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Characterization of fine-grained wastes generated during carbon steel and stainless steel production

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SUMMARY

This work is focused on characterization of dusts generated as a by-product during steel production. These wastes are due to high content of heavy non-ferrous metals (Zn, Cd, Pb, etc.) legally classified as hazardous wastes. On the other hand, this material could be used as a secondary raw material in zinc, chrome or/and iron production. One of the most important step before designing a recycling technology is detailed characterization of the material. In this work, chemical analysis (AAS), phase analysis (XRD), granulometric analysis and observation through optical microscop of dusts from carbon steel and stainless steel production were carried out. The samples studied in this work came from real steelmaking plants, espesially from electric arc furnaces (EAF). The results obtained by these analysis are discussed and evaluated in this work.

Keywords: *EAF dust, stainless steel, carbon steel, XRD diffraction phase analysis,*

1. INTRODUCTION

Fine-grained wastes coming from steelmaking processes are clasiffied as hazardous waste according to the US EPA classification [1]. These steelmaking dusts are generated in amount of 15 to 20 kg per a tone of produced steel [2-4]. Steelmaking dusts contain high amount of hazardous elements, such as Cr, Pb, Ni, Cd, Zn. Therefore are these materials harmful to the environment, especially to the human health [5-6]. On the other hand, concerning high content of iron, nickel and chromium, this material could be used as a secondary raw material in stainless steel production [5].

The nature of steelmaking dust depends mainly on [7]:

- steelmaking process – Electric arc furnace (EAF), Basic oxygen furnace (BOF), argon oxygen decarburization converter (AOD)
- chemical composition of input material (steel scrap) – biggest influence in case EAF
- type of produced steel – carbon steel (higher Zn content) or stainless steel (higher content of Cr, Ni and other alloy elements)

The biggest influence on chemical and mineralogical composition of steelmaking dust has type of produced steel. In Tab.1, there are listed several chemical analysis from different sources concerning steelmaking dust coming from both carbon and stainless steel production.

Tab. 1 Chemical composition of dust from both carbon and stainless steel production

Elements	**steelmaking dusts from production of:**							
	carbon steel				**stainless steel**			
	[wt. %]							
Fe	26.5	36.46	24	45	19.37	22.1	35.88	34
Zn	33	28.47	29.1	17.99	5.2	4.11	0.96	-
Ca	0.9	1.73	3.16	3.85	4.71	9.22	6.45	7
Cr	0.2	0	0.14	0.46	10.9	9.99	16.3	10.2
Ni	0.1	0.04	-	0.03	4.1	2.2	6.7	1.4
Mn	2.3	1.95	4.11	1.94	4.55	3.94	-	1.7
Mg	-	-	-	-	2.56	3.28	2.19	3.7
Pb	2.17	4.05	3.64	0.2	1.4	0.36	0.29	-
Ti	-	-	-	-	0.096	0.048	0.08	-
Al	-	-	-	-	0.39	0.21	0.34	-
Si	-	1.12	0.34	0.42	2.69	2.25	2.4	1.7
Source	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[3]

It results from the literature sources that main elements like Zn, Cr, Fe and Ni are mostly present as complex oxides with spinel structure. Main phases identified in steelmaking dust from carbon steel production are: franklinite $ZnFe_2O_4$, zincite ZnO, magnetite Fe_3O_4, quartz SiO_2 [8-10]. The most frequently occurring phases in dusts from stainless steel production are: chromite $FeCr_2O_4$, magnetite Fe_3O_4, calcite $CaCO_3$ and calcium silicate $CaSi_2O_4$ [3, 12-14].

It can be seen from Tab.1, that compositions of dust from carbon steel and stainless steel differ significantly. Dusts coming from carbon steel production are specific by high content of zinc (up to 40 %) and dust from stainless steel production are typical by high content of chromium, nickel and others metals used as alloys. The source of zinc in dust is galvanized steel scrap.

The main reasons for recovering metals (especially zinc, chromium and nickel) are:

- decreasing supply of primary raw materials,
- increasing price of chromium, nickel and zinc,
- higher content of metals that in primary raw materials.

Tab. 2 shows comparison in metal content between primary and secondary raw materials together with recent market prices.

Tab. 2 Content of Zn, Ni and Cr in ores, in steelmaking dusts and metal prices.

Metal	**Metal content [wt.%]**		**Price [$/t]** [18-20]
	Primary ore [15-17]	**Steelmaking dust** *(from Tab. 1)*	
Zn	5 – 10	17 – 33	2 150 $/t
Ni	0.5 – 2.5	1 – 7	18 300 $/t
Cr	28 – 37	9 – 17	13 500 $/t

As can be seen from Tab. 2, nickel and zinc content is significantly higher than that in primary raw materials.

