THE MINERALOGICAL COMPOSITION OF DUST FROM AN ELECTRIC ARC FURNACE

MINERALOŠKA SESTAVA PRAHA IZ OBLOČNE ELEKTRIČNE PEČI

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A very important waste produced during the manufacturing of steel is the dust from the electric arc furnace (EAF). This dust is emitted from the EAF with the fume gases. Because of its physical and chemical properties it is categorised as a hazardous industrial waste.

To prevent improper handling of this hazardous waste and stop or reduce pollution of the environment, and to find solutions for recycling of the EAF dust, it is important to carry out a systematic investigation of its physical and chemical characteristics, with a determination of its chemical and mineralogical composition, morphological characteristics and its interaction with the environment.

In this article we report on the mineralogical, i.e., phase, composition of EAF dust determined with X-ray diffraction (XRD) analyses. The mineralogical phase in various grain size fractions of dust was identified on the basis of XRD patterns. The results of the investigation show that some phases appear in all samples and size fractions, some in most of the analysed samples and some only in individual samples.

The results of the phase composition analysis will be of use both for a determination and explanation of the potential harmful impact of dust on the environment as well as in the selection of the most suitable method for managing and re-cycling the EAF dust.

Key words: electric-arc-furnace, dust, mineralogical composition, metallurgical waste

Prah je pomembna sestavina odpadkov pri izdelavi jekla v električni obločni peči (EOP). Iz peči izhaja z odpadnimi plini. Zaradi fizikalnih in kemijskih lastnosti so rizični industrijski odpadek.

Določitev fizikalnih in kemijskih značilnosti, kot so kemijska in mineraloška sestava, morfologija in interakcija z okoljem, je potrebna, da bi preprečili neustrezno razmerje med prahom in onečiščenje okolja in našli pot za njegovo recikliranje.

V tem članku poročamo o mineraloški sestavi prahu EOP, določeni z rentgensko difrakcijo prahov z različno velikostjo. Nekatere faze najdemo v vseh vzorcih in velikostih, druge v večini, nekatere pa samo v posameznih vzorcih.

Rezultati analiz bodo uporabljeni za razlago in oceno škodljivosti prahu za okolje in za izbiro najbolj primerne metode za njegovo recikliranje.

Ključne besede: elektro obločna peč, prah, mineraloška sestava, metalurški odpadek

1 INTRODUCTION

Dust from an electric arc furnace (EAF), which is separated from the EAF along with the fume gases, is one of the most important wastes produced during the manufacture of steel. Because of its physical and chemical properties it is categorised as hazardous technological waste.

Before 1991 the Sisak Steelworks used the EAF dust from the steel production process at the Sisak Steel Mill as an additive to the sintering mixture for the production of blast-furnace pig iron. In this way, the iron part of the EAF dust was used. However, concentrated toxic heavy metals were present in the dust, and so they were simply moved from the EAF dust to the sludge in the blast-furnace waste-gases rinsing unit.

The pig-iron production in the blast furnace at the Sisak Steelworks has been shut down. For this reason, the EAF dust is not recycled in the described way, but it is temporarily stored within the factory grounds, where it is an environmental hazard.

With the aim of preventing improper handling of this hazardous waste and stopping the increase in environmental pollution, to assess the EAF dust as a secondary raw material and to find a solution for the recycling, a systematic determination of dust's physical and chemical characteristics, with the identification of its chemical and mineralogical composition, morphological characteristics and behaviour in interaction with the environment was performed.

2 EXPERIMENTAL PROCEDURE

2.1 Sampling

For our investigations we used samples of EAF dust generated in the manufacturing of carbon steel in the Sisak Steel Mill during 2001, samples of EAF dust from

the Split Steel Mill, and EAF dust from the Felis Steel Castings Foundry in Sisak. The samples were taken from the discharge of the de-dusting unit during every heat production in the EAF 30 t. In this way a raw monthly average sample with a mass of approximately 5.0 kg was obtained. After homogenisation by stirring and reduction of mass by quartering, the sample was reduced to a size of about 2.0 kg. The monthly average samples were marked and kept in glass bottles.

