

## **CHEMICAL AND STRUCTURAL CHARACTERIZATION OF DIFFERENT STEELMAKING DUSTS FROM STAINLESS STEEL PRODUCTION**

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### **Abstract**

Steelmaking dust is considered to be a hazardous waste from steel production. On the other side it is also valuable source of metals like Zn, Cr, Mn and Ni. However, because of its large heterogeneity and anisotropy it is difficult to design suitable process for its recycling. The first and the most important step for designing a recycling process is characterization of the material from different points of view. Characterization of the material includes chemical, structural and morphological composition. The aim of this work was to characterize five samples of steelmaking dusts from three different stainless steelmaking equipment from Outokumpu Stainless (Tornio, Finland). In particular, two sample of electric furnace (EAF) dust, two sample of argon oxygen decarburization (AOD) converter dust and one sample of ferro-chrome converter (CrK) dust were characterized. Chemical analysis was carried out by Atomic absorption spectroscopy (AAS). For structural characterization of the samples the X-ray diffraction phase analysis was used. Morphological analysis was carried out by optical microscopy and scanning electron microscopy with semi-quantitative analysis of dust particles.

**Keywords:** steelmaking dust, AAS, XRD analysis, granulometry, SEM

### **1 Introduction**

Steelmaking dust is generated as a by-product from steelmaking processes in amount around 10 to 20 kg per ton of produced steel [1]. Main compounds of steelmaking dust are represented by iron oxides [2]. Due to its chemical and physical properties, steelmaking dust is categorized as hazardous waste according to US EPA classification [3].

However, it can be also considered as valuable secondary source of Zn, Cr, Mn and Ni. The increasing demand for metals has stimulated the development of new technologies worldwide to treat secondary resources like steelmaking dusts, which can present risks to the public health and/or to the environment if managed in an incorrect way [4].

The methods for steelmaking dust processing can be divided into following categories: pyrometallurgical, hydrometallurgical processes, or their combination. Hydrometallurgical processing appears to be more perspective in the future mainly from environmental and economical point of view [5, 6].

One of the major problem regarding steelmaking dusts processing is their heterogeneity in chemical and mineralogical composition. Especially in case of dusts generated during stainless steel production. From this reason it is difficult to design "versatile" technology for their processing and every technology must be adjusted to the certain steelmaking dust. From this reason, chemical and structural characterization of the material is a very important stage to evaluate the recycling feasibility.

Both chemical and mineralogical composition depends on:

- Steelmaking process – Electric arc furnace (EAF), Argon oxygen decarburization converter (AOD) a. o.,
- Chemical composition of raw material – steel scrap (mainly in EAF)
- Type of steel to be produced – carbon steel (high Zn content) or stainless steel (high Cr content).

There are several papers [1, 7-9] dealing with characterization of EAF dust from carbon steel production but only very few papers dealing with steelmaking dust from stainless steel production. This work responds to the lack of information on the composition of dusts coming from stainless steel production.

Tab. 1 shows an example of chemical composition for EAF dust and AOD converter dust from stainless steel production.

**Tab.1** Chemical composition of EAF dust and AOD converter dust from stainless steel production [1, 4]

| Sample          | Content [%] |      |     |     |     |    |     |     |      |                  |      |      |                                |
|-----------------|-------------|------|-----|-----|-----|----|-----|-----|------|------------------|------|------|--------------------------------|
|                 | Fe          | Cr   | Ni  | Pb  | Zn  | Ca | Mg  | Mn  | CaO  | SiO <sub>2</sub> | MgO  | MnO  | Fe <sub>2</sub> O <sub>3</sub> |
| <b>EAF dust</b> | -           | 10.9 | 4.1 | 1.4 | 5.2 | -  | -   | -   | 6.59 | 5.76             | 4.25 | 5.88 | 39.56                          |
| <b>AOD dust</b> | 34          | 10.2 | 1.4 | -   | -   | 7  | 3.7 | 1.7 | -    | -                | -    | -    | -                              |

The aim of this paper is to characterize five samples of steelmaking dust from stainless steel production. Samples of steelmaking dust came from different steelmaking equipment. The characterization was carried out through chemical, mineralogical, morphological and granulometric analysis.

