

Characterization of steel mill electric-arc furnace dust

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Abstract

In order to make a complete characterization of electric-arc furnace (EAF) dust, as hazardous industrial waste, and to solve its permanent disposal and/or recovery, bearing in mind both the volumes formed in the Croatian steel industry and experiences of developed industrial countries, a study of its properties was undertaken.

For this purpose, samples of EAF dust, taken from the regular production process in the Željezara Sisak Steel Mill between December 2000 and December 2001, were subjected to a series of tests.

The chemical composition of EAF dust samples was investigated by means of a several different analytical methods. The results from the chemical analysis show that the approximate order of abundance of major elements in EAF dusts is as follows: Fe, Zn, Mn, Ca, Mg, Si, Pb, S, Cr, Cu, Al, C, Ni, Cd, As and Hg.

Granular-metric composition of single samples was determined by applying sieve separation. Scanning electron micro-structural examination of EAF dust microstructure was performed and results indicated that all twelve EAF dusts were composed of solid spherical agglomerates with Fe, Zn, Pb, O, Si and Ca as the principal element.

The investigation of grain morphology and the mineralogical composition of EAF dust were taken by combination of high resolution Auger electron spectroscopy (HR AES), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction analysis. The analysis of XPS-spectra determined the presence of zinc in the form of ZnO phase and the presence of lead in the form of PbO phase, i.e. PbSO₃/PbSO₄ forms.

The results of the X-ray diffraction phase analysis show that the basis of the examined EAF dust samples is made of a mixture of metal oxides, silicates and sulphates.

The metal concentration, anions, pH value and conductivity in water eluates was determined in order to define the influence of EAF dust on the environment.

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1. Introduction

The share of the electric-arc furnace (EAF) procedure in the world's steel output is increasing. This is evident from the yearly data on steel production in 1970, amounting to 595 million tonnes, 14% of which was produced by the electric-arc furnace procedure. In 1980, the electric-arc furnace process accounted for 23% of the total world output of

716 million tonnes, in 1990 the share was 28% of the total of 770 million tonnes, and in 1998 it was 34% of the total of 776 million tonnes [1].

Major pollution that is released into the atmosphere during the steel making process includes solid particles (dust), carbon (II) oxide, nitrogen oxides, and volatile organic compounds.

Due to its chemical and physical properties, the electric-arc furnace dust was categorized as hazardous waste according to the US EPA classification of 1980 [2]. Being treated as hazardous waste, it is partly disposed of permanently at appropriate, regulation-prescribed waste

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dumps, or it can be used as secondary raw material in the production of zinc, iron, lead, etc.

Most of the so far developed and commercialized processes are predominantly applied to the re-cycling of electric furnace dust and, to a lesser extent, to its inactivation, i.e. its stabilization prior to permanent disposal.

The seriousness of the problem of the disposal electric-arc furnace dust arises from the fact that its annual output produced in the electric steel making process is constantly increasing. A total of 20 kg of dust per ton of steel is produced, which, according to reports [2,3] for 1996, makes a volume of 4.72 million tonnes.

As early as in 1998, the total volume of electric-arc furnace dust in the USA reached 0.9–0.925 million tonnes [2]. According to the same source, this volume will surpass one million tonnes in 2002.

From December 2000 to December 2001, Željezara Sisak produced 26,619 tonnes of electric-arc furnace steel and 400 tonnes of electric-arc furnace dust resulted from the process.

Collecting EAF dust while treating smoke gases in electric filters is just a partial solution to the emission problem, whereas the volumes of the produced dust as well as its chemical composition point to the necessity to define and apply integral solutions for its complete and final disposal.

This research involved examination of the chemical and phase composition and physical properties of 12 average monthly samples of EAF dust for the purpose of its detailed characterization.

2. Experimental

2.1. Analysis and characterization of samples

In order to investigate the chemical and phase composition of EAF dust, the average monthly samples taken at the outlet of the dust suppression system were analyzed, with the exception of July 2001 when the steel mill was out of operation.

The samples were homogenized and successive quartering provided 1000 g of each sample (average samples). All samples were dried for 2 h at 105 °C and stored above silica gel in a desiccator. They were marked with numbers 1–12.

The chemical composition of average EAF dust samples was investigated by means of a traditional chemical analysis (EN 196-21:1989, ASTM E 277-69:1984, ASTM E 247-82:1986), atomic absorption spectrometry (AAS), emission spectrometry by inductively coupled plasma (ICP) and absorption of IR-radiation.

For determination of the sample metal content by atomic absorption spectrometry, the samples were prepared by dissolution in an acid admixture.

The prepared samples were analyzed on a Perkin-Elmer 503 atom absorption spectrometer using the flame technique. Contents of As and Hg were determined by ICP-spectrometry on a Perkin-Elmer 3100 RL Optima spectrometer.

The CS-444 Carbon and sulphur system with HF-400 induction furnace and infrared detector was used for determination of carbon and sulphur contents.

The accuracy of the used analytical methods was tested by analysing one electrical furnace dust reference material (ECRM 876-1). Recovery factors for all analytes identified by means of the stated methods in this paper were within the range of $100 \pm 4\%$. The applied methods have displayed satisfactory linearity when defining the stated analytes within the selected operational area and the correlation coefficients for all analytes and all applied methods were >0.997 .

Granular-metric composition of single samples was determined by applying sieve separation according to DIN-4188, and the obtained fractions had the following particle size: $>125 \mu\text{m}$, 125–100 μm , 100–90 μm , 90–63 μm , 63–50 μm , and $<50 \mu\text{m}$.

For scanning electron microscopy, the samples were prepared on a graphite support. Electron micrographs were taken on the Philips XL 30 scanning electron microscope with BSE detector and EDS analyzer.

The grain morphology and mineralogical composition of EAF dust were investigated by a combination of high resolution Auger electron spectroscopy (HR AES) and X-ray photoelectron spectroscopy (XPS). Vacuum Generators Microlab 310-F system with Mg $K\alpha$ X-ray source (1253.6 eV; pass energy 25 eV CAE mod; anode voltage 14.5 mA \times 14 kV 200 W) was used in these investigations.

For the X-ray powder diffraction analysis, all the separated fractions were subsequently ground and homogenized in a Spex Mixer Mill tungsten-carbide grinding container for 10 min.

Standard procedures were applied to prepare the samples for analysis by X-ray diffraction [4]. The phase composition of EAF dust was determined using a Philips counter diffractometer with monochromatized (graphite monochromator) Co $K\alpha$ -radiation.

