1.3 $MgCl_2$		1.59
1.4 MgO	0.67		3.1.4 $ZnCl_2$		5.13
1.5 PbO	0.34		3.1.5 $CaCl_2$		6.18
1.6 CaO	1.85		3.1.6 H_2SiO_3		1.77
1.7 CaSiO3	2.63		3.1.7 H2O		113.38
1.8 Fe2O3	13.00		3.2 Residue:	30.42	
1.9 C	1.12		3.2.1 Fe_2O_3	14.52	
1.10 Fe	2.94		3.2.2 $PbCl_2$	0.42	
1.11 Other	5.42		3.2.3 $ZnFe_2O_4$	11.12	
2. HCl (8.5%)		121.24	3.2.4 Other	4.36	
Included:					
2.1 HCl		10.31			
2.2 H2O		110.94			
Total	41.11	121.24		30.42	131.32
Overall	162.36			161.74	

Table 9: Material balance by the flows

After leaching stage 1, the bottom drain of the thickener is directed to the second stage to achieve the most complete extraction of the valuable component. The material balance of the stage 2 is shown in Tables 10-12. In calculation of balance of products after the 2nd stage of leaching the following parameters are taken into account:

- Zinc extraction into solution: 85%;
- Iron extraction into solution: 20%;
- Residue yield: 74%;
- Residue humidity after filtration: 20%

This stage also produces circulating solution, which is fed into the process header to rationally consume hydrochloric acid and to ensure closure of the process. The balance of the initial leaching phase including the recycled solution is shown in Table 13.

Content, t					
Element / ***Compound***	Fe	Zn	Cl	Other	Σm
$ZnCl_2$		2.55	2.78		5.33
$FeCl_3$	3.07		5.83		8.90
Other			10.19	136.72	146.91
Σm	3.07	2.55	18.81	136.72	161.14

Table 10: Daily composition of the solution after the 2nd stage of leaching

Content, t							
Element / ***Compound***	Fe	Pb	Zn	Cl	O	Other	Σm
Fe_2O_3	11.49				4.93		16.42
$PbCl_2$		0.31		0.11			0.42
$ZnFe_2O_4$	1.55		0.90		0.89		1.67
Other						4.01	4.01
Σm	13.04	0.31	0.90	0.11	5.81	2.34	22.51

Table 11: Daily composition of the residue after the 2nd stage of leaching

Compound	***Inflow, t***		***Reacted, m***	***Formed, t***	***Outflow, t***	
	S	***L***			***S***	***Ж***
Fe_2O_3	14.52					
$PbCl_2$	0.42					
$ZnFe_2O_4$	11.12					
Other	4.36					
HCl		10.19	8.86			1.33
$ZnCl_2$				5.33		5.33
$FeCl_3$				8.90		8.90
H_2O		132.36		2.18		134.54
Fe_2O_3				16.42	16.42	
$PbCl_2$				0.42	0.42	
$ZnFe_2O_4$				1.67	1.67	
Other				4.01	4.01	
Total	30.42	142.55			22.51	150.10
Overall	172.97				172.62	

Table 12: Material balance by the compounds

Compound	***Inflow, t***		***Reacted, m***	***Formed, t***	***Outflow, t***	
	S	***L***			***S***	***L***
CuO	0.07					
ZnO	2.86					
$ZnFe_2O_4$	10.22					
MgO	0.67					
PbO	0.34					
CaO	1.85					
$CaSiO_3$	2.63					
Fe_2O_3	13.00					
C	1.12					
Fe	2.94					
Other	5.42	136.72				136.72
HCl		10.19	10.10			0.09
$CuCl_2$				0.11		0.11
$FeCl_3$		8.90		3.15		12.05
$MgCl_2$				1.59		1.59
$ZnCl_2$		5.33		5.13		10.47
$CaCl_2$				6.18		6.18
H_2SiO_3				1.77		1.77
H_2O		107.63		2.45		110.08
Fe_2O_3					14.52	
$PbCl_2$					0.42	
$ZnFe_2O_4$					11.12	
Other					4.36	
Total	41.11	268.77			30.42	279.06
Overall	309.89				309.48	

Table 13: Material balance of the 1st leaching stage including recycled solution

Material flow calculations provide a clear understanding of the composition of reagents and products, their consumption at each stage and the scope of the projected work. Material flow estimates also analyse possible losses. When the technology is implemented on an industrial scale, the real values obtained are compared with the theoretical data to determine how close the production data is to the figures obtained under ideal conditions.

2.3 The rationale for a solution to the technical problem

Having analysed the possible technological schemes for extraction of zinc from steelmaking dusts and the composition of raw materials, the technology of zinc dust processing of a given composition has been developed, which is presented in Figure 6. The technological scheme includes the following stages:

- 2-stage leaching of zinc-containing dust with hydrochloric acid in order to transfer the valuable component into solution;
- Zn extraction from the obtained solution into the organic phase;
- Re-extraction to return the valuable component to a solution suitable for zinc electrolytic extraction;
- Purification of the solution from Ca and Mg;
- Decomposition of iron chlorides in "Ruthner" furnace to recover HCl;
- Electrolysis to produce a saleable product (zinc).

This technology allows the processing of anthropogenic raw materials of ferrous metallurgy with the aim of additional extraction of a valuable component. At the same time, it produces iron-containing products for use in cast iron/steel production.

The choice of hydrometallurgical technology is justified by a number of advantages:

1. The possibility of adjusting process parameters to improve process performance (product yield, presence of impurities, etc.);
2. Application of different types of solvents allows selective extraction of the required metals;
3. Raw materials with low content of a component can be used as a feedstock;
4. The possibility of recycling of dust with variable composition;
5. More efficient recycling compared to pyro-processing;
6. Reduced impact on the environment;
7. Low energy consumption (Leclerc et al., 2003, p.12).

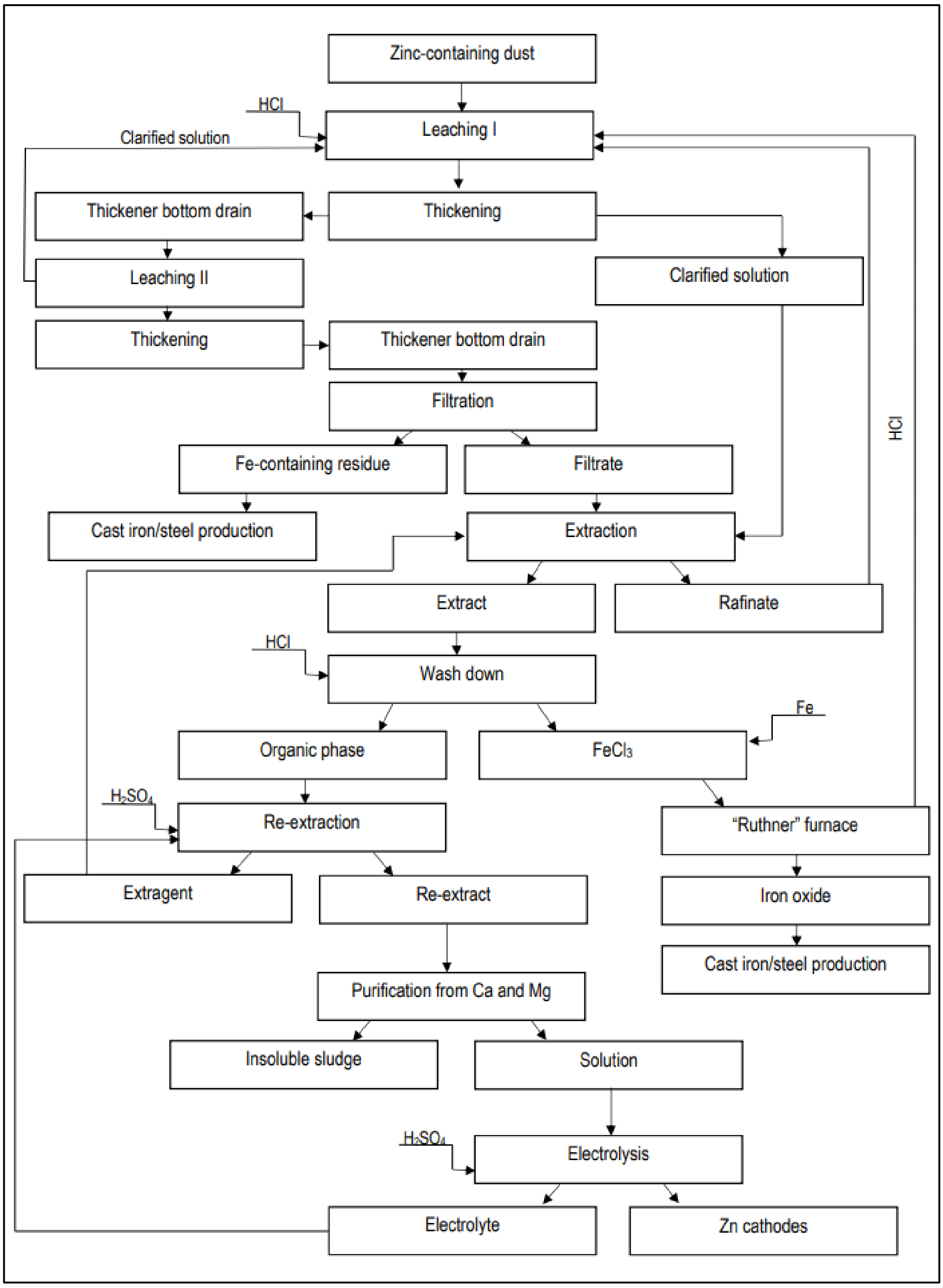

Figure 6: Process flowchart for EAFD recycling.

Hydrochloric acid is the most suitable acid for the leaching operation for the following reasons:

- Hydrochloric acid has a lower contaminating effect;
- The possibility of economical decomposition of iron chloride in further stages;
- The possibility of carrying out hydrochloric acid regeneration.

There are several ways of hydrochloric acid regeneration. Sheftel N.I. in his work "Production of steel calibrated bars" considered three options for regeneration of pickling solutions. Basically, all technologies are aimed at acid regeneration after the steel pickling operation. Although the composition of the pickling solutions differs from the circulating solution after extraction, this technology can be considered as an implementable process step, providing a closed-loop technology. A comparison of the technologies described by N. I. Scheftel was made by K. Eisenhut. Comparative Table 14 (Source: Sheftel, 1970, p.35) includes the Ruthner (1), Otto (2) and Lurgi-Keram-Chemi (3) processes.

Process indicator	Method		
	1	2	3
Operating temperature, °C	500	600	875
Max. quantity of solution to be processed, l/h	300	600	700
Quantity of recycled solution established during the experiments, l/h	250	450	100
Liquid fuel consumption, kg/m^3			
- with pre-vaporisation	80	-	100
- without pre-vaporisation	100	125	-
Ratio of cooling water volume to solution volume:			
- with pre-vaporisation	1:1	-	0.9:1
- without pre-vaporisation	1.6:1	2:1	-
The ratio of the volume of regenerated water to the volume of the solution:			
- with pre-vaporisation	1:1	-	1:1
- without pre-vaporisation	1:1	1:1	-

Table 14: Comparison of hydrochloric acid regeneration method.

From the presented data it is clear that acid regeneration in the Ruthner spray kiln (method 1) is the most profitable, because this unit is superior to the others in all respects, except for the amount of recycled liquor. On this basis, the Ruthner furnace was chosen as the HCl recovery aggregate for the development of a closed-loop process flowchart. The operating principle of the spray kiln consists in spraying the solution simultaneously with the excess air and combustion gases in the reactor

8 which activates the evaporation of the solution (Fig. 7; Source: Sheftel, 1970). This results in decomposition of iron chloride to produce iron oxide and HCl according to the reaction (Habashi, 1995, p.34):

$$2FeCl_2+2H_2O+{}^{1}/_{2}\,O_2 \rightarrow Fe_2O_3+4HCl \qquad (12)$$

The resulting iron oxide is precipitated in the reactor 8 itself and additionally in the cyclone 10, as some of it is carried away with the waste gases and is recovered as a by-product. The percentages of Fe_2O_3 in the reactor and cyclone are 80 and 20 % respectively.

The process of converting iron chloride to oxide is carried out according to the following steps:

- Inert heating of droplets: after the solution is injected into the reactor, the droplets are heated to the boiling point of water;
- Boiling of free water: as iron chloride forms hydrates, some of the water that evaporates at 373 K is bound to the iron chloride
- Evaporation of water bound to iron chloride;
- Decomposition of $FeCl_2$.

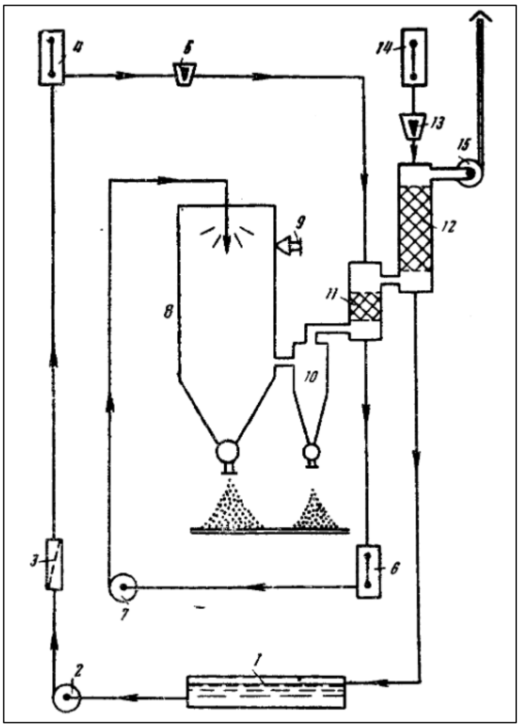

Figure 7: Ruthner furnace
1 - pickling tank, 2 - pump, 3 - filter, 4 - top collector, 5 - valve, 6 - intermediate collector, 7 - high pressure pump, 8 - reactor, 9 - burner, 10 - cyclone, 11 - pre-evaporator, 12 - condensation column, 13 - valve, 14 - top tank, 15 – fan

The important parameters are the volume of hot gases and of the bath with the solution to be treated 1. These are selected so that the temperature in the reactor is maintained at about 480°C (the decomposition temperature of the iron chloride in the above reaction (12).

There are two operating modes of the Ruthner furnace: with and without pre-evaporation. Pre-evaporation is necessary to increase the chloride concentration. In the pre-evaporator 11 the pickling solution is partially evaporated by the counterflow of hot gas coming from the reactor. However, this mode is not essential and successful regeneration may be carried out without it.

Sheftel N.I. states that the acid regeneration is 94-95%. Losses occur in the scrubber and with the exhaust gases (Sheftel, 1970, p.32).

According to the brochure "Regeneration Systems" from ANDRITZ AG, a spray roasting furnace is used at Novolipetsk Iron & Steel Works in Russia[3].

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[3] ANDRITZ.COM/METALS

In the 9th edition of the journal "Industrial and Environmental Safety, Occupational Health and Safety" in 2009 the use of a Ruthner furnace with a capacity of 5,500.00 t/a at “Nizhnekamskshina” was mentioned[4]. During the period of operation from 1989 to 2009 87,456.6 tons of waste (including third-party waste) were neutralised.

A disadvantage of application of HCl as a reagent is corrosive activity of the acid. However, this problem can be solved by leaching in rubber lined equipment.

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[4] https://prominf.ru/article/effektivnyy-recikling

3 RESEARCH PART

3.1 Scientific review and the state of research in the area under study

Many industries are now forced to dump metal-containing waste (secondary raw materials) due to lacking of sufficiently economical recycling methods. Due to increasingly strict environmental regulations, rising disposal costs and a lack of internal storage capacity, it is becoming increasingly important to study treatment processes. One example of anthropogenic raw materials is electric steel furnace dust, which usually contains significant amounts of zinc and iron. Dust from the steel production process causes profit loss, regardless of whether it is disposed of or recycled. As the dust contains heavy metals and halogen compounds, some of which can leach out. It is classified as a hazardous waste. In addition to the steel industry, this problem also affects the non-ferrous metals industry, which produces large quantities of waste that contain significant quantities of recoverable metals such as zinc, iron, copper, lead and others. The problem of recycling these substances has only been studied for a few years. The driving forces behind this are, on the one hand, the increase in metal prices in recent years and, on the other hand, the constantly rising demand for metals and, consequently, the demand for raw materials.

Zinc is the largest metal part of the EAF dust (with the exception of iron). Its content varies from 7 to 40 %. It is generally believed that the presence of large quantities of zinc is due to the increased use of galvanised steel in automobiles (Salihoglu and Pinarli, 2008, p.6). This necessitates the extraction of the valuable component, which can be carried out using pyro- and hydrometallurgical techniques.

PYROMETALLURGICAL TECHNOLOGY

About 90% of dust generated during steel production is recycled using pyrometallurgical processes. The difficulty is due to the presence of the volatile, but difficult to recover metal, zinc, in the dust. Condensation of oxidised metal on the charge, which causes increased coke consumption, is the main problem. In addition, the formation of scale leads to the destruction of the furnace lining.

By now, different technologies have been developed and implemented in the laboratory and industrial scale.

Waelz process

The Waelz process is the most common process for the recovery of valuable raw materials. This process takes a leading position due to the ability to extract a relatively low percentage of zinc in the dust and the lack of copper clinker, which would incur additional disposal costs.

The pulverisation process is about recovery of metals from their oxide form at high temperatures and their subsequent removal Figure 8.

According to the article "Technology for treatment of dust from electric arc furnaces of JSC "‘Severstal’" in the waelz-combination of JSC "ChPZ" the dust formation in the domestic industry reaches 168 thousand t/a (Pan’shin et al., 2012, p.5). However, there is no recycling. In 2012, at JSC "Chelyabinsk Zinc Plant" two-stage technology for zinc extraction from EAF dust was implemented for the first time on an industrial scale on the basis of the waelz-complex of the enterprise. After the first stage of Waelz-process waelz-oxide is formed, into which zinc is sublimed, which is captured by bag filters and directed to the second stage of Waelz process. The produced clinker from the first stage can be used in the sintering branch of the iron ore industry as an additive or as an inert material for reclamation of mine workings in road construction (Pan’shin et al., 2012, p.3). After double Waelz process, zinc is concentrated in the clinker, while halogenates, oxidised organics and non-volatile charge components (iron etc.) are volatilised.