## 2 Material and methods

Five samples of steelmaking dust produced in Outokumpu Stainless (Tornio, Finland) were analyzed. Description and labeling of the samples are shown in Tab. 2.

**Tab. 2** Labeling of five different steelmaking dusts from stainless steel production

| Sample   | Labeling    |
|--|-------------|
| Electric furnace dust from production line 1                       | <b>EAF1</b> |
| Electric furnace dust from production line 2                       | <b>EAF2</b> |
| Argon oxygen decarburization converter dust from production line 1 | <b>AOD1</b> |
| Argon oxygen decarburization converter dust from production line 2 | <b>AOD2</b> |
| Ferro-chrome converter   | <b>CrK</b>  |

### 2.1 Chemical analysis

All five samples were submitted to the chemical analysis by using method AAS on atomic absorption spectrophotometer Varian Spectrophotometer AA20+. The results of the analysis are listed in Tab. 3.

Tab. 3 Chemical composition of the samples

| Sample | content [%] |       |      |       |      |      |      |       |      |       |
|--------|-------------|-------|------|-------|------|------|------|-------|------|-------|
|        | Zn          | Fe    | Ni   | Cr    | Mn   | Pb   | Cd   | Ca    | Mo*  | LOI** |
| EAF1   | 8.10        | 20.23 | 1.45 | 18.16 | 1.67 | 0.46 | 0.48 | 10.84 | 0.07 | 0.67  |
| EAF2   | 6.40        | 15.44 | 2.40 | 17.19 | 1.61 | 0.88 | 0.38 | 15.10 | 0.51 | 2.93  |
| AOD1   | 9.75        | 29.20 | 0.67 | 18.56 | 1.35 | 0.09 | 0.19 | 5.50  | 0.11 | 1.35  |
| AOD2   | 5.20        | 18.75 | 2.70 | 13.39 | 1.68 | 0.39 | 0.15 | 17.20 | 1.25 | 1.30  |
| CrK    | 7.35        | 13.94 | 0.12 | 22.08 | 0.24 | 0.11 | 0.12 | 17.40 | 0.01 | 2.18  |

\* analysis of Mo content have been done at Aalto University

\*\* LOI – lost of ignition

It results from the Tab. 3, that these dusts are typical by high content of chromium (13 – 23 %), zinc (5 – 10 %) and iron (13 – 30 %). The source of chromium in dusts from stainless steel production is ferrochrome used as an alloy whilst zinc originates from the galvanized iron scrap [2]. As it was already mentioned there is a significant difference between chemical composition of EAF dust from carbon steel production and stainless steel production. EAF dust from carbon steel production contains mainly iron (24 – 49%) and zinc (8 – 30%) [10] whilst dusts from stainless steel production contain mainly Fe and Cr (Tab.3).

These results show that besides considering these dusts as a hazardous waste they might be also valuable secondary raw materials for chromium and/or zinc production. However, when designing a recycling process it is necessary to take into account mineralogical form of the metals.

## 2.2 Mineralogical analysis

Mineralogical analysis was carried out through X-Ray diffraction qualitative phase (XRD) analysis on the PANalytical X'Pert PRO MRD X-ray diffractometer using Co K $\alpha$  radiation. The main phases identified in each sample are given in Tab. 4. Evaluating the results of XRD analysis was carried out using software HighScore.