X-ray diffraction patterns were analyzed both visually and by the comparison technique using the Joint Committee of Powder Diffraction Standard (JCPDS) data [5–8]. Mass share of the phases Fe_3O_4 , $\alpha\text{Fe}_2\text{O}_3$, and FeO was determined with an outer standard method [9,10].

The eluates for examination were prepared by shaking 10 g of an EAF dust sample with 100 ml of redistilled water. Samples were equilibrated for 1, 10 and 30 days. After shaking, the samples were filtered through a 0.45 μm filter FP 030/2 (Schleicher, Germany), and determination was carried out on a 25 ml aliquot. Eluted metals were established by the AAS method.

The metal concentration, pH value and conductivity in water eluates were determined in order to define the influence of EAF dust on the environment. Changes in pH, conductivity and chemical composition of water eluates were monitored for 1, 10 and 30 days. Conductivity and pH were measured on the INOLAB pH/cond Level 1, type 1E 10-111401 (WTW) instrument.

2.1.1. Determination of leached anions

Anions, which are relevant because of their impact on the environment (F^- , Cl^- , Br^- , NO_2^- , NO_3^- and SO_4^{2-}), were determined by the ion-chromatographic method. Eluted anions were detected using a combination of ion exchange columns and conductivity detection on an Ion Chromatograph 690 (Metrohm) with IC anion column Super Sep –6.1009.000 (Metrohm).

3. Results and discussion

3.1. Characterization of samples

3.1.1. Chemical analysis

The chemical composition of electric-arc furnace dust depends on the quality of steel scrap processed, the type of steel being produced, technological and operating conditions and the degree of return of the dust into the process. Reference data [11–24] imply that the prevailing elements in EAF dust vary in concentration: Fe 10–45%, Zn 2–46%, Pb 0.40–15.14%, Cr 0.2–11%, Cd 0.01–0.30%, Mn 1–5%, Cu < 3%, Si 1–5%, Ca 1–25%, Mg 1–12%, Al 0.1–1.5%, C 0.11–2.36%, S 1.5–2.5%, Na 0.5–1.8%, K 0.35–2.30%. The analyzed samples of EAF dust formed within the stated time frame had the following metal concentration ranges: Fe 41.08–48.58%, Zn 3.75–8.10%, Pb 0.94–2.07%, Cr 0.19–0.33%, Cd 0.010–0.027%, Mn 5.00–5.96%, Cu 0.22–0.30%, Si 1.79–2.24%, Ca 3.61–4.95%, Mg 2.0–2.83%, Al 0.21–0.28%, C 0.27–0.44%, S 0.54–1.20%, Na 0.36–0.66%, K 0.48–1.26%.

The results of the chemical analysis of the EAF dust samples are shown in Table 1.

The results of individual metal content analysis in the EAF dust point to the need of examining its physical and

Table 2
Granular-metric analysis of EAF dust

Sample	Fraction (μm) mass share (%)					
	<50	50–63	63–90	90–100	100–125	>125
1	11.07	2.84	36.65	0.91	32.89	15.63
2	8.51	5.80	33.33	4.60	34.93	12.81
3	4.04	4.04	18.26	0.50	63.07	10.09
4	7.17	2.66	37.60	1.64	38.11	12.81
5	11.62	3.01	26.95	1.20	43.29	13.83
6	8.42	4.21	42.38	1.30	32.46	11.22
7	9.12	3.91	42.58	2.91	26.65	15.83
8	7.24	3.32	29.14	7.14	42.71	10.45
9	14.36	6.37	32.56	0.91	28.71	17.09
10	4.22	1.71	17.49	8.04	15.88	52.66
11	18.31	15.79	16.90	2.21	36.92	9.86
12	16.35	9.83	39.32	2.31	25.08	7.12

chemical properties, since it is considered to be a type of industrial waste. Special attention was given to the content of heavy metals in water leachates [25,26] in order to find the proper solution for its disposal.

The samples were subjected to granular-metric analyses in order to determine the grain size and the mass share of individual granular-metric fractions. Table 2 shows the results of these analyses.

The results of granular-metric analysis have shown that a sample of electric furnace dust basically consists of 100–125 μm particles, while 90–100 μm particles are least represented.

Although the results of granular-metric analysis show that the smallest measured fraction has the grain size <50 μm , this is not the final picture of the actual grain size of the examined EAF dust. Namely, the micrographs obtained by means of search microanalysis, Fig. 1, point to the particles with grain diameter = 1 μm which mostly form agglomerates, the size of which can exceed 200 μm , Fig. 3.

Table 1
The chemical composition of EAF dust

Element	Waste (%)											
	1	2	3	4	5	6	7	8	9	10	11	12
C	0.27	0.42	0.29	0.40	0.37	0.35	0.44	0.37	0.36	0.38	0.29	0.35
Na	0.39	0.66	0.65	0.50	0.60	0.61	0.58	0.40	0.57	0.57	0.36	0.50
Mg	2.35	2.42	2.83	2.42	2.32	2.00	2.56	2.30	2.24	2.16	2.41	2.58
Al	0.21	0.24	0.25	0.28	0.28	0.26	0.28	0.28	0.27	0.20	0.27	0.28
Si	1.90	2.24	2.00	2.15	2.12	1.91	1.96	2.19	2.00	1.91	2.17	1.79
S	0.67	0.72	0.62	0.61	0.52	0.66	0.71	1.20	0.54	0.55	0.65	0.61
K	0.83	0.89	1.13	0.91	1.26	0.78	0.70	0.71	0.75	0.67	0.48	0.68
Ca	4.07	3.97	4.10	4.26	4.10	4.07	3.97	4.37	4.95	3.79	3.82	3.61
Cr	0.29	0.27	0.21	0.19	0.33	0.21	0.23	0.24	0.22	0.22	0.28	0.33
Mn	5.48	5.42	5.48	5.22	5.58	5.18	5.90	5.50	5.00	5.76	5.96	5.88
Fe	46.62	45.23	44.11	46.64	44.67	41.08	43.86	43.83	41.88	48.58	46.90	44.11
Ni	0.033	0.032	0.016	0.018	0.035	0.023	0.024	0.027	0.025	0.019	0.031	0.035
Cu	0.27	0.28	0.29	0.28	0.30	0.27	0.29	0.27	0.26	0.22	0.25	0.27
Zn	4.84	5.24	5.08	4.52	5.16	8.10	5.45	5.56	7.45	3.75	4.40	6.60
As	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	0.019	0.014	0.016	0.012	0.010	0.025	0.012	0.027	0.021	0.011	0.012	0.025
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	1.85	1.15	1.37	1.16	1.77	2.07	1.58	1.38	1.42	1.02	0.94	1.19

