Investigation of hazardous waste
A case study of electric arc furnace dust characterization

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Abstract

Dust from an electric arc furnace is formed as the main by-product of the steel production process from the secondary iron-based raw materials. This dust has significant contents of Zn and Fe, as well as Pb, Cd, Ca, Mg, Cr, Mn, Si, Ni, Cu, F, Cl and other elements and is considered hazardous industrial solid waste since it contains heavy metals. In order to protect the environment and public health from the negative impact of this type of hazardous waste, it is necessary, even mandatory, to carry out its treatment in accordance with the legislation of the country where it is located. Before applying any treatment of the electric arc furnace (EAF) dust, it is necessary to perform its detailed characterization. In this paper, the following characterization of EAF dust originating in the Republic of Serbia was performed: physical-mechanical and chemical characterization, determination of granulometric composition, and mineralogical characterization. Also, the EAF dust impact on the environment and human health was assessed (Leachability and Toxicity Characteristic Leaching Procedure (TCLP) tests). The results have shown that the Zn content is in the range 32 to 35 % and that the main mineralogical phases of the dust are zincite, franklinite, magnetite, and magnesioferrite. Granulometric analysis has shown that 80 % of the sample consists of particles less than 26 µm in size. According to the leaching test results, the EAF dust is characterized as a hazardous waste due to the increased chloride content, while the TCLP test indicated dust toxicity due to the increased contents of Zn, Cd, and Pb.

Keywords: industrial waste; EAF dust; environmental impact.

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1. INTRODUCTION

Use of the secondary raw materials, the so-called scrap iron, as a raw material, and electricity as the energy source of this process, steel production in electric arc furnaces has become more prominent than any other steel production process in the world [1,2]. The main sources of secondary raw materials for steel production are construction material waste, old cars, appliances, and household waste, which means that waste can contain a large number of different metals, plastics and rubber, glass, paint, oil, and even salts [1-8]. Due to the high process temperature (1600 °C) in the electric arc furnace, during melting of a batch, some elements evaporate and together with solid particles carried away with the gas phase, form one of the by-products - electric arc furnace dust (EAF dust) [3,8,9]. The amount of EAF dust generated during the production of 1 t of crude steel is about 10-20 kg [3,10]. A typical EAF dust has a reddish-brown or dark brown appearance, and very fine particles that can spread in the air [3,5]. Composition of EAF dust can widely vary depending on the operating conditions of the electric arc furnace, characteristics of scrap iron charged in the furnace, the working period, specifications of the steel produced, and is also specific to each plant [1,4,6,11]. EAF dust is actually the final result of a series of physical and chemical changes that the EAF dust-producing substances undergo. These phenomena, which begin in the electric arc furnace and take place within different environments along the gas path, define its physical aspect, chemical, and mineral composition. In ideal case, EAF dust should consist of iron oxide,

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only, however, due to the presence of different types of scrap iron, containing different elements, its composition becomes complex [12].

Thus, EAE dusts usually have significant contents of Zn, Fe, and Pb, as well as variable contents of Cd, Ca, Mg, Cr, Mn, Si, Ni, Cu, F, Cl, etc. [1,4,6,12-16]. The Zn content varies from 2 to 40 wt.% [2,6,17]. Zinc present at higher concentrations in the EAF dust is most often due to its widespread use to protect steel from corrosion or it is derived from scrap brass. Since the EAF dust is formed under oxidative conditions, most of the metals are present in oxide forms. Zinc occurs in the EAF dust in the form of ZnO and $ZnFe_2O_4$, while iron mainly occurs as oxides (such as Fe_3O_4 and Fe_2O_3) [18,19].

Presence of heavy metals such as Zn, Pb, and Cd in EAF dust can pose a threat to the environment and human health due to the mobility of these toxic elements, and for this reason, EAF dust is considered hazardous industrial solid waste in many countries [20,21]. According to the United States Environmental Protection Agency (EPA), the EAF dust is listed as a hazardous solid industrial waste K061 [22], and according to the Brazilian standard ABNT 10004: 2004, the EAF dust is listed as hazardous waste from certain source K061 [23]. In the European Union Waste Catalogue [24] the EAF dust is classified as a hazardous substance with the designation 10 02 13* and 10 02 07*, depending of the gas treatment process [4]. Leachability of heavy metals such as Zn, Cu, Ni, Cd, Cr, and Pb, as well as F and Cl from waste [25] leads to significant environmental pollution and improper disposal of the EAF dust has a negative impact on the environment [5]. Thus, in the hazardous waste landfills, the EAF dust must be protected from rain, to prevent formation of leachate that could pollute the surrounding areas [25].

Zinc is an essential element needed by the human body, especially for building cells and enzymes, and it also helps wound healing. Reduced Zn content in the human body leads to negative health effects such as anorexia (loss of appetite and eating disorders), loss of taste, lethargy (fatigue and lack of energy), growth retardation, slower wound healing, *etc.* The recommended intake of zinc by the World Health Organization (WHO), through the daily diet, is 5.5 to 9.5 mg day^{-1} for men and 4.0 to 7.0 mg day^{-1} for women. Despite the great importance of Zn for human health, it should not be overlooked that it is also carcinogenic and that its excessive intake (100-500 mg day^{-1}) can be toxic. Zinc is also an important nutrient for plants. The deficiency of zinc in plants can cause chlorosis (change in leaf color) and necrosis of the root tip (death) and can also lead to reduced yields [26]. Although zinc is an important part of living organisms and the environment, this element belongs to the group of toxic metals.

In this paper, hazardous industrial waste was investigated, *i.e*. dust from an electric arc furnace originating from a steel plant in the Republic of Serbia was characterized in detail. In specific, the dust was characterized regarding physical-mechanical, chemical, and mineralogical properties as well as regarding granulometric composition and the analyses are supplemented with the assessment of the dust impact on the environment and human health.

2. EXPERIMENTAL

2. 1. Materials

Hazardous waste, which was investigated in this paper, is dust from an electric arc furnace obtained from the dry dust collecting system of a steel plant in the Republic of Serbia. Four samples (10 kg each) of the EAF dust were taken from the production process for investigating purposes. Samples were taken at random from jumbo bags from the landfill located under the canopy in the circle of the steel plant (not directly from the filter bags in which the EAF dust is collected from the electric arc furnace).

2. 2. Sample preparation

Homogenization of each of the four samples was performed by mixing the sample on foil. From the total amount of each of the EAF dust samples, representative samples were taken by the quartering procedure (Fig. 1) and marked as U1, U2, U3, and U4.

Triplicate samples from all four representative EAF dust samples (U1, U2, U3, and U4), in quantities of 0.5, 1.0, and 2.0 kg, for physical-mechanical and chemical characterization were obtained by drying in a dryer at the temperature of 105 °C, for 24 h.