Tab. 4 Main phases identified in each sample

| Sample   |                                  |                                  |  |                                  |
|--|----------------------------------|----------------------------------|--|----------------------------------|
| EAF1   | EAF2                             | AOD1                             | AOD2   | CrK                              |
| FeCr <sub>2</sub> O <sub>4</sub>                                     | FeCr <sub>2</sub> O <sub>4</sub> | FeCr <sub>2</sub> O <sub>4</sub> | FeCr <sub>2</sub> O <sub>4</sub>                                     | FeCr <sub>2</sub> O <sub>4</sub> |
| ZnFe <sub>2</sub> O <sub>4</sub>                                     | ZnFe <sub>2</sub> O <sub>4</sub> | ZnFe <sub>2</sub> O <sub>4</sub> | ZnFe <sub>2</sub> O <sub>4</sub>                                     | ZnFe <sub>2</sub> O <sub>4</sub> |
| Ni <sub>0.25</sub> Fe <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub> | NiFe <sub>2</sub> O <sub>4</sub> | ZnCr <sub>2</sub> O <sub>4</sub> | Ni <sub>0.25</sub> Fe <sub>0.75</sub> Fe <sub>2</sub> O <sub>4</sub> | Cr <sub>2</sub> O <sub>3</sub>   |
| ZnO  | CaO                              | Fe <sub>3</sub> O <sub>4</sub>   | ZnO  | Fe <sub>2</sub> O <sub>3</sub>   |
| CaO  | CaCO <sub>3</sub>                | Fe <sub>2</sub> O <sub>3</sub>   | CaCO <sub>3</sub>  | ZnO                              |
|  | MnO <sub>2</sub>                 | ZnO                              | Ca(OH) <sub>2</sub>  | CaO                              |

As it results from XRD analysis, all five samples are very similar from point of view mineralogical composition. The main phases present in almost every sample are:

- oxides - CaO, ZnO and Fe<sub>2</sub>O<sub>3</sub>
- ferrites – FeCr<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, and Ni<sub>0.25</sub>Fe<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub>

From hydrometallurgical point of view it is very important to know mineralogical form of the metals in order set up optimal leaching conditions. As can be seen in Tab. 4, zinc is present mainly as ZnO and/or ZnFe<sub>2</sub>O<sub>4</sub>, that is very resistant against any kind of treatment. Nickel is

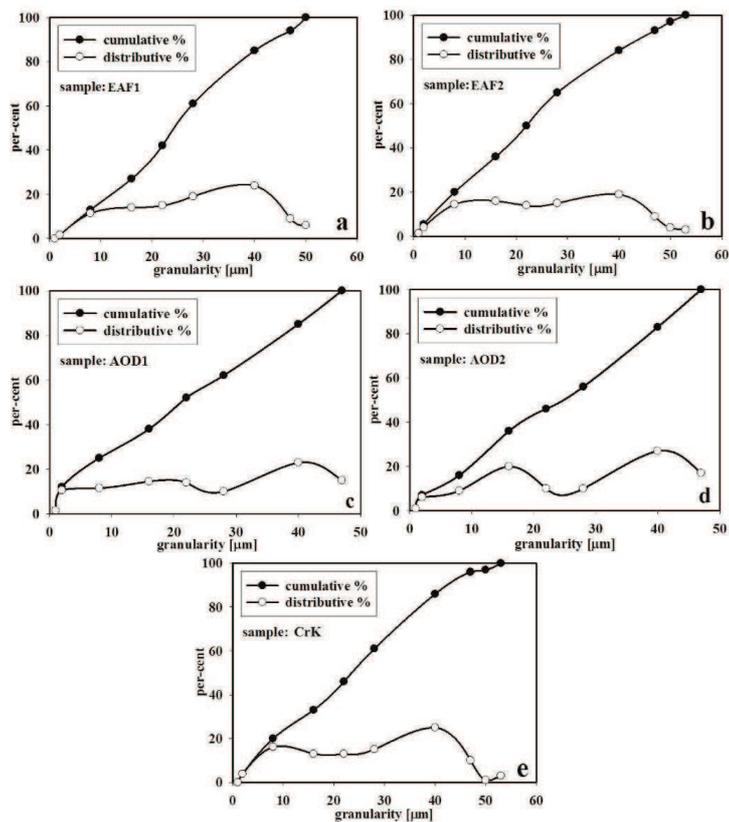
present as spinel compound  $(\text{NiFe})\text{Fe}_2\text{O}_4$ . Chromium is present in all samples mainly as chromite,  $\text{FeCr}_2\text{O}_4$ .