Standard sieves (DIN 4188:1957) were used for the granulometrical analyses, and the size fractions were marked with codes containing the number of the sample and the grain size of the fraction in μm (e. g. 1/>125 μm; 1/125–100 μm etc.). Finally, all the samples were dried for 2 h in a dryer at 105 °C and subsequently stored in a silica-gel desiccator.

2.2 Sample Analysis

The dust-size assessment was performed with dry sieving on a Tyler-sieve set according to DIN 4188:1957, and fractions with sizes >125 μm, 125–100 μm, 100–90 μm, 90–63 μm, 63–50 μm, and <50 μm were obtained.

The mineralogical phase present in the samples of dust and their granulometric fractions were identified with X-ray diffraction analysis of the diffractograms recorded with a Philips PW 1410 X-ray spectrometer with a proportional counter in the angular range from 5°/2Θ to 145°/2Θ. CoK$_\alpha$ radiation and a graphite monochromator were used in the following recording conditions: voltage of the X-ray tube 35 kV, anode current 20 mA, recording speed 0.25° min^{-1} and paper speed 2.5 mm min^{-1}. Some diffractograms were also obtained with a Philips PW 1710 X-ray spectrometer with a proportional counter in the angular range from 3 to 85°/2Θ, with CuK$_\alpha$ radiation, an X-ray tube voltage of 45 kV, an anode current of 30 mA and a recording speed of 0.02° min^{-1}.

Before the diffraction analysis, samples of EAF dust as well as their granulometric fractions were ground in a vibration mill, with the aim to crush the agglomerates, and then homogenised for 10 min. After the preparations, the samples were placed in a rotating metal carrier and submitted for analysis.

For a reliable identification of franklinite with X-ray diffraction, dust samples were treated with HCl (1.00 mol L^{-1}) in the ratio S/L = 1/3 and mixed for 24 h at ambient temperature. In this way, phases whose diffraction lines disturb the identification of franklinite were removed.

3 RESULTS AND DISCUSSION

The proper interpretation of the obtained results is possible on the basis of the knowledge of the dust generated during the EAF processing of steel. The ele-

mentary factors that directly influence the composition of the EAF dust are as follows: the quality and composition of the steel scrap used as raw base material, the non-metal additives and their mass share in the EAF charge (bauxite, fluorite, dolomite, lime, coke, etc.), the type and volumes of ferroalloys (Fe-Mn, Fe-Si, Fe-Cr, etc.) as well as the technological parameters, such as the volume of oxygen blowed in the melt, the regime in the furnace and the technique and dynamics of slag separation.

The type of EAF dust depends strong on the technology of steel melting, and for this reason, dusts from different processes differ significantly in terms of the quantity and mineralogical composition.

According to P. Rocabois et al.[1], EAF dust consists of three elementary groups of material: volatile particles of metal (e.g. Zn, Pb, Cd, Bi), particles produced by mechanical separation (dust) from steel scrap (dust, i. e., metal oxides) and non-metal inclusions and particles produced by expelling drops of liquid metal and slag in the furnace atmosphere. The last group accounts for the largest mass share in the dust.

V. R. Daiga et al.[2] find EAF dust to consist essentially of only two groups of compounds: volatile and non-volatile. In the volatile group are compounds of Zn, Pb, Cd, Na, and K, and the non-volatile group contains oxides of Ca, Mg, Al, and Si.