Two dry representative U1 samples (5.0 g) were prepared for morphological analyses by dipping in epoxy resin after which they were ground and polished with silicon carbide and then polished with a diamond suspension. The samples were first analyzed by a polarizing microscope (JENAPOL-U, Carl Zeiss-Jena, Germany) and then coated with gold and analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS, JSM IT 300LV, JOEL, Japan).

Figure 1. Preparation of the EAF dust representative sample

Two dry representative U1 samples (1.0 g each) were prepared by comminution in an agate mortar and used for X-ray diffractometer recording.

2. 3. Characterization methods

2. 3. 1. Physico-mechanical and chemical characterization

Physico-mechanical characterization of the initial representative samples of EAF dust involves the determination of moisture, pH value of the sample, bulk density, and density of the sample.

For the determination of metals, initial EAF dust samples were dissolved in 4 acids (HCl, HNO_3, $HClO_4$, and HF), and the obtained solutions were analyzed. Concentrations of Fe, Mn, Cu, Pb, Bi, Co, Ni, Cr, Mo, P, As, Sb, Sn, Ca, Cd, Al, Si, Na, K, and Mg were measured using inductively coupled plasma atomic emission spectrometer (ICP-AES) Spectro Ciros. In addition, concentrations of metals with relatively higher content such as Zn, Fe, Mn, Cu, Pb, Ni, Ca, Na, K, and Mg were confirmed using atomic absorption spectrophotometer (AAS) PerkinElmer PinAAcle 900F. Since the concentration of Zn in EAF dust was the highest of all metals, a more accurate Zn concentration was determined by titration with ethylenediaminetetraacetic acid with methylthymol blue as an indicator. The contents of silver and gold were determined using fire assay (FA). The content of mercury was measured using flameless atomic absorption spectrophotometer AMA-254 (AAS-Hg). The content of sulfur was determined using Thermo Horiba EMIA-920V2 carbon sulfur analyser (CSA). To determine chloride (Cl^-), fluoride (F^-), and pH value, leachates were prepared by suspending initial EAF dust samples in demineralized water in a ratio of 1:10, shaking, and filtration. Concentrations of Cl^- and F^- were measured both using spectrophotometer (SF) HACH DR 3900 and ion chromatograph (IC) Thermo Dionex ICS-1600. pH values were measured by pH meter IM-23P.

2. 3. 2. Granulometric composition

Particle size distribution was determined in a representative EAF dust U1 sample without any prior preparation by using a laser device MASTERSIZER 2000 (MALVERN Instruments, UK).

2. 3. 3. Mineralogical characterization

Mineralogical characterization of a dry representative EAF dust U1 sample included analyses by using a polarization microscope (JENAPOL-U, Carl Zeiss-Jena, Germany), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), and X-ray diffraction analysis (XRD).

A SEM-EDS microscope (JSM IT 300LV, JOEL, Japan), with an accelerator voltage of 20 kV, was used to examine the morphology and elemental mapping of the EAF dust sample.

The XRD analysis was applied to determine the phase composition of a representative U1 EAF dust sample as a polycrystalline sample (powder) by using a PHILIPS X-ray diffractometer (PW-1710, PHILIPS, Netherlands), with a curved graphite monochromator and a scintillation counter. The measurement was carried out in the 2θ range from 4 to 70°, with a scan rate of 5° min^{-1}.

2. 3. 4. Assessment of the EAF dust impact on the environment and human health

A representative U1 EAF dust sample was assessed regarding the impact on the environment and human health after disposal, following the Rulebook on categories, testing, and classification of waste (Official Gazette of RS 93/2019, 39/2021). Laboratory tests were performed according to the accredited standard methods: SRPS EN 12457-2 for testing the leachability of materials, and EPA 1311 for testing the toxicity of materials. For Leachability test, after determining the moisture content of the sample, the EAF dust sample in the amount of 0.090 kg (calculated on dry mass) was mixed with distilled water in the liquid : solid ratio = 10 L : 1 ± 0.02 kg, in a plastic bottle. The bottle was placed on a rotary shaker and rotated at 30 rpm for 24 hours. The suspension was then filtered, the pH value and conductivity of the filtrate were measured, and a chemical analysis was performed. Based on the dry mass of the original EAF dust sample, the amount of the ingredient leached from it was calculated. To perform the TCLP test, a 100 g sample of EAF dust was mixed with 2 dm^3 of extraction liquid (acetic acid) in a plastic bottle. The plastic bottle was placed on a rotating shaker at 30 rpm for 18 hours. After the suspension was filtered, the pH value of the extract was measured, and immediately aliquot and chemical analysis of the extract was performed. The EAF dust samples for both tests were not previously additionally prepared, and both tests were performed with two samples each.

The obtained results were compared to the legislation of the Republic of Serbia, based on which the toxicity and leachability of the tested material samples were determined.

3. RESULTS AND DISCUSSION

3. 1. Characterization of the EAF dust

3. 1. 1. Physical and chemical characterization

The results of physical characterization of the representative EAF dust samples (U1, U2, U3, and U4) are presented in Table 1.

Table 1. Physical characteristics of the representative EAF dust samples

Characteristic	Sample			
	U1	U2	U3	U4
Moisture, wt.%	0.36	2.90	43.30	1.60
pH	11.42	8.05	9.10	7.15
Bulk density, kg m^{-3}	654	712	n.a.	686
Density, g cm^{-3}	4.351	4.550	n.a.	4.446

n.a. – not analyzed

The moisture contents in the EAF dust samples U1, U2, and U4 are low (below 3 wt.%), while the moisture content is higher (43.3 wt.%) in the sample U3. All EAF dust samples were taken from jumbo bags from the landfill located under the canopy. However, the sample marked as U3 was taken from a jumbo bag that stood at the very end of the canopy and was damaged (torn). For this sample, the difference in the size of EAF dust particles compared to the other taken samples could be already noticed by the visual inspection, since the EAF dust particles were in the form of larger agglomerates. The research has shown that the particle size distribution of EAF dust is closely related to the moisture content, and for this reason, dust particles will also coagulate in reaction with water [3,28].

It was shown that long-term storage of the EAF dust in conditions with increased humidity can lead to the formation of large agglomerates of the dust particles [3]. The increased humidity of the U3 sample indicates that its storage is not adequate because the EAF dust contact with water resulted in agglomeration and formation of large and solid agglomerates of the otherwise very small and powdery EAF dust particles. For this reason, bulk density was not measured for the U3 sample. The pH values of the dust samples range from 7.15 to 11.42 (Table 1), which indicates that the EAF dust is a material with basic characteristics.

Results of the chemical characterization of the four representative EAF dust samples, as well as the analytical methods used for chemical characterization, are presented in Table 2.