Others work [4] dealing with characterization of AOD converter dust from stainless steel production also confirmed the presence of phases such as: chromite  $\text{FeCr}_2\text{O}_4$ , magnetite  $\text{Fe}_3\text{O}_4$ , hematit  $\text{Fe}_2\text{O}_3$  and calcite  $\text{CaCO}_3$ .

The results of the XRD analysis show that zinc, iron and chromium are mainly present as ferrites which are very resistant against any kind of treatment. Because of that, it is necessary to use more aggressive conditions (high temperature or stronger leaching reagent) for metals recovery.

### 2.3 Granulometry analysis

Granulometry was determined by Scanning-foto-sedimentograph, Fritsch – GmbH, Analysette. Cumulative and distribution curves of the particles size in individual samples are illustrated in Fig. 1.



**Fig. 1** Granulometry of the samples: Cumulative and distribution curve  
a) EAF1; b) EAF2; c) AOD1; d) AOD2; e) CrK

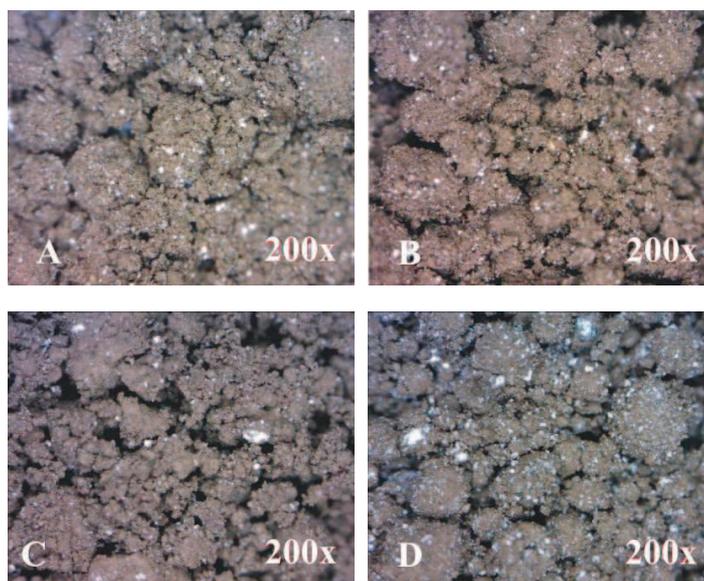
The results of granulometric analysis showed that all samples have a very similar granulometry, where 100 % of particles are below 55  $\mu\text{m}$ . From distributive curve of all five samples can be clearly seen that there are two major fractions in size range 0 to 22  $\mu\text{m}$  and 28 to 47  $\mu\text{m}$  for the samples EAF1 and EAF2. For the samples AOD1 and AOD2 it was 8 to 22  $\mu\text{m}$  and 28 to 47  $\mu\text{m}$ . For the sample CrK the size ranges were 0 to 22  $\mu\text{m}$  and 27 to 47  $\mu\text{m}$ .

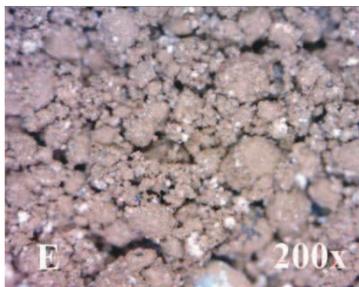
If we compare chemical composition and granulometry analysis we could find correlation between Ca content and quantity of the size fraction 0 to 22  $\mu\text{m}$ . In the samples where the Ca content was highest (samples EAF2, AOD2, CrK, - over 15 %) the size fraction 0 to 22  $\mu\text{m}$  was clearly visible in distributive curves (Fig. 1b,d,e). On the other side in samples where the Ca content was lowest (EAF1 and AOD1) the size fraction 0 to 22  $\mu\text{m}$  was hardly visible in distributive curves (Fig. 1a,c). From these results it concludes that Ca (white spots in Fig. 2) is mostly concentrated in the size fraction 0 to 22  $\mu\text{m}$ .