In general, there are two groups of processing methods: pyrometallurgical and hydrometallurgical or their combination [8]. One of the major problem regarding steelmaking dust processing is its heterogeneity in chemical and mineralogical composition. This is a main reason why it is difficult to design “versatile” technology for processing steelmaking dusts. Every technology must be adjusted to chemical and mineralogical composition of certain steelmaking dust. Therefore, proper chemical and mineralogical analysis is a very important stage to evaluate the recycling technology [7].

2. EXPERIMENTAL

2.1. MATERIAL

In this work two samples (Sample 1 and Sample 2) of electric furnace dust were investigated. One sample (Sample 1) came from carbon steel production from Železiarne Podbrezova a.s. Slovakia whilst another one (Sample 2) came from stainless steel production from Outokumpu Stainless (Tornio, Finland).

2.2. METHODS

2.2.1. CHEMICAL ANALYSIS

Both samples were submitted to elemental analysis by using atomic absorption spectrophotometer (AAS) Varian Spectrophotometer AA20+.

2.2.2. PHASE ANALYSIS

Phase analysis was carried out by using X-ray diffractometer PANalytical X'Pert PRO MRD with Co Kα radiation.

2.2.3. GRANULOMETRY ANALYSIS

Granulometry was determined by Scanning-foto-sedimentograph, Fritsch – GmbH, Analysette.

2.2.4. OPTICAL MICROSCOPY

The samples were introduced to observation by optical microscopy using Digital microscope MZK 1701. Magnifications of 20x, 60x and 195x were used during the observation. No optical filters were used. These observations allowed not only the appreciation of macromorphology of the samples, but also the color resolution, what is impossible by using SEM microscopy.

3. RESULTS

3.1 CHEMICAL ANALYSIS

The results of chemical analysis are listed in Tab. 3

Tab. 3 Chemical composition of Sample 1 and Sample 2

Sample	**Content [wt.%]**								
	Fe	**Zn**	**Cr**	**Mn**	**Cd**	**Ni**	**Ca**	**Pb**	**LOI***
Sample 1	27.23	17.05	0.81	1.03	0.9	0	4.42	1.28	7.08
Sample 2	20.23	8.1	18.16	1.67	0.48	1.45	10.84	0.46	0.67

* *Lost of ignition*

These results correspond with the results listed in Tab. 1. Dust from carbon steel production (Sample 1) has significant content of zinc while dust from stainless steel production has really high content of chromium, nickel and calcium. For recovering metals like zinc, chromium and nickel is very important in which phase they are present in dust.

3.2 PHASE ANALYSIS

Obtained XRD patterns were evaluated using software High-Score. The XRD patterns as well as lists of identified phases are present below.

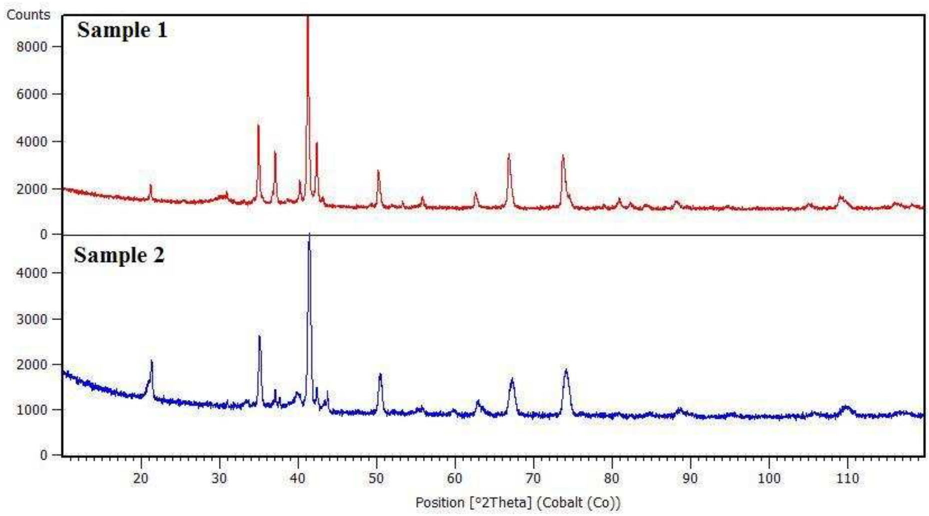

Fig. 1. Comparison of XRD patterns of Sample 1 and Sample 2

Tab. 4 Phases identified in Sample 1

Ref. code	Compound name	Chemical formula
01-089-1012	Zinc Iron Oxide	$ZnFe_2O_4$
01-075-1609	Iron Oxide	Fe_3O_4
00-005-0664	Zinc Oxide	ZnO
01-089-8936	Silicon Oxide	SiO_2