Table 2. Chemical composition of the representative EAF dust samples U1-U4 and analytical methods used for determination

Element	U1	U2	U3	U4	Analytical method*
	Content, wt.%				
Zn	32.44	32.95	35.21	32.38	V/AAS
Fe	18.92	21.92	22.93	28.28	ICP-AES/AAS
Mn	1.81	2.07	1.48	2.29	ICP-AES/AAS
Cu	0.19	0.20	0.23	0.19	ICP-AES/AAS
Pb	1.39	1.74	2.37	1.11	ICP-AES/AAS
Bi	0.013	<0.01	0.016	<0.01	ICP-AES
Co	0.0017	0.0013	0.0024	0.0018	ICP-AES
Ni	0.036	0.0099	0.017	0.014	ICP-AES/AAS
Cr	0.25	0.25	0.28	0.40	ICP-AES
Mo	<0.0050	0.0029	0.0053	0.0028	ICP-AES
S	0.51	0.38	0.41	0.44	CSA/ICP-AES
P	0.15	0.11	0.12	0.11	ICP-AES
As	0.0041	0.004	0.0058	0.045	ICP-AES
Sb	0.022	0.017	0.023	0.014	ICP-AES
Sn	0.037	0.044	0.055	0.035	ICP-AES
Ca	3.85	2.89	2.07	3.05	ICP-AES/AAS
Cd	0.040	0.06	0.059	0.032	ICP-AES
Ag	0.00604	0.00747	0.017	0.00730	FA/AAS
Au	0.00004	<0.00001	-	-	FA/AAS
Cl	2.85	2.23	0.16	2.50	SF/IC
Al	0.73	0.63	0.58	0.77	ICP-AES
Si	1.34	1.68	-	-	ICP-AES
Hg	0.0001	0.00006	-	-	AAS-Hg
Na	1.28	0.91	0.35	0.92	ICP-AES/AAS
K	0.87	0.69	0.22	0.74	ICP-AES/AAS
Mg	0.93	0.68	0.55	0.57	ICP-AES/AAS
F	-	-	0.52	0.023	SF/IC

**V- Volumetry; AAS – Atomic Absorption Spectrophotometry; ICP-AES - Inductively Coupled Plasma Atomic Emission Spectrometry*
CSA – Carbon/Sulfur analyzer; FA – Fire Assay; FOT – Photometry; SF – Spectrophotometry; IC – Ion Chromatography
AAS-Hg - Flameless Atomic Absorption Spectrophotometry (mercury analysis)

Comparison of the obtained results for the four dust samples from the same steel plant indicates variability of the EAF dust composition depending on the operational parameters of the melting process in the electric arc furnace and the type of charged scrap iron, which is in accordance with the literature [11,29].

Apart from the fact that treatment of EAF dust is primarily performed for environmental protection, which can be carried out by a hydrometallurgical process, for example, could be also economically viable if the EAF dust contains Zn at concentrations higher than 15 wt.%. After the treatment, returns from the obtained by-products, which can be used for production of metals could compensate the capital and operating costs of such a process [20,28]. The most significant deviations in the analyzed EAF dust samples in this work were observed in the contents of Zn, Fe, Mn, Pb, Cl, Na, and Ca. The lowest Fe content and the highest Ca content were determined in the U1 sample. The increased Ca content in this sample is attributed to lime addition during the furnace operation, which is also the reason for the increased pH value of this sample compared to the other three analyzed samples. Zn contents in the samples can be characterized as high (32.38-35.21 wt.%), since the content of this metal varies from 2-40 wt.% in EAF dusts. For further characterization of the EAF dust, the U1 sample was selected, *i.e*. the sample with the Zn content of 32.44 wt.% and the Fe content of 18.92 wt.%.

Considering the need for EAF dust treatment, whether for environmental or economic reasons, choice of the processing methods depends on the dust chemical composition and the available quantity for exploitation. In the case of processing the investigated EAF dust, due to the limited quantities and high content of Zn, hydrometallurgical process is the most suitable in order to separate Zn and transform hazardous waste into non-hazardous waste.

3. 1. 3. Granulometric composition

Graphical presentation of particle size distribution in the U1 EAF dust sample is presented in Figure 2. Based on the obtained granulometric analysis results, it was determined that 80 vol.% of the sample consists of particles <26 µm in size. Such a fine grain distribution in the EAF dust can result in difficult filtration during the hydrometallurgical treatment.

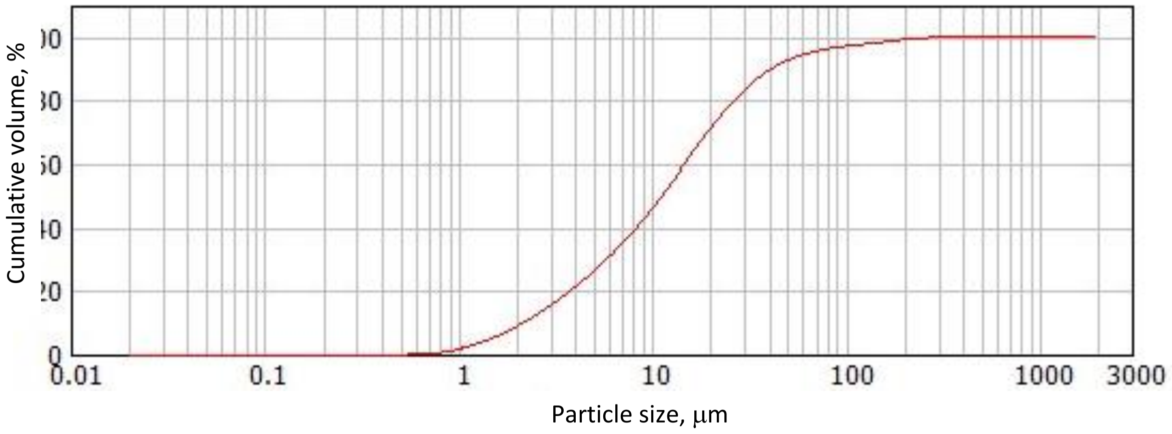


Figure 2. Granulometric composition of the representative EAF dust sample

Due to differences in methods for steel production in electric arc furnaces and methods of dust collection, physical characteristics of EAF dusts may be variable in a certain range. There are three main dust collection methods resulting in 3 EAF dust particle size intervals: 1) collection by gravity collectors, where 85 % of the particles are <10 µm in size, 2) collection in filter bags where 90 % of the particles are 50 µm in size, and 3) collection by electrostatic collectors where more than 90 % of the particles are less than 100 µm in size [3].

In this work, the investigated EAF dust was collected in filler bags, and the obtained results of the particle size distribution agree with the literature results [3,29].