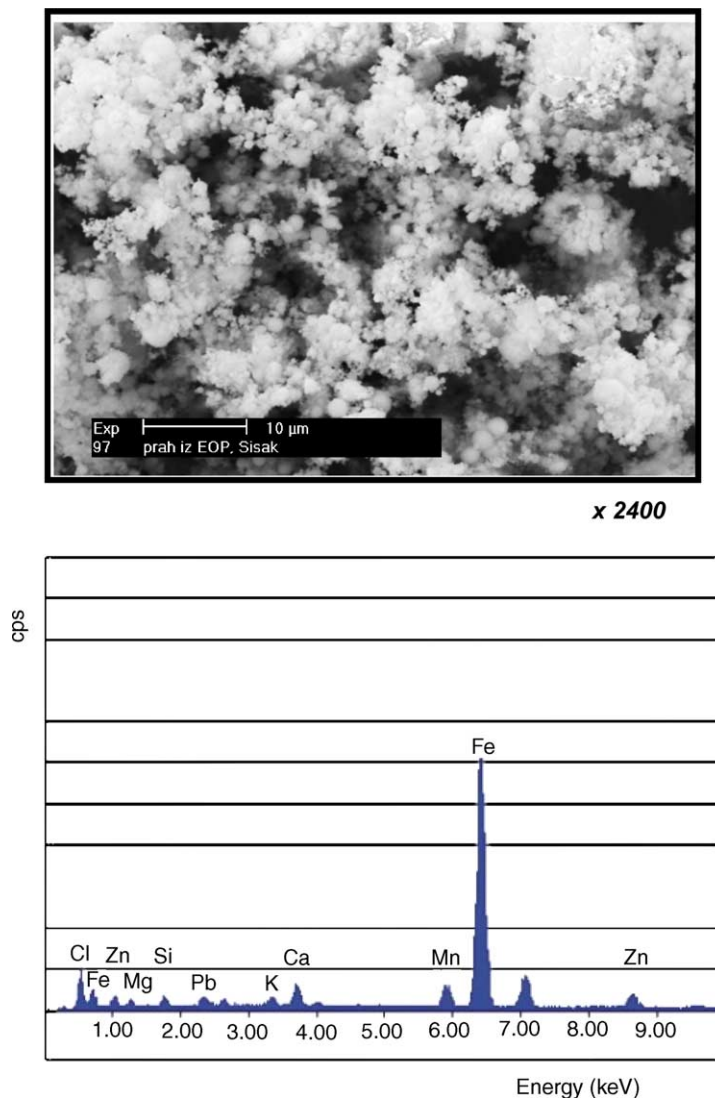


Fig. 1. Scanning electron micrograph (magnification 2400 \times) and EDS spectre of EAF dust sample number 9.

It is important to say that the granular-metric fractions obtained by screening the dry sample without previous ultrasound treatment, which is very often used in spite of the potential grain erosion, i.e. additional fragmentation. The reference data imply a comparatively substantial difference in the measured sizes of EAF dust particles.

Delalio et al. [20] have found that over 85% of EAF dust sample mass is accounted for by particles $<40\ \mu\text{m}$, whereas Li and Tsai [11] have found two groups of particles in the examined dust sample: one $<37\ \mu\text{m}$ and the other $>37\ \mu\text{m}$. Cruells et al. [34] have determined different mass shares of particles over $100\ \mu\text{m}$ (92% in one sample and 12% in the other).

Thus, have for example Sekula et al. [30] examined the dust having 94% of particles $<56\ \mu\text{m}$ 94%, as defined by screening analysis. Wet screening accounted for the mass share of particles $<10\ \mu\text{m}$ of 53%. Similar results were obtained by both Nyirenda and Lugtmeijer [35] and Vinals et al. [33], respectively.

3.1.2. Scanning electron micro-structural examination

Scanning electron micro-structural examination of EAF dust microstructure was performed and the results are shown in Figs. 1–3. Based on this microphotographs and the results of X-ray energy dispersive spectrometry (EDS), it can be seen that the samples were not completely homogeneous. The grain size of the EAF dust samples was 1–200 μm .

The references most often present the results of this type of research implying the dominance of spherical particle, i.e. agglomerate form of comparably the same size, and the agglomerate diameter varies from 1 to around 30 μm . Spherical particles with wrinkled surface and elongated non-defined forms were also observed. Škvara et al. [32] have recorded the predominant presence of spherical particles, just like Li and Tsai [11], whereas Rocabois et al. [24] have pointed out to spherical forms of the spinel-type metal oxides (Fe, Zn, Mn)OFe₂O₃, and they have proven the presence of angular-shaped particles which he considers to be zinkite ZnO. The

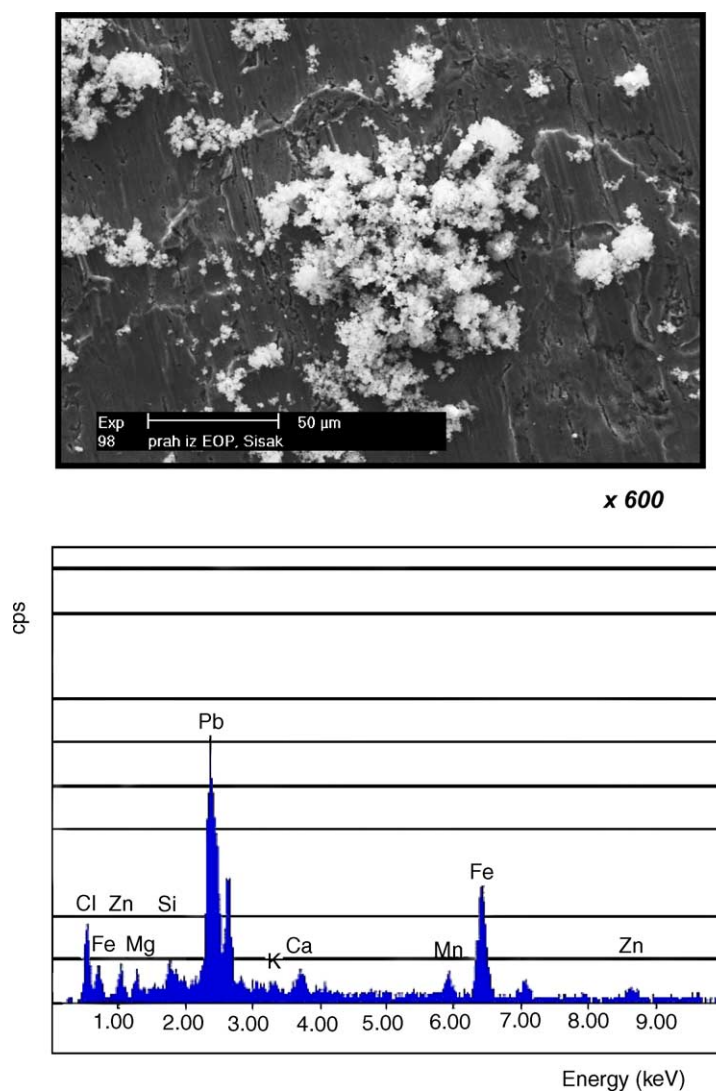


Fig. 2. Scanning electron micrograph (magnification 600×) and EDS spectre of EAF dust sample number 9.

elongated acicular shapes $<1 \mu\text{m}$, in addition to the mandatory spherical shapes, were described by Stegemann et al. [36] as well.