Tab. 5 Phases identified in Sample 2

Ref. code	Compound name	Chemical formula
01-089-3855	Iron Chromium Oxide	$FeCr_2O_4$
01-070-2551	Zinc Oxide	ZnO
00-052-0279	Nickel Zinc Iron Oxide	$Ni_{0.25}Zn_{0.75}Fe_2O_4$
01-087-0674	Calcium Hydroxide	$Ca(OH)_2$
01-078-0649	Calcium Oxide	CaO
01-073-1963	Zinc Iron Oxide	$ZnFe_2O_4$

As can be seen from Tab. 4 and 5, zinc, is present as zinc oxide – ZnO and/or zinc ferrite $ZnFe_2O_4$. Similar composition have been found also in other works [2,8]. The mineralogical form of zinc in steelmaking dust is very important aspect especially in hydrometallurgical processing. ZnO is very easy soluble even in low concentrated acidic or an alkaline solution, but zinc ferrite – ZnFe2O4 is a very stable phase which is soluble only in very strong acid solutions at high temperature.

The major chrome phase identified in the Sample 2 is chromite – $FeCr_2O_4$, which is also very stable phase. Zinc phases are the same in both samples. Calcium is present in Sample 2 as oxide or/and hydroxide.

Reason why these two samples have a very similar XRD patterns even if they contain different phases is that main metals (Fe, Zn, Cr, Ni) are mostly present in a ferritic form and ferrites have very similar peak positions.

3.3 Granulometry analysis

Cumulative and distribution curves of the particles size in both samples are illustrated in Fig. 2.

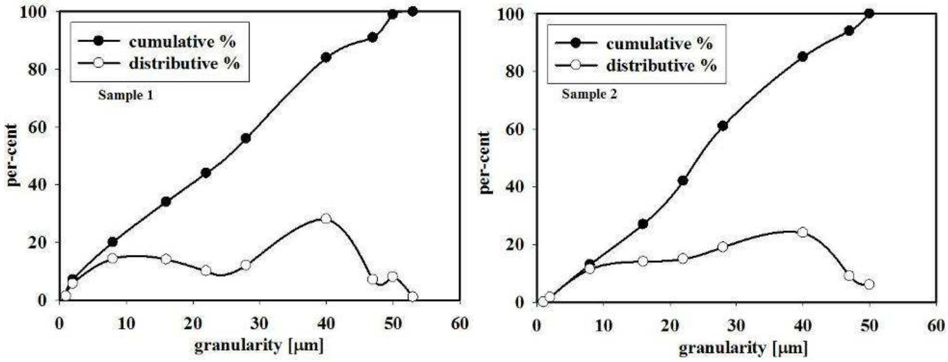

Fig. 2. Granulometry of the Sample 1 and Sample 2

It results from the analysis that both samples have very similar particle size distribution. All particles in both samples were smaller that 53 µm. As can be seen from distributive curves (Fig. 2) there are two major fraction: 0 to 22 µm and 27 to 47 µm. This fact is especially evident in the case of Sample 1.

3.4 OPTICAL MICROSCOPY

Results of optical microscopy observation are showed in Fig. 3 and 4.