3. 1. 4. Mineralogical characterization

3. 1. 4. 1. Polarized light microscopy

Table 3 presents a semi-quantitative mineralogical analysis of the U1 representative EAF dust sample.

Table 3. Presence of minerals in the U1 representative sample

Mineral	Presence	Mineral	Presence
Zinc metal	Substantial	Magnesioferrite	Low
Zincite	Substantial	Maghemite	Occurs in trace amounts
Magnetite	Substantial	Wustite	Occurs in trace amounts
Franklinite	Low	Crystalline coke	Substantial

Based on the obtained qualitative microscopic analyses in reflected light, the following composition was determined in the representative U1 dust sample: zinc metal, zincite, magnetite, franklinite, Mg-spinels, maghemite, wustite, crystalline coke (graphite), and amorphous phase. Structural-textural properties of grains containing zinc and iron minerals are presented in Table 3 and in micrographs in Figure 3. The main mineral phases of zinc in the sample are zincite (ZnO) and zinc metal (Zn). Grains with zinc (Fig. 3b) appear in the form of small white "lumps". Zinc metal is a common metal phase, mostly occurring in free grains, which are spherical with circular cross-sections (Fig. 3b-d). Zinc metal grains are sometimes surrounded by the annular franklinite ($ZnFe_2O_4$) or the central parts may be filled with Zn-Fe-Mg spinels and their eutectics (Fig. 3d). The main iron minerals that are well represented in the sample are magnetite (Fe_3O_4) and various (Fe, Mg)-spinels, which regularly occur in free spherical grains (up to 50 µm) with circular cross-sections. Other mineral phases with iron are less represented. Carbon phases are largely presented by crystalline, semi-crystalline, and amorphous coke (Fig. 3c). All coke grains (graphite) are tabular or rod-shaped, with appearance of black stripes along their foliation (glass).

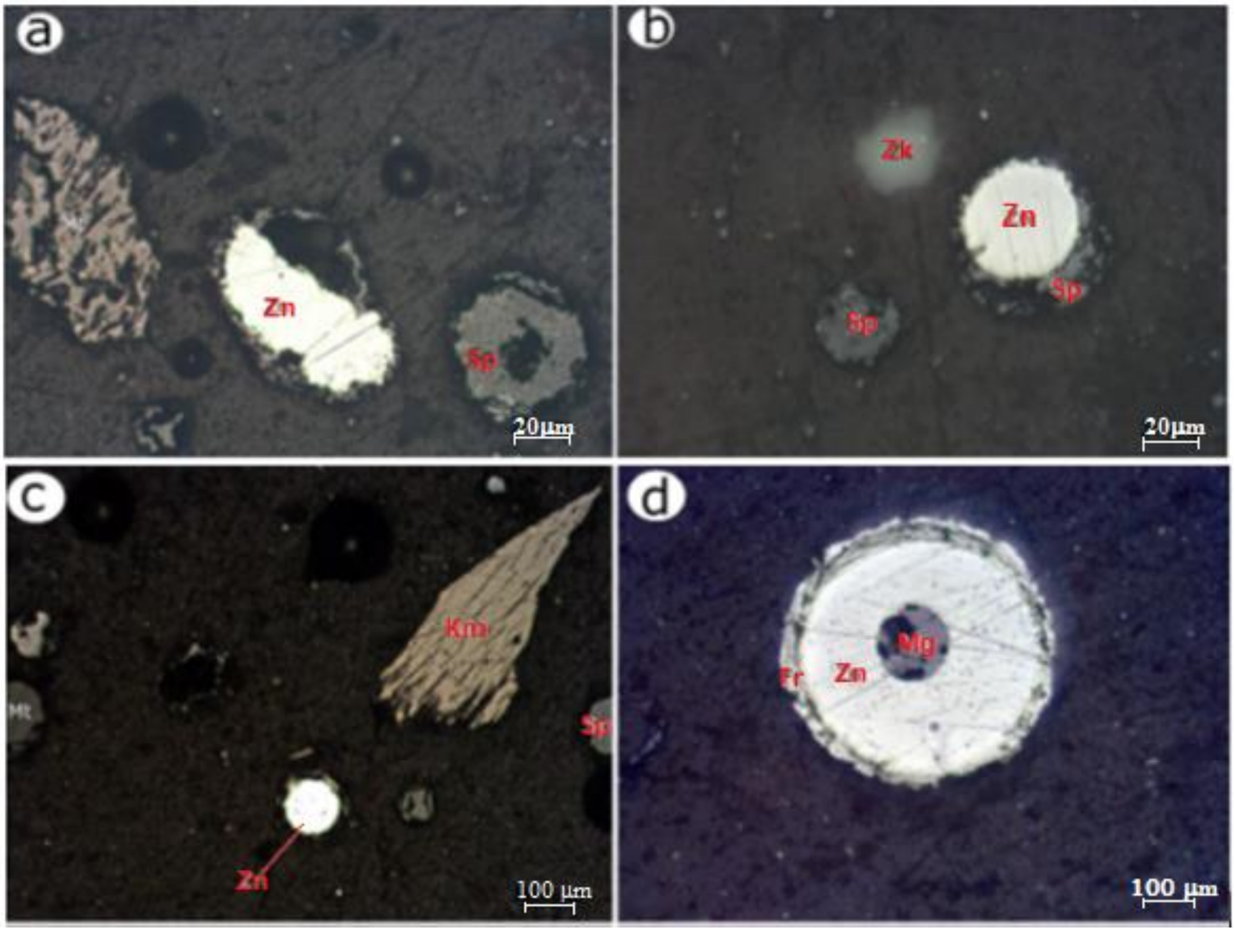


Figure 3. Micrographs of the representative EAF dust sample: a) Zn metal and spinel grains; b) zincite, spinel and Zn metal grains; c) Zn metal, crystalline coke and spinel grains; d) magnetite grain in Zn metal grain in franklinite grain
Indications of present phases: Km - crystalline coke; Mg - magnetite; Zk - zincite; Zn – zinc metal; Fr - franklinite; Sp – spinel

The obtained results are in accordance with literature data [3,4,16].

3. 1. 4. 2. SEM-EDS analysis

Figure 4 presents a SEM micrograph of the U1 EAF dust sample showing agglomerates of irregularly shaped particles, as well as agglomerates of spherical particles, which differ in size.