The individual particles were generally spherical and very often in aggregate forms. The same samples were also subjected to the element distribution analysis (O, Zn, Mg, Al, Si, S, Pb, Ca, Mn, Fe and Cu), and the results are shown as elemental distribution images in Fig. 4. Fig. 4 shows the match of metal and oxygen distribution in accumulations, implying the possible presence of metal–oxygen structural forms, which corresponds to the XRD analysis results.

In some of the EAF dust samples examined by means of high resolution Auger electron spectrometry, AES-spectra were detected at several points and they were subjected to quantitative chemical analysis. Fig. 5 shows the microphotograph of EAF sample 9 and the AES-spectrum at points P1–P5. Qualitative compositions of individual

analysed points are almost identical, and the absence of certain elements at particular points is the result of their concentration, which lies below the limit of detection.

The analysis of XPS-spectra, Fig. 6, determined the presence of zinc in the form of ZnO phase and the presence of lead in the form of PbO phase, i.e. $\text{PbSO}_3/\text{PbSO}_4$ forms.

The X-ray diffraction technique was applied to analyze all of the studied samples as well as all fractions obtained by the granular-metric analysis. The results of the X-ray diffraction phase analysis are shown in Table 3.

According to JCPDS data from file card numbers: 1-0201, 1-1247, 3-0125, 3-0676, 3-1062, 4-326, 5-0490, 5-0661, 5-0664, 6-005, 6-0283, 6-0504, 6-0615, 6-0696, 7-26, 7-230, 7-302, 8-243, 8-247, 9-6, 9-307, 9-327, 9-464, 10-173, 10-352, 10-2356, 10-380, 10-430, 10-476, 11-88, 11-99, 11-164, 11-284, 11-614, 11-695, 12-102, 12-174, 12-181, 12-205, 12-224, 12-284, 12-301, 12-408, 12-714,

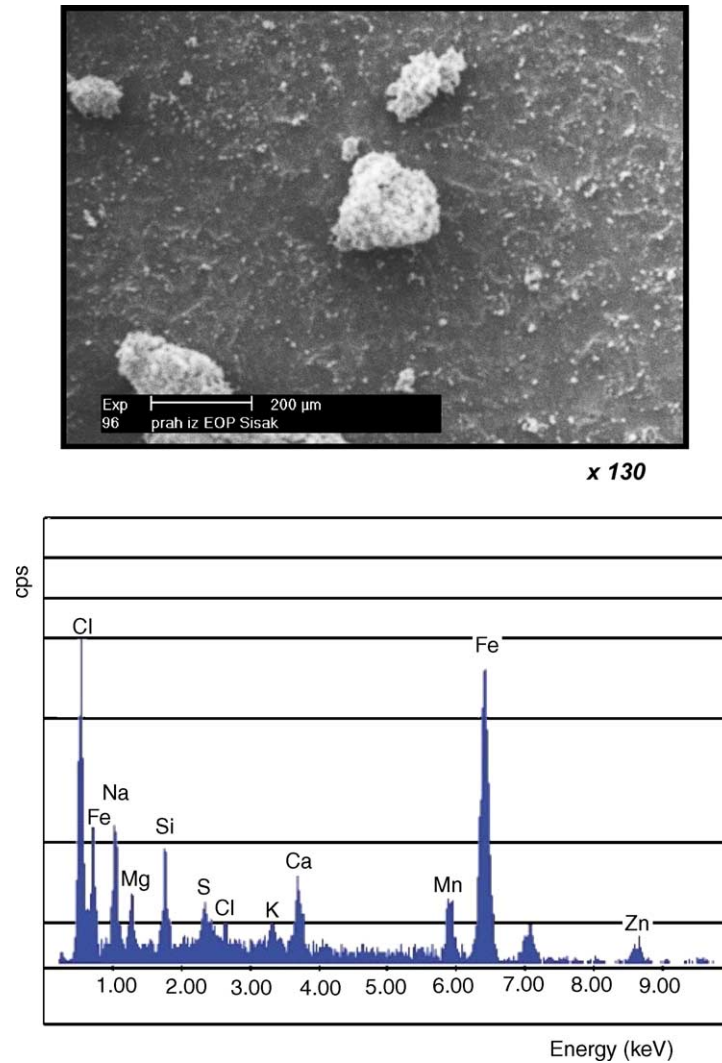


Fig. 3. Scanning electron micrograph (magnification 130 \times) and EDS spectre of EAF dust sample number 9.

13-122, 13-309, 13-534, 14-260, 14-326, 14-364, 14-444, 15-157 and 15-776 in the examined samples, the following phases were identified.

- in all average samples and all separated fractions: Fe_3O_4 , $\alpha\text{Fe}_2\text{O}_3$, FeO , Fe-met. , $2\text{FeO}\cdot\text{SiO}_2$; ZnO , SiO_2 (quartz), $3\text{CaO}\cdot 2\text{SiO}_2$; $4\text{PbO}\cdot\text{PbSO}_4$ This basis of EAF dust is confirmed with results of X-ray diffraction analysis obtained by other authors [11,24,27–33].
- in most of the average samples and separated fractions – FeS ; $\text{Cu}_{1,96}\text{S}$; $\text{Cu}_2\text{O}\cdot 2\text{Fe}_2\text{O}_3$; $3\text{CdSO}_4\cdot 2\text{H}_2\text{O}$; Ni_7S_6 ; NiS_2 ; $\alpha\text{CaO}\cdot\text{Cr}_2\text{O}_3$; MnO ; $\alpha\text{Al}_2\text{O}_3$; SiO_2 (cristobalite); SiO_2 (tridymite); $3\text{Mg}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$; $\text{CaO}\cdot 2\text{SiO}_2\cdot 1/2\text{H}_2\text{O}$; $\text{CaO}\cdot\text{SiO}_2\cdot \text{YH}_2\text{O}$; $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; $\text{Al}_2\text{O}\cdot\text{SiO}_2$; $\text{Al}_2\text{O}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ and S ;
- only in some of the examined samples – Fe_9S_8 ; $\text{Fe}_2(\text{SO}_4)_3\cdot \text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$; $\text{FeSO}_4\cdot 4\text{H}_2\text{O}$; $\text{Fe}_2(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$; $3(\text{Cu}, \text{Zn})\text{SO}_4\cdot 4\text{H}_2\text{O}$; $\text{Zn}_3(\text{AsO}_4)_2\cdot 4\text{H}_2\text{O}$; $\text{ZnS}_2\text{O}_4\cdot \text{Na}_2\text{S}_2\text{O}_4\cdot n\text{H}_2\text{O}$; $3(\text{Zn}, \text{Mg})\text{O}\cdot 4(\text{Si}, \text{Al})\text{O}_2\cdot \text{H}_2\text{O}$;