The main disadvantages of Waelz process are:

- Significant fuel consumption;
- Ingress of iron oxides into the zinc concentrate.

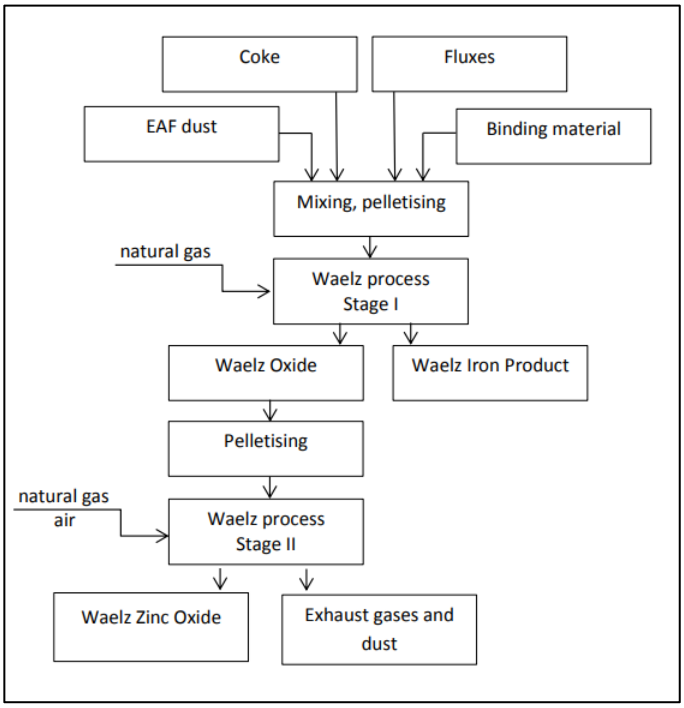

Figure 8: Technological scheme for EAFD processing by Waelz process

The result is a 96.5% zinc recovery in clinker.

The prospects for the development of Waelz technology are positive, as more and more end-of-life galvanized steel products (e.g. scrap) are being recycled into steel production. Environmental regulations for waste storage and storage also play an important role and are becoming stricter over time.

Smelting in a rotary hearth furnace

This technology is the second most common process after the Waelz process. The patent "Method of metallurgical processing" describes a method of obtaining zinc-containing slag and granulated pig iron by two-stage heat treatment in a rotary furnace at 1200-1300°C and at 1280-1500°C respectively (Odegov et al., n.d., 2017, p.6). The furnace is a horizontal rotary kiln on which a pelletized mixture of iron and zinc dust, mill scale, carbon reducing agent and slag-forming components is loaded. The whole mixture is subjected to heat treatment by means of installed burners. The resulting slag is a zinc oxide concentrate containing at least 60% Zn, and granulated pig iron, with about 94% iron, 1.0 to 4.5% carbon and low sulphur content (less than 0.09%), which defines the application of the products as raw materials for zinc metal and steel production respectively.

In the paper "Review of methods of electric arc furnace dust processing", Yu.I. Toporkova considers different technologies of zinc reduction by melting in the rotary-furnace (Nakagawa et al., 2010, p.2):

1. ITmk3 (Ironmaking Technology Mark Three) - when processing zinc-containing raw materials the technology makes it possible to obtain three products: granulated pig-iron, which does not yield to blast-furnace iron, slag and zinc-containing dust. The resulting pig iron is used in steel production, while the slag is used in road construction, cement and concrete industry.

2. Fastmet and Fastmelt - these technologies produce sponge iron and cast iron/steel respectively. The latter product is obtained by means of an electric furnace in the Fastmelt process chain. Fastmet has found application on a production scale. Hirohata Works of Nippon Steel Co. launched a zinc product with a high zinc content of 50-70% in 2000.

3. ZincOx - technology developed by a Korean company was recognised as more efficient in comparison to the Waelz process due to higher zinc throughput, better economics obtained by replacing coke with coal, improved zinc oxide quality, heat recovery and recycling and a cycle organisation that almost entirely prevents waste generation.

4. DryIron - the distinguishing feature of this technology is conversion of initial fine-grained raw material into pulverized coal briquettes by means of pelletizing. Zinc recovery is also high (95-97%).

5. Inmetco - mainly characterised by recycling of stainless steel waste, but EDS dust can also be used as material for zinc and lead substrates and alloyed pig iron. Some facilities in the USA, Thailand and Canada are known to operate on this technology.

6. Comet - the distinguishing feature is the method of loading the material into the rotary kiln. The raw material and carbon reducing agent are loaded in layers of 3-6 mm alternately. The process is characterised by lower productivity due to the degree of material grinding (2 mm).

Technological scheme with pelletising

In the paper "Recycling electric furnace steelmaking dusts for zinc and iron extraction" the technology of zinc and iron extraction from EAF dust with initial pelletizing of starting material was proposed (Nemchinova et al., 2016, p.11).

Smelting was carried out in a high-temperature furnace LHT 08/17 (Germany), and the extraction of waste metal-containing gases was forced by a water-cooled gas duct. In the course of melting, iron carbidisation took place, which resulted in the formation of granulated iron. Zinc recovery was 90%. The distribution of iron between pig iron and slag was 1:1, i.e. 50% in each product.

The disadvantages of this technology are:

- Increased chlorine and fluorine content in the zinc concentrate;
- Difficulty in obtaining pig iron in a single metallic phase (only the fraction of 6 mm or less);
- Rather low iron recovery into pig iron;
- Contamination of the resulting zinc by condensing lead.

Primus technology

One technology that has found industrial application is the Primus technology, which has been developed for implementation at the A.K. Serov Metallurgical Plant for the production of DSP-80. Primus was developed by Paul Wurth and is based on a direct reduction process. The products of steelmaking waste processing are zinc oxide (with more than 60% metal content) and granulated pig iron (Loshkarev and Matyunina, 2015, p.4). The Primus technology is based on passing the sludge through chambers of a multi-hearth furnace, where reduction and metallization takes place. A simplified technological scheme of the process is shown in Figure 9 (Source: Loshkarev and Matyunina, 2015 p.5).

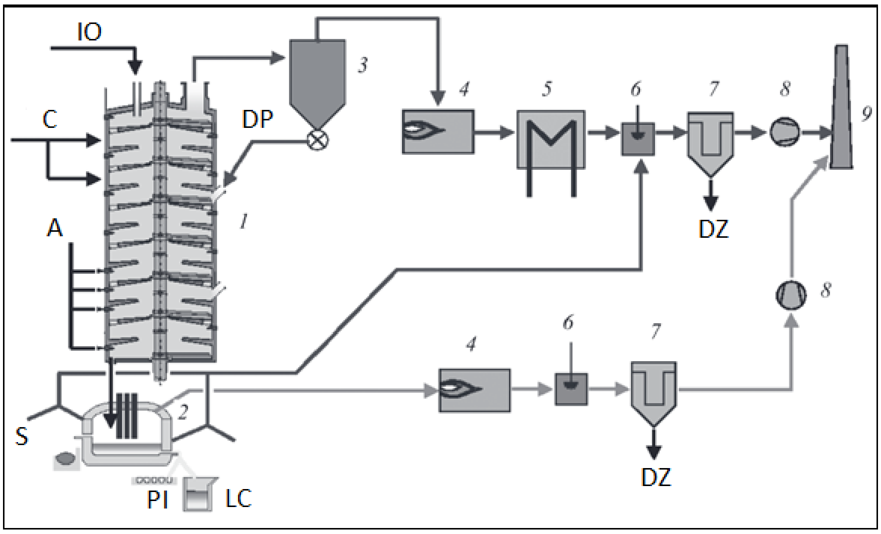

Figure 9: Primus technology
1 - multi-hearth furnace; 2 - cyclone; 3 - gas afterburning chambers; 4 - combustion air recuperator-heater; 5 - coolers; 6 - fabric filters; 7 - smokeboxes; 8 - chimney; 9 - melting aggregate; IO - iron ore; C - coal; A - air; S - slag; PI - pig iron; LC - liquid cast iron; CP - combustion products; EFG - electric furnace process gas; AG - aspiration gases; DP - dust for Primus process recycling; DZ - dust for zinc and lead production

The lead and zinc contained in the feedstock is removed from the process after reduction, evaporation and oxidation by gas. A distinctive feature of the multi-hearth furnace (another name is the multi-chamber boiler aggregate (DSP-80)) is the possibility of separate extraction of gaseous products. Thus, at a temperature of 950-1050 ° C lead, chlorides and alkali metals are first extracted in sub carbons. The further addition of carbon activates the zinc recovery process. Using the preliminary sublimation of the elements, the process allows the production of a product with a higher zinc content of up to 90%.

The products of the Primus process are granulated pig iron, which has the properties of blast furnace iron, and dust with a zinc content sufficient to be used as a raw material in the zinc industry.

According to the author, two smelters are using the Primus process: in Luxembourg and Taiwan, with capacities of 85,000 t/a and 120,000 t/a respectively.

OXYCUP process

The technology was developed by Germany's Küttner GmbH & Co. In 2004 the OXYCUP process was commercialised by Thyssen-Krupp Steel (Hamburg, Germany) (Holtzer et al., 2015, p.7).

The starting material is formed briquettes (C-bricks), the composition and appearance of which are shown in Figure 10.

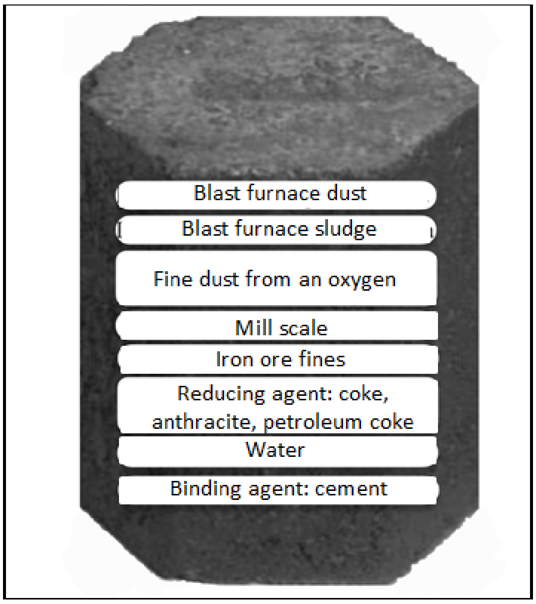

Figure 10: The elements C-briquettes consist of.

The OXYCUP process combines the melting function of traditional blast furnaces with the reduction function of blast furnaces. In contrast to electric arc and blast furnaces, cupola furnaces can easily process large quantities of zinc contained in the charge, which can be obtained either from metallurgical waste or from automotive scrap (Li et al., 2014, p.2).

Further distribution of the products obtained:

- Pig iron - to the converter shop;
- Slag - for granulation;
- Bottom combustion gas - to be used as fuel;
- Bottom combustion dust - to be converted into briquettes.

When zinc content in subsoil becomes sufficient for the product to be considered economically viable, it (subsoil) is recovered and sold as zinc concentrate (Kurunov, 2012, p.8).

In the paper "Prospects of recycling all metallurgical wastes on a plant or regional scale" the author describes the principle of the OXYCUP furnace in details and considers variants of industrial application of this technology in Russia (Ushakova et al., 2011, p. 13). The introduction of the OXYCUP process into the existing production facilities is possible due to the use of traditional industrial waste typical of the domestic industry as raw materials (pig iron, slag, gases and dust), the flexibility of operation in the factory environment, and the low cost of pig iron production.

Mintek

The American company Mintek has developed a technology based on plasma-arc dust melting. The heart of the process is a furnace consisting of a cathode, represented by a single graphite electrode, and an anode, which is a melt in the furnace bath. The company has developed 4 furnaces, one of which operates at high power (1 MW), the others at lower power (50, 100 and 200 kVA) (Schoukens et al., 1991, p.65).

A pilot plant using the developed furnaces was tested by the company. Zinc and lead oxide recovery was tested on both high-power and low-power furnaces. As a result, double the amount of zinc and lead oxides were recovered. The iron content in the substrates was reduced by a factor of 10 in comparison to steelmaking dust.

The disadvantage of the Mintek technology is that it can be applied to a limited type of raw material: dust from carbon steel production with high zinc content, dust from alloy steel production with high and low zinc content and lead smelting slag.

The Enviroplas process

The above mentioned Mintek company has also developed the Enviroplas technology, which includes 3 possible implementations depending on the type of raw material (Barcza et al., 1995, p.43):

- Envirodust - electric arc furnace dust and argon-oxygen decarburisation;
- Enviroslag - slags from lead generation and smelting furnaces;
- Envirores - calcined zinc/lead leaching residue.

In the paper "Pilot production of Prime Western zinc from lead blast furnace slag using Enviroplas technology" the process of zinc production from lead blast furnace slag using Enviroplas process which consists in reduction of zinc and lead oxides to metals in 2 plasma arc furnaces developed by Mintek, their (metals') transition to gaseous state and condensation in lead splash condenser (ISP) (Schoukens et al., n.d.,2016, p.4). A schematic of the Enviroplas technology is shown in Figure 11 (Source: Schoukens et al., n.d., 2016, p.5).

The distinguishing feature between the pre-melting furnace and the melting furnace is the presence of two openings in the second one for discharge of the formed products - slag and metal-bearing gas. Also in the body of the melting furnace there was a bottom intake opening, necessary for loading the already molten slag.

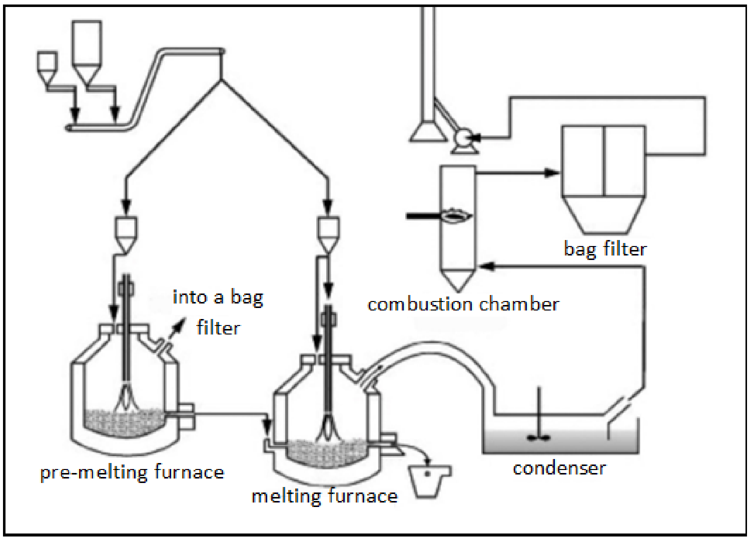

Figure 11: Scheme of Enviroplas technology

The temperatures in the furnaces are 1300ºC and 1450ºC respectively. These temperature values were chosen to minimise zinc losses in the pre-melting furnace, to ensure the required slag fluidity and a high zinc recovery rate. In the condenser, the inlet gas temperature was kept constant (1000-1100ºC), as was the pressure (about 5 mm H_2O), to prevent oxidation of gaseous metals, which is the cause of accretion - the process of mass increase by adding new layers or parts.

Moreover, the author analysed the effect of changing temperature while maintaining a constant CO to CO_2 ratio (percentage of coke added). These conditions influence the occurrence of a reverse reaction of vapour zinc with CO_2, re-oxidation of zinc and the occurrence of undesirable side reactions such as magnesium and silicon monoxide evaporation. Excessively high temperatures can also lead to destruction of the furnace lining.

According to the author, this technology was successfully commissioned in 1994. Approximately 600 tonnes of EAF dust were processed, and one-time slag with zinc and lead contents of less than 1.5 and 0.2% respectively was obtained. The zinc recovery efficiency was 80%.

Tetronics

Tetronics is a technology similar to the Enviroplas process described above. The difference is the way the feed material is loaded. In Tetronics, the charge is loaded through feed ports built into the vault. Whereas in Enviroplas the charge is loaded through the central opening of the graphite electrode.

Dust and coke breeze EAF are fed through ports located in the vault of a cylindrical DC furnace. Electric power is supplied through the central graphite electrode. The zinc, lead and cadmium oxides contained in the EAFD are selectively reduced and evaporated, and the safety slag rich in iron oxide is periodically discharged from the furnace.

Elkem

The Elkem process for processing EAF dusts is based on the Elkem Furnace (EMPF) combined with an ISP Zinc Spray Condenser. The EMPF is a sealed three-phase furnace equipped with a thermal oil cooling system to produce a frozen slag liner. The furnace, which was commissioned in 1992, had an annual design capacity of 40,000 tonnes of EAFD. The Elkem process is similar to the Tetronics process. The main differences are that a three-phase slag furnace is used instead of a DC arc furnace, and briquettes are used instead of unagglomerated raw materials.

Zewa

The Zewa process was developed and applied at VitkoviceSteelworks (Czech Republic). The disadvantage of the technology is the limited use of metallurgical waste as a feedstock - it is economical to process only dusty waste with high zinc and iron content. The distinctive feature is the set of end products, which includes the production of steel, lean slag, and a secondary product of gas purification (Toporkova et al., 2021, p.23). Consequently, another disadvantage of the technology is the lack of zinc concentrate as an end product that is sent to the consumer. However, obtaining high quality steel and a zinc-rich and lead-rich dust product (50-70%) makes this process economically viable.

ScanDust

A number of companies have developed and implemented technologies that use plasma to process iron-containing waste (ScarArc, ScanDust, etc.). Since 1984, more than one million tonnes of dust have been recycled using the technology developed by ScanDust (Sweden). Approximately 600 000 tonnes of metal have been produced using this method. In this technology, a pre-dried dust and sand mixture is injected into plasma jets at the bottom of the reactor and coke is fed into the reactor above the plasma zone. The exhaust gases are returned to the plasma zone after cleaning. A total of 240 kg of coke and 100 kg of sand are consumed to produce 1 ton of secondary dust. The products are 480 kg of metal, 500 kg of slag and 170 kg of high zinc content sludge (Doronin and Svyazhin, 2011, p.3). An advantage of the technology is the possibility to recycle all kinds of metallurgical dust and sludge and to recover the heat of flue gases, which keeps the energy efficiency at a high level. The disadvantage of the technology is the high capital investment.

