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# Variability of chemical composition of metallurgical slags after steel production

## Raznolika kemična sestava jeklarskih žlinder

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## Abstract

Chemical composition of slags after steel production is variable and depends on: the type of the used charge material, fluxes, refining additives and a used melt technology. Slags contain these elements, which participated in the metallurgical process; they often contain some quantities of heavy metals. For using slags as a secondary material it is very important to know the forms of metals occurrence and their relationship with the slag components. Knowing waste material we can choose a right way of wastes management.

**Key words:** slags after steel production, chemical composition, heavy metals

## Izvleček

Kemična sestava žlinder, ki nastajajo med proizvodnjo jekla, je raznolika. Odvisna je od vložka, žlindrotvornih dodatkov in legur ter tehnologije izdelave. Elementi se vežejo v žlindre med metalurškimi procesi v reaktorju, zato pogosto vsebujejo tudi sledi težkih kovin.

Pri uporabi žlinder kot sekundarnih surovin je zelo pomembno, v kakšni obliki so kovine vezane v žlindri, prav tako pa je potrebno poznati povezavo teh spojin z drugimi komponentami v žlindri. Le tako lahko izberemo pravilno metodo ravnanja z odpadki.

**Ključne besede:** jeklarske žlindre, kemična sestava, težke kovine

## Introduction

Upper Silesia, situated in the southern part of Poland, is one of the best industrialized regions. The beginnings of mining and smelting date here back to the Middle Ages. Besides coal mining, iron and steel industry has become one of the most developed industries in Upper Silesia. But on the other hand, iron and steel industry has become especially problematic, because of considerable amounts of wastes – mainly metallurgical slags. In Poland, there are waste dumps left after industrial establishments' activities from previous centuries. At present there are propositions to apply slag for the production of road aggregate, aggregate for the production of concrete mixtures, there are also attempts to return slags to metallurgical processes, such an activity is popular not only in Poland.[1, 2]

Before using slags as a secondary material it is very important to know their chemical composition, forms of metals occurrence, the resistance of minerals to weathering processes and in which conditions metals are liberated from slag components.[3] This knowledge will be useful in economic activities because utilization of slags should be economically viable and ecologically safe for the environment.

## Research methods

To show the chemical composition of the slag the following research methods were used: INAA – Instrumental Neutron Activation Analysis and, TD-ICP – Total Digestion with Inductively Coupled Plasma. The researches were done in Activation Laboratories Ltd. – Actlabs in Canada. The microscopy analysis in transmitted light (on thin plates) was carried out in the Institute of Applied Geology of the Faculty of Mining and Geology of the Silesian University of Technology using the microscope Axioplan 2 of the firm ZEISS for the research in transmitted light and reflected one. The research with the application of scanning microscopy was carried out in the Scanning Microscopy Laboratory of Biological and Geological Sciences of the Department of Biology and Earth Sciences of the Jagiellonian University (Laboratory in the Institute of Geological Sciences). For the research a scanning electron microscope with field emission Hitachi S-4700, furnished with the EDS analysis system (energy dispersion spectrometry) Noran Vantage was applied.

## Characteristic of waste material

A number of samples was taken from two dumps located in Upper Silesia (Figure 1).

The first examined dump is the remainder of the activities of steel works, which started working as a production plant on 25th October 1802. But at this moment that steelworks is already closed, after its work only a waste dump has remained. The waste material collected on the dump was stored up not selectively and it contains slag from smelting processes, raw slag from other processes and casting slag. For that reason in the part of the dump remaining after exploitation four strata characterized by a different colour (grey and brown) can be recognized. Vitrified fragments of metallurgical slag can also be seen on the dump. Slags which have