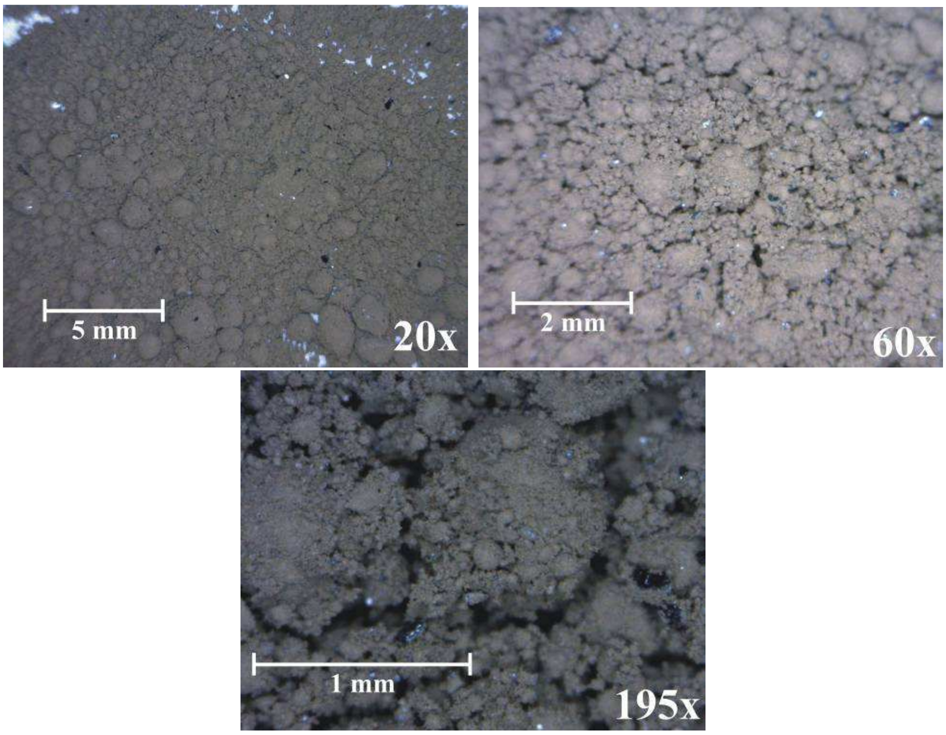

Fig. 3. Morphology of Sample 1 at 20x, 60x and 195x magnification

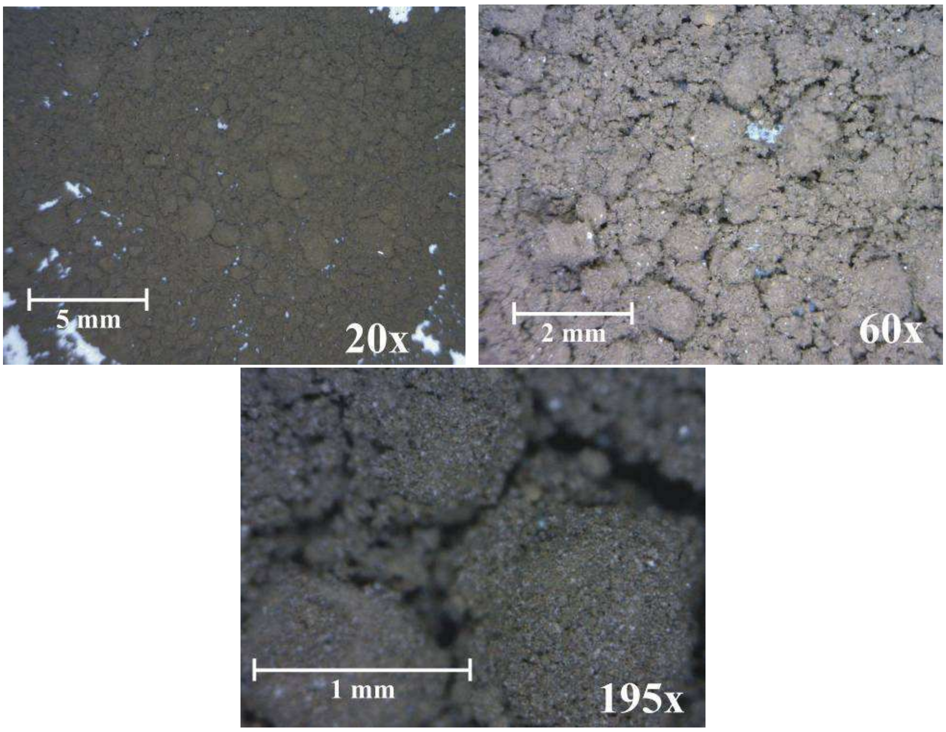

Fig. 4. Morphology of Sample 2 at 20x, 60x and 195x magnification

From Fig. 3 and 4 it is clearly seen that almost all particle have a spherical shape where bigger particles are covered with smaller ones. From point of granularity both samples are very similar. This similarity is most likely caused by the same mechanisms of creating dust particles regardless of type of steel being produced. These mechanisms are decribed in work of Guezennec et. al. [21].

4. CONCLUSION

Two samles of steelmaking dusts were investigated in this work. Sample 1 coming from carbon steel production and Sample 2 coming from stainless steel production. Both samples were analysed by chemical, phase and granulometric analysis. Morphology of the samples was observed through optical microscopy.

The results confirmed that the main elements in case of steelmaking dust coming from carbon steel production (Sample 1) are iron and zinc. Content of zinc in this material was 17.05 %, what is much higher than in zinc primary raw materials. Zinc is present mostly as zinc ferrite (franklinite) $ZnFe_2O_4$ and as oxide ZnO.

Sample 2 was characteristic by high content of chrome, iron, calcium and zinc. Also content of nickel (1.45 %) was very interesting in this sample. Metals like zinc, iron and chrome were present as ferrites, mostly $FeCr_2O_4$ and $ZnFe_2O_4$, which are very resistant to any kind of treatment. Calcium was present as oxide

CaO and hydroxide $Ca(OH)_2$. Content of calcium is very important aspect especially during hydrometallurgical treatment as it consumes acid preferentially.

Both samples have very similar granulometric composition where 100 % particles were under 53 µm. This implies that in both cases it is very fine-grained material. This fact must be taken into account in order to avoid problem with high dustiness during transport. From morphological point of view are the samples also very similar. They consist of particles mostly with spherical shape where bigger particles are covered with smaller ones.

The results of this work show that steelmaking dust could be suitable secondary raw materials for zinc, iron, chrome or nickel production. Content of these metals are in some cases much higher than in primary ores.

5. ACKNOWLEDGEMENTS

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