ArcFume

At the 9th International Symposium on Lead and Zinc Recycling, testing of the ArcFume technology was conducted. The aim of the test was to find out whether the depleted residue could be re-melted and a good quality slag could be recovered and several metals could be recovered. Using the ScanArc furnace, oxides are recovered into the gaseous phase which contains valuable metals (Zn, Pb, Ag, In, Ge, Sb) as well as impurities (As, Cd, Tl, F, Cl).

The reduction process consists of two stages (Siegmund et al., 2020, p.6):

1. Oxidation and reduction in the ArcFume reactor;

2. Melting of the granulated slag in a flame reactor in a reducing atmosphere (reduction of volatile metals).

The oxide steam is then treated hydrometallurgically: halogenide washing, selective leaching to produce Pb-Ag residue and separate extraction of In and Ge. As is precipitated as iron arsenate.

Zinc is reduced and sublimed. The Zn stream, captured by bag filters, is routed to the zinc plant cycle.

Conclusion to the section

To date, a large number of technologies have been developed to process anthropogenic waste from steelmaking production in order to recover useful components. However, most of them remain at the development stage. Some have been tested on a large industrial scale, but have not been introduced into production for various reasons:

1. The size of the capital investment;
2. The reliability of the process (flaring types of melting);
3. Difficulties in maintaining melting units (multi-hearth furnace)
4. High power costs (plasma melting types);
5. Low capacity;
6. The selectivity of used raw materials, etc.

Despite the variety of invented technologies, all of them are not designed to solve the overall problem of waste recycling. The processes are aimed at solving only particular problems and have many disadvantages which limit the breadth of their application.

HYDROMETALLURGICAL PROCESSES

In addition to pyrometallurgical processes, many hydrometallurgical processes have also been developed.

Although hydrometallurgical technologies have a number of advantages, the efficiency of zinc leaching using hydrometallurgical processes is rather low, because the most part of zinc in EAF dust is in the form of $ZnFe_2O_4$. This compound is very stable and insoluble in alkaline or acidic environment under moderate conditions.

The basis of hydrometallurgy is the transfer of a valuable component in a solution in the form of different compounds (depending on the solvent composition) and its separation from a solid residue. The use of electrolysis in the last stage of hydrometallurgical technologies allows obtaining a useful product in the form of pure metal, which is one of the distinctive features compared to pyrometallurgical processes, where the final product is an oxide form of metal. Since the main operation of hydrometallurgical technologies is the leaching process, technologies can be classified according to the type of reagent used - acidic, alkaline and complexing.

Hydrometallurgy is still developing. Quite a number of hydrometallurgical technologies have been devised to extract zinc from steelmaking dusts. However, most of them have not yet found wide application on an industrial scale. In the domestic industry the implementation of hydrometallurgical processes is progressing particularly slowly.

The present hydrometallurgical technologies for the processing of zinc-containing dust generated during steel production are discussed below.

ACID LEACHING

Acid leaching is a highly efficient method of converting metals to solution. A characteristic feature of this method is the rapid kinetics of the chemical processes. A disadvantage however, is that in addition to zinc, iron is actively leached in an acidic environment. Consequently, the main objective of many studies is to find optimal solutions that will concentrate the zinc in solution and the iron in an insoluble precipitate.

Sulphuric acid leaching

Sulphuric acid is a cheap reagent that is produced in copper and zinc smelters. The sulphuric gases produced during the metal production process are collected by filters and routed for further acid production. Sulphuric acid leaching is an effective and intensive method of zinc recovery. It has the disadvantage, however, that the dust contains other, more soluble elements, such as iron, calcium and magnesium, which absorb about 90% of the sulphuric acid consumption. Thus, the target zinc only accounts for about 10% of the leachate. Consequently, the solutions after leaching contain large quantities of iron and are poor in zinc. The subsequent treatment of iron is in turn expensive and difficult to achieve.

In hydrometallurgical processes zinc is first leached with sulphuric acid solution and then the enriched Zn solution and solid extraction residue containing non-extractable Zn and some heavy metal compounds such as Pb, Cd and Mn are obtained by separating liquid and solid phases using a rotary filter. The zinc-rich solution is purified and the zinc is extracted by electrolysis, while the solid residue from the extraction process is usually landfilled. These residues are considered hazardous waste due to the presence of heavy metals (Altundog et al., 2016, p.5).

The main objective of this technology is to transfer zinc into solution in the form of sulphate. The interaction processes are described by the following stoichiometric reactions (Cruells et al., 1992, p.67):

$$ZnO_{(s)}+H_2SO_{4(aq)}\rightarrow ZnSO_{4(aq)}+H_2O \tag{13}$$

$$Ca[Zn(OH)_3]_2\cdot 2H_2O\ _{(s)}+H_2SO_{4(aq)}\rightarrow CaSO_{4(aq)}+2ZnSO_{4(aq)}+8H_2O \tag{14}$$

$$CaCO_{3(s)}+H_2SO_{4(aq)}\rightarrow CaSO_{4(aq)}+CO_{2(g)}+H_2O \tag{15}$$

$$ZnO\cdot Fe_2O_{3(s)}+4H_2SO_{4(aq)}\rightarrow ZnSO_{4(aq)}+Fe_2(SO_4)_{3(aq)}+4H_2O \tag{16}$$

$$Fe_3O_{4(aq)}+4H_2SO_{4(aq)}\rightarrow FeSO_{4(aq)}+Fe_2(SO_4)_{3(aq)}+4H_2O \tag{17}$$

Reaction (16) occurs slowly at room temperature and proceeds more rapidly as the temperature rises. Despite its occurrence, the iron mostly remains in an insoluble residue.

The occurrence of reaction (15) leads to the consumption of sulphuric acid. The occurrence of this chemical interaction is extremely difficult to prevent, as it occurs at any concentration of H_2SO_4.

The process of zinc leaching in the presence of sulphuric acid has been studied in many studies. Works are devoted to tracing the trend of leaching degree depending on various factors: temperature, duration of process, acid concentration, stirring speed and liquid to solid ratio.

In the article " Electric arc furnace flue dusts: characterization and leaching with sulphuric acid" a study was carried out to identify the most suitable conditions and parameters for zinc extraction from dusts of a particular composition. The best parameters are (Cruells et al., 1992, p.34):

- H_2SO_4 concentration - 1 M;
- Molar activity of H_2SO_4- 0.135;
- Room temperature;
- Leaching duration - 3 h;
- Liquid/solid ratio – 10/1.

These figures ensure high zinc and low iron recovery rates of 80 and 40% respectively. Additional metals transferred into solution are Ca, Cd, Cr and As.

The author found that the extraction of metals is practically independent of the liquid/solid ratio. However, maintaining a ratio of 5/1 resulted in highly viscous slurry, which made it difficult to separate the liquid phase from the solid. In work " Hydrometallurgical processing of carbon steel EAF dust" the dependence of metal extraction on the ratio S/L was revealed (Havlík et al., 2006, p.3). It was found that a reduction in the leaching portion of the charge leads to an increase in the amount of iron transferred to the solution. This is explained by the fact that the amount of free acid with which the more active iron will interact increases. Consequently, the maximum amount of acid should be consumed for the extraction of non-ferrous metals.

Regarding the activity of sulphuric acid it was found that zinc recovery is almost independent of the value of this factor, unlike iron recovery, which has a direct correlation, which explains the choice of H_2SO_4 with minimum activity.

Conducting the leaching at room temperature excludes this factor from the group of influencing factors. In T. Gavlik's work, temperature is part of the study. Experiments were carried out at high temperature (100ºC-250ºC) and pressure. It was found that the amount of iron leached is relatively high at lower temperatures, but using higher temperatures such as 70ºC and 90ºC reduces the iron content in the solution. However, the iron content at 100ºC is many times higher than at 80ºC (Havlik et al., 2005, p.4). Therefore, an increase in temperature is one of the factors causing the transfer of unfavourable impurities such as iron into the solution.

In the study " Pressure Leaching of EAF Dust with Sulphuric Acid " the author considered not only high temperature (100ºC-250ºC) but also related pressure in autoclave as factors of influence (Havlik and Friedrich, 2004, p.2). It was found out that these factors do not have a strong influence. Only an increase of temperature to 150 and correspondingly pressure to 4.1 bars led to a slight increase of zinc recovery into solution. In this case, most of the iron will precipitate. It is interesting, that at conducting the process at a temperature of 100ºC and 150ºC and further settling of a solution within one or two days a white sediment in the form of calcium sulphate appears. In other cases, the calcium remains in a soluble form almost permanently. High values of temperatures and pressures at a particular a/d ratio (acid/dust - mass ratio of mass of acid to mass of dust in pulp (in grams)) lead to an increase in zinc yield. Consequently, achieving optimum zinc recovery from solution with minimum iron and calcium content at the next stage of electrolysis is possible by regulating the above mentioned leaching parameters.

In paper " Atmospheric leaching of EAF dust with diluted sulphuric acid" the author analyses influence of k/p ratio on zinc recovery. The conclusion is that this ratio (or concentration of sulphuric acid) is the most important factor influencing the leaching process, as increasing the amount of feed through the feeder entails a decrease in the degree of zinc transfer into the solution. The best concentration was taken as 0.4 $mol{\cdot}dm^{-3}$, which achieved a Zn recovery of 67% (Havlik et al., 2005, p.3). The amount of acid applied to leach dust of a particular composition also depends on the pH value which varies with the process at different temperatures. More concentrated acid solutions (0.5 and 1.0 $mol{\cdot}L^{-1}$) raise the pH to around a unit value (Havlík et al., 2006, p.3). The $Fe\text{-}S\text{-}H_2O$ system allows the pH dependent behaviour of iron to be monitored. The stability region of the Fe^{2+} ion lies between pH values up to 1.6 at 100 °C and pH = 0.4 at 250°C (Havlik et al., 2005, p.4). If the $Fe\text{-}S\text{-}H_2O$ system has a pH outside the stability range of the Fe^{2+} ion, the iron will precipitate insoluble.

The duration of leaching is also an influencing factor. With time the zinc recovery gradually decreases, which can be explained by the theoretical assumption of metal deposition in the form of $ZnFe_2O_4$.

Another factor influencing the leaching process was analysed by T. Yoshida. At higher temperature and lower pH, the leaching rate also increases (Yoshida, 2003, p.5). Also the relatively lower activation energy and the relationship between leaching rate and sample rotation rate indicate that the reaction rate of zinc oxide leaching is controlled by mass transfer through the liquid boundary layer. The speed of rotation of the sample acted as an additional influence because the design of the laboratory setup was as follows: a glass flask containing 0.5 dm^3 of leaching solution acted as the reaction vessel in which a zinc oxide disk sample was immersed and attached to a rod. The rod and sample were rotated by a variable speed motor.

The aim of the study " Atmospheric leaching of steel-making wastes and the precipitation of goethite from the ferric sulphate solution" was to determine the conditions for both selective zinc leaching and complete zinc and iron extraction with sulphuric acid for two different types of wastes. The goethite process was chosen for the precipitation of iron from the iron sulphate solution as it does not require increased pressure. The goethite process consists of diluting the leached solution to an iron content of 0.123 g per 1 l and adjusting the pH to 2.15 (Langová et al., 2007, p.4). These conditions were optimal for the precipitation of goethite. The solution was heated in a closed beaker and the pH monitored until it remained almost constant after 2 hours, after which the process was stopped. An even lower dissolution rate could be achieved by a longer precipitation time. The final concentration of Fe in the solution was 0.0284 g/l, i.e. 23 % of the initial amount. Further reduction of iron content in the solution was achieved by the addition of a small amount of ZnO, which reduced the iron concentration in the solution to 3.9 mg/l. The sulphur content in the sludge was reduced to less than 2% by strict pH control. The process can be carried out with a small amount of alkali, provided that there is sufficient dilution. Therefore, the costs for hydrometallurgical treatment of steelmaking dust and sludge could be reduced. The contamination of the sludge with zinc and sulphur was low and amounted to 0.044% and 2.7% respectively. The main drawback of this precipitation method is the high water consumption. If the solution was neutralised with fresh dust, the amount of water needed to dilute the leaching solution could be significantly lower. Also, only small quantities of zinc can be extracted successfully in the solution without accompanying dissolution of iron. The remaining zinc is represented by low-soluble zinc ferrite compound $ZnFe_2O_4$, which can be successfully transferred into solution (almost 100%) at elevated temperatures by hydrochloric or sulfuric acid at concentrations of 2 M and 3 M, respectively (Jandová et al., 2013, p.3). When using dilute acids, zinc yield is within 20-40%. One solution to this problem could be the use of additional solution purification operations prior to electrolysis. If all dust constituents pass into solution, then lead, cadmium and other metals should be extracted by cementation and iron by extraction or precipitation as jarosite, goethite, hematite or magnetite.

In the paper " Hydrolysis of Ferric Sulfate in the Presence of Zinc Sulfate at 200 °C: Precipitation Kinetics and Product Characterization " a similar method of Zn extraction was studied. Only the precipitation of iron was in the form of hematite. This process is a commercially available precipitation process which produces no waste. Lead and cadmium are removed from the zinc solution by cementation. Interestingly, zinc sulphate increases the stability range of hematite (Cheng and Demopoulos, 2004, p.3). Over 92% of zinc can be leached in 100 min using 0.3 M H_2SO_4 solution at 260°C. Wustite and magnetite are the source of Fe (II), which remains in solution, while most of the Fe(III) is hydrolytically precipitated as hematite. In the presence of hydrogen peroxide most of the iron precipitates and zinc recovery increases to ~99%. The zinc/iron ratio in the solution has suitable values for subsequent treatment. The content of iron and zinc in the residue was 90 and 0.2-0.3 % respectively. Minor amounts (a few percent) of $PbSO_4$, $CaSO_4$ and graphite were also observed. Compared to a zinc recovery study by atmospheric leaching conducted by the same author, the leached solutions contain low iron concentration, which eliminates the need to add alkali to the solution for iron precipitation. On the other hand, the zinc concentration is lower, which may be the reason for the increased cost of the thickening stage.

According to P. Ustadakis et al. the optimum conditions for dust of a given composition are: acid normality = 3N, temperature = 60°C and solid/liquid ratio = 10% (Oustadakis et al., 2010, p.2). As a result, 80% of zinc and 45% of iron were recovered. This study is further evidence that the zinc present in the EAFD as zincite is much easier to dissolve than the ferritic form (according to SEM/EDS and X-ray diffraction analysis).

The author of the study "Environmental risk assessment and stabilization/solidification of zinc extraction residue: I. Environmental risk assessment" was analysed the residue after the dust leaching operation. The solid residue contains non-extractable Zn and some heavy metal compounds such as Pb, Cd and Mn and is usually stockpiled (Özverdİ and Erdem, 2010, p.3). The heavy metal content is responsible for the toxicity of these residues. The toxicity characteristic leaching procedure (TCLP) conducted showed that the concentrations of Pb and Cd dissolved in the residue are about 65 and 2.9 mg/l respectively. As these values exceed the threshold values of 5 mg/l for Pb and 1 mg/l for Cd, the residue should be considered a hazardous pollutant and should not be disposed of with domestic waste. Further the author proposed a variant of stabilization in solid form of zinc extraction residue using Portland cement, fly ash and lime using solidification/stabilization process (hereinafter S/S) (Erdem and Özverdi, 2011, p.4). S/S technologies are widely used for the treatment of hazardous wastes such as slimes, slags and ashes containing heavy metals. The main objectives of S/S processes are to reduce the hazard of waste by converting the pollutants into less soluble, mobile or toxic forms and to encapsulate the waste into a monolithic solid body with high structural integrity using certain additives such as metal stabilisation additives and binders (Conner and Hoeffner, 1998, p.31). S/S processes not only improve the physical and chemical properties of the waste but also have low cost compared to other treatment methods by using the cheapest binders such as cement, lime and pozzolan (Pereira et al., 2001, p.8). S/S processes have been applied to many industrial wastes containing heavy metals such as copper slag (Zain et al., 2004, p.5), galvanic sludge (Luz et al., 2006, p.4), electric arc furnace dust (Pelino et al., 2002, Bulut et al., 2009, p.3-4), heavy metal sludge (Andrés et al., 1998, Diet et al., 1998, p.6-7) and foundry sludge (Ruiz, 2004, p.3). The S/S process found portland cement to be the best binder among those tested, with a minimum of 40% of it in the mixture. The release of Pb and Zn was highly dependent on the reagent used in the S/S operation. For example, lime was found to be unsuitable for use as a reagent. The efficiency of S/S decreases in the sequence Portland cement > fly ash >> lime. By using Portland cement, combinations based on Portland cement and a minimum of 30% fly ash as reagents it was possible to successfully immobilise extractable heavy metals. Their concentrations were reduced to values below the TCLP limits. Pb in the form of anglesite, which is the main pollutant in the solid residue, was converted into susannite [$Pb_4SO_4(CO_3)_2(OH)_2$] and cerrusite [$PbCO_3$] (Salihoglu et al., 2007, p.4).

The Zincex process is another example of the extraction of impurities that pass with the zinc into solution during the leaching process. A modified Zincex process is used to produce high quality zinc boards from recycled raw materials. Atmospheric leaching, purification of the leached solution (mainly from iron and aluminium by precipitation), solvent extraction and conventional electrolysis are used to deal with impurities and to recover zinc ingots. At the Anglo-American Skorpion Zinc refinery, impurities such as iron, aluminium and silica are removed from the solution by precipitation after leaching with sulphuric acid. Zinc is then selectively extracted with di(2-ethylhexyl) phosphoric acid, which allows electrochemical extraction of zinc in the next stage (Cole et al., 2006, Maccagni, 2016, p.4). This technology studied in paper "Hydrometallurgical process for zinc recovery from EAFD. Part II: Downstream processing and zinc recovery by electrowinning", consists of the following stages (Tsakiridis et al., 2010, p.6):

- **Removal of iron by chemical precipitation**

The process has been patented by the National Technical University of Athens and consists in the precipitation of iron, aluminium and chromium ions from sulphate-nickel leach solutions in the form of crystalline, easily filterable chemical precipitates, such as jarosite, under atmospheric pressure without the addition of alkali.