These results of granulometric analysis are important in designing conditions for hydrometallurgical treatment.

#### 2.4 Optical microscopy

The samples were introduced to observation by optical microscopy using Digital microscope MZK 1701. Magnification of 200x was 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.





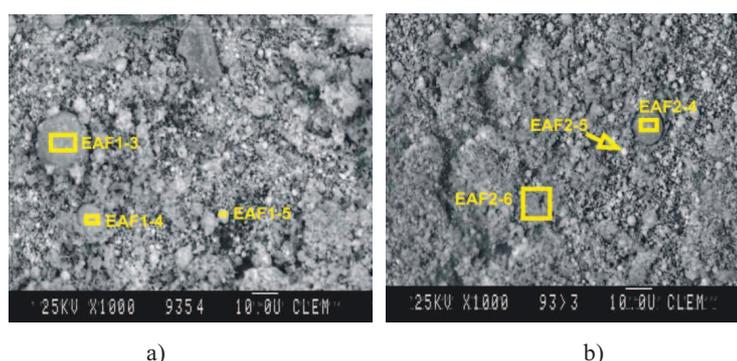
**Fig. 2** Morphology of five different dusts from stainless steel production:  
a) EAF1; b) EAF2; c) AOD1; d) AOD2; e) CrK

As can be seen from the Fig.2, particles in all five samples have predominantly spherical shape where bigger particles are covered with the smaller ones. The presence of two fractions was also confirmed by granulometry analysis (Fig.1). It is possible to observe small white spots in all samples, which represent CaO, whose presence was confirmed by XRD analysis. The smallest amount of white spots was observed in the sample AOD1 where the content of calcium comparing to the other samples was the lowest. On the other hand the highest amount of white particles was observed in samples AOD2 and CrK where the calcium content was higher than 17 wt.%.

### 2.5 Scanning electron microscopy SEM-EDX

Both of morphology of the samples and chemical microanalysis were carried out on scanning electron microscope JEOL JSM-35CF with EDX analyzer LINK ANALYTICAL AN 10/85S.

This observation serves to closer investigation of chemical composition individual particles and areas on the sample surface. During the observation several areas were chosen for chemical analysis in order to find out how individual elements occur in the samples. Fig. 3a represents the sample EAF1 where the chosen areas contain mainly Fe, Ca and Zn (Tab. 5). In the area EAF1-3 was also relatively high content of Si (19.8 %), what can indicate also local presence of Si phases.



**Fig. 3** Morphology of the samples EAF1(a) and EAF2 (b) with magnifications 1000x

Tab. 5 Chemical composition of certain areas in the sample EAF1 and EAF2

| AREA   | CONTENT [WT. %] |      |      |     |     |      |     |      |      |
|--------|-----------------|------|------|-----|-----|------|-----|------|------|
|        | Mg              | Si   | Ca   | Cr  | Mn  | Fe   | Cu  | Zn   | Ni   |
| EAF1-3 | 2.9             | 19.8 | 17.7 | 4.8 | 6.8 | 29.2 | 1.9 | 12.2 | 0.2  |
| EAF1-4 | 0.9             | 9.5  | 35.3 | 4.6 | 2.3 | 38.5 | 1.9 | 5.4  | 0.2  |
| EAF1-5 | 3.3             | 4    | 2    | 12  | 3.2 | 53.2 | 2.2 | 17.7 | 0.8  |
| EAF2-4 | 3.3             | 16.3 | 25.9 | 5.7 | 9   | 22.8 | 2.5 | 4.1  | 3.1  |
| EAF2-5 | 1.3             | 8    | 10.8 | 8.9 | 2.7 | 39   | 3.4 | 8.4  | 13.6 |
| EAF2-6 | 1.7             | 5.1  | 46.5 | 9.4 | 2.5 | 18.1 | 2.3 | 6.8  | 2.1  |

The areas in the sample EAF2 (Fig. 3b) are by their chemical composition similar to the areas in the sample EAF1. However, this sample is characteristic by significantly higher content of Ca (area EAF2-6), what is also confirmed by chemical analysis of the sample listed in Tab.1. According stoichiometry composition Ca present in the area EAF2-6 can be present as  $\text{Ca}(\text{OH})_2$ , which was also found by the XRD analysis (Tab.4).