According to J. C. Huber et al.[3] the EAF dust consists mostly of metal oxides of the spinel type (Fe, Zn, Mn)O·Fe$_2$O$_3$, zinc oxide, ZnO, and various glass phases (FeO$_x$, SiO$_2$, CaO). The dust, according to these authors, is the product of the emission of particles from the steel melt and of the chemical/physical transformations of these particles in the furnace zone and in the zone of fume-gases discharge, as well as their agglomeration and coalescence processes. These chemical-physical transformations in the gaseous stage still have not been accounted for in detail, while the various emission mechanisms have been identified.
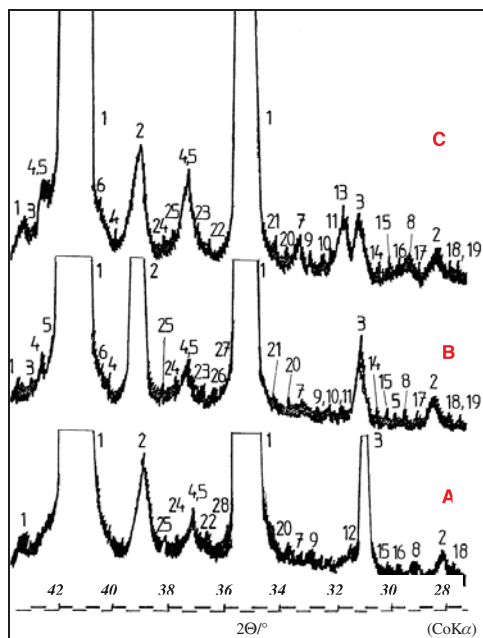
C. L. Li and M. S. Tsai[4] assumed that the zinc and manganese ferrites are generated by the oxidation of Zn and Mn in liquid steel to ZnO and MnO, which, at high temperatures and in the presence of Fe$_2$O$_3$ or Fe$_3$O$_4$, form solid solutions of the ZnFe$_2$O$_4$ / MnFe$_2$O$_4$, (Mn, Fe)Fe$_2$O$_4$ and (Mn,Fe)O types.

The surface slag layer on the steel melt contains compounds of the type (Mn, Zn)Fe$_2$O$_4$, (Mn, Zn) Fe$_2$O$_4$–Fe$_3$O$_4$, Fe$_3$O$_4$–(Mn, Fe)O and (Mn, Fe)O. When the bubbles of carbon (II) oxide exit from the melt, these compounds are ejected in the furnace atmosphere, generating a fine spinel-ferrite dust with the composition (Mn, Zn)Fe$_2$O$_4$ or (Mn, Zn)Fe$_2$O$_4$–Fe$_3$O$_4$.

For the purpose of this paper XRD analysis was applied to identify the qualitative mineralogical, i. e., phase, composition of all the average samples of EAF dust and their granulometric fractions obtained. Charac-

teristic sections of the diffractograms are shown in **Figures 1 to 4**.
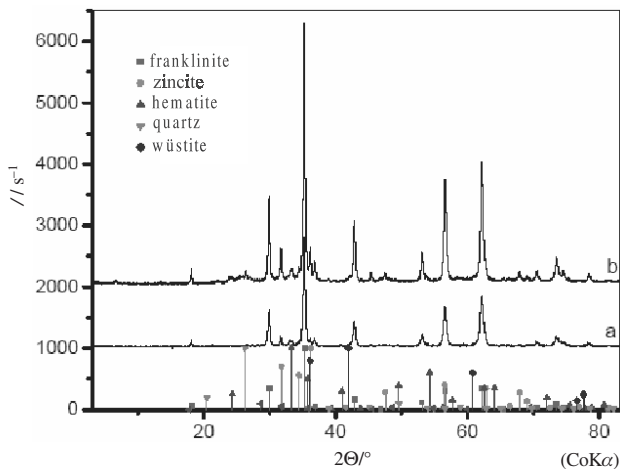
The crystalline phases were identified by comparing the intensity and position of the recorded Bragg peaks to the JCPDS (The Joint Committee on Powder Diffraction Standards) data[5-8] in 53 cards.