The precipitation follows a hydrolysis reaction (Dutrizac, 1996, p.45):

$$2[Fe_2(SO_4)_3]_{(aq)}+[Al_2(SO_4)_3]_{(aq)}+H_2SO_4+12H_2\rightarrow \qquad (18)$$
$$2H[Fe_2Al(SO_4)_2(OH)_6]_{(s)}+6H_2SO_4$$

This step is necessary because it is known that iron levels even as low as 0.001% in the sulphate electrolyte significantly reduce the zinc current yield.

- **Zinc recovery by extraction**

Extraction by di(2-ethylhexyl)phosphoric acid occurs by the mechanism of cationic liquid ion exchange. An oxygen atom of the phosphoric group ensures coordination with extractable ions, forming chelation products (the process of the formation of substances whose solutions, when interacting with metal ions, form chelates - substances whose molecules can form several bonds with a single metal ion).

- Zinc electrowinning

This stage is the main application of this chain of hydrometallurgical operations. It is also highly important in extracting zinc from primary sources. About 80 % of world metal production is realized by this method (Gürmen and Emre, 2003, p.12). The process is possible because of the high overvoltage hydrogen formation on the zinc layer covering the aluminium cathode (as aluminium does not form alloys with zinc).

The main problem in zinc electro winning, which becomes more serious when the raw material is metallurgical waste, is the detrimental effect of metallic impurities as they reduce the current yield and the purity of the zinc precipitate (Mureşan et al., 1996, p.54). Iron can be removed from solution as an easily filterable crystalline basic sulphate salt of the jarosite type at atmospheric pressure and temperature of 95°C by chemical precipitation. Zinc is then extracted using Cyanex 272 (an acid-based extractant which provides cation exchange recovery), leaving the other metals in solution. The zinc-rich organic phase is then purified with spent zinc electrolyte to produce a solution suitable for zinc electrolysis. The magnesium and manganese formed in the solution can be removed by hydrolytic precipitation as an easily filterable crystalline precipitate at ambient temperature, using calcium hydroxide as a neutralising agent (Karidakis et al., 2005, p.7 and Zhang and Cheng, 2007, p.12).

In the study " Zinc recovery from purified electric arc furnace dust leach liquors by chemical precipitation" the chemical precipitation of zinc from metal-saturated solution obtained by sulphuric acid leaching was successfully performed as insoluble compounds of hydrozincite and zinc basic carbonate hydrate ($Zn_5(OH)_6(CO_3)_2$ and $Zn_4(CO)_3(OH)_6 \cdot H_2O$ respectively). The precipitating reagent was sodium carbonate (Na_2CO_3). As a result, a high zinc recovery of 99.5% was achieved (Xanthopoulos et al., 2017, p.3).

The authors of the study "A novel method to recover zinc and iron from zinc leaching residue" developed a new method of zinc and iron simultaneous extraction from solid leach residue including three stages: reduction roasting, acid leaching and magnetic separation (Yan et al., 2014, p.5). Zinc ferrite in the residue was selectively converted to ZnO and Fe_3O_4 in an atmosphere of CO, CO_2 and Ar. Acid leaching was then carried out to extract zinc from the reduced residue. Iron remained in the residue and was extracted by magnetic separation. The effect of firing and leaching conditions was investigated under the following optimum conditions: firing at 750°C for 90 min with 8% CO and CO/(CO + CO_2) = 30%; leaching at 35°C for 60 min with sulphuric acid at 90 g/l and a liquid/solid ratio of 10/1. Iron was extracted by magnetic separation for 20 min. At optimal performance, 61.38% zinc and 80.9% iron were extracted. The author claims that this method not only allows for simultaneous extraction of iron and zinc, but also solves the environmental problem regarding the disposal of large quantities of solid residue after leaching.

Although the leaching technology in all of the reviewed works is similar, each case is important and unique. This is due to the different composition of the raw materials and the conditions under which the process is carried out.

Hydrochloric acid leaching

Leaching with hydrochloric acid can be an alternative method of converting the metal into a solution. The basic reaction of the chloride formation process is as follows (Van Weert and Peek, 1992, p.14):

$$ZnO + 2HCl = ZnCl_2 + H_2O \qquad (19)$$

In the work "Leaching of Zinc Oxide in Acidic Solution" a zinc oxide disc was used for the leaching test. The experimental parameters were varied: pH, temperature, leaching time and rotation speed of the disk sample. It was found that the zinc yield increased with time and decreasing pH value (Yoshida, 2003, p.13). Also, the recovery is directly proportional to the temperature of the process, i.e., increases with increase. Regarding the speed of the disc sample, it was found that the thickness of the liquid boundary layer on the disc sample decreases as the speed of the sample increases. Consequently, the zinc yield increased. This relationship is fundamental due to the fact that the leaching reaction is controlled by mass transfer.

Hydrochloric acid was found to be a very effective reagent for the leaching of zinc ferrite. This process is described by the following reactions (Langová et al., 2009, p.17):

$$ZnFe_2O_{4(s)}+2HCl_{(aq)}=ZnCl_2+Fe_2O_{3(s)}+H_2O \quad (20)$$

$$ZnFe_2O_{4(s)}+8HCl_{(aq)}=ZnCl_2+2FeCl_{3(aq)}+4H_2O \quad (21)$$

Iron can also be precipitated from a chloride solution as hematite by the reaction:

$$2FeCl_{3(aq)}+3H_2O =Fe_2O_{3(s)}+6HCl_{(aq)} \quad (22)$$

It is desirable to suppress reaction (21) in favour of reaction (20). In other words, shift the equilibrium of reaction (22) to the right. From the equation of the equilibrium constant of reaction (22), it can be concluded that dilute hydrochloric acid should be used to minimize the formation of $FeCl_3$. However, the amount of acid must be sufficient to extract the maximum amount of zinc. In this particular example the choice of hydrochloric acid is due to the fact that thermodynamic data indicate a much less intense reverse dissolution of hematite. The effective parameters for conversion of zinc to solution are:

- t = 260°C;
- p = 85 bar;
- duration = 100 min;
- C(HCl) = 0.3 M.

The yields were: Zn - 93% and α-Fe_2O_3 - 98% in solution and residue respectively. The iron can be used directly to smelt iron or as a pigment. The leaching solution contains less than 3 g/l of iron, which can be removed by precipitation after Fe(II) oxidation. The zinc/iron ratio in the solution obtained with dilute acid leaching at elevated pressure is much more favourable than that obtained by leaching and dissolving the whole material in strong acids.

In the study "Determination of the optimal parameters for dezincification of converter sludge of hydrochloric acid solutions" a particular case of BOF dust processing of JSC "ArcelorMittal Temirtau", one of the leading steelmaking companies in Kazakhstan, has been considered. Sixteen experiments with variation of leaching parameters: C_{HCl}, t, L/S have been conducted. At the same time researches were conducted at room temperature and atmospheric pressure. As a result, 87.90% zinc recovery was achieved. The most suitable conditions are (Katrenov et al., 2017, p.18):

- C_{HCL} = 15%;
- t = 90 min;
- L/S = 6/1.

This technology was developed for converter production; however, it can also be suitable for leaching of EAF waste, provided that the leaching parameters are well selected and optimized.

V.I. Kazyuta proposed a scheme of two-stage counter-current HCl leaching resulting in conversion of all metals into soluble divalent chlorides (Kazyuta, 2014, p.4). The iron chlorides are then reduced to Fe(III) first by scrap and then to powdered iron. Concerning zinc, powdered lime, gas purification dust from limestone firing furnaces, soda ash and other Ca-containing products are used for its precipitation. Thus, extraction rates are 95% for Fe, 90% for Zn and a recovery rate of 90% for HCl. In conclusion, the author emphasises another problem that arises when trying to treat dusts from steelmaking. To date, no technology has been developed to ensure the reuse of filter media after the leaching process.

The author of the paper "Processing of electric arc furnace dust via chloride hydrometallurgy" considered a two-stage method of leaching of zinc-containing dust. The technology consists of atmospheric leaching using excess ferric chloride as a source of hydrochloric acid (McElroy, 1994, p.19):

$$2FeCl_2+3ZnO+H_2O=2FeO\cdot OH+3ZnCl_2 \tag{23}$$

The pulp is further atmospheric leached at 175°C and appropriate vapour pressure to fully convert zinc ferrite to more perceptible and filterable hematite. The final product is a commercially pure ZnCl2 solution containing 60 g/l zinc. The resulting zinc to chloride yield was about 99%.

Although Reyad A. Schawabke found that at higher concentrations hydrochloric acid provides higher zinc recovery than sulphuric acid and has a strong activator (Cl^-) that can dissolve both zinc and iron, leaching using these acids is quite difficult as they dissolve large amounts of iron (Shawabkeh, 2010, p.21).

The study "Hydrometallurgical Extraction of Zinc and Iron from Electric Arc Furnace Dust (EAFD) using Hydrochloric Acid" examined the effect of hydrochloric acid concentration and leaching temperature on the amount of zinc in solution and iron in the insoluble precipitate. The present study shows that using 5 M HCl with a dust to acid ratio of 3 g per 100 ml after 15 minutes of leaching at 70°C, the maximum zinc and iron recoveries are about 70% and 60% respectively (Teo et al., 2018, p.7).

П. Halley et al. investigated the leaching of Cr, Fe, Mn, Pb and Zn from EAF dust using 16 different leaching media at different concentrations. The study showed that in the absence of oxygen scavenging, the highest zinc yield into solution (>75%) with good iron selectivity (<5%) was achieved using 1.2 M HCl and 10% aqua regia. In addition, 48-49% Pb can be removed with partial dissolution of Mn and Cr (Halli et al., 2017,p.12).

Nitric acid leaching

Mert Zoraga and his colleagues analysed the kinetics of steelmaking dust leaching with nitric acid. HNO_3 is a strong acid and dissociates completely in aqueous solutions by reaction (Zoraga et al., 2020, p.3):

$$HNO_{3(aq)} \rightarrow H^{+}_{(aq)} + NO^{-}_{3(aq)} \tag{24}$$

The process of zinc and iron transfer into solution is described by the following reactions:

$$\frac{1}{2}ZnO_{(s)} + H^{+}_{(aq)} \rightarrow \frac{1}{2}Zn^{2+}_{(aq)} + \frac{1}{2}H_2O \tag{25}$$

$$\frac{1}{8}ZnFe_2O_{4(s)} + H^{+}_{(aq)} \rightarrow \frac{1}{4}Fe^{3+}_{(aq)} + \frac{1}{8}Zn^{2+}_{(aq)} + \frac{1}{2}H_2O \tag{26}$$

$$\frac{1}{6}Fe_2O_{3(s)} + H^{+}_{(aq)} \rightarrow \frac{1}{3}Fe^{3+}_{(aq)} + \frac{1}{2}H_2O \tag{27}$$

When ore or metallurgical dust is processed, preferably in a loose, granular or finely divided state, leaching is carried out with nitric acid to form a mixture of calcium nitrate and other metals. The nitrates that are in solution are removed from the process and dried at room temperature to about 200°C to remove moisture. The solid sludge is then heated to between 200 and 500°C to break down the metal nitrates into oxides and oxygen in gaseous form. The gases are then removed. The calcium nitrate remains in solid form, which is then leached with water. The calcium nitrate passes back into solution, while the metal oxides remain as solids and are thus separated from the calcium nitrate. If desired, calcium nitrate can be used as a product in its current form or heated to above 550 °C to decompose it to lime (CaO) (Drinkard et al., 1998, p.75).

P. Halley found that the use of 1.5 M HNO_3 in a mixture with 0.94 M citric acid leads to a high yield of Zn in solution (> 75%) with some dissolution of Fe (15-17%) (Halli et al., 2017, p.15).

In the paper "Basic Consideration on EAF Dust Treatment Using Hydrometallurgical Processes" the process chain consists of nitric acid leaching and electrolysis (Nakamura et al., 2008, p.9). The EAFD is first leached with water to remove chlorine from the dust. The dust is then leached with diluted nitric acid solution to extract Zn. After filtration the residue is returned to the EAF as a source of iron. The filtrate is purified by adding zinc powder and precipitation of metallic impurities and then filtered. Finally, electrolysis in solution is carried out. Zn or ZnO is precipitated at the cathode and O_2 is produced at the anode where nitric acid is regenerated. Although there are virtually no differences between leaching with nitric acid solution and other acid solutions, the electrodeposition of Zn in nitric acid solution is very different from that in other acidic solutions due to the formation of powdery/dendritic Zn/ZnO. This is a disadvantage of the process. The regenerated nitric acid returns to the leaching stage. In this way, a perfectly closed system is achieved. No data is available on the percentage yield of elements.

Despite a number of patents, the process is considered to be expensive, environmentally unfriendly and unsafe.

Leaching with organic acids

A common feature of this technique is the careful washing of the dust of chlorides before leaching. This operation is of high importance because even small amounts of chloride compounds cause intense iron transfer to the solution.

Dreisinger et al in cooperation with Chaparral Steel have developed a hydrometallurgical process on a laboratory scale based on leaching with dilute acetic acid to dissolve lime to produce calcium acetate, further processing of which consists in ammonia leaching to remove zinc from the residue. Zinc is precipitated with carbon dioxide at boiling point as basic zinc carbonate and the residue is leached with hot acetic acid to remove lead so that recycling is possible. As a result, the yield of Zn as $ZnCO_3 \cdot Zn(OH)_2$ compound is 55-60% (Dreisinger et al., 1990, p.76).

In the paper "A hydrometallurgical process to treat carbon steel electric arc furnace dust" leaching using concentrated acetic acid at room temperature with further residue treatment in electric furnace to extract Fe from iron oxides and zinc ferrite in insoluble residue was investigated (Barrett et al., 1992, p.32). The heavy metals in solution (zinc, lead, copper and cadmium) are precipitated as a bulk sulphide product (by acetic acid regeneration) for delivery to the zinc refinery. The process is based on the concept of reusing dust in the electric furnace while removing components that are undesirable in steelmaking.

The aim of the work "Hydrometallurgical recovery of zinc and lead from electric arc furnace dust using mononitrilotriacetate anion and hexahydrated ferric chloride" was to study the possibility of applying a process designed to extract zinc and lead from chipboard dust without destroying the iron oxide matrix. The material could then be recycled in the steel industry. The proposed process consists of atmospheric dust leaching using sodium hydrogenonitrile triacetate solutions to selectively dissolve easily leachable compounds such as ZnO and Pb(OH)Cl, further zinc and lead extraction from the filtrate by sulphide precipitation and $ZnCl_2$ recovery by treating the solid residue with $FeCl_3$-$6H_2O$. The reaction consists of an exchange of O^{2-}/Cl^- particles, allowing zinc to be extracted as chloride and iron as Fe_2O_3 hematite (Leclerc et al., 2002, p.2). The separation of these products is carried out by simple aqueous leaching. The author noted the following regularities:

- With increasing temperature, zinc extraction increases, but there is also an increase in the iron content of the solution;
- The optimum ratio is $HNTA^{2-}/ZnO = 8/1$.
- The resulting residue after leaching is suitable for safe disposal.

The process can be applied to other zinc or lead containing solids (burnt sulphides, waelz oxides, metallurgical scrap, etc.). The process can also be adapted according to the composition of the sample. For example if the sample to be analysed is predominantly zinc in the form of ZnO, only the first step will be carried out. On the other hand, if the predominant mineralogical form is zinc ferrite, the solid will be directly treated with $FeCl_3$-$6H_2O$.

Some experiments carried out with calcined sulphide and waelz-oxide samples have shown that zinc recovery yields can be as high as 99.5%.

Application of citric acid as a leaching agent for zinc extraction from steelmaking dust was considered in the article "Selection of leaching media for metal dissolution from electric arc furnace dust". The research showed, that this reagent at a concentration of 0.94 M transfers >75% of zinc into solution. A good iron selectivity (<15%) is observed (Halli et al., 2017, p.4).

P. Halli and co-authors in the article "Developing a sustainable solution for recycling electric arc furnace dust via organic acid leaching" have developed a new two-step process for the treatment of steelmaking dust. The technological approach uses an alkaline roasting with NaOH at 450°C followed by leaching with 0.8 M citric acid at 40°C with an oxygen purge for two hours (Halli et al., 2018, p.3). It has been observed that roasting converts $ZnFe_2O_4$ to the favourable form of sodium zincate (Na_2ZnO_2) and sodium dioxoferrate ($NaFeO_2$), the former being an easily leachable zinc compound and the latter retaining the iron in a solid state. The optimum parameters are: t = 40ºC. With citric acid = 0.8 M. This technique ensures that more than 90% of the zinc is transferred to the solution. Only leaching with citric acid without pre-flame was also investigated. In this case it is possible to reduce the acid concentration to 0.4 M as there is no need for pH maintenance. In this case, an extraction of only 78% Zn is achieved (Halli et al., 2020, p.4). The next processing steps of the resulting solution are the precipitation and extraction of Zn and Pb. Lead is removed as lead sulphate ($PbSO_4$) by precipitation with the addition of sulphuric acid at pH=2. In this process the loss of zinc is minimal. Zn is then extracted into an organic solution and further treated with sulphuric acid. The purified zinc solution is suitable for electrolysis. Consequently, the EAF dust, which is a waste product, can be used as an anthropogenic raw material for the production of secondary metals Zn, Fe and Pb.