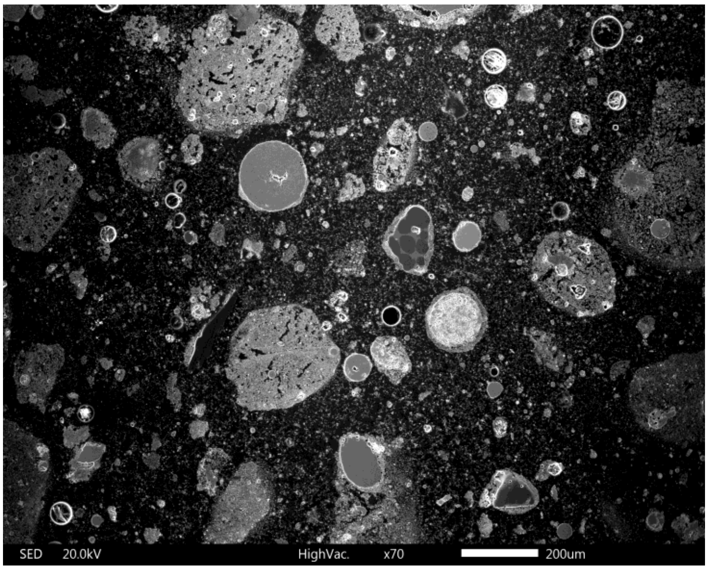
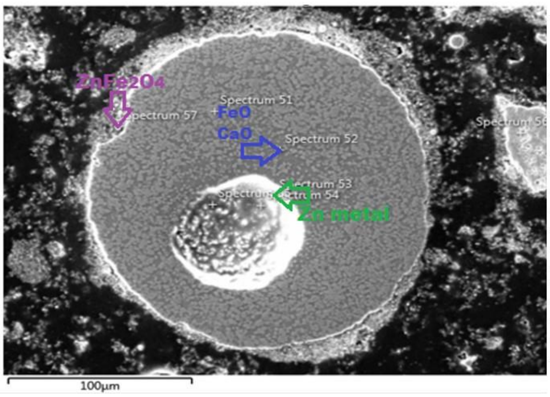


Figure 4. SEM image of the representative U1 EAF dust sample showing agglomerates of irregularly shaped as well as spherical particles

Melting of scrap iron in an electric arc furnace induces metal evaporation, resulting in EAF dust formation by two ways: by heterogeneous and homogeneous nucleation. Depending on the nucleation process, dust particles will be larger or smaller. Most of deposition of volatile metals on the surface of solid metal particles is carried out by heterogeneous nucleation, leading to formation of larger particles, *i.e.* particles with a diameter of about 200 µm. In the case that the amount of solid particles is not sufficient for agglomeration, homogeneous nucleation takes place and particle growth up to 0.02-100 µm. All interactions that occur during the formation of EAF dust make the final dust complex in terms of its chemical and physical characteristics [1, 30].

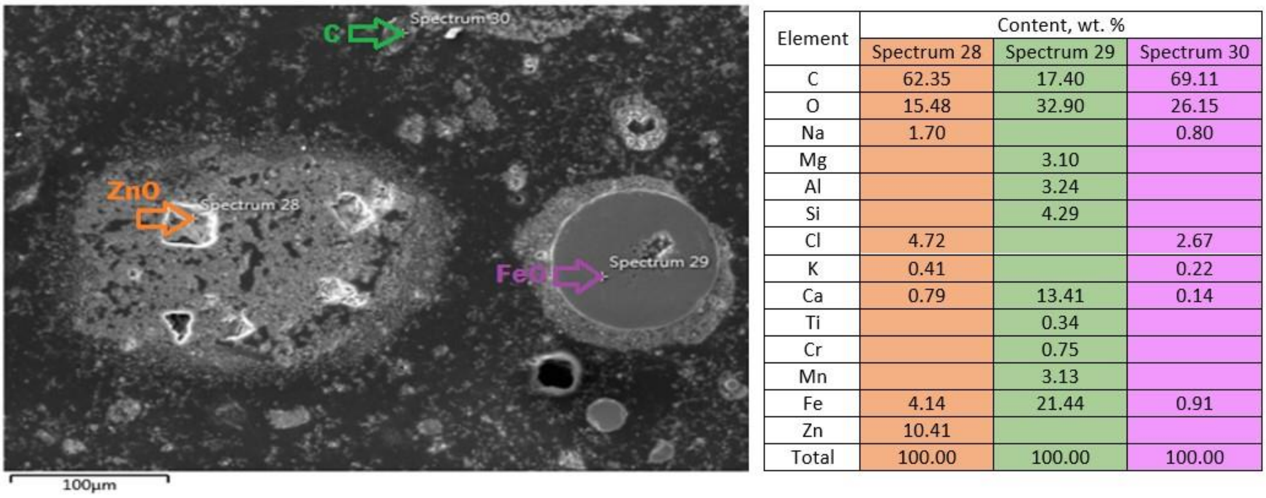
The SEM-EDS analysis has also shown an encapsulation phenomenon in the EAF dust particles, *i.e.* zinc metal particles are in some cases trapped within a sphere of magnetite and various types of glass, confirming the results obtained by polarized light microscopy. Cross-section of an EAF dust particle is presented in Figure 5, indicating that the larger particles are composed of an inner core of iron oxide (Fe_3O_4/Fe_2O_3), Zn metal, CaO, Ca-Si-Al-Ti glass, and graphite; middle layer of FeO, CaO, and graphite and a most distant layer of $ZnFe_2O_4$, leading to the assumption of heterogeneous nucleation.



Element	Content, wt. %						
	Spectrum 51	Spectrum 52	Spectrum 53	Spectrum 54	Spectrum 55	Spectrum 56	Spectrum 57
C	20.21	23.26	12.67	12.02	11.66	20.05	21.29
O	33.82	32.15	10.37	5.91	7.98	24.41	35.44
Na						2.08	
Mg	3.01						
Al	4.69	2.66	0.45	0.20	0.48		1.53
Si		6.26	1.14	0.59	1.66		1.58
Cl						0.13	
Ca	0.45	16.91	22.81	28.81	28.92		1.11
Ti		0.52		0.93	0.92		
Cr	20.91						
Mn	2.44	1.75	4.75	3.89	3.67		1.89
Fe	14.15	16.48	45.94	43.60	42.17	41.07	34.15
Zn	0.31		1.87	1.27		12.27	3.03
Te				2.77	2.53		
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Figure 5. SEM-EDS analysis of a cross-section of a spherical particle

Figure 6 shows SEM-EDS analysis of the U1 EAF dust sample, which also identified the presence of ZnO, along with graphite and FeO in irregularly shaped particles.