CuO ; $5\text{CuO}\cdot 2\text{As}_2\text{O}_5\cdot 10\text{H}_2\text{O}$; $\text{Cd}_3\text{Zn}(\text{SO}_3)_4$; $\text{PbO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; Cr_2O_3 ; ρMnO_2 ; Mn_xO_y ; γMnS ; MnSO_4 ; $\alpha\text{MnO}\cdot\text{SiO}_2$; MnS_2 ; $\alpha 2\text{CaO}\cdot\text{SiO}_2$ (Narita⁹); $\gamma 2\text{CaO}\cdot\text{SiO}_2$ (Narita⁹); $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$; $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 12\text{H}_2\text{O}$; $\text{Na}_2\text{O}\cdot 4\text{SiO}_2$; $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$; $\text{BaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$.

Based on the results of the X-ray diffraction analysis, individual heavy metal phase forms were identified solely in some of the fractions obtained by means of screen analysis. However, the same forms were not identified in average samples, obviously due to their low concentration, which lies below the susceptibility limit of this method.

The results of the X-ray diffraction phase analysis confirm the conclusions about the phase composition of electric-arc furnace dust samples derived from the results of elementary and quantitative analyses. The basis of the examined EAF dust samples is made of a mixture of metal oxides, silicates and sulphates. Other identified phases, as compared to the

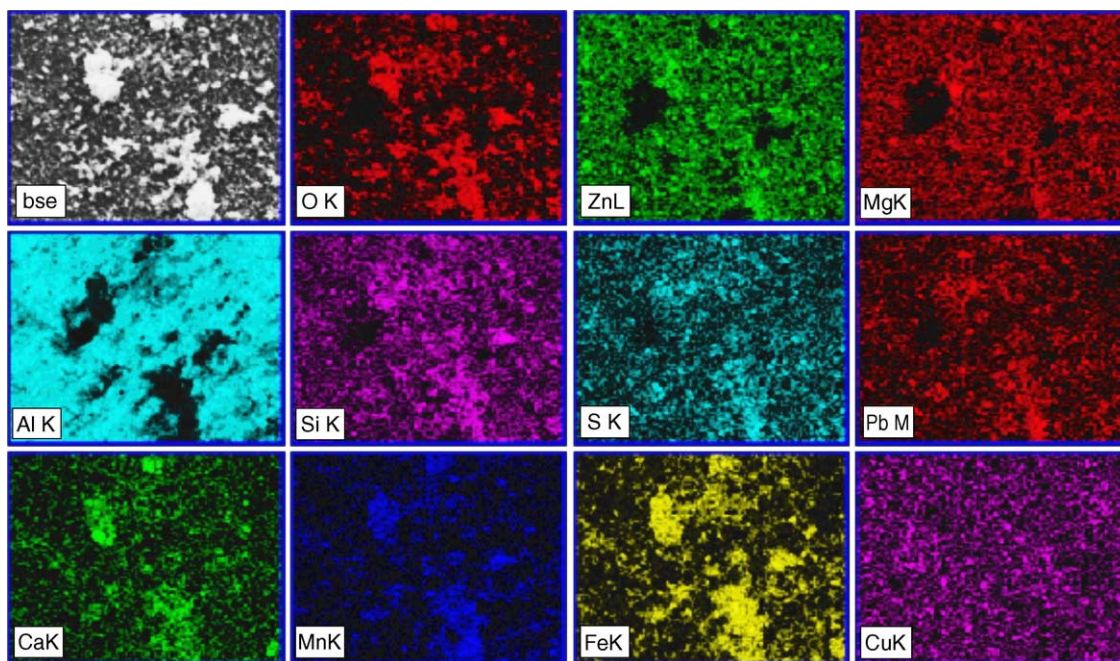


Fig. 4. Scanning electron micrograph (SEM) and elemental distribution (BSE) image of EAF dust sample number 9.

basic phases, are found in a smaller or considerably smaller concentration.

Most of the identified phases account for a very low mass share in the examined samples, and some of them are at the limit of measurability.

On the other hand, the Fe_3O_4 phase makes up the matrix of all examined samples and its mass share exceeds 50%.

Apart from the most often identified oxides (Fe_2O_3 , Fe_3O_4 , FeO , ZnO , PbO , MnO , NiO , Cr_2O_3 , CuO , Al_2O_3 , MgO , SiO_2 , CaO , Na_2O and K_2O) the references [11,36] rarely refer to the compounds of the spinel-ferrite type such as $(\text{Mn}_x\text{Zn}_y\text{Fe}_{1-x-y})\text{Fe}_2\text{O}_4$, i.e. $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ (or ZnFe_3O_4), MnFe_2O_4 , $(\text{Mn}, \text{Zn})\text{Fe}_2\text{O}_4\text{--Fe}_2\text{O}_4\text{--Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4\text{--}(\text{Mn}, \text{Fe})\text{O}$, and even less frequently they [11,35,37,38] mention compounds such as NaCl , KCl , $\text{ZnCl}_2\cdot 4\text{Zn}(\text{OH})_2\cdot \text{H}_2\text{O}$, PbOHCl , CaSiO_3 , FeCr_2O_4 , FeCr_2S_2 , Mn_3O_4 , NiCr_2O_4 , Zn_2SiO_4 , FeAl_2O_4 , FeNi , $\text{Ca}[\text{Zn}(\text{OH})_3]_2\cdot 2\text{H}_2\text{O}$ or $[\text{CaZn}_2(\text{OH})_6\cdot 2\text{H}_2\text{O}]$.

Due to the relatively high level of heavy metals and their classification as hazardous industrial waste, electric-arc furnace dust cannot be disposed of unless there is a dump complying with all technical environmental protection measures postulated by statutory regulations.