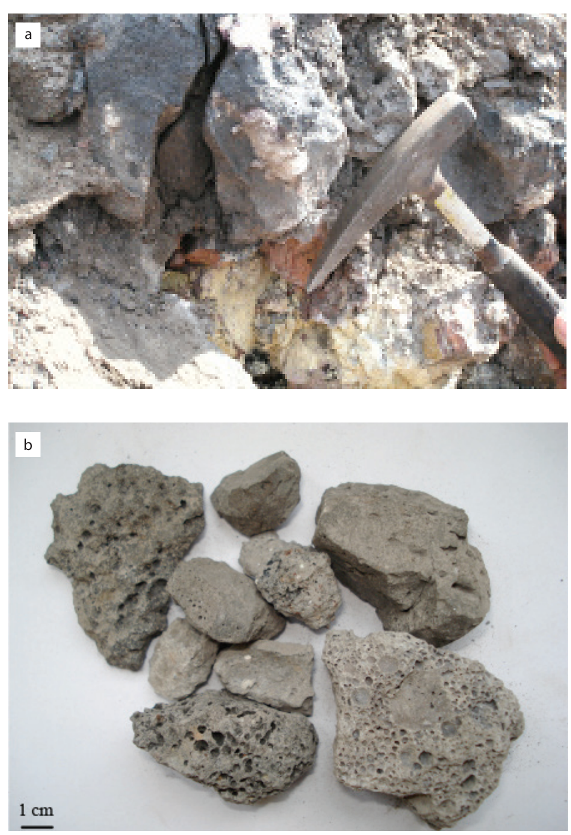



**Figure 1:** *Slags from the first (a) and the other dump (b).*

been exposed to weathering processes are covered with a white deposit of re-crystallized gypsum and calcite. Currently, the area occupied by the dump is reclaimed. As the material has been stored non-selectively; the studied samples consist of a mixture of slags from various steelmaking processes. At the moment, due to the strong weathering processes, it is difficult to distinguish between different kinds of slags. The other group of samples was taken from the dump of steel works – one of the biggest iron and steel works in Poland, which started production in 1975. The dump of this steelworks occupies an open-air area of 28 ha. Wastes gathered on the dump represent mainly converter slag. Slags are not weathered; the oldest of them have been gathered on the dump for several years.

## Tests results

The following components are present in the chemical composition of wastes:
— non-metals,
— metals,
— and also trace amounts of lanthanides.

Examples of an analysis of the chemical composition of slags from the studied dumps are given below. Concentration of individual elements has been determined in the average and representative sample from each dump (Table 1).
Slag after steel production contains these elements, which participated in the metallurgical process. Therefore, its chemical composition can be determined for the presence of metals such as iron. In the waste material the content of this element should be as low as possible, because this is the determinant of a well-run process of steel production.
Slag from the dump No 1 representing wastes from different steelmaking processes contains the mass fraction $w$ = 11.90 % of iron, while the converter slag from the dump No 2 – 14.20 %. In comparison, based on the research carried out by the author, in the slags from Siemens-Martin process content of iron ranges from $w$ = 4.20 % to 15.90 %[5], while in the wastes from the production of cast steel it has only reached 1.59 %.

**Table 1:** *Detailed chemical composition of studied slags (examples of characteristic analyses of slags from each dump)*

| Element | Unit | Limit of detection | No of dump 1* | 2 |
|---|---|---|---|---|
| Ag | µg/g | 0.3 | 1.2 | 1 |
| Al | % | 0.01 | 4.04 | 3.19 |
| As | µg/g | 0.5 | 3.3 | 6.1 |
| Ba | µg/g | 50 | 530 | 370 |
| Au | ng/g | 2 | 13 | < 2 |
| Be | µg/g | 1 | 6 | 1 |
| Bi | µg/g | 2 | < 2 | < 2 |
| Br | µg/g | 0.5 | < 0.5 | 1.1 |
| Ca | % | 0.01 | 12.00 | 20.00 |
| Cd | µg/g | 0.3 | 0.4 | 5.4 |
| Co | µg/g | 1 | 36 | 6 |
| Cr | µg/g | 2 | 214 | 1180 |
| Cs | µg/g | 1 | 2 | < 1 |
| Cu | µg/g | 1 | 837 | 109 |
| Fe | % | 0.01 | 11.90 | 14.20 |
| Hf | µg/g | 1 | 3 | < 1 |
| Hg | µg/g | 1 | < 1 | < 5 |
| Ir | ng/g | 5 | < 5 | 6 |
| K | % | 0.01 | 0.53 | 0.18 |
| Mg | % | 0.01 | 2.94 | 3.74 |
| Mn | µg/g | 1 | 14 900 | 11 400 |
| Mo | µg/g | 0.3 | < 1 | 32 |
| Na | % | 0.01 | 0.17 | 0.13 |
| Ni | µg/g | 1 | 93 | 0.284 |
| P | % | 0.001 | 0.088 | 975 |
| Pb | µg/g | 3 | 19 | < 15 |
| Rb | µg/g | 15 | < 15 | < 15 |
| S | % | 0.01 | 0.03 | 0.2 |
| Sb | µg/g | 0.1 | 0.9 | 48.4 |
| Sc | µg/g | 0.1 | 11.8 | 2.7 |
| Se | µg/g | 3 | < 3 | < 3 |
| Si | % | 0.01 | 18.64 | 8.28 |
| Sn | % | 0.01 | < 0.01 | < 0.01 |
| Sr | µg/g | 1 | 232 | 168 |
| Ta | µg/g | 0.5 | < 0.5 | < 0.5 |
| Th | µg/g | 0.2 | 4 | 1.7 |
| Ti | % | 0.01 | 0.23 | 0.16 |
| U | µg/g | 0.5 | 3.9 | < 0.5 |
| W | µg/g | 1 | 24 | 47 |
| Zn | µg/g | 1 | 463 | 812 |
| La | µg/g | 0.5 | 16.1 | 7.9 |
| Ce | µg/g | 3 | 28 | 13 |
| Nd | µg/g | 5 | 7 | < 5 |
| Sm | µg/g | 0.1 | 2.2 | 1.1 |
| Eu | µg/g | 0.2 | 0.6 | 0.2 |
| Tb | µg/g | 0.5 | < 0.5 | < 0.5 |
| Yb | µg/g | 0.2 | 1.3 | 0.6 |
| Lu | µg/g | 0.05 | 0.22 | 0.16 |
| V | µg/g | 2 | 266 | 686 |
| Y | µg/g | 1 | 26 | 9 |