Marja Rinne et al. in "Alternative Method for Treating Electric Arc Furnace Dust: Simulation and Life Cycle Assessment" compared the roasting and further leaching in citric acid process (hereinafter LCAP) described above with the conventional waelz process in order to identify possible disadvantages and advantages of the developed technology. The mass and energy balances of the processes as well as the environmental impact were analysed. The disadvantage of LCAP is the high consumption of chemicals, which, on a global scale, has an impact on global warming (Rinne et al., 2022, p.5). One option to reduce the environmental impact is to reduce the consumption of caustic soda during the firing phase.

Increased consumption of citric acid has also been reported due to its decomposition during leaching and interaction with alkali, which is a barrier to its reuse. Optimisation of the roasting stage and cleaning of the roasted cinder with diluted inorganic acid solutions to remove easily soluble alkali and unreacted caustic soda can reduce the excessive consumption of citric acid in the leaching process.

The advantage is that the hematite residue can be returned to the EAF for iron extraction. LCAP is also more resistant to the presence of halogens in the starting material.

In the article "Sustainable methodology for recycling electric arc furnace dust" the parameters affecting the recovery of metals (Fe, Zn, Mg, Cr and Pb) during EAF dust leaching with citric acid were investigated. It was found that increasing the concentration of the reagent increases the extraction of all metals while the temperature decreases it. The latter is explained by the decomposition of organic acid during heating. In addition, it was found that the maximum zinc recovery achieved by direct leaching with citric acid was only 78% (Sun et al., 2018, p.12). The reason is the presence of Zn in the dust in the form of hard to dissolve ferrite. The solution to this problem is the use of pre-treatment in the form of alkaline roasting, which has increased the Zn recovery to 99.98%.

In "Citric acid as an alternative lixiviant for zinc oxide dissolution" the ability of ZnO to dissolve in citric acid in electrolytic media with the addition of chlorides, nitrates and sulphates was studied. Dissolution of up to 98%, 84% and 67% of zinc oxide was observed, respectively (Larba et al., 2013, p.3). In fact, citric acid without additives dissolved 90.4% of ZnO after 1 hour at 50°C. Consequently, the presence of chlorides leads to an increase in solubility and the addition of nitrates and sulphates leads to a decrease.

In general, citric acid is the only organic reagent capable of transferring more than 75% of the zinc into solution. However, acetic acid can also be considered as a leaching agent as it provides a Zn yield of over 50% with a very low accompanying iron recovery (<5%) compared to 20% with citric acid (Sun et al., 2018, p.4).

ALKALINE LEACHING

As mentioned earlier, zinc in EAF dust is present as $ZnFe_2O_4$ (franklinite) and ZnO (zincite). Zinc oxide leaching is not a problem with either acid or alkali. The use of alkali as a reagent has several advantages: the solid residue is much less toxic than the original EAFD as most heavy metals (such as cadmium and lead) are leached and the solid phase is rich in iron oxides and quartz and also contains some zinc ferrite. Alkaline leaching is the most profitable compared to acidic leaching due to the transfer of small amounts of iron into the solution (Dutra et al., 2006, p.3). However, the disadvantage of this method is the alkali consumption as the process must be carried out in a relatively concentrated medium (Youcai and Stanforth, 2000, p.6).

Leaching in NaOH solution

In the article "The selective alkaline leaching of zinc oxide from Electric Arc Furnace dust pre-treated with calcium oxide" the process of alkaline leaching of dust pre-treated with CaO to convert $ZnFe_2O_4$ to zinc oxide and $Ca_2Fe_2O_5$ without carbothermic reduction (Chairaksa-Fujimoto et al., 2016, p.4). The CaO treatment also results in the volatilisation of lead, chlorides and fluorides. The effect of temperature, leaching time, NaOH concentration and solid/liquid (S/L) ratio was also investigated. It was found that almost complete zinc recovery from CaO-treated dust could be achieved without any appreciable dissolution of iron and calcium, which remained as $Ca_2Fe_2O_5$ and $Ca_3Fe_2(OH)_{12}$ in the leaching residue. However, less than 50% of the zinc was recovered from the incoming raw dust, i.e., dust not subjected to CaO treatment. Optimal parameters were (Ghani et al., 2016, p.3):

- T = 70°C;
- NaOH concentration = 2M;
- S/L = 1/300;
- t = 2 h.

The following relationships were observed:

- Zinc recovery increases with increasing temperature;
- An increase in S/L ratio lowers the efficiency of zinc recovery because of ZnO solubility limit in the solution;

- Zinc leaching efficiency increases with increasing NaOH concentration.

In the paper "Alkaline leaching of zinc from steel dust from electric arc furnace" 4 types of leaching were analysed: conventional leaching with stirring; under pressure; conventional leaching after microwave pre-treatment and leaching with stirring provided by ultrasonic probe. Conventional leaching proved to be the most optimal with the following parameters:

- t = 4 h;
- C (NaOH) = 6 M;
- T = 90°C.

The zinc recovery was 74%.

In the article "Study of Zinc Leaching of EAF Flue Dust Using Sodium Hydroxide" 90% of zinc was converted into solution by leaching with alkali solution with concentration of 4 M (Ghani et al., 2016, p.6).

Jiachao Jiang et al. obtained zinc recovery equal to 84% under the following optimum parameters (Jiang et al., 2010, p.12):

- C (NaOH) 250 g/l;
- S/L = 1/10;
- T = 90°C;
- t = 2 h.

After leaching, the zinc solution was subjected to electrolysis, after which a powder of 98.5% purity was obtained. The solid residue is suitable for safe disposal and the residue after purification can be sold for lead extraction as it is concentrated there after precipitation with sodium sulphide.

In the article "Lead and zinc selective precipitation from leach electric arc furnace dust solutions" the technological scheme including hydrolysis, melting and strong alkaline leaching is described. Subsequent chemical precipitation using sodium sulphide as precipitant is carried out for selective extraction of zinc and lead from solution (Lenz and Martins, 2007, p.4).

LI Honghsiu and co-authors achieved 73.4% zinc transfer into solution by leaching in alkaline medium under conditions (Li et al., 2010, p.3):

- T = 90 °C;
- C (NaOH) = 6 mol/l;
- t = 60 min;
- average particle size = 0.69 µm.

A pattern of increased zinc yield with increasing NaOH concentration and leaching time was also noted.

In their paper "Optimized Hydrometallurgical Route to Produce Ultrafine Zinc Powder from Industrial Wastes in Alkaline Medium" Qiang Li et al. proposed the technology of zinc extraction, including alkaline leaching, purification stage and electrolysis (Li et al., 2012, p.2). The Zn recovery was over 80%. In addition, the residue was completely decontaminated. In the purification section, Pb, Sn and Al were separated by addition of Na_2S, Zn and CaO respectively.

In the article "Leaching properties of electric arc furnace dust prior" the focus was also on residue decontamination. The results showed that the following procedure is required for permanent disposal of EAF dust: alkaline leaching (followed by filtrate purification and alkaline zinc electrolysis), chromate recovery (if needed), drying of the solid residue and analysis for residual toxic components. The reduction of Cr(VI) to Cr(III) was carried out with $FeSO_4$-$7H_2O$ solution (Oreščanin et al., 2007, p.12).

In "Leaching and cementation of heavy metals from electric arc furnace dust in alkaline medium" a recovery of 85% zinc was achieved when leached in alkaline medium. Optimal conditions are (Orhan, 2005, p.7):

- S/L = 1/7;
- C (NaOH) = 10 M;
- t = 2 h;
- T = 95°C.

The filtrate was further purified by zinc cementation at 50 °C to remove metallic impurities (Pb, Cu, Cd, etc.) and to make it suitable for electrolysis. Also Pb can be removed selectively and quantitatively as sulphide mixtures by adding Na_2S and keeping the NaS/Pb weight ratio at 1.8-2.0 (Youcai and Stanforth, 2001, p.2).

In the article "Hydrothermal treatment of electric arc furnace dust" the technology of producing nano-rods from ZnO crystals with high zinc purity (99%) by means of multistage leaching, further purification and hydrothermal synthesis was considered (Yu et al., 2011, p.4). Zinc oxide can be widely used in industry in the form of one-dimensional ZnO nano-rods, which is a promising key to the world of nanotechnology as it has several advantages

- Wide band gap (3.37 eV);
- High exciton binding energy (60 MeV);
- High breakdown strength.

The results of this study show promising prospects for the alkaline treatment of EAF dust. However, as the content and type of zinc in the EAFD are different and depend on the source, more research is needed before the alkaline process can be applied to anthropogenic raw materials of a given composition on an industrial scale.

Ammonia leaching

Another method of zinc recovery from steelmaking dusts is ammonia leaching. As an aqueous ammonia solution is a base, this method belongs to the group of alkaline methods and is carried out according to the reaction:

$$ZnO + 4(NH_3 \cdot H_2O) \rightarrow [Zn(NH_3)_4(OH)_2] + 3H_2O \qquad (28)$$

Leaching in aqueous ammonia is an inefficient process as zinc recovery is only 20-30% due to the presence of ferrite, which is resistant to leaching in this environment. However, the process is efficient with respect to selectivity as only zinc is transferred to the solution. Neither iron nor calcium are practically leached (Mining University et al., 2016, 2). Dissolution of copper and nickel can be observed, but the concentration of these metals is too low to provide any appreciable effect on cost effectiveness as Cu and Ni are more costly metals than Zn (Popov, 2015, p.4).

There is a large number of studies on this technology. Thus, in the article "Selective leaching of zinc from blast furnace dust using monoligand and mixed-ligand complex leaching systems" the highest zinc yield was observed using a two-molar ammonium chloride solution at T = 70°C and t = 2 h . Iron remained in the residue in the form of the compound $Ca_2Fe_2O_5$.

The authors of the paper "Selective leaching of zinc from blast furnace dust with mono-ligand and mixed-ligand complex leaching systems" achieved 85% Zn recovery. Leaching was carried out using ammonium sulphate as a reagent. The suitable parameters were (Zhang et al., 2017, p.3):

- $C((NH_4)_2SO_4) = 4\ mol/dm^3$;
- T = 90°C;
- t = 4 h.

Fidarov B.F. and Petrov G.V. converted 93.2% of zinc using $(NH_4)_2SO_4 \cdot Fe(SO_4)$. The leaching was conducted in an autoclave at T = 220°C and t = 10 h (Fidarov and Petrov, 2016, p.4).

Technologies of ammonia leaching require the use of sealed equipment not only at the stage of leaching itself but also for subsequent operations.

This method of extraction of zinc from steelmaking dust is of little industrial applicability.

LEACHING WITH CHLORIDE SOLUTIONS

In the article "Leaching of zinc dust in $Zn(II)$-$(NH_4)_2SO_4$-H_2O system" the dependence of zinc recovery on ultrasonic cavitation application in thiourea and choline chloride leaching solution was determined. Optimal parameters were (Tang et al., 2007, p.5):

- Solvent flow rate = 115 cm^3/1g dust;
- T = 60°C.

It was found that the use of ultrasound for 5 min increased zinc yield by 25%.

The authors of "Efficient and selective hydrothermal extraction of zinc from zinc-containing electric arc furnace dust using a novel bifunctional agent" achieved 97% zinc extraction. Leaching was carried out using ammonium chloride as a reagent under the following parameters (Wang et al., 2016, p.10):

- $C(NH_4Cl) = 4.93\ mol/dm^3$;

- $T = 80°C$;
- $t = 2$ h.

The "EZINEX" technology is one of the most promising leaching methods. The process is based on zinc dissolution using ammonia salts as a more efficient reagent than water-based ammonia solutions. In 1996 this technology was implemented on the industrial scale and ensured the annual capacity of 12 thousand tons of Zn. Transition of oxides contained in the dust to the solution is carried out according to the following reaction:

$$MeO + 2NH_4Cl \rightarrow [Me(NH_3)_2]Cl_2 + H_2O \, , \qquad (29)$$

where Me – Zn, Cd, Cu, Ni, Mn, 2Ag, Ca, Mg.

Optimal parameters for the leaching are (Steer and Griffiths, 2013, p.4):

- Reagent - waste electrolyte with zinc concentration = 10-15 g/dm^3;
- $T = 60°C$;
- $t = 1$ h.

In this case ZnO passes into solution at a high rate, while iron and zinc ferrite remain in the residue, which is mixed with coal dust, dried to a moisture content of about 5% and sent to the electric arc furnace. The more electropositive impurities are removed from the zinc-rich solution by cementation on zinc powder; the more electronegative ones are further precipitated (Kania and Saternus, 2023, p.7).

3.2 Research methodology

The conduct of the scientific research includes the following aspects:

- Analysis of developed technologies aimed at zinc extraction from steelmaking dust;
- Study of material composition of zinc-containing waste of ‘Severstal’;
- Determination of optimal parameters of ‘Severstal’ zinc-containing waste leaching process.
- Development of the basic technological scheme of zinc-containing steelmaking waste processing.
- Calculation of material flows in the leaching process;
- The carrying out of experiments on the selection of optimum parameters (temperature, duration) of leaching stage.

A literature analytical study helps to form an idea of possible methods of processing technogenic raw materials and to compare them in order to find the most suitable process for a certain dust composition. The analysis is made by comparing many characteristics influencing the processing of raw materials: the degree of extraction of the valuable component, availability and low cost of reagents, simplicity of apparatus design, multistage, the degree of associated extraction of contaminants and so on.

The analysis of the material composition is carried out by means of X-ray phase and optical analysis, atomic emission spectrometry and IR spectrometry. Based on the mineralogical, particle size distribution and chemical compositions studied, the possible behaviour of the dust components during the leaching operation and the likely recovery percentage of the valuable component are determined.

The development of a schematic process flowchart makes it possible to assess the feasibility of introducing the technology into the production cycle and to assess the feasibility of processing waste by the developed method.

By calculating material flows, a clear understanding of the composition of reagents and products, their consumption at the leaching stage and the scope of the designed works is formed. If necessary, further comparison of experimental mass flow data with the data obtained in theoretical calculations of material balances will make it possible to assess the behaviour of components at each stage and to trace and analyse losses.

Laboratory studies were carried out in a glass reactor under mechanical agitation and given parameters. During the leaching process hydrochloric acid was heated to the desired temperature, after which the test dust was added and the time was monitored. The slurry level was kept constant. At the end of the leaching the pulp was filtered and a sample taken for analysis. The residue was washed with three portions of water, dried in the desiccator at 105ºC until a constant mass value was established, then weighed, abraded, quartered and sampled for analysis. Based on the results of experiments and data on distribution of zinc and iron in the leaching products the feasibility of using hydrochloric acid leaching is determined.

3.3 Theoretical and experimental research

Selection of the most appropriate reagent for the leaching process

The Mining University Research Centre has carried out tests on the selection of promising reagents for leaching. A number of experiments were conducted in which the following reagents were used as reagents: NaCl, NH_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, NH_4+NH_4Cl, NH_4Cl, $(NH_4)_2SO_4$+$(NH_4)_2CO_3$, NaOH, HCl, H_2SO4+NaCl, H_2SO_4. Reagent consumption data and distribution of components between solution and leaching residues are shown in Table 15 and Figure 12.

№	***Type of reagent***	***Reagent consumption***		***Residue yield, %***	***Content in the residue***		***Extraction into solution***	
		Main	***Add.***		***Zn***	***Fe***	***Zn***	***Fe***
		kg/t	***kg/t***		***%***	***%***	***%***	***%***
1	H_2O	-	-	99,98	13,90	38,51	0,00	0,00
2	NaCl	248,78	-	99,71	13,94	38,61	0,00	0,00
3	NH_4	144,59	-	91,33	6,40	42,15	7,80	0,00
4	$(NH_4)_2SO_4$	280,68	-	95,11	12,86	40,48	12,00	0,00
5	$(NH_4)_2CO_3$	204,13	-	94,12	12,94	40,91	12,40	0,00
6	NH_3+NH_4Cl	144,59	227,52	86,31	11,63	44,61	27,80	0,00
7	NH_4Cl	227,52	-	86,81	11,51	44,35	28,10	0,00
8	$(NH_4)_2SO_4$+ $(NH_4)_2CO_3$	280,68	204,13	90,1	11,06	42,73	28,30	0,00
9	NaOH	2240,00	-	76,6	10,65	50,21	41,30	0,10
10	HCl	155,22	-	73,4	10,55	50,30	44,30	4,10
11	H_2SO_4+NaCl	208,38	248,78	78,8	9,37	43,09	46,90	11,80
12	H_2SO_4	208,38	-	78,9	8,84	42,50	49,80	12,90

Table 15: Parameters and indicators for processing zinc-containing EAFD[5].

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[5] Data provided by „Severstal“

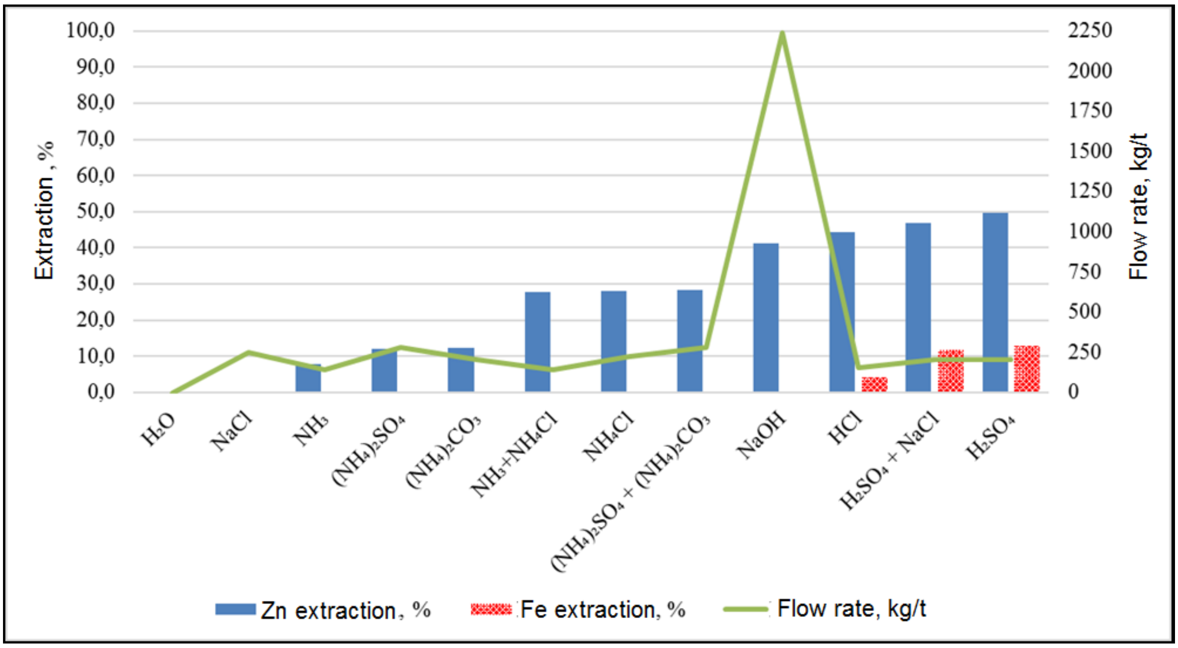

Figure 12. Zinc and iron recovery in the processing of zinc-containing waste by hydrometallurgical methods using different reagents

From the presented data, it is clear that NaOH leaching is unprofitable due to high consumption, water and NaCl does not ensure the transfer of Zn and Fe into the solution. Sulphuric and hydrochloric acids are the reagents that provide maximum transfer of the valuable component to the solution. However, the main problem with acid leaching is the inability to selectively transfer zinc into the solution, as acids also dissolve iron. Also a disadvantage of using H_2SO_4 is the transition of calcium into insoluble sulphate and its accumulation in the residue, which negatively affects the possibility of reuse of insoluble residue in iron and steel industry.