Otherwise, electric-arc furnace dust as toxic waste can be taken care of either by applying an EAF dust recovery method, or by stabilizing heavy metals.

EAF dust, as hazardous waste, is a material that requires special investigation in order to examine its influence on the environment. To complete the information on the behaviour of the EAF dust at final destination, it was decided to carry out leaching test with water (toxicity characteris-

tics leaching test according to DIN-38414 S4). For this reason, the EAF dust samples were leached in water to establish the chemical composition of eluates. The results of the quantitative chemical analysis are shown in Table 4. Extraction with water caused dissolution of some components. It was observed in all samples that the pH value slightly decreased with time (1–30 days), while conductivity slightly increased.

Reference data about measuring pH values in eluates of electric-arc furnace dust samples are relatively poor. Leclerc et al. [37] examined the eluate reaction on five different types of electric-arc furnace dust and determined the pH values of 8.2; 9.3; 10.4; 11.0 and 11.4 respectively.

Chemical composition in one of the observed samples (Fe 44%, Zn 7.4%, Pb 0.2%, Ni 0.07%, Mn 4.4%) was relatively similar to the average chemical composition of the samples examined in the present study and the pH value of its eluate was 10.4.

As can be seen, in all samples, we observed that the iron concentration retained identical values in the course of time. In all samples zinc concentrations retained similar values in the course of time (1 and 10 days) and it showed increasing after 30 days. The results of lead and cadmium are similar in the course of time. The metal concentration in the leachate are in all cases under the level established as toxic by Croatian Regulations on waste handling terms [26].

Other authors have also recorded rather poor solubility of EAF dust samples in water. Very similar results were provided Vinals et al. [33] who subjected EAF dust to elution and measured the concentration of zinc to be 0.360 mg l^{-1} and lead 0.05 mg l^{-1} . The pH value of eluates was 11.6.

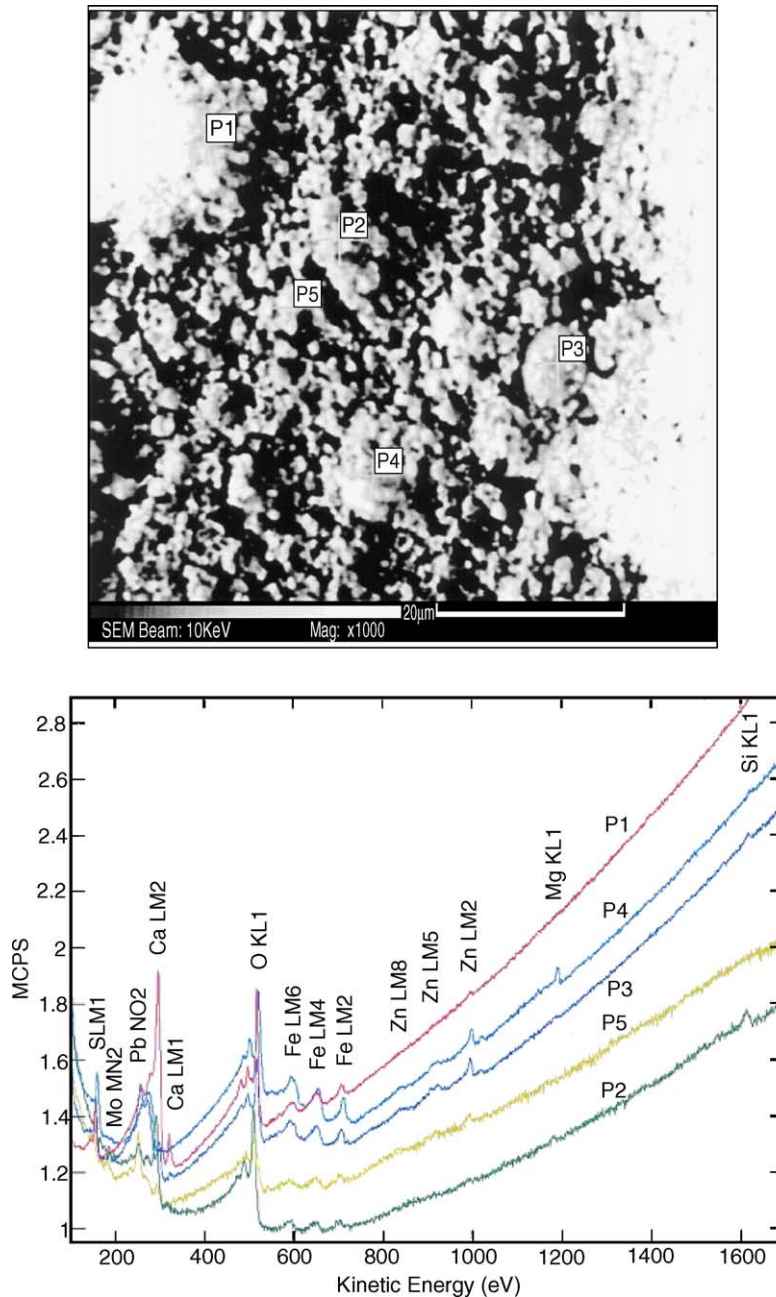


Fig. 5. SEM micrograph of EAF dust sample number 9 and AES spectra measured at marked points (P1–P5).

As opposed to him, Delalio et al. [20] provided a parallel display of EAF dust elution results according to DIN 38414-S4 and TCLP-method: the concentration of zinc in eluates was 4 mg l^{-1} and lead 320, i.e. 330 mg l^{-1} ; the pH value of water eluate was 12.8.

In the work of Delalio et al. [20], we can observe rather poor solubility of zinc from EAF dust, although the mass concentration of zinc in the sample is significantly higher compared to the dust examined in the present paper or to the dust examined by Vinalsa et al. A relatively high solubility of lead in water is interpreted by Delalio as its potential presence within the dust in the chloride form.

At the same time, some of the EAF dust samples (samples 9–11) were leached in water to establish the concentration of some anions and cations (F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). The results of this investigation show that some anions were not detected in analyzed eluates (F^- , Br^- , NO_2^-) and as can be seen, we observed that the Cl^- and NO_3^- concentrations retained similar values in the course of time, while concentration of SO_4^{2-} ions slightly increased.