Explanation:
*according to Jonczy 2008[4]

In slags significant amounts of: copper, chromium, manganese and vanadium were also shown. The presence of these elements is connected with the metallurgical process and the type of produced steel. These elements are the additives which improve the properties of steel. In the studied slags special attention is paid to a quite large concentration of manganese (11 400 μg/g and 14 900 μg/g) and chromium (214 μg/g and 1 180 μg/g). A similar situation was observed in the slags from Siemens-Martin process, in which a significant concentration of Mn (20 000 μg/g) and Cr (13 600 μg/g) was noticed.[5]

Slags contain also considerable amounts of zinc. The presence of this element is often associated with the charge material, to which a scrap is added. Slags from the first dump contain 463 μg/g of zinc, while in the slags from the dump No 2 the amount of zinc is increased to 812 μg/g. But the highest concentration of this element was noticed in slags from Siemens-Martin process – 40 500 μg/g.

Slags after iron and steel production usually are characterized by very good technical properties, often compared to properties of natural rocks. At present in Poland, in view of a widely accepted pro-ecological policy, attention has been drawn to the possibility of reusing metallurgical slags, both the slags collected on dumps and the slags generated by ongoing production processes. In this way it will be possible to acquire new materials for example for the production of road aggregate and at the same time to recover the lands previously occupied by dumps.

Therefore, multi-directional research of metallurgical slag should be carried out. Such researches should be applied not only to the determination of the technical properties of slags, but also to the determination of their chemical composition. A very important issue is also to determine the forms of elements occurrence, especially in respect of heavy metals. In the slags metals can form metallic aggregates, their own minerals; on the other hand metals can make substitution in the internal structure of silicates. A considerable amounts of metals are dispersed in glaze and amorphous substance. All these forms of metals occurrences were found in the studied slags (Figures 2–4).