Element	Content, wt. %		
	Spectrum 28	Spectrum 29	Spectrum 30
C	62.35	17.40	69.11
O	15.48	32.90	26.15
Na	1.70		0.80
Mg		3.10	
Al		3.24	
Si		4.29	
Cl	4.72		2.67
K	0.41		0.22
Ca	0.79	13.41	0.14
Ti		0.34	
Cr		0.75	
Mn		3.13	
Fe	4.14	21.44	0.91
Zn	10.41		
Total	100.00	100.00	100.00

Figure 6. SEM-EDS analysis of the representative U1 EAF dust sample

3. 1. 4. 3. XRD analysis

In the analyzed U1 EAF dust sample, presence of the following phases was determined by the XRD analysis: zincite (ZnO), zinc metal (Zn), magnetite (Fe_3O_4), franklinite ($ZnFe_2O_4$), magnesioferrite ($MgFe_2O_4$), maghemite (Fe_2O_3), wustite (FeO) and poorly crystallized graphite (C) as shown in the diffractogram (Fig. 7). The main phases identified in the analyzed dust sample are in accordance with the results published in literature [2,3,5,10].

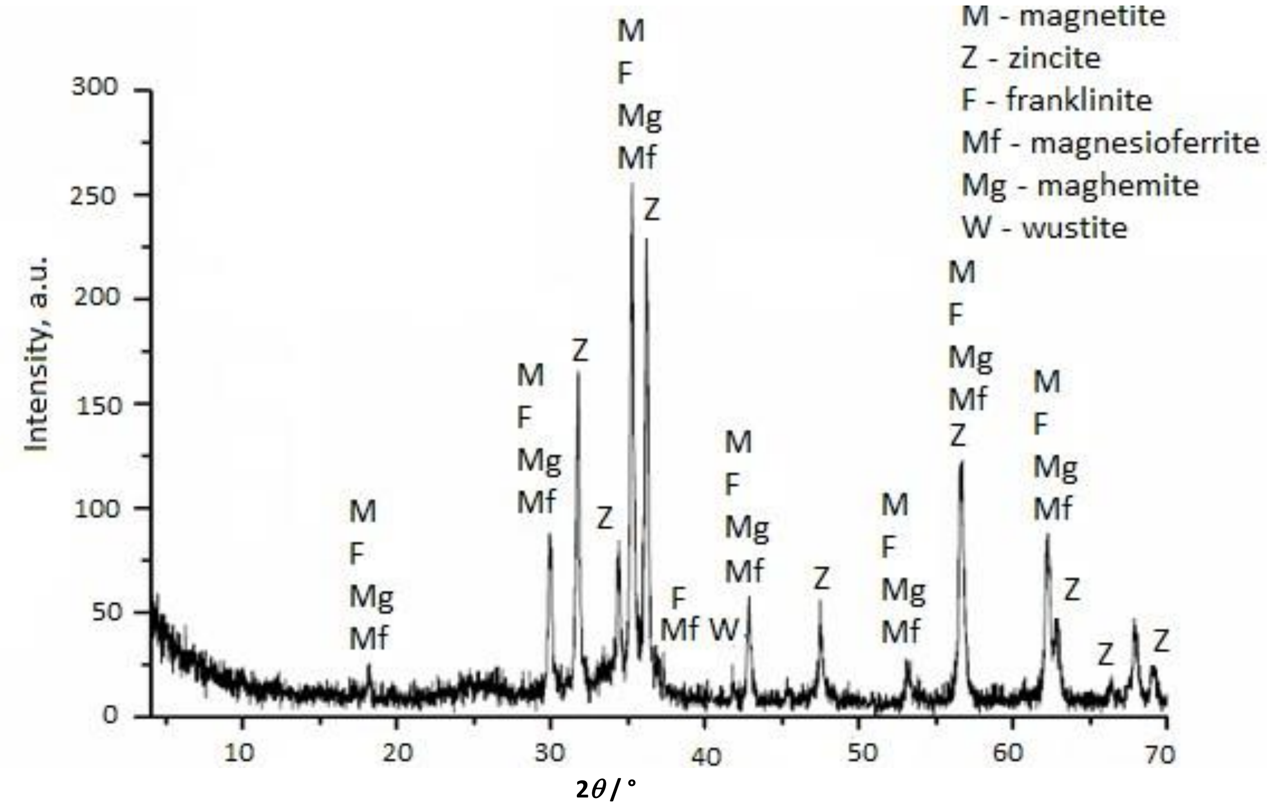


Figure 7. Diffractogram of the representative U1 EAF dust sample

Positions and relative intensity of the most intense diffraction peaks correspond to zincite, *i.e*. the most common phase, followed by the spinel phases (magnetite (Fe_3O_4), franklinite ($ZnFe_2O_4$), magnesioferrite ($MgFe_2O_4$)), while the diffraction peaks of zinc metal (Zn), graphite (C) and maghemite (Fe_2O_3) are less expressed. Peaks of the wustite (FeO) mineral show that it appears in traces in the sample.

3. 1. 5. Assessment of the impact of EAF dust on the environment and human health

3. 1. 5. 1. Leachability test

Results of the Leachability test of the representative U1 EAF dust sample according to SRPS EN 12457-2: 2008 are presented in Table 4.

Table 4. Leachability test results for the representative U1 EAF dust sample

Parameter	Measured value	Reference value for non-hazardous waste[1]	Reference value for hazardous waste[2]
pH	11.31	6-13[3]	-
Conductivity, µS cm^{-1}	8288	-	-
		Content, mg kg^{-1} of dry matter	
Vanadium	<0.08	200	-
Chromium	<0.05	10	70
Nickel	<0.07	10	40
Copper	<0.05	50	100
Zinc	3.00	50	200
Arsenic	<0.20	2	25
Selenium	<0.33	0.5	7
Silver	<0.05	50	-
Cadmium	<0.08	1	5
Barium	2.60	100	300
Mercury	<0.005	0.2	2
Lead	10.00	10	50
Molybdenum	4.70	10	30
Antimony	<0.50	0.7	5
Chlorides, as Cl^-	**30900**	**15000**	**25000**
Fluorides, as F^-	36.30	150	500
Sulfates, as SO_4^{2-}	7400	20000	50000
Phenol index	0.24	1000	-

[1,2] Annex 10 of the Rulebook on categories, investigation and classification of waste (Official Gazette of RS 93/2019, 39/2021), Article 2, Parameters for testing waste and leachate from non-hazardous waste landfills[1] and hazardous waste[2]. Ambient temperature 21°C, humidity 52 %, pressure 970 hPa

[3] Reference value for pH according to the Rulebook 93/2019, 39/2021 Annex 7, H15- Waste that has the property of producing another substance in any way after disposal, *e.g.* leachate that has any of the following characteristics (H1-H14), is 6-13. The measured pH value is within the allowable range.

Based on the leaching test results, the EAF dust sample is categorized as a hazardous waste in terms of disposal, due to the increased chloride content in the leaching eluate (leaching solution) above the permitted limits, even for the waste disposal on a hazardous waste landfill. These results indicate that the dust has to be subjected it to the prior treatment before the final disposal.