Thus, after analysing the data provided by "‘Severstal’", it was concluded that the most suitable reagent for dust leaching operation for the purpose of subsequent zinc cathode production is HCl. Further experimental studies were carried out using this reagent.

The influence of changing temperature on the hydrochloric acid leaching process on zinc and iron recovery rates

The characteristics of the experiment:

- Temperature range - 20-80°C (step - 20°C);
- HCl flow rate - 420 kg/t;
- W:T=5:1;
- t = 2 h.

The data obtained are shown in Table 16 and Figure 13.

№	*T,°C*	*Residue yield, %*	*Content in the residue*		*Extraction*	
			Zn	**Fe**	**Zn**	**Fe**
			%	**%**	**%**	**%**
1	20	73,47	10,54	50,25	44,30	4,10
2	40	73,51	10,74	50,65	43,20	3,30
3	60	73,42	10,49	50,03	44,60	4,60
4	80	73,40	11,00	49,36	41,90	5,90

Table 16: Process values for hydrochloric acid leaching of EAFD with varying process temperatures

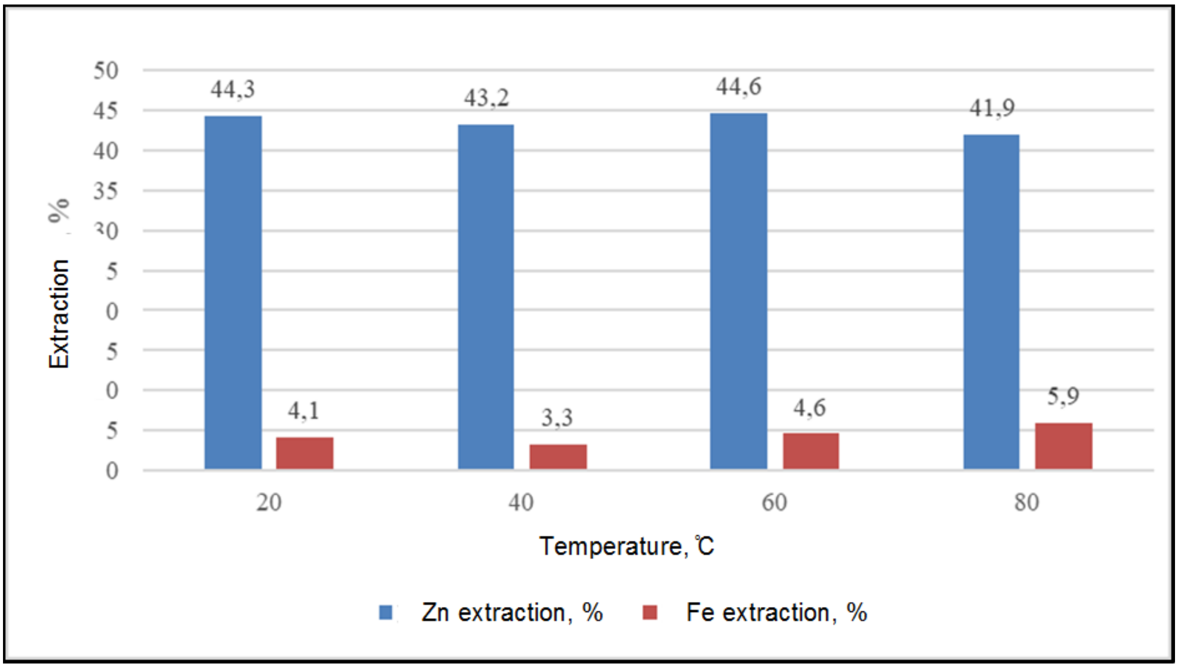

Figure 13. Zinc and iron extraction in hydrochloric acid leaching of EAFD with varying process temperatures

It can be concluded from the data obtained that leaching between 20 and 80°C is not feasible as the percentage of zinc transfer into solution in this range remains constant. Leaching at higher temperatures requires the use of autoclaves and the aggressiveness of the acid used makes the process too expensive and therefore unprofitable.

The optimum temperature for hydrochloric acid leaching of steelmaking dust is therefore 20°C.

The influence of the duration of hydrochloric acid leaching on zinc and iron extraction yields

The characteristics of the experiment:

- T=20°C;
- HCl consumption - 420 kg/t;
- S/L =5;
- t = 24 h.

The data obtained are shown in Table 17 and Figure 14.

№	*Time, h*	*Residue yield, %*	*Content in the residue*		*Extraction*	
			Zn	*Fe*	*Zn*	*Fe*
			%	*%*	*%*	*%*
1	0,5	85,98	11,15	44,73	31,00	0,10
2	1	79,43	10,85	47,94	38,00	1,10
3	1,5	73,88	10,71	50,60	43,10	2,90
4	2	73,47	10,75	50,67	43,20	3,30
5	4	73,44	10,75	50,59	43,20	3,50
6	6	73,42	10,73	50,60	43,30	3,50
7	8	73,42	10,75	50,50	43,20	3,70
8	12	73,31	10,73	50,52	43,40	3,80
9	24	73,28	10,70	50,59	43,60	3,70

Table 17: Process values for hydrochloric acid leaching of EAFD with varying process durations

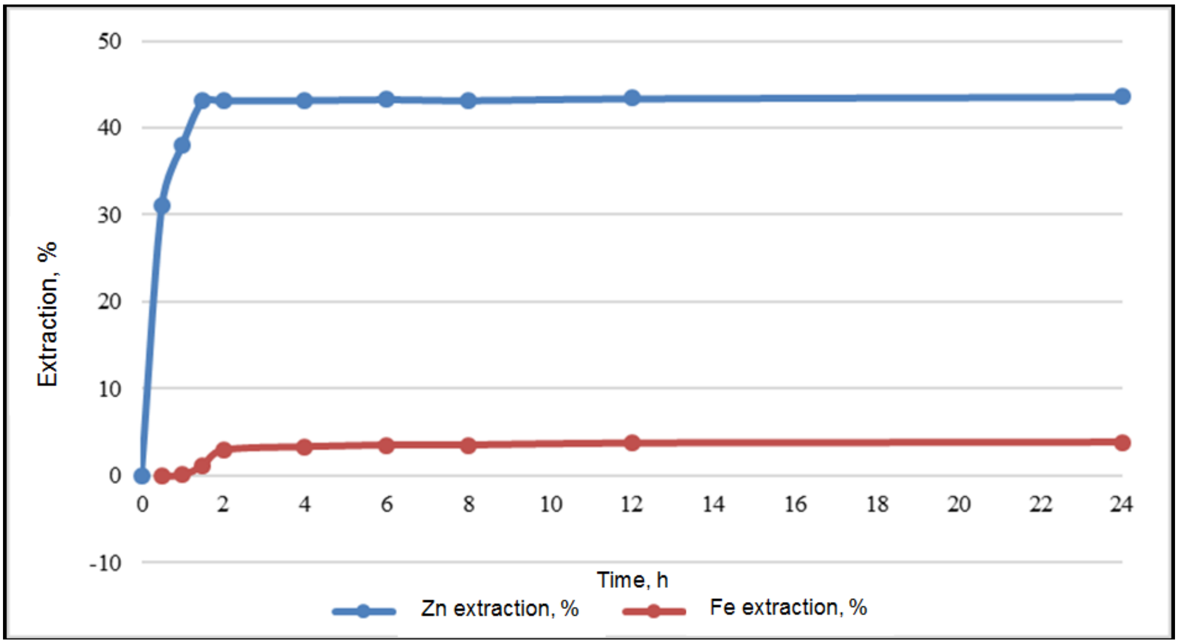

Figure 14. Dynamics of zinc and iron extraction

The data shows that it is not advisable to run the leaching process for a long time, as the recovery is most complete in the first two hours. Thereafter it remains at the same level.

3.4 Analysis of research outcomes

1. The analysis of the mineralogical composition showed that the predominant mineral phases in the dust are Zn ferrite, spinel, Zn, Fe and Mn oxides, metallic iron and graphite.

2. By means of analysis of the chemical composition the main elements in the composition of technogenic raw materials have been determined. These are iron, zinc, calcium and silicon.

3. Analysis of the experimentally received data allows to conclude that the optimum parameters of leaching are:

- T=20°C;
- HCl consumption is 420 kg/t;
- S/L =5/1;
- t = 2 h.

4. Analysis of the developed technological scheme allows to distinguish its advantages:

- Extraction of valuable product - commodity cathode zinc;
- Getting a by-product – solid iron consisting residue, which can be used in steel production;
- Ensuring product recycling in the process;
- Solution of hydrochloric acid regeneration problem.

5. Based on the calculation of material flows, processing of 41 tons of dust will yield about 5 tons of cathode zinc. Further analysis of economic indicators will allow to figure out the payback period of this technology and make a conclusion about the expediency of its introduction into production.

4 ECONOMICS

4.1 Analysis of the factors influencing the economic performance of the process

The implementation of the proposed technology is one of the possible ways to improve ‘Severstal’'s economic efficiency.

In the course of the process it is ensured:

- Waste recycling

It allows reducing expenses for organization of dust storage, formed during electric arc furnace steelmaking process.

- Extraction of the valuable zinc component

While calculating the material flows in each process stage, it was found out that by processing the daily dust mass (41 tons), the theoretical yield of Zn will be about 5 tons. According to data on zinc value for 2023 (Table 18), profit will be 3,866.32 thsd €.

Cost of Zn, US$/t	***The produced daily volume, t***	***$/€ exchange rate***	***Cost of Zn, € /t***	**Income,th THSD €/d**	**Income, THSD €/a**
2,312.00	4.98	0.92	2,127.04	10.59	3,866.32

Table 18: Data on the theoretical profit of marketable products[6]

As described above, steelmaking dusts can be treated by either hydro or pyrometallurgical processes. In terms of finished product, zinc recovery by leaching is more profitable as it results in a saleable product, cathode zinc, which is more expensive than ZnO from pyrometallurgical processes. For example, the product of Waelz process is zinc-containing oxide (92-96% Zn), the cost of which is 21 € per tonne. However it is necessary to take into account, that the obtained oxide is not a

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[6] Data up to 23.06.2023

commodity product and requires further hydrometallurgical processing in order to obtain metal zinc.

Another advantage of the application of hydrometallurgical technologies in relation to pyro is the reduced carbon dioxide emissions into the atmosphere. Consequently, the costs of purchasing greenhouse gas emission permits would not have a major impact on the payback of the technology.

Based on the data on non-ferrous metal quotations presented in Figure 15 (Source: LME) and considering the cyclicality of the price formation, zinc prices can be predicted to increase in the near future (as the price decrease is observed since the beginning of 2023), which makes the commercial zinc obtained an even more profitable product in the foreseeable future.

Figure 15. Graph of zinc costs

- use of recycled solutions

The HCl solution introduced in leaching stage 2, the raffinate of the extraction stage and the extractant of the re-extraction stage are used in leaching stage 1. After zinc cathode recovery by electrolysis, the electrolyte is sent to the re-extraction stage.

In addition, the use of a Ruthner furnace enables the recovery of hydrochloric acid, which is required to transfer the valuable component into solution in the second leaching stage. According to material flow calculations, 37.47 tonnes of HCl are generated per day during iron chloride evaporation. Given the data presented in Table 19, the theoretical profit due to acid turnover is 1,625.87 euro per year.

HCl cost, €/t	***The produced daily volume, t***	***The produced annual volume, t***	***Income, €/d***	***Income, € THSD/a***
118.88	37.47	13,676.55	4,454.45	1,625.87

Table 19: Data on the theoretical profit of HCl regeneration

Moreover, the use of hydrochloric acid as a reagent is an advantageous solution due to its relatively low cost compared to other solutions capable of transferring a valuable component into solution. The comparative cost of the reagents is shown in Table 20.

Reagent	***Cost, ₽/t***
HCl	11,000.00
H_2SO_4	6,500.00
HNO_3	16,700.00
NaOH	23,900.00
CH_3COOH	88,000.00
Ammonia	12,500.00

Table 20: Reagent costs

Although sulphuric acid is the cheapest reagent for leaching operations in many hydrometallurgical processes, the most suitable acid for zinc transfer in solution, due to the reasons given in the section "Rationale for the solution of a technical problem".

- Maintaining optimum leaching parameters

The research part of this work presents experiments determining the optimum leaching process parameters. Based on the data presented, it is worth noting that the selected temperature and time are most beneficial from an economic point of view. Conducting zinc transfer into liquor at 20ºC shows that there are no costs for pulp heating (i.e., for electric power). In addition, duration of 2 hours allows more dust to be handled, thereby increasing the productivity of the leaching stage.

It is also worth noting that the use of anthropogenic waste as raw material excludes the use of beneficiation operations (crushing, grinding, etc.). It is known that about

30% of all losses of a valuable component come from these stages. Thus, the elimination of additional losses has a positive impact on the economic effect.

Conclusion to the section

In this section, the main aspects of the developed technological scheme have been analysed, which can increase the economic efficiency if the technology is implemented in production. In the future, the analysed data should be taken into account when calculating the economic indicators in order to identify the payback period.

5 OCCUPATIONAL SAFETY

5.1 The analysis of working conditions and occupational health and safety

1. Working with hydrochloric acid

Leaching is carried out in HCl, which is a strong acid and an extremely aggressive reagent with toxic effects on the human body.

2. Lack of sufficient natural light

Due to the constant work inside the workshop space, a lack of natural light for workers may occur, which may contribute to diseases of the heart, blood vessels and other vital parts of the body.

3. Working with ammonia

Ammonia is a colourless, explosive substance with a pungent odour. Ammonia poisoning causes the following symptoms: suffocating cough, agitation and delirium, swelling of the skin, vesicular burns accompanied by pain. Cases of severe poisoning are fatal.

4. Handling of sulphuric acid

At the re-extraction stage the organic phase is mixed with sulphuric acid to convert the valuable component back into a solution - zinc sulphate, suitable for electrolysis. H_2SO_4 is a strong acid and an extremely aggressive reagent, which has toxic effects on the human body

5. Operation of electrolysers

When carrying out zinc electrolysis, particular attention should be paid to safety measures concerning electrolysers, as the equipment is under high voltage.

6. The operation of metallurgical furnaces

Hydrochloric acid regeneration in Ruthner furnaces takes place at temperatures of around 1300ºC. The surface of the furnace therefore presents a risk of work-related injuries.

7. Working area air temperature.

When working in production at high temperatures, there is always the risk of not being able to follow the temperature of the working area, which also takes into account the ambient air temperature. Staying in an uncomfortable temperature regime for a long period of time can provoke a deterioration in the condition of workers.

5.2 Safety precautions

Depending on the type of adverse impact on the human body, the company implements workplace safety measures and takes various measures to protect against serious factors

SAFETY MEASURES WHEN HANDLING HYDROCHLORIC ACID

Due to the highly toxic nature of acid when evaporated, it must be stored in different types of sealed containers:

- Gummed tanks;
- Containers;
- Plastic drums;
- Glass bottles.

Rubber or polyethylene gaskets can be used to ensure proper sealing. It is worth bearing in mind that not only filled but also empty containers are concerned.

HCl in gaseous and liquid form is a hazardous substance which can cause damage to the eyes, respiratory organs and other mucous membranes. Therefore, protective equipment must always be worn when handling this reagent:

- A respirator;
- Safety goggles;
- Rubber gloves;
- Acid-resistant boots;
- Gown or overalls (long sleeves, with fasteners).

In the event of a hazardous situation, workers should observe the safety regulations:

- If acid comes into contact with the skin, it should be washed with warm water and blotted with a soft cloth;
- If there are signs of poisoning from hydrochloric acid vapour, remove the victim to the air immediately. If necessary, perform artificial respiration and call a doctor. Workers must wear a mask to avoid this situation;
- If acid comes into contact with the mucous membrane of the eyes, rinse immediately with water and call a doctor. Workers are required to wear safety glasses to avoid this situation;
- The most dangerous situation is when acid enters the stomach. In this case it must be removed immediately by inducing a gag reflex (multiple times if necessary).

SAFETY PRECAUTIONS WHEN HANDLING SULPHURIC ACID

In the re-extraction process, sulphuric acid is used to convert components in solution to sulphate for electrolysis. Sulphuric acid is a hazardous and toxic reagent, class 2. Sulphuric acid affects the respiratory tract, skin, eyes and mouth, causing burning, pain, burns and blisters.

To prevent workers from coming into contact with sulphuric acid, the following preventive measures must be followed:

- Ventilation;
- Local exhaust ventilation;
- Respiratory protection equipment;
- Protective gloves and clothing;
- Face mask.