The analysis of the recorded position and the relative intensity of the specific diffraction lines confirmed the presence of basic phases (Fe_3O_4, αFe_2O_3, FeO, ZnO, SiO_2-quartz, $ZnO \cdot Fe_2O_3$) occurring in all samples of dust regardless of its origin (**Figure 2**). The same diffraction lines recorded for different samples differ to a large extent in terms of their relative intensity, due to the difference of the mass share of the different phases. This finding was later confirmed with a quantitative chemical analysis.

The same diffraction lines of different samples differ significantly from one another in terms of the relative intensity (**Figure 3**), which implies a different mass share of these phases within the observed samples. In

1 – Fe_3O_4; 2 – αFe_2O_3; 3 – SiO_2; 4 – ZnO; 5 – $2FeO \cdot SiO_2$; 6 – αAl_2O_3; 7 – $3CaO \cdot 2SiO_2$; 8 – $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; 9 – $CaO \cdot Al_2O_3 \cdot 2SiO_2$; 10 – $4PbO \cdot PbSO_4$; 12 – $PbO \cdot Al_2O_3 \cdot 2SiO_2$; 13 – $BaO \cdot Al_2O_3 \cdot 2SiO_2$; 14 – $3Al_2O_3 \cdot 2SiO_2$; 15 – $Cu_{1.96}S$; 16 – $MnSO_4$; 17 – $3MgO \cdot 2SiO_2 \cdot 2H_2O$; 18 – $Na_2O \cdot 4SiO_2$; 19 – $Cu_2O \cdot 2Fe_2O_3$; 20 – $CaO \cdot SiO_2 \cdot 1/2H_2O$; 21 – MnS_2; 22 – Ni_7S_6; 23 – NiS_2; 24 – $\alpha MnO \cdot SiO_2$; 25 – $\alpha 2CaO \cdot SiO_2$; 26 – $Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$; 27 – $Cd_3Zn(SO_3)_4$; 28 – $ZnS_2O_4 \cdot Na_2S_8O_4 \cdot nH_2O$

Figure 1: X-ray diffraction patterns of EAF dust from Sisak Steel Mill number 1(A), 4(B) and 6(C)

Slika 1: Spekter analize z rentgensko difrakcijo za vzorce prahov 1(A), 4(B) in 6(C) iz EOP v jeklarni Sisak

Figure 3: X-ray diffraction patterns of the phases with the largest mass shares in EAF dust (a – Sisak Steel Mill, b – Split Steel Mill, c – Felis Foundry Sisak)

Slika 3: Spekter analize z rentgensko difrakcijo za faze z največjim masnim deležem v EOP-prahu (a – jeklarna Sisak, b – jeklarna Split, c – Felis, livarna Sisak)
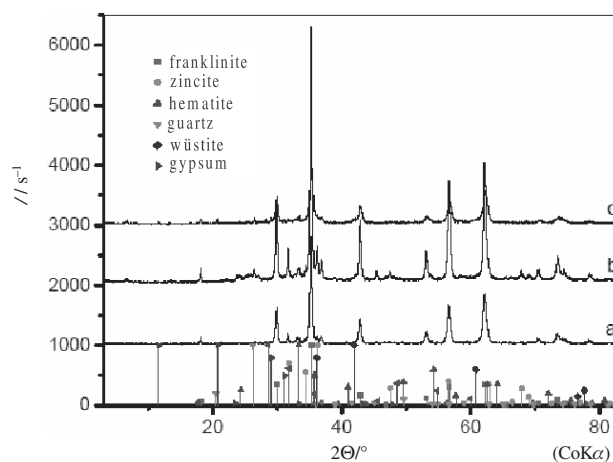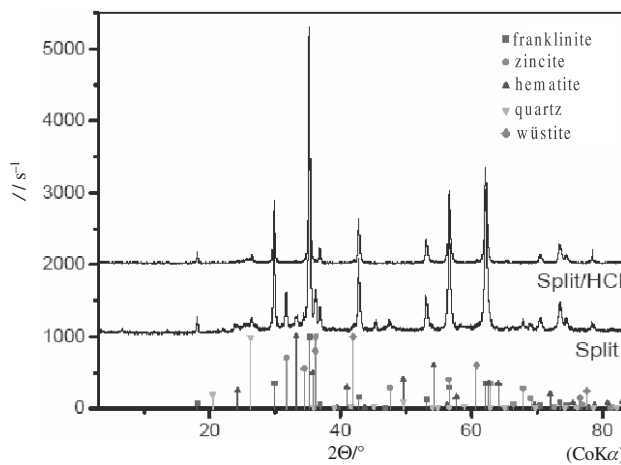