The areas in the sample AOD1 (Fig. 4a and Tab. 6) are characteristic by high content of Fe (in the area AOD1-5 over 62.6%), Cr (over 20 % in the area AOD1-5) and Ca (36.6 % in the area AOD1-6). The highest content of Ca was found in the areas of the sample AOD2 (Fig. 4b and Tab. 6) that correspond with the chemical composition in the Tab. 3. The highest content 93.6 % of Ca was found in the area AOD2-4.

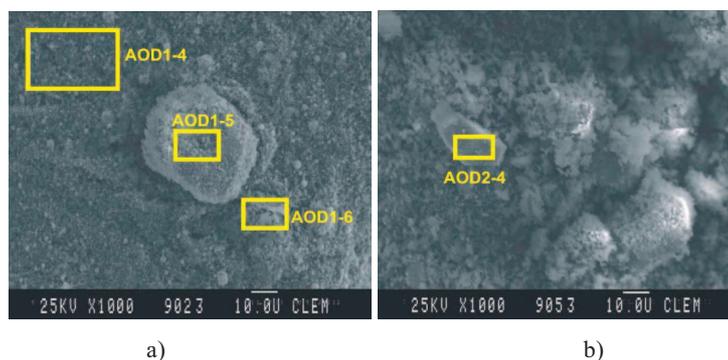


Fig. 4 Morphology of the sample AOD1 and AOD2 with magnifications 1000x

Tab. 6 Chemical composition of certain areas in the sample AOD1

| AREA   | CONTENT [WT. %] |     |      |      |     |      |     |     |     |
|--------|-----------------|-----|------|------|-----|------|-----|-----|-----|
|        | Mg              | Si  | Ca   | Cr   | Mn  | Fe   | Cu  | Zn  | Ni  |
| AOD1-4 | 2               | 1.7 | 2.8  | 12.2 | 4.4 | 50.7 | n.a | 3.1 | 1.1 |
| AOD1-5 | 1.3             | 1   | 1.2  | 20.5 | 5.4 | 62.6 | n.a | 2.1 | 1.2 |
| AOD1-6 | 1               | 1.2 | 36.6 | 9    | 3.7 | 33.7 | n.a | 2.1 | 0.5 |
| AOD2-4 | 0.5             | 0.5 | 93.6 | 0.7  | 0.3 | 1.9  | n.a | 2.1 | 0   |