Control of food and drink consumption in the immediate vicinity of the workplace is an important aspect.

First aid should be given whenever workers come into contact with hazardous chemicals.

In case of inhalation:

- Provide a supply of fresh air to the victim's airway;
- Rest in a semi-sitting position;
- If necessary, carry out artificial respiration;

- Call a doctor immediately.

In case of contact with skin:

- Wear gloves for first aid only;
- Rinse contact area with plenty of water for at least 15 minutes;
- Remove contaminated clothing and repeat point 3;
- Call a doctor immediately.
- In case of contact with eyes:
- Rinse with plenty of water;
- Call a doctor immediately.

In case of ingestion:

- Rinse out mouth;
- Do not allow fluids to enter victim's mouth;
- Do not induce vomiting;
- Call a doctor immediately.

SAFETY MEASURES WHEN WORKING WITH METALLURGICAL FURNACES

There is a risk of thermal burns from working in furnaces at high temperatures.

In order to avoid contact with high temperatures you should:

1. Perform work according to strict rules, instructions and other regulations;
2. Wear personal protective equipment (PPE);
3. Cover as much area as possible with thermal insulation materials;
4. Periodically check compliance with the technology.

SAFETY PRECAUTIONS FOR WORKING WITH AMMONIA

Ammonia is a colourless substance with a pungent odour, which can ignite in the presence of a flame source or explode when vessels are heated. Ammonia mixture is poisonous and first aid should be given in case of poisoning:

- Gas mask protection or a gauze bandage moistened with water or a 5% citric acid solution;
- Artificial respiration;
- Inhalation of warm water vapour mixed with vinegar or citric acid;
- If the mixture enters the stomach - induce vomiting;

- In case of contact with the eyes, rinse the face;
- In case of contact with exposed skin, flush with copious amounts of water;
- In case of burns, apply an anesthetic and bandage the affected areas.

Storage of ammonia solutions is also an important aspect. Tanks are equipped with visible level gauges, pressure gauges, safety valves and discharge lines.

SAFETY MEASURES FOR WORKING WITH ELECTRICAL EQUIPMENT

The electrolytic zinc bath has a high current (20·103 A) and a low voltage (3.3-3.6 V). In order to avoid injuries, measures must be taken to improve the literacy of workers. Exposure to electricity primarily affects the heart and blood vessels. Electric shock causes severe spasm of muscles throughout the skeleton, which explains the lack of reflexive withdrawal of the person receiving the shock from the object of exposure. As the strength of the current increases, the person's ability to move decreases. The degree of injury from electric shock is also influenced by the following parameters:

1. The time of exposure of the body to the electricity;
2. The threshold resistance of the upper epidermis to the action of electricity;
3. The presence of additional conductive substances on the body surface;
4. The size of the affected area (it is not necessary to touch the conductive device, being in the affected area is sufficient).

The operation of the electrolysis unit (hereinafter referred to as OEU) shall be carried out in accordance with the safety regulations:

1. Wearing PPE is mandatory;
2. No smoking in the room of the electrolysis unit;

Prohibition of use of open fire in the room of the electrolysis installation;

3. Prohibition of storage of flammable explosives in OEU premises;
4. Contact with any part of the OEU and unprotected parts of the body is strictly prohibited;
5. Rubber dielectric mats and earthing devices must be checked.

Methods and means of protection when working with live parts of the equipment are as follows:

- Protective sheathing;
- Protective guards;
- Safe arrangement of live parts;
- Insulation of live parts;
- Insulation of the workplace;
- Low voltage;
- Safety disconnection;
- Warning signalisation;
- Safety signs.

Non-current-carrying parts should also not be neglected, as they pose no less of a risk if the insulation layer is damaged. To prevent the conductivity of currents, apply:

- Protective earthing;
- Grounding;
- Equalisation of potential;
- Safety wire system;
- Safety disconnection;
- Electrical separation of the network;
- Insulation monitoring;
- Compensation of earth-fault currents;
- Personal protective equipment.

Every worker in the workplace must be aware not only of his own safety options, but also those of the other worker. To do so, it is necessary to be aware of first aid procedures:

1. Disconnect a source generating electricity;
2. If it is not possible to comply with point 1, contact between the extremities of the injured person and the power source must be stopped;
3. Move the injured person away from the area of exposure to a safe area (pull only by parts of the clothing, do not touch the body);
4. Assess for vital signs of the victim (breathing, pulse, pupil size, etc);
5. Take life-sustaining measures (indirect heart massage, artificial respiration, etc.) until the ambulance arrives.

5.3 Optimising the workplace

Every company is concerned with improving workers' working conditions, which is ensured by means of sanitary, technical and organisational measures and by preventing occupational hazards from affecting workers.

MEASURES TO ENSURE OPTIMAL LIGHTING

Lighting illuminates surfaces in order to facilitate the visual perception of objects. Depending on the source of light it is divided into:

- Natural - sunlight;
- Artificial - lighting fixtures;
- Combined - a combination of natural and artificial light.

Based on the location of the work area, lighting sources need to be selected correctly. Since the leaching area in the plant is located in a closed area, the most suitable is the use of combined lighting. Periodic regular checking of the lighting in the rooms, medical examination of the eyesight and installation of additional light sources (in case of insufficient light).

MEASURES TO ENSURE OPTIMUM TEMPERATURE IN THE WORKPLACE

‘Severstal’ is based in Cherepovets, which is located in a temperate climate zone. This climate is characterised by warm summers and cold or very cold winters. Therefore, the following measures are necessary to establish normal temperatures in production facilities and workplaces:

1. Barometric pressure control devices;
2. Ventilation;
3. Cleaning and air-conditioning units;
4. Heating;
5. Automatic temperature level control;
6. Alarm in case of temperature disturbance.

FIRE SAFETY OF AN INDUSTRIAL FACILITY

The measures to protect the property of workers and their lives in the event of fire are an important factor in industrial safety. Although there is a specific person responsible for fire safety in the workplace, each worker has certain responsibilities:

1. Training in the fire safety minimum program;
2. Being briefed on fire safety;
3. Being trained in the use of fire extinguishers;
4. Compliance with the requirements when conducting evacuation drills;
5. Studying the information provided on fire safety.

Management, in turn, should implement the following safety measures:

1. Development of evacuation plans;
2. Installation of safety signs on the territory;
3. The availability of fire extinguishers and primary firefighting equipment;
4. Installation of fire alarms;
5. Supervision of the operation of fire-fighting equipment;
6. Availability of a sufficient number of emergency exits;
7. Provision of fire escape ladders for the enterprise;
8. Fire protection treatment of structures;
9. Installation of devices for smoke removal and fire extinguishing;
10. Contract with an organisation responsible for the maintenance of fire-fighting equipment.

5.4 Occupational emergencies

The occurrence of an emergency (OE) poses a risk to the health and life of personnel. In the event of an emergency, immediate emergency rescue actions must be taken to eliminate it.

Possible causes of emergencies at ‘Severstal’ are as follows:

1. Wear and tear of equipment;
2. Technical systems failure;
3. Abnormalities in equipment operation;
4. Natural events (cataclysms etc.);
5. Lack of regular professional training;
6. Leakage of reagents (ammonia, hydrochloric and sulphuric acid);
7. Equipment integrity is compromised.

Emergencies are the cause of increased injury rates. Occupational injuries, in turn, are a measure of the effectiveness of industrial safety measures. The number of injuries in the company over the last ten years has decreased 2.5 times and Lost Time Injury Frequency Rate (LTIFR) over the same period from 1.33 to 0.65 (Figure 16; Source: https://severstal.com).

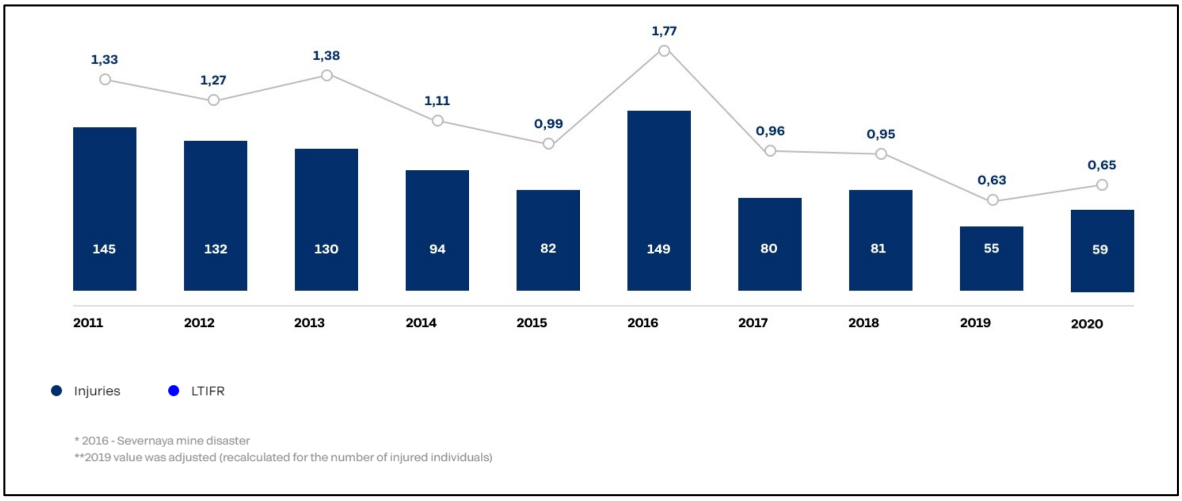

Figure 16. Lost-time injury frequency rate across ‘Severstal’

Precautionary actions should be taken in advance to avoid the risk of emergencies, which include:

1. Forecasting of possible emergencies and planning of response actions;

2. Control and implementation of measures to improve safety of technological equipment;

3. Conducting safety briefings on a regular basis.

To improve safety operations of ‘Severstal’ are certified according to the international standard ISO 45001. The certification increases the transparency of the Company's processes, and assures stakeholders of continuous improvement of our health and safety management system. The strategic goal is to have all of the Company's facilities certified to ISO 45001 by 2025.

Section Conclusion

In this section the underlying factors to ensure safe working in the workplace have been examined and described. A neglect or negligent attitude towards safety can result in a disruption to the production process. In order to avoid this, measures to prevent and remedy safety failures have been suggested. To ensure the success of any company, it is imperative that all conditions are met. As there are people behind any breach, the main challenge is to train highly skilled personnel who are responsible for the actions taken. To summarise, safety is the most important part of successful production organisation.

6 CONCLUSION

Steelmaking dust recycling is an important development in the field of metallurgical waste recycling, allowing to consider the poor raw material as an additional source of valuable components and to achieve an improved environmental situation.

Both pyro- and hydro technologies can be effective. The choice has to be based on a qualitative analysis of the components that make up the dust and their behaviour when the proposed technology is applied.

In the scientific review different metallurgical technologies for zinc recovery from steelmaking dusts were analysed. On this basis the following conclusions could be made:

1. It is necessary to extract zinc from dust in order to reduce or completely eliminate the negative impact on the structural elements of the furnace during steel production;
2. Hydrometallurgical technologies are more and more used for processing of steelmaking wastes, which is connected with possibility of using raw materials with low content of useful components;
3. All processes depend on tailored approaches for specific waste chemistries;
4. The joint recovery of iron and zinc wastes was still an issue, and finding a suitable reagent to ensure that these components were distributed between the solution and the slag was required;
5. Residue composition needs to be controlled in order to maintain the quantities of the constituents within the 'safe waste' category.

Involvement of secondary deposits of zinc-containing steelmaking dust in processing allows expanding the raw material base of zinc industry, increasing the efficiency of steel production and reducing the negative impact on the environment.

7 BIBLIOGRAPHY

1. Altundog, H.S., Erdem, M., Orhan, R., Zer, A.O., Men, F.T., 2016. Heavy Metal Pollution Potential of Zinc Leach Residues Discarded in C¸ inkur Plant. Tr J Eng. Environ. Sci. 167–177.
2. Andrés, A., Ibáñez, R., Ortiz, I., Irabien, J.A., 1998. Experimental study of the waste binder anhydrite in the solidification/ stabilization process of heavy metal sludges. J. Hazard. Mater. 57, 155–168. https://doi.org/10.1016/S0304-3894(97)00079-4
3. Barcza, N.A., Robertson, D.G.C., Schoukens, A.F., Shaw, F., Denton, G.M., 1995. Enviroplas technology for the recovery of lead and zinc from lead blast furnance slags. Presented at the Recycling lead and zinc into the 21st century, Madrid, Spain.
4. Barrett, E.C., Nenniger, E.H., Dziewinski, J., 1992. A hydrometallurgical process to treat carbon steel electric arc furnace dust. Hydrometallurgy 30, 59–68. https://doi.org/10.1016/0304-386X(92)90077-D
5. Chairaksa-Fujimoto, R., Maruyama, K., Miki, T., Nagasaka, T., 2016. The selective alkaline leaching of zinc oxide from Electric Arc Furnace dust pre-treated with calcium oxide. Hydrometallurgy 159, 120–125. https://doi.org/10.1016/j.hydromet.2015.11.009
6. Cheng, T.C., Demopoulos, G.P., 2004. Hydrolysis of Ferric Sulfate in the Presence of Zinc Sulfate at 200 °C: Precipitation Kinetics and Product Characterization. Ind. Eng. Chem. Res. 43, 6299–6308. https://doi.org/10.1021/ie030711g
7. Cole, P.M., Sole, K.C., Feather, A.M., 2006. Solvent extraction developments in southern africa. Tsinghua Sci. Technol. 11, 153–159. https://doi.org/10.1016/S1007-0214(06)70169-9
8. Conner, J.R., Hoeffner, S.L., 1998. The History of Stabilization/Solidification Technology. Crit. Rev. Environ. Sci. Technol. 28, 325–396. https://doi.org/10.1080/10643389891254241
9. Cruells, M., Roca, A., Núñez, C., 1992. Electric arc furnace flue dusts: characterization and leaching with sulphuric acid. Hydrometallurgy 31, 213–231. https://doi.org/10.1016/0304-386X(92)90119-K
10. Doronin, I.E., Svyazhin, A.G., 2011. Commercial methods of recycling dust from steelmaking. Metallurgist 54, 673–681. https://doi.org/10.1007/s11015-011-9356-z
11. Dreisinger, D.B., Peters, E., Morgan, G., 1990. The hydrometallurgical treatment of carbon steel electric arc furnace dusts by the UBC-Chaparral process. Hydrometallurgy 25, 137–152. https://doi.org/10.1016/0304-386X(90)90035-Z
12. Drinkard, W.F., Woerner, H.J., Pleasant, M., Metalox, D., 1998. SEPARATION OF CALCIUM FROM METAL COMPOUNDS.
13. Dutra, A.J.B., Paiva, P.R.P., Tavares, L.M., 2006. Alkaline leaching of zinc from electric arc furnace steel dust. Miner. Eng. 19, 478–485. https://doi.org/10.1016/j.mineng.2005.08.013
14. Dutrizac, J.E., 1996. The effect of seeding on the rate of precipitation of ammonium jarosite and sodium jarosite. Hydrometallurgy 42, 293–312. https://doi.org/aboratory-scale investigation of alkaline zinc electrowinning
15. Erdem, M., Özverdi, A., 2011. Environmental risk assessment and stabilization/solidification of zinc extraction residue: II. Stabilization/solidification. Hydrometallurgy 105, 270–276. https://doi.org/10.1016/j.hydromet.2010.10.014