Figure 2: X-ray diffraction patterns of the elementary phase in EAF dust (a – Sisak Steel Mill, b – Split Steel Mill)

Slika 2: Spekter analize z rentgensko difrakcijo za temeljne faze v EOP-prahu (a – jeklarna Sisak, b – jeklarna Split)

Figure 4: X-ray diffraction patterns of the EAF dust from Split Steel Mill before and after treatment with hydrochloric acid

Slika 4: Spekter analize z rentgensko difrakcijo za EOP-prah iz jeklarne v Splitu pred obdelavo in po njej s solno kislino

some cases, the analysis of individual average samples and their granulometrical fractions showed the absence of certain diffraction lines, implying the absence of the corresponding phase within the sample or, on the other hand, a very low mass share of phases below the sensitivity limit of the applied diffraction-analysis method (**Table 1 and 2**).

Table 1: Results of X-ray diffraction phase analysis of average samples of EAF dust from the Split Steel Mill and Felis Foundry in Sisak.
Tabela 1: Rezultati analize z rentgensko difrakcijo za povprečne vzorce iz EOP-jeklarne Split in livarne Felis v Sisku

Identified phase	EAF dust	
	Split Steel Mill	Felis Foundry
Fe_3O_4	+	+
αFe_2O_3	+	+
FeO	+	+
$2FeO \cdot SiO_2$	+	+
Fe–met.	+	+
SiO_2	+	+
ZnO	+	+
ZnS	+	–
$ZnFe_2O_4$	+	––
αAl_2O_3	+	+
MnS_2	+	–
MnO	+	+
$\alpha MnO \cdot SiO_2$	+	–
$3Al_2O_3 \cdot 2SiO_2$	+	–
$3CaO \cdot 2SiO_2$	+	+

+/- confirmation of phase presence

The share of zinc as zincite (ZnO) in the total zinc in the EAF dust sample varies from 70 % to 85 %, according to reference data [9-11]. The rest of the zinc (15–30 % of the total zinc present in the dust) is accounted for by all the other phases, such as ($ZnFe_2O_4$; $3(Cu,Zn)SO_4 \cdot 4H_2O$; $Zn_3(AsO_4)_2 \cdot 4H_2O$; $ZnS_2O_4 \cdot$ $Na_2S_2O_4 \cdot nH_2O$; $3(Zn,Mg)O \cdot 4(Si,Al)O_2 \cdot H_2O$; $Cd_3Zn(SO_3)_4$; and $Zn_{12}(SO_4)_3Cl_3(OH)_{15} \cdot 5H_2O$).

Though franklinite is the second most abundant of the zinc phases, right after zincite, its identification is difficult because of the relatively small mass share in the dusts with poor zinc content and due to the interference of its diffraction lines with the lines of other spinel-type phases.

In order to reliably identify franklinite with x-ray diffraction some researchers[4] processed the samples of dust with acids to remove the ZnO phase and other zinc compounds, if any (e. g. $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$), as their diffraction lines might be covering the franklinite lines.

In our investigation samples of EAF dust were processed with chloride acid and the presence of franklinite was determined reliably, although this is sometimes difficult for dust with a low zinc content, (**Figure 4**).