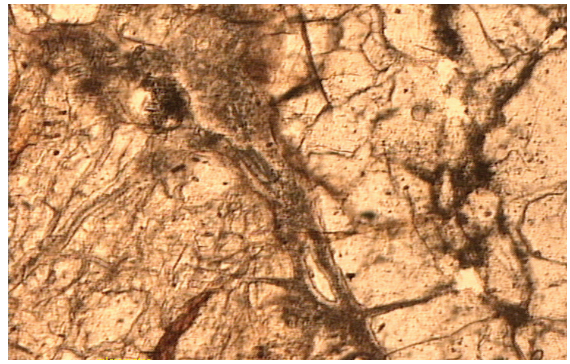


**Figure 2:** *Metals in cracks of glaze: transmitted light, magnification 100 ×, one nicol.*

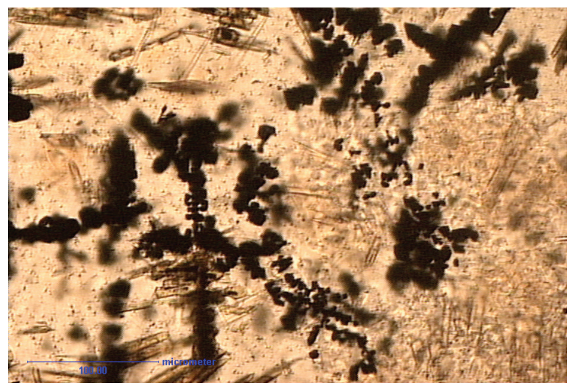



**Figure 3:** *Magnetite; transmitted light, magnification 200 ×, one nicol[6].*

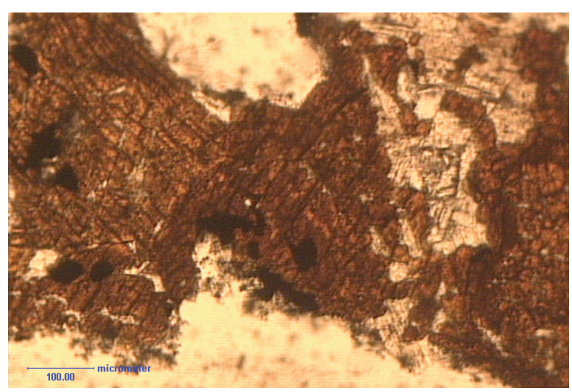



**Figure 4:** *Inclusions of metal in pyroxenes; transmitted light, magnification 100 ×, one nicol[7].*

Chemical and mineral composition of steel slags is often very diversified. Phases which crystallized in a furnace can be identified with the minerals forming as a result of geological processes. However, its chemical composition is usually much richer than their natural counterparts.

To show it the studies in microarea, from which the chemical composition of the individual slag components could be determined, are very useful. Varieties of chemical composition of phases, in two microareas of the same sample from the dump No 2, were shown (Figure 5, Tables 2, 3 and Figure 6, Tables 4, 5).

It should be noted that in one sample of the converter slag, in two studied microareas, different phase composition was found. The first microarea is dominated by calcium silicates surrounded by glaze. In the other microarea, oxide phases can be distinguished; they are represented by solutions of mixed oxides of Fe, Mn, Mg and Ca. This shows a very high variability and diversity of mineralogical and chemical composition of the slag. In Tables 3 and 5, the contributions of individual oxides at a given point of analysis calculated to 100 % were shown.