16. Fidarov, B.F., petrov, G.V., 2016. Ferrite-containing technogenic waste from metallurgical industries. Presented at the Week of Science SPbPU: mater. Scientific conf. with international participation of the Institute of Metallurgy, Mechanical Engineering and Transport, Изд-во Политехнического ун-та, Saint-Petersburg, pp. 125-128.
17. Ghani, A.A., Saleem, J., Al Hameed, Z., Lal, H., Shoaib, M., 2016. Study of Zinc Leaching of EAF Flue Dust Using Sodium Hydroxide. Pak. J. Anal. Environ. Chem. 17. https://doi.org/10.21743/pjaec/2016.06.005
18. Gürmen, S., Emre, M., 2003. A laboratory-scale investigation of alkaline zinc electrowinning. Miner. Eng. 16, 559–562. https://doi.org/10.1016/S0892-6875(03)00081-5
19. Habashi, F., 1995. The leaching of sulfide minerals in chloride media. Hydrometallurgy 38, 219. https://doi.org/10.1016/0304-386X(95)00003-Y
20. Halli, P., Agarwal, V., Partinen, J., Lundström, M., 2020. Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction. Sep. Purif. Technol. 236, 116264. https://doi.org/10.1016/j.seppur.2019.116264
21. Halli, P., Hamuyuni, J., Revitzer, H., Lundström, M., 2017. Selection of leaching media for metal dissolution from electric arc furnace dust. J. Clean. Prod. 164, 265–276. https://doi.org/10.1016/j.jclepro.2017.06.212
22. Havlik, T., Friedrich, B., 2004. Pressure Leaching of EAF Dust with Sulphuric Acid. World Metall.
23. Havlík, T., Souza, B.V. e, Bernardes, A.M., Schneider, I.A.H., Miškufová, A., 2006. Hydrometallurgical processing of carbon steel EAF dust. J. Hazard. Mater. 135, 311–318. https://doi.org/Atmospheric leaching of EAF dust with diluted sulphuric acid
24. Havlik, T., Turzakova, M., Stopic, S., Friedrich, B., 2005. Atmospheric leaching of EAF dust with diluted sulphuric acid. Hydrometallurgy 77, 41–50. https://doi.org/Pressure Leaching of EAF Dust with Sulphuric Acid
25. Holtzer, M., Kmita, A., Roczniak, A., 2015. The Recycling of Materials Containing Iron and Zinc in the OxyCup Process. Foundry Comm. Pol. Acad. Sci. 15, 126–130.
26. Jandová, J., Dvorák, P., Jiričný, V., Mráz, R., 2013. Recycling of ZnO Flue Dust to Produce Zinc by Hydrometallurgical Routes, in: Young, C., Alfantazi, A., Anderson, C., James, A., Dreisinger, D., Harris, B. (Eds.), Electrometallurgy and Environmental Hydrometallurgy. John Wiley & Sons, Inc., Hoboken, NJ, USA, pp. 1593–1603. https://doi.org/10.1002/9781118804407.ch39
27. Jiang, J.C., Yang, X.Y., Zhao, Y.C., 2010. Recovery of Zinc from EAF Dust by Alkaline Extraction. Adv. Mater. Res. 113–116, 2299–2304. https://doi.org/Lead and zinc selective precipitation from leach electric arc furnace dust solutions
28. Kania, H., Saternus, M., 2023. Evaluation and Current State of Primary and Secondary Zinc Production—A Review. Appl. Sci. 13, 2003. https://doi.org/10.3390/app13032003
29. Karidakis, T., Agatzini-Leonardou, S., Neou-Syngouna, P., 2005. Removal of magnesium from nickel laterite leach liquors by chemical precipitation using calcium hydroxide and the potential use of the precipitate as a filler material. Hydrometallurgy 76, 105–114. https://doi.org/Manganese metallurgy review. Part II: Manganese separation and recovery from solution
30. Katrenov, B.B., Zhumashev, K.Z., Narembekova, A.K., Mysina, A.E., 2017. Determination of the optimal parameters for dezincification of converter sludge of hydrochloric acid solutions // Fundamental research and applied development of

processes for processing and utilization of technogenic formations. Presented at the V Forum “Ural market of scrap, industrial and municipal waste”: tr. Congress with the international participation and the Conference of Young Scientists, UB RAS, Yekaterinburg, pp. 174–177.
31. Kazyuta, V.I., 2014. Utilization of dust from metallurgical industries and waste filtered materials 9, 95–102.
32. Kurunov, I.F., 2012. Environmental aspects of industrial technologies for recycling sludge and dust that contain iron and zinc. Metallurgist 55, 635. https://doi.org/Prospects for recycling all metallurgical waste products on a combine scale or regional scale
33. Langová, Š., Leško, J., Matýsek, D., 2009. Selective leaching of zinc from zinc ferrite with hydrochloric acid. Hydrometallurgy 95, 179–182. https://doi.org/10.1016/j.hydromet.2008.05.040
34. Langová, Š., Riplová, J., Vallová, S., 2007. Atmospheric leaching of steel-making wastes and the precipitation of goethite from the ferric sulphate solution. Hydrometallurgy 87, 157–162. https://doi.org/10.1016/j.hydromet.2007.03.002
35. Larba, R., Boukerche, I., Alane, N., Habbache, N., Djerad, S., Tifouti, L., 2013. Citric acid as an alternative lixiviant for zinc oxide dissolution. Hydrometallurgy 134–135, 117–123. https://doi.org/10.1016/j.hydromet.2013.02.002
36. Leclerc, N., Meux, E., Lecuire, J.-M., 2003. Hydrometallurgical extraction of zinc from zinc ferrites. Hydrometallurgy 70, 175–183. https://doi.org/10.1016/S0304-386X(03)00079-3
37. Leclerc, N., Meux, E., Lecuire, J.-M., 2002. Hydrometallurgical recovery of zinc and lead from electric arc furnace dust using mononitrilotriacetate anion and hexahydrated ferric chloride. J. Hazard. Mater. 91, 257–270. https://doi.org/10.1016/S0304-3894(01)00394-6
38. Lenz, D.M., Martins, F.B., 2007. Lead and zinc selective precipitation from leach electric arc furnace dust solutions. Matér. Rio Jan. 12, 503–509. https://doi.org/Zinc leaching from electric arc furnace dust in alkaline medium
39. Li, H., Wang, Y., Cang, D., 2010. Zinc leaching from electric arc furnace dust in alkaline medium. J. Cent. South Univ. Technol. 17, 967–971. https://doi.org/10.1007/s11771-010-0585-2
40. Li, K., Zhang, J., Liu, Z., Mao, R., Yang, T., 2014. Comprehensive Evaluation of OxyCup Process for Steelmaking Dust Treatment Based on Calculation of Mass Balance and Heat Balance. J. Iron Steel Res. Int. 21, 575–582. https://doi.org/10.1016/S1006-706X(14)60089-3
41. Li, Q., Zhao, Y., Jiang, J., Zhang, C., 2012. Optimized Hydrometallurgical Route to Produce Ultrafine Zinc Powder from Industrial Wastes in Alkaline Medium. Procedia Environ. Sci. 16, 674–682. https://doi.org/10.1016/j.proenv.2012.10.093
42. Loshkarev, A.N., Matyunina, I.V., 2015. Implementation of the PRIMUS process in the EAF-80 JSC Metallurgical Plant named after A.K. Serov". FGAOU HPE Ural Fed. Univ. Named First Pres. Russ. BN Yeltsin.
43. Luz, C., Rocha, J., Cheriaf, M., Pera, J., 2006. Use of sulfoaluminate cement and bottom ash in the solidification/stabilization of galvanic sludge. J. Hazard. Mater. 136, 837–845. https://doi.org/10.1016/j.jhazmat.2006.01.020
44. Machado, J., Brehm, F., Moraes, C., Santos, C., Vilela, A., Cunha, J., 2006. Chemical, physical, structural and morphological characterization of the electric arc furnace dust. J. Hazard. Mater. 136, 953–960. https://doi.org/10.1016/j.jhazmat.2006.01.044

45. McElroy, R.O., 1994. Processing of electric arc furnace dust via chloride hydrometallurgy. Springer Science+Business Media Dordrecht, Canada. https://doi.org/10.1007/978-94-011-1214-7
46. Mureşan, L., Maurin, G., Oniciu, L., Avram, S., 1996. Effects of additives on zinc electrowinning from industrial waste products. Hydrometallurgy 40, 335–342. https://doi.org/10.1016/0304-386X(95)00008-5
47. Nakagawa, T., Inoue, H., Hashimura, T., Inoue, K., Maeda, Y., Motoyuki, M., Nishikawa, T., Oi, K., Shimizu, H., Yoshimura, S., 2010. Kobelco technology review. Secr. Public. Dept Secr. Public. Dept Kobe Steel Ltd 85–92.
48. Nakamura, T., Shibata, E., Takasu, T., Itou, H., 2008. Basic Consideration on EAF Dust Treatment Using Hydrometallurgical Processes. Resour. Process. 55, 144–148. https://doi.org/10.4144/rpsj.55.144
49. National Mineral Resources University (Mining University), Popov, A., Petrov, G., National Mineral Resources University (Mining University), 2016. DISPOSAL OF STEEL INDUSTRY ZINC-CONTAINING DUST. Proc. Irkutsk State Tech. Univ. 111, 177–185. https://doi.org/10.21285/1814-3520-2016-4-177-185
50. Nemchinova, N.V., Chernykh, V.I., Tyutrin, A.A., Patrushov, A.I., 2016. Processing of dusts from electric steelmaking to extract zinc and iron. FSBEI HE Irkutsk Natl. Res. Tech. Univ. 5, 68–71.
51. Odegov, S.Yu., Fedosov, I.B., Baranov, A.P., Chernykh, V.I., Patrushov, A.I., n.d. Processing method of metallurgical production. 2626371.
52. Oreščanin, V., Mikelić, L., Sofilić, T., Rastovčan-Mioč, A., Užarević, K., Medunić, G., Elez, L., Lulić, S., 2007. Leaching properties of electric arc furnace dust prior/following alkaline extraction. J. Environ. Sci. Health Part A 42, 323–329. https://doi.org/10.1080/10934520601144576
53. Orhan, G., 2005. Leaching and cementation of heavy metals from electric arc furnace dust in alkaline medium. Hydrometallurgy 78, 236–245. https://doi.org/Stanforth R. SELECTIVE SEPARATION OF LEAD FROM ALKALINE ZINC SOLUTION BY SULFIDE PRECIPITATION
54. Oustadakis, P., Tsakiridis, P.E., Katsiapi, A., Agatzini-Leonardou, S., 2010. Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). J. Hazard. Mater. 179, 1–7. https://doi.org/10.1016/j.jhazmat.2010.01.059
55. Özverdİ, A., Erdem, M., 2010. Environmental risk assessment and stabilization/solidification of zinc extraction residue: I. Environmental risk assessment. Hydrometallurgy 100, 103–109. https://doi.org/10.1016/j.hydromet.2009.10.011
56. Pan'shin, A.M., Leont'yev, L.I., Kozlov, P.A., Dyubanovo, V.G., Zatonskiy, A.V., Ivakin, D.A., 2012. Technology for processing dust from electric arc furnaces of OAO 'Severstal' in the Welz complex of OAO "ChPZ." Ecol. Ind. Russ. 4–6.
57. Pelino, M., Karamanov, A., Pisciella, P., Crisucci, S., Zonetti, D., 2002. Vitrification of electric arc furnace dusts. Waste Manag. 22, 945–949. https://doi.org/10.1016/S0956-053X(02)00080-6
58. Pereira, C.F., Rodrıguez-Piñero, M., Vale, J., 2001. Solidification/stabilization of electric arc furnace dust using coal fly ash Analysis of the stabilization process.
59. Pereskoka, V.V., Kamnina, L.V., Proydak, YU.S., Stovpchenko, A.P., Kvichanskaya M.I., 2010. REDUCTION-THERMAL TREATMENT OF ELECTRIC FILTER DUST FROM AN ARC STEEL FURNACE. Bull. Azov State Tech. Univ. 13–16.

60. Popov, A.A., 2015. To the issue of the problem of utilization of zinc-containing dust of steel-smelting industries. ФГБОУ ВПО «Национальный Минерально-Сырьевой Университет «Горный»» 7. https://doi.org/0.15862/124TVN215
61. Rinne, M., Halli, P., Aromaa, J., Lundström, M., 2022. Alternative Method for Treating Electric Arc Furnace Dust: Simulation and Life Cycle Assessment. J. Sustain. Metall. 8, 913–926. https://doi.org/10.1007/s40831-022-00531-x
62. Ruiz, M., 2004. Environmental behavior of cement-based stabilized foundry sludge products incorporating additives. J. Hazard. Mater. 109, 45–52. https://doi.org/10.1016/j.jhazmat.2003.12.011
63. Salihoglu, G., Pinarli, V., 2008. Steel foundry electric arc furnace dust management: Stabilization by using lime and Portland cement. J. Hazard. Mater. 153, 1110–1116. https://doi.org/10.1016/j.jhazmat.2007.09.066
64. Salihoglu, G., Pinarli, V., Salihoglu, N.K., Karaca, G., 2007. Properties of steel foundry electric arc furnace dust solidified/stabilized with Portland cement. J. Environ. Manage. 85, 190–197. https://doi.org/10.1016/j.jenvman.2006.09.004
65. Schoukens, A.F., Jones, R.T., Denton, G.M., n.d. Pilotplant production of Prime Western grade zinc from lead blast-furnace slag using the Enviroplas process [WWW Document]. MINTEKSpesialists Miner. Metall. Technol. URL https://www.pyrometallurgy.co.za/RTJones/LBFS/LBFS.htm (accessed 1.5.23).
66. Schoukens, A.F., Nelson, L.R., Barcza, N.A., 1991. Plasma-arc treatment of steel-plant dust and zinc-containing slag - theoretical and practical consideration. Presented at the The International Lead and Zinc Study Group Conference, Mintek. Pyrometellurgy Division, Rome, pp. 1–16.
67. Shawabkeh, R.A., 2010. Hydrometallurgical extraction of zinc from Jordanian electric arc furnace dust. Hydrometallurgy 104, 61–65. https://doi.org/10.1016/j.hydromet.2010.04.014
68. Sheftel, N.I., 1970. Production of steel calibrated bars. Metallurgy, M.
69. Siegmund, A., Alam, S., Grogan, J., Kerney, U., Shibata, E. (Eds.), 2020. PbZn 2020: 9th International Symposium on Lead and Zinc Processing, The Minerals, Metals & Materials Series. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-030-37070-1
70. Steer, J.M., Griffiths, A.J., 2013. Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry. Hydrometallurgy 140, 34–41. https://doi.org/10.1016/j.hydromet.2013.08.011
71. Sun, Z., Wang, C., Guillen, D.P., Neelameggham, N.R., Zhang, L., Howarter, J.A., Wang, T., Olivetti, E., Zhang, M., Verhulst, D., Guan, X., Anderson, A., Ikhmayies, S., Smith, Y.R., Pandey, A., Pisupati, S., Lu, H. (Eds.), 2018. Energy Technology 2018: Carbon Dioxide Management and Other Technologies, The Minerals, Metals & Materials Series. Springer International Publishing, Cham. https://doi.org/10.1007/978-3-319-72362-4
72. Tang, M.-T., Zhang, P., He, J., Yuan, X., Chen, Y., 2007. Leaching zinc dust in system of Zn(II)-(NH4)2SO4-H2O. Zhongnan Daxue Xuebao Ziran Kexue BanJournal Cent. South Univ. Sci. Technol. 38, 867–872.
73. Teo, Y.Y., Lee, H.S., Universiti Tunku Abdul Rahman, Malaysia, Low, Y.C., Universiti Tunku Abdul Rahman, Malaysia, Choong, S.W., Universiti Tunku Abdul Rahman, Malaysia, Low, K.O., IOP Specialists Sdn. Bhd., Malaysia, 2018. Hydrometallurgical Extraction of Zinc and Iron from Electric Arc Furnace Dust (EAFD) using Hydrochloric Acid. J. Phys. Sci. 29, 49–54. https://doi.org/10.21315/jps2018.29.s3.6

74. Toporkova, Yu.I., Bludova, D., Mamyachenkov, S.V., Anisimova, O.S., 2021. A review of processing methods for electric arc furnace dust. IPolytech J. 25, 643–680. https://doi.org/10.21285/1814-3520-2021-5-643-680
75. Tsakiridis, P.E., Oustadakis, P., Katsiapi, A., Agatzini-Leonardou, S., 2010. Hydrometallurgical process for zinc recovery from electric arc furnace dust (EAFD). Part II: Downstream processing and zinc recovery by electrowinning. J. Hazard. Mater. 179, 8–14. https://doi.org/10.1016/j.jhazmat.2010.04.004
76. Ushakova, M.V., Chernousov, P.I., Rostovskii, A.V., Klyuev, M.P., 2011. Prospects for recycling all metallurgical waste products on a combine scale or regional scale. Metallurgist 55, 478–482. https://doi.org/10.1007/s11015-011-9455-x
77. Van Weert, G., Peek, E.M.L., 1992. Reagent recovery in chloride hydrometallurgy —some missing links. Hydrometallurgy 29, 513–526. https://doi.org/10.1016/0304-386X(92)90030-4
78. Wang, H., Jia, N., Liu, W., Zhang, M., Guo, M., 2016. Efficient and selective hydrothermal extraction of zinc from zinc-containing electric arc furnace dust using a novel bifunctional agent. Hydrometallurgy 166, 107–112. https://doi.org/10.1016/j.hydromet.2016.10.013
79. Xanthopoulos, P., Agatzini-Leonardou, S., Oustadakis, P., Tsakiridis, P.E., 2017. Zinc recovery from purified electric arc furnace dust leach liquors by chemical precipitation. J. Environ. Chem. Eng. 5, 3550–3559. https://doi.org/10.1016/j.jece.2017.07.023
80. Yan, H., Chai, L., Peng, B., Li, M., Peng, N., Hou, D., 2014. A novel method to recover zinc and iron from zinc leaching residue. Miner. Eng. 55, 103–110. https://doi.org/10.1016/j.mineng.2013.09.015
81. Yoshida, T., 2003. Leaching of Zinc Oxide in Acidic Solution. Mater. Trans. 44, 2489–2493. https://doi.org/10.2320/matertrans.44.2489
82. Youcai, Z., Stanforth, R., 2001. SELECTIVE SEPARATION OF LEAD FROM ALKALINE ZINC SOLUTION BY SULFIDE PRECIPITATION. Sep. Sci. Technol. 36, 2561–2570. https://doi.org/10.1081/SS-100106110
83. Youcai, Z., Stanforth, R., 2000. Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium. J. Hazard. Mater. 80, 223–240. https://doi.org/10.1016/S0304-3894(00)00305-8
84. Yu, B.-S., Wang, Y.-R., Chang, T.-C., 2011. Hydrothermal treatment of electric arc furnace dust. J. Hazard. Mater. 190, 397–402. https://doi.org/10.1016/j.jhazmat.2011.03.056
85. Zain, M.F.M., Islam, M.N., Radin, S.S., Yap, S.G., 2004. Cement-based solidification for the safe disposal of blasted copper slag. Cem. Concr. Compos. 26, 845–851. https://doi.org/10.1016/j.cemconcomp.2003.08.002
86. Zhang, D., Zhang, X., Yang, T., Rao, S., Hu, W., Liu, W., Chen, L., 2017. Selective leaching of zinc from blast furnace dust with mono-ligand and mixed-ligand complex leaching systems. Hydrometallurgy 169, 219–228. https://doi.org/10.1016/j.hydromet.2017.02.003
87. Zoraga, M., Ilhan, S., Kalpakli, A.O., 2020. Leaching kinetics of electric arc furnace dust in nitric acid solutions. Int. J. Chem. Kinet. 52, 933–942. https://doi.org/10.1002/kin.21411

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10 LIST OF ABBREVIATIONS

A/d ratio	Acid/dust ratio
AG	Aktiengesellschaft – public limited company
CHPZ	Chelyabinsk Zinc Plant
DC	Direct current
EDS	Energy dispersive X-ray spectroscopy
EMPF	Elkem Furnace
ITmk3	Ironmaking Technology Mark Three
JSC	Join-stock company
LCAP	Leaching in citric acid process
LLC	Limited liability company
LTIFR	Lost Time Injury Frequency Rate
OE	Occurrence of an emergency
OEU	Operation of the electrolysis unit
PJSC	Public join-stock company
PPE	Personal protective equipment
S/S	Solidification/stabilization
SEM	Scanning electron microscopy
TCLP	Toxicity Characteristic Leaching Procedure