3. 1. 5. 2. Toxicity characteristic leaching procedure

Results of the toxicity characteristic leaching procedure (TCLP) test (EPA 1311) of the representative U1 EAF dust sample intended for disposal are presented in Table 5.

The obtained results of the TCLP test show that the EAF dust sample exhibited toxic characteristics, due to the increased contents of zinc, cadmium and lead in the TCLP eluate (leaching solution), which are above the permissible limits prescribed by the regulations. This type of hazardous waste needs further attention in order to protect the environment and work conditions.

Table 5. TCLP test results for the representative U1 EAF dust sample (element contents in the extraction procedure extract)

Element	Measured content, mg dm^{-3}	Waste toxicity reference content*, mg dm^{-3}
Vanadium	<0.008	24
Chromium	<0.005	5
Nickel	0.068	20
Copper	0.050	25
Zinc	**2690.67**	**250**
Arsenic	<0.020	5
Selenium	<0.033	1
Silver	<0.005	5
Cadmium	**13.880**	**1**
Barium	0.880	100
Mercury	<0.0005	0.2
Lead	**61.160**	**5**
Molybdenum	<0.007	350
Antimony	<0.050	15

*Annex 10 of the *Rulebook* on categories, investigation and classification of waste (Official Gazette of RS *93/2019, 39/2021*), Article 1, Parameters for testing the toxic characteristics of waste intended for disposal

4. CONCLUSION

This paper presents a detailed investigation of hazardous waste, *i.e*. EAF dust from a steel production plant in Serbia. Chemical characterization has confirmed the Zn content in the dust in the range of 32 to 35 wt.%, while the main mineralogical phases were zincite, franklinite, magnetite and magnesioferrite. Granulometric analysis showed that 80 % of the sample consisted of particles less than 26 µm in size. Impact on the environment and human health was assessed by the leachability test, which characterized the EAF dust as a hazardous waste due to the increased chloride content, while the TCLP test indicated toxicity of the dust due to the increased Zn, Cd and Pb contents.

Thus, treatment of this type of hazardous waste is necessary to protect the environment and human health. With appropriate processing, it would be possible to achieve concentration and separation of valuable metals that are in the waste, which is in the present case zinc, the most abundant metal in the investigated EAF dust. In order develop hydrometallurgical processes for zinc separation and stabilization of solid residues, as well as to design safe disposal of the resulting non-hazardous waste, further experimental studies of the treatment of the investigated EAF dust are necessary.

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REFERENCES

[1] Siame MC, Kaoma J, Hlabangana N, Danha G. An Attainable Region Approach for the Recovery of Iron and Zinc from Electric Arc Furnace Dust. *S Afr J Chem Eng*. 2019; 27: 35–42 https://doi.org/10.1016/j.sajce.2018.12.002.

[2] Wu CC, Chang FC, Chen WS, Tsai MS, Wang YN. Reduction Behavior of Zinc Ferrite in EAF-Dust Recycling with CO Gas as a Reducing Agent. *J Environ Manage*. 2014; 143: 208-213 https://doi.org/10.1016/j.jenvman.2014.04.005.

[3] Wang J, Zhang Y, Cui K, Fu T, Gao J, Hussain S, AlGarni TS. Pyrometallurgical Recovery of Zinc and Valuable Metals from Electric Arc Furnace Dust - A Review. *J Clean Prod.* 2021; 298: 126788 https://doi.org/10.1016/j.jclepro.2021.126788.

[4] Kukurugya F, Vindt T, Havlík T. Behavior of Zinc, Iron and Calcium from Electric Arc Furnace (EAF) Dust in Hydrometallurgical Processing in Sulfuric Acid Solutions: Thermodynamic and Kinetic Aspects. *Hydrometall.* 2015; 154: 20–32 https://doi.org/10.1016/j.hydromet.2015.03.008.

[5] Silvaa VS, Silvaa JS, Costaa BdS, Labesb C, Oliveira RMPB. Preparation of Glaze Using Electric-Arc Furnace Dust as Raw Material. *J Mater Res Technol*. 2019; 8(6): 5504–5514 https://doi.org/10.1016/j.jmrt.2019.09.018.

[6] Hazaveh PK, Karimia S, Rashchia F, Sheibania S. Purification of the Leaching Solution of Recycling Zinc from the Hazardous Electric Arc Furnace Dust Through an As-Bearing Jarosite. *Ecotoxicol Environ Saf*. 2020; 202: 110893 https://doi.org/10.1016/j.ecoenv.2020.110893.

[7] Čerňan M, Müller Z, Tlustý J, Valouch V. An Improved SVC Control for Electric Arc Furnace Voltage Flicker Mitigation. *Int. J. Electr. Power Energy Syst*. 2021; 129: 106831 https://doi.org/10.1016/j.ijepes.2021.106831.

[8] Bruckard WJ, Davey KJ, Rodopoulos T, Woodcock JT, Italiano J. Water Leaching and Magnetic Separation for Decreasing the Chloride Level and Upgrading the Zinc Content of EAF Steelmaking Baghouse Dusts. *Int J Miner Process*. 2005; 75: 1 – 20 https://doi.org/10.1016/j.minpro.2004.04.007.

[9] Trifunović V, Avramović Lj, Jonović R, Milić S, Đorđievski S, Jonović M. Hydrometallurgical Treatment of EAF Dust in aim of Zinc Separation, Proceedings/52nd International October Conference on Mining and Metallurgy - IOC 2021. In: *Proceedings of The 52nd International October Conference on Mining and Metallurgy*, Bor, Serbia, 2021, pp. 209-212 ISBN:978-86-6305-119-5.

[10] Halli P, Hamuyuni J, Revitzer H, Lundström M. Selection of Leaching Media for Metal Dissolution from Electric Arc Furnace Dust. *J Clean Prod*. 2017; 164: 265-276 https://doi.org/10.1016/j.jclepro.2017.06.212.

[11] Havlik T, Turzakova M, Stopic S, Friedrich B, Atmospheric Leaching of EAF Dust With Diluted Sulphuric Acid, *Hydrometall*. 2005; 77: 41–50 https://doi.org/10.1016/j.hydromet.2004.10.008.

[12] Keglevich de Buzin PJW, Heck NC, Vilela ACF. EAF dust: An Overview on the Influences of Physical, Chemical and Mineral Features in its Recycling and Waste Incorporation Routes. *J Mater Res Technol*. 2017; 6(2): 194–202 https://doi.org/10.1016/j.jmrt.2016.10.002.

[13] Halli P, Hamuyuni J, Leikola M, Lundström M. Developing a Sustainable Solution for Recycling Electric Arc Furnace Dust via Organic Acid Leaching. *Miner Eng*. 2018; 124: 1–9 https://doi.org/10.1016/j.mineng.2018.05.011.