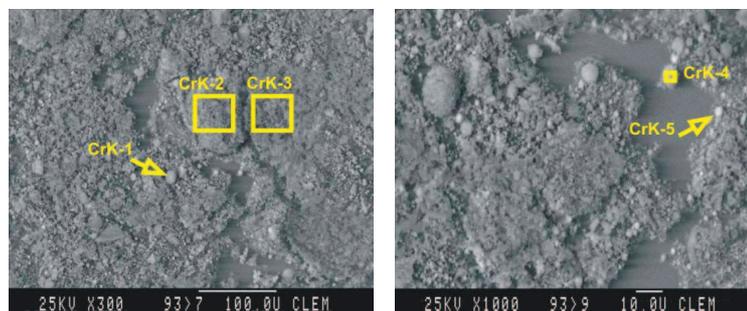


Fig. 5 Morphology of the sample CrK with magnifications 300x and 1000x

Tab. 7 Chemical composition of certain areas in the sample CrK

| AREA  | CONTENT [WT. %] |     |      |      |     |      |     |      |    |
|-------|-----------------|-----|------|------|-----|------|-----|------|----|
|       | Mg              | Si  | Ca   | Cr   | Mn  | Fe   | Cu  | Zn   | Ni |
| CrK-1 | 2.5             | 8.6 | 12.5 | 12.7 | 0.5 | 17.4 | 1.9 | 42.9 | 0  |
| CrK-2 | 4.6             | 3.1 | 30.9 | 20.3 | 1   | 16.8 | 1.8 | 20.7 | 0  |
| CrK-3 | 1.2             | 0.9 | 88.7 | 2    | 0   | 2.1  | 1.6 | 3.1  | 0  |
| CrK-4 | 0.7             | 0.5 | 7.3  | 19.3 | 0   | 64   | 3.4 | 3.9  | 0  |
| CrK-5 | 1.2             | 3.5 | 10.1 | 19.7 | 0.4 | 18.5 | 2.8 | 43.3 | 0  |

Particle CrK-1 in the sample CrK (Fig. 5 and Tab. 7) contains almost 43 % of Zn and area of the particle CrK-5 more than 43 % of Zn. It results from the Tab.7 that both particles have very similar chemical composition. Area CrK-4 contains 64 % of iron what is value close to the stoichiometric amount of Fe in Fe<sub>2</sub>O<sub>3</sub>. This iron oxide was identified also by XRD analysis. Area CrK-3 is typical by highest amount of Ca. However, this high amount of Ca was expected as the CrK sample, according to Tab.3, has the highest content of Ca from all five samples.

### 3 Conclusion

Five samples of steelmaking dusts from stainless steel production were investigated in this paper. The samples were delivered from Outokumpu Stainless (Tornio, Finland).

All five samples were submitted to chemical, mineralogical and granulometric analysis as well as to observation by SEM-EDX.

Chemical analysis was carried out by AAS method. The results show that the main elements in all five samples were Fe, Cr, Zn and Ca. Content of Zn was in range 5-10%, iron 13-30%, chromium 13-23% and calcium 5-18 %. In the samples AOD2 and EAF2 was Ni content more than 2 %. Cadmium and lead contents were lower than 1 %. It results from chemical analysis that Cr, Fe and Zn content is significant for its recovery from this kind of waste.

Mineralogical analysis shows that Cr and Fe are present mostly as chromite, FeCr<sub>2</sub>O<sub>4</sub>. Zn is present as zinkit, ZnO and franklinite, ZnFe<sub>2</sub>O<sub>4</sub>. Calcium was found in the form of calcite, CaCO<sub>3</sub> and calcium oxide CaO. Nickel was found in the sample EAF2 as a ferrite NiFe<sub>2</sub>O<sub>4</sub> and in the samples EAF1 and AOD2 as a complex ferrite Ni<sub>0.25</sub>Fe<sub>0.75</sub>Fe<sub>2</sub>O<sub>4</sub>. Information regarding mineralogical composition is very important from point of view recycling feasibility.

By means of optical microscopy it was found out that almost all particles in all five samples have spherical shape. Also it was observed that bigger brown particles (consisted mainly of Fe, Zn, Cr) are covered with smaller white particles (consisted of Ca). The size range of the bigger

particles was from 27  $\mu\text{m}$  to 47  $\mu\text{m}$  and size range for the smaller particles was 0 to 22  $\mu\text{m}$ . Granulometry of all five samples was very similar where 100 % particles were below 55  $\mu\text{m}$ .

SEM-EDX confirmed spherical shape of most particles in all samples. SEM-EDX observation shows that selected particles consist of more than only one phase. The main elements in most spherical particles were Fe, Ca and Zn. In the sample EAF2 there was also small particle (EAF2-5 in Fig. 3b) with Ni content 13.6 %. Small spherical particles in the sample CrK (CrK-1 and CrK-4 in Fig. 5) contain more than 42 % of Zn. Rectangular particle in the sample AOD2 (AOD2-4 in Fig. 4) contains almost pure Ca (93.6%).

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