The increased concentration of sulfate ions in sample 9 eluates compared to the concentration of sample 10 and 11 eluates (>2.5 times) could be related to the results of

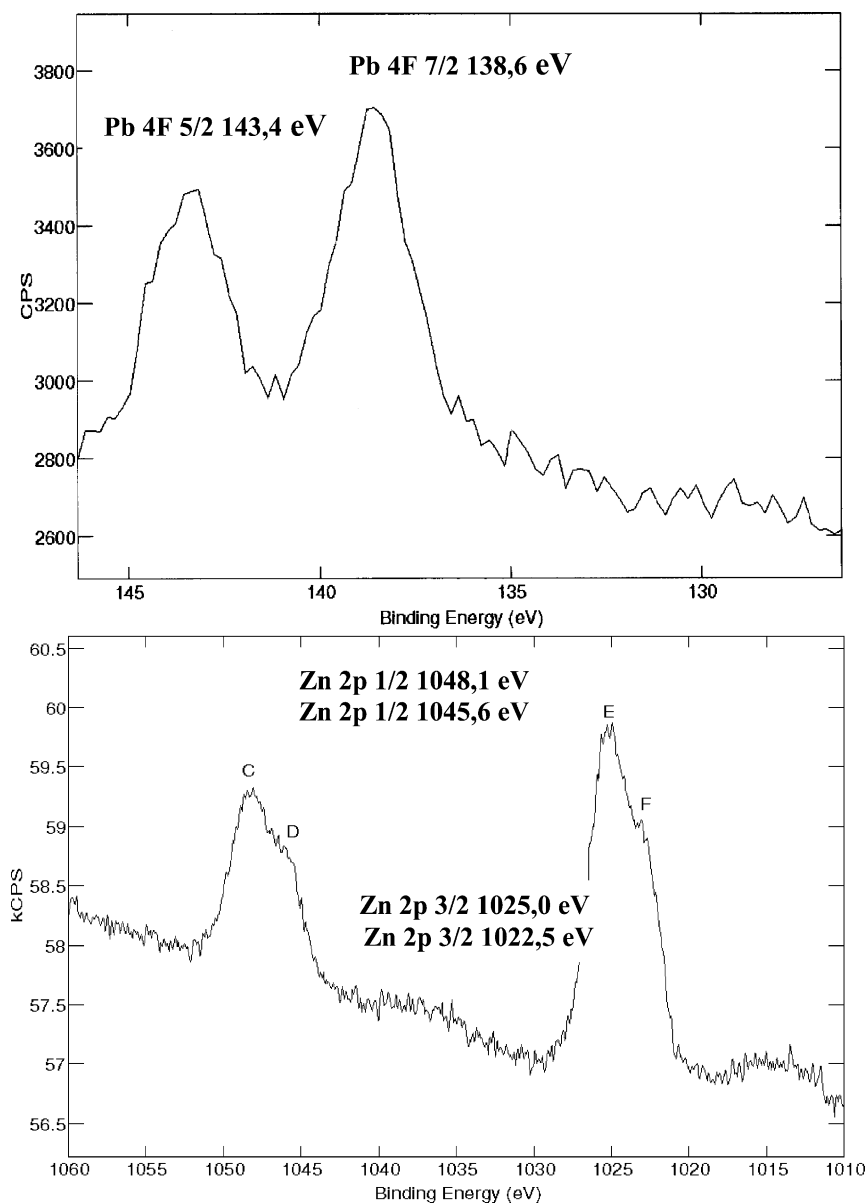


Fig. 6. XPS spectre of EAF dust sample number 9, Pb 4F5/2; Pb 4F7/2 and Zn 2P1/2; Zn 2P3/2.

phase analysis by means of X-ray diffraction. Namely, sample 9 has displayed the presence of soluble sulfates such as MnSO_4 , $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ and $3(\text{Cu}, \text{Zn})\text{SO}_4 \cdot 4\text{H}_2\text{O}$ but these phases were not identified in the averaged sample 10. They were identified in some granular-fraction fractions only, implying their relatively low concentration. The average sample 11 displayed only MnSO_4 and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The insoluble $\text{PbO} \cdot \text{PbSO}_4$ was identified in all samples.

The results of cation concentration determination (Na^+ , K^+ , and Ca^{2+}) retained similar values in the course of time, with the exception of Mg^{2+} .

The results of defining the contents of Na^+ , K^+ , Ca^{2+} and Cl^- in EAF sample eluate with water and 1-day elu-

tion time were presented by Delalio et al. [20] in his work.

Comparing the obtained results with the content of these elements in the examined sample they have found that more than 99% out of the total Na contained in the sample was resolved, over 96% Cl, and 91% K resolved into eluate, whereas Ca solved between 2 and 8% (depending on the solid-liquid ratio).

If the results provided in the present paper are considered this was, i.e. if the concentrations of K^+ , Na^+ and Ca^{2+} in eluates are compared to the concentrations obtained by means of chemical analysis of the average dust sample, e.g. sample 9, then they refer to the possibility of a similar conclusion.