The diffraction analysis of the series of EAF dust samples from the Sisak Steel Mill shows the presence of the same basic phases, both in the average samples and in their granulometric fractions. Namely, all diffracto-grams recorded the diffraction lines corresponding to specific phases that provided the bulk part of all the observed samples of EAF dust, as well as their granulometric fractions: Fe_3O_4, αFe_2O_3, FeO, Fe-met., $2FeO \cdot SiO_2$; ZnO, $ZnFe_2O_4$, SiO_2 (quartz), $3CaO \cdot 2SiO_2$; $4PbO \cdot PbSO_4$.

In addition to the group of identified phases, which occur in all samples and their fractions, a cluster of phases was identified in most, but not in all, recorded samples, whereas some phases occur rarely and then only in individual samples.

The phases occurring in most samples are FeS; $Cu_{1.96}S$; $CuO \cdot 2Fe_2O_3$; $3CdSO_4 \, 2H_2O$; Ni_7S_6; NiS_2; $\alpha CaO \cdot Cr_2O_3$; MnO; αAl_2O_3; SiO_2 (crystobalite); SiO_2

Table 2: Results of the X-ray diffraction phase analysis of the EAF dust from the Sisak Steel Mill
Tabela 2: Rezultati analiz z rentgensko difrakcijo za EOP-prah iz jeklarne v Sisku

Identified phase	Average sample	Fraction, grain size $d/\mu m$					
		> 125	125-100	100–90	90–63	63–50	< 50
Fe_3O_4	+	+	+	+	+	+	+
αFe_2O_3	+	+	+	+	+	+	+
FeO	+	+	+	+	+	+	+
$2FeO \cdot SiO_2$	+	+	+	+	+	+	+
Fe-met.	+	–	+	-	+	+	+
SiO_2	+	+	+	+	+	+	+
ZnO	+	+	+	+	+	+	+
αAl_2O_3	+	–	+	+	+	–	+
MnS_2	+	+	–	+	+	+	+
MnO	+	–	+	-	+	+	–
$\alpha MnO \cdot SiO_2$	+	–	–	-	+	+	–
$3Al_2O_3 \cdot 2SiO_2$	+	–	–	-	+	+	–
$3CaO \cdot 2SiO_2$	+	–	+	+	+	–	–

+/– confirmation of phase presence

(tridimite); $3Mg \cdot 2SiO_2\ 2H_2O$; $CaO \cdot 2SiO_2 \cdot \frac{1}{2}H_2O$; $CaO \cdot SiO_2 \cdot yH_2O$; $CaO \cdot Al_2O_3 \cdot 2SiO_2$; $Al_2O \cdot SiO_2$; $Al_2O \cdot 2SiO_2 \cdot 2H_2O$ and elementary S.

Phases occurring rarely, i.e., in individual samples only, are Fe_9S_8; $Fe_2(SO_4)_3 \cdot H_2SO_4 \cdot 2H_2O$; $FeSO_4 \cdot 4H_2O$; $Fe_2(SO_4)_3 \cdot 9H_2O$; $3(Cu, Zn)SO_4 \cdot 4H_2O$; $Zn_3(AsO_4)_2 \cdot 4H_2O$; $ZnS_2O_4 \cdot Na_2S_2O_4 \cdot nH_2O$; $3(Zn,Mg)O \cdot 4(Si, Al)O_2 \cdot H_2O$; CuO; $5CuO \cdot 2As_2O_5 \cdot 10H_2O$; $Cd_3Zn(SO_3)_4$; $PbO \cdot Al_2O_3 \cdot 2SiO_2$; Cr_2O_3; ρMnO_2; Mn_xO_y; γMnS; $MnSO_4$; $\alpha MnO \cdot SiO_2$; MnS_2; $\alpha 2CaO \cdot SiO_2$; $\gamma 2CaO \cdot SiO_2$; $CaO \cdot Al_2O_3 \cdot 10H_2O$; $3CaO \cdot Al_2O_3 \cdot 6H_2O$; $3Al_2O_3 \cdot 2SiO_2$; $Al_2O_3 \cdot 2SiO_2 \cdot 12H_2O$; $Na_2O \cdot 4SiO_2$; $Na_2O \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$; $BaO \cdot Al_2O_3 \cdot 2SiO_2$.