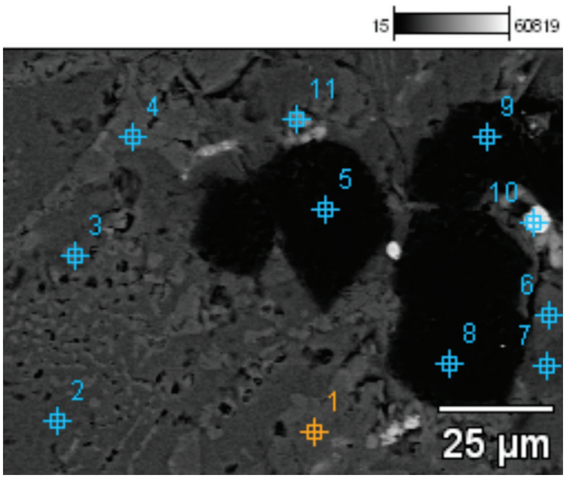



**Figure 5:** *Microphotography of slag by scanning Microscopy (1) (BSE).*

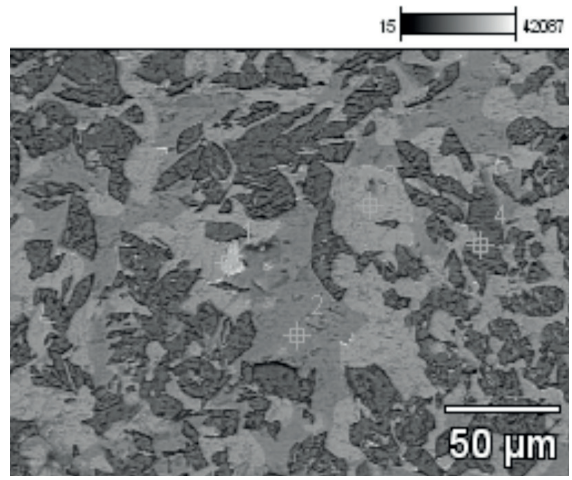



**Figure 6:** *Microphotography of slag by scanning Microscopy (2) (BSE).*

**Table 2:** *Chemical composition of slag phases according to Figure 5*

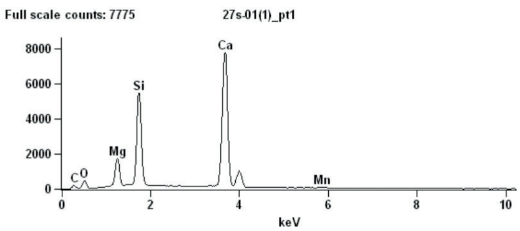
| Point of analysis | Oxides [*w*/%] | | | | | | | | | | | Σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | FeO | MnO | MgO | CaO | $K_2O$ | $V_2O_5$ | $SO_3$ | $P_2O_5$ | |
| 1 | 36.19 | - | - | - | 0.61 | 11.38 | 51.83 | - | - | - | - | 100.01 |
| 2 | - | - | 49.63 | - | - | - | 50.13 | - | - | - | 0.24 | 100.00 |
| 3 | 29.67 | - | 9.65 | - | 0.38 | 4.72 | 55.59 | - | - | - | - | 100.01 |
| 4 | 35.39 | 0.32 | - | - | 1.05 | 5.22 | 58.01 | - | - | - | - | 99.99 |
| 5 | 0.73 | - | - | - | 2.65 | 95.96 | 0.66 | - | - | - | - | 100.00 |
| 6 | 35.96 | - | - | - | 0.66 | 11.32 | 52.06 | - | - | - | - | 100.00 |
| 7 | 21.23 | - | 35.73 | - | 0.36 | - | 42.68 | - | - | - | - | 100.00 |
| 8 | 0.77 | - | - | - | 2.84 | 95.63 | 0.77 | - | - | - | - | 100.01 |
| 9 | 0.64 | - | - | - | 4.51 | 93.22 | 1.22 | - | - | - | 0.42 | 100.01 |
| 11 | 8.95 | 2.94 | 1.11 | 0.49 | 6.35 | 2.65 | 39.96 | 0.44 | 0.03 | 37.07 | - | 99.99 |

| Point of analysis | Elements [*w*/%] | | | | | | | | Σ |
|---|---|---|---|---|---|---|---|---|---|
| | Si | Cr | Al | Fe | Mn | Mg | Ca | P | |
| 10* | 0.20 | 1.63 | 0.42 | 80.66 | 15.40 | 0.52 | 0.98 | 0.19 | 100.00 |

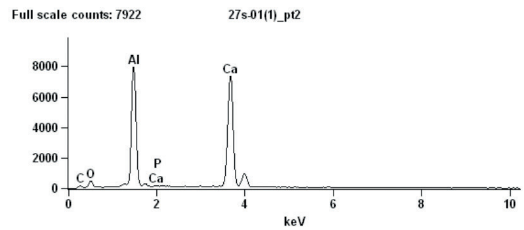
Explanation:
*in the point no 10 oxygen was not determined
Points: 3, 4, 6, 7 – calcium or dicalcium silicates, 2 – calcium aluminate, 5, 8, 9 – periclase, 11 – glaze

**Table 3:** *EDS spectrums (Scanning Microscopy) according to Figure 5*

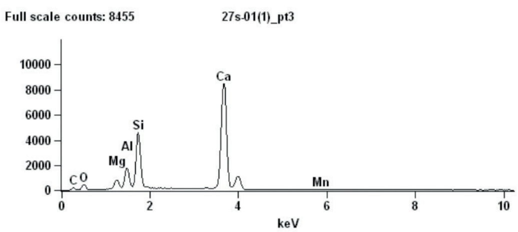
Point 1



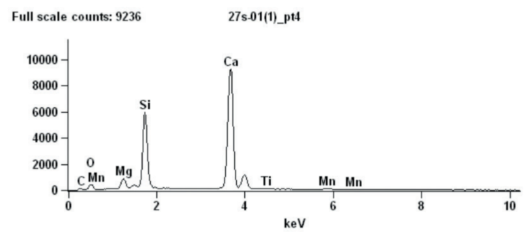

Point 2