[14] Omran M, Fabritius T. Effect of Steelmaking Dust Characteristics on Suitable Recycling Process Determining: Ferrochrome Converter (CRC) and Electric Arc Furnace (EAF) Dusts, *Powder Technol*. 2017; 308: 47–60 https://doi.org/10.1016/j.powtec.2016.11.049.

[15] Al-harahsheh M, Al-Nu'airat J, Al-Otoom A, Al-hammouri I, Al-jabali H, Al-zoubi M, Abu Al'asal S. Treatments of Electric Arc Furnace Dust and Halogenated Plastic Wastes: A Review. *J Environ Chem Eng*. 2019; 7: 102856 https://doi.org/10.1016/j.jece.2018.102856.

[16] Omran M, Fabritius T. Effect of Steelmaking Dust Characteristics on Suitable Recycling Process Determining: Ferrochrome Converter (CRC) and Electric Arc Furnace (EAF) Dusts, *Powder Technol*. 2017; 308: 47–60 https://doi.org/10.1016/j.powtec.2016.11.049.

[17] Ruiz O, Clemente C, Alonso M. Alguacil FJ. Recycling of an Electric Arc Furnace Flue Dust to Obtain High Grade Zno. *J Hazard Mater*. 2007; 141: 33–36 https://doi.org/10.1016/j.jhazmat.2006.06.079.

[18] Pickles CA, Marzoughi O. Thermodynamic Analysis of Metal Speciation During the Chlorosulphation of Electric Arc Furnace Dust. *Miner Eng*. 2019; 140: 105874 https://doi.org/10.1016/j.mineng.2019.105874.

[19] Khattab RM, El-Sayed Seleman MM, Zawrah MF. Assessment of Electric Arc Furnace Dust: Powder Characterization and its Sinterability as Ceramic Product. *Ceram Int.* 2017; 43: 12939–12947 https://doi.org/10.1016/j.ceramint.2017.06.192.

[20] Alencastro de Araújo J, Schalch V, Recycling of Electric Arc Furnace (EAF) Dust for Use in Steel Making Process, *J Mater Res Technol*. 2014; 3(3): 274–279 https://doi.org/10.1016/j.jmrt.2014.06.003.

[21] Li YC, Zhuo SN, Peng B, Min XB, Liu H, Ke Y. Comprehensive Recycling of Zinc and Iron From Smelting Waste Containing Zinc Ferrite by Oriented Transformation with SO_2. *J Clean Prod*. 2020; 263: 121468 https://doi.org/10.1016/j.jclepro.2020.121468.

[22] Environmental Protection Agency, Land Disposal Restrictions for Electric Arc Furnace Dust (K061) - Federal Register Notice, Vol. 56 No. 160, August 19, 1991 p 41164.

[23] Norma Brasileira, ABNT 10004:2004, Solid waste Classification, 2004.

[24] Commission of the European Communities, Guidance on classification of waste according toEWC-Stat categories, Supplement to the Manual for the Implementation of the Regulation (EC) No 2150/2002 on Waste Statistics, version 2, December 2010.

[25] Ledesma EF, Lozano-Lunar A, Ayuso J, Galvín AP, Fernández JM, Jiménez JR. The Role of pH on Leaching of Heavy Metals and Chlorides from Electric Arc Furnace Dust in Cement-Based Mortars. *Constr Build Mater*. 2018; 183: 365–375 https://doi.org/10.1016/j.conbuildmat.2018.06.175.

[26] Ng KS, Head I, Premier GC, Scott K, Yu E, Lloyd J, Sadhukhan J. A Multilevel Sustainability Analysis of Zinc Recovery from Wastes. *Resour Conserv Recycl*. 2016; 113: 88–105 https://doi.org/10.1016/j.resconrec.2016.05.013.

[27] Pickles CA. Thermodynamic Modelling of the Multiphase Pyrometallurgical Processing of Electric Arc Furnace Dust. *Miner Eng*. 2009; 22: 977–985 https://doi.org/10.1016/j.mineng.2009.03.007.

[28] Miki T, Chairaksa-Fujimoto R, Maruyama K, Nagasaka T. Hydrometallurgical Extraction of Zinc from CaO Treated EAF Dust in Ammonium Chloride Solution. *J Hazard Mater*. 2016; 302: 90–96 https://doi.org/10.1016/j.jhazmat.2015.09.020.

[29] Rudnik E. Investigation of Industrial Waste Materials for Hydrometallurgical Recovery of Zinc. *Miner Eng*. 2019; 139: 105871 https://doi.org/10.1016/j.mineng.2019.105871.

Ispitivanje opasnog otpada
Studija slučaja karakterizacije prašine iz elektrolučne peći

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Izvod

Kao međuprodukt procesa dobijanja čelika topljenjem sekundarnih sirovina na bazi gvožđa u elektrolučnoj peći, nastaje prašina. Ova prašina iz elektrolučne peći ima značajan sadržaj Zn i Fe, kao i Pb, Cd, Ca, Mg, Cr, Mn, Si, Ni, Cu, F, Cl i dr. elemenata i smatra se opasnim industrijskim čvrstim otpadom obzirom da u svom sastavu sadrži teške metale. U cilju zaštite životne sredine i javnog zdravlja od negativnog uticaja ove vrste opasnog otpada, neophodno je, čak i obavezno, sprovesti tretman otpada u skladu sa zakonodavstvom zemlje u kojoj se nalazi. Pre nego što se primeni bilo koji tretman prerade prašine iz elektrolučne peći, potrebno je izvršiti njenu detaljnu karakterizaciju. U ovom radu, izvršena je sledeća karakterizacija uzoraka prašine iz elektrolučne peći iz postrojenja u Republici Srbiji: fizička, hemijska, kao i mineraloška karakterizacija, određen je granulometrijski sastav, a određena je i procena uticaja prašine na životnu sredinu i zdravlje ljudi (testovi toksičnosti i lužljivosti). Rezultati istraživanja ove vrste opasnog otpada pokazali su da je sadržaj Zn u prašini iz elektrolučne peći iznosio od 32 mas.% do 35 mas.% i da su glavne mineraloške faze prašine cinkit, franklinit, magnetit i magnezioferit. Granulometrijska analiza je pokazala da se 80 % uzorka sastoji od čestica veličine manje od 26 µm. Što se tiče rezultata testa lužljivosti, prašina je okarakterisana kao opasan otpad zbog povećanog sadržaja hlorida, dok je testom toksičnosti utvrđeno da ispitivana prašina pokazuje toksična svojstva zbog povećanog sadržaja Zn, Cd i Pb.

Ključne reči: industrijski otpad, EAF prašina, uticaj na životnu sredinu