The recorded diffractograms also showed diffraction lines that could not be attributed with any certainty to specific phases. Nevertheless, this leaves us with the option of their existence in the observed samples. So, for example, based on the recorded diffraction lines, although having a weak relative intensity, it is possible that phases such as $Pb_{12}O_{19}$, $Zn_{12}(SO_4)_3Cl_3(OH)_{15} \cdot 5H_2O$, or $(Al,Fe)_3AsO_4(OH)_5 \cdot 5H_2O$, $CaAl_2Si_7O_{18} \cdot 6H_2O$, $BaAl_2Si_2O_8$ etc. also exist.

Different simple oxides are the phases identified in the analysed samples, and quoted in references most frequently as 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, and rarely, phases of the spinel-ferrite type, such as $(Mn_xZn_yFe_{1-x-y})Fe_2O_4$, i.e., $ZnO \cdot Fe_2O_3$ (or $ZnFe_3O_4$), $MnFe_2O_4$, $(Mn,Zn)Fe_2O_4$-Fe_2O_4-Fe_3O_4, Fe_3O_4-$(Mn,Fe)O$ were identified[4,11], and even more rarely, it is reported[4,12,15] in the identification of the compounds $NaCl$, KCl, $ZnCl_2 \cdot 4Zn(OH)_2 \cdot H_2O$, $PbOHCl$, $PbSO_3$, $CaSiO_3$, $FeCr_2O_4$, $FeCr_2S_2$, Mn_3O_4, $NiCr_2O_4$, Zn_2SiO_4, $FeAl_2O_4$, $FeNi$, $Ca[Zn(OH)_3]_2 \cdot 2\ H_2O$, $[CaZn_2(OH)_6 \cdot 2\ H_2O]$, $(Fe,Mg)(Ti, Fe)O_3$, $Mn_6Si_4O_{10}(OH)_8$, $Pb_9Ca_6[(Si_2O_7)_3(SiO_4)_3])$ ili $Ca_2Al_2Mn(SiO_4)(Si_2O_7)(O,OH)_2$.

4 CONCLUSIONS

The mineralogical composition of several specimens of dust was examined in order to obtain information relevant for the temporal disposal of dust generated in the processing of steel in an electric arc furnace (EAF) in the Sisak Steel Mill, and to be able to decide on the proper solution for the management of this type of hazardous waste in an environmentally friendly and economically beneficial way.

EAF dusts generated in the electric arc processing of steel differ essentially from one another by their physical and chemical characteristic to a significant extent. This supports the assumption of the non-existence of a unique model of solution for every EAF dust. The recovery and disposal of EAF dust is to be approached individually, in a way determined by the physical and chemical characteristics of every sample of dust.

In this work the mineralogical composition of several dust specimens was determined with X-ray diffraction analysis. The identification was performed on diffraction images obtained by recording samples of different dusts and their granulometric fractions.

The results of the X-ray diffraction phase analysis confirm the earlier conclusions based on the elementary and quantitative chemical analyses. The bulk mass of the examined EAF dust samples consist of a mixture of metal oxides, silicates and sulphates. Other identified phases are found in smaller or considerably smaller concentrations.

Based on the results of a phase analysis of EAF dust samples and the fractions obtained in screen analysis we concluded that some identified phases occur in all samples and their fractions, some occur in the majority of the analysed samples and some occur, but in individual samples.

For the case of EAF dust generated in the steel processing in the Sisak Steel Mill, in the light of the results of an examination of its physical and chemical properties, the results of this investigation will be applied for the evaluation and explanation of the dust's potential environmentally hazardous impact as well as for the selection of the best method of managing waste dust disposal or its recovery.

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