Table 3
Results of phase analysis of EAF dust samples

Basic element	Identified phases	Sample											
		1	2	3	4	5	6	7	8	9	10	11	12
Fe	Fe ₃ O ₄	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	αFe ₂ O ₃	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	FeO	●○	●	●	●○	●○	●○	●○	●○	●○	●○	●○	●○
	Fe-met.	●○	●	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	2FeOSiO ₂	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	FeS	●			●○	●	●	●○	●	●○	●○	●○	●○
	Fe ₉ S ₈	●○	●		●○	●○	●						
	Fe ₂ (SO ₄) ₃ ·H ₂ SO ₄ ·2H ₂ O	●		●	●	●			●			●	
	FeSO ₄ ·4H ₂ O	●			●		●			●			
Fe ₂ (SO ₄) ₃ ·9H ₂ O	●				●	●			●		●	●	
Zn	ZnO	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	3(Cu,Zn)SO ₄ ·4H ₂ O	●		●		●		●	●	●			
	Zn ₃ (AsO ₄) ₂ ·4H ₂ O		●	●		●							
	ZnS ₂ O ₄ ·Na ₂ S ₂ O ₄ ·nH ₂ O	●		●○	●	●							
3(Zn,Mg)O·4(Si,Al)O ₂ ·H ₂ O				●	●					●			
Cu	CuO	●	●			●○		●	●				
	Cu _{1.96} S	●○	●	●	●○	●	●	●		●○	●○	●○	●○
	5CuO·2As ₂ O ₅ ·10H ₂ O		●	●	●	●	●				●		
	Cu ₂ O·2Fe ₂ O ₃	●	●	●○	●○	●	●	●			●	●	●
Cd	3CdSO ₄ ·2H ₂ O	●	●	●○	●	●	●			●		●	●
	Cd ₃ Zn(SO ₃) ₄			●○	●○					●			
	4PbO·PbSO ₄	●○	●	●○	●○	●○	●	●○	●○	●	●○	●○	●○
Pb	PbO·Al ₂ O ₃ ·2SiO ₂	●		●		●	●		●				●
	NiS ₂	●	●	●○	●○	●○	●○				●○		●
Ni	Ni ₇ S ₆	●○	●○			●○	●	●		●			●
	Cr ₂ O ₃			●	●○	●	●			●			
Cr	αCaO·Cr ₂ O ₃	●	●		●○	●				●	●		●
	MnO	●	●	●○	●	●	●○		●	●	●○	●	●○
	ρMnO ₂	●							●		●		
	Mn _x O _y				●	●	●		●				
Mn	γMnS					●			●		●○	●	
	MnSO ₄	●			●	●	●	●	●		●	●	●
	αMnO·SiO ₂	●			●	●	●	●				●	●
	MnS ₂	●			●○	●○			●			●	
Si	SiO ₂ quartz	●	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	SiO ₂ cristobalite	●	●	●○	●	●	●	●		●	●		
	SiO ₂ tridimite	●	●	●○	●	●	●○	●		●	●		
Mg	3MgO·2SiO ₂ ·2H ₂ O	●	●	●	●	●	●			●	●	●	●○
	3CaO·2SiO ₂	●	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○	●○
	CaO·2SiO ₂ ·1/2H ₂ O	●	●	●	●○	●	●○	●		●	●○	●	●
	CaO·SiO ₂ ·yH ₂ O	●			●	●		●	●	●	●	●	●
	α2CaO·SiO ₂	●	●		●	●	●				●		●
Ca	γ2CaO·SiO ₂		●			●			●		●		●
	CaO·Al ₂ O ₃ ·10H ₂ O	●	●	●		●							
	3CaO·Al ₂ O ₃ ·6H ₂ O		●		●		●					●○	
	CaO·Al ₂ O ₃ ·2SiO ₂	●○	●	●		●	●○			●			●
	αAl ₂ O ₃	●○	●○	●	●	●○	●○		●	●	●○	●	●
	Al ₂ O ₃ ·SiO ₂	●	●	●	●○	●○	●						
Al	3Al ₂ O ₃ ·2SiO ₂			●		●○	●			●		●○	●
	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	●○	●	●	●○	●	●○	●○	●		●	●	●
	Al ₂ O ₃ ·2SiO ₂ ·12H ₂ O	●					●	●		●			●
Na	Na ₂ O·4SiO ₂	●	●	●	●	●							
	Na ₂ O·Al ₂ O ₃ ·SiO ₂ ·H ₂ O		●	●	●					●			
Ba	BaO·Al ₂ O ₃ ·2SiO ₂						●			●○			
S	S	●○	●	●	●	●	●			●○	●	●○	●

(●) Identified phases in average samples; (○) identified phases in each separated fraction.

Table 4
Monitoring of leaching effects on samples of EAF dust during 30 days

Sample	Time (days)	pH value	Conductivity ($\chi(\text{mS cm}^{-1})$)	Concentration (mg/l)			
				Fe	Zn	Pb	Cd
1	1	9.65	4.03	0.04	0.014	0.098	0.013
	10	9.32	4.22	0.04	0.013	0.107	0.015
	30	8.91	4.29	0.04	0.256	0.114	0.017
2	1	9.62	4.28	0.06	0.107	0.098	0.019
	10	9.10	4.36	0.07	0.088	0.100	0.020
	30	8.86	4.46	0.06	0.304	0.105	0.020
3	1	9.69	4.74	0.07	0.072	0.111	0.019
	10	9.24	4.83	0.07	0.088	0.118	0.019
	30	8.94	4.90	0.07	0.316	0.107	0.021
4	1	9.67	3.88	0.04	0.018	0.080	0.015
	10	9.33	3.83	0.04	0.015	0.078	0.018
	30	8.85	3.98	0.04	0.230	0.098	0.018
5	1	9.56	4.89	0.05	0.012	0.094	0.018
	10	9.31	4.76	0.04	0.038	0.111	0.019
	30	8.94	5.02	0.04	0.232	0.126	0.020
6	1	9.37	5.23	0.05	0.038	0.116	0.018
	10	9.14	5.46	0.05	0.012	0.116	0.019
	30	8.95	5.44	0.05	0.359	0.120	0.026
7	1	9.50	4.54	0.05	0.016	0.085	0.019
	10	9.34	4.69	0.05	0.017	0.086	0.019
	30	8.99	4.62	0.05	0.338	0.109	0.020
8	1	9.27	4.96	0.05	0.028	0.089	0.019
	10	8.95	4.94	0.05	0.036	0.087	0.020
	30	8.50	5.07	0.05	0.202	0.087	0.022
9	1	8.57	6.24	0.05	0.127	0.110	0.078
	10	8.35	6.59	0.05	0.179	0.160	0.052
	30	8.09	6.55	0.05	0.443	0.140	0.033
10	1	9.34	3.29	0.05	0.010	0.110	0.018
	10	9.27	3.47	0.05	0.021	0.080	0.003
	30	9.11	3.59	0.05	0.024	0.130	0.005
11	1	9.46	3.60	0.05	0.010	0.030	0.013
	10	9.32	3.90	0.05	0.012	0.088	0.018
	30	8.93	3.93	0.05	0.015	0.086	0.020
12	1	9.41	4.99	0.05	0.040	0.096	0.022
	10	8.77	5.19	0.05	0.060	0.102	0.021
	30	8.40	5.21	0.05	0.110	0.109	0.023

Further investigations should deal with the change of elution agents (rain, acid rain, wastewater, etc.).

4. Conclusion

The obtained research results show that the volume of EAF dust formed per tonne of crude steel in Croatia does not differ from the volumes of EAF dust formed in other steel mills in the world using the electric-arc furnace procedure.

The chemical composition of the domestic EAF dust is mostly identical to the chemical composition of EAF dust of other steel producers. Major differences refer to the zinc content, which has a mass share not greater than 10% in

EAF dust samples from domestic steel mills. This is a direct consequence of applying high-quality steel scrap (containing very little galvanized steel).

Granular-metric analysis of EAF dust, examination of the phase composition, determination of chemical composition, pH value and conductivity of EAF eluates were performed in order to provide a more comprehensive view of the possibility to stabilize heavy metals for the purpose of their permanent disposal. At the same time, these results provide a better analysis of the possibility to use EAF dust in other industrial branches or to recover and reuse EAF dust.

The final evaluation of the applicability of EAF dust, the potential reasons for its recovery, as well as the choice of methods for its stabilization in case of permanent disposal, can be made once all relevant ongoing research has been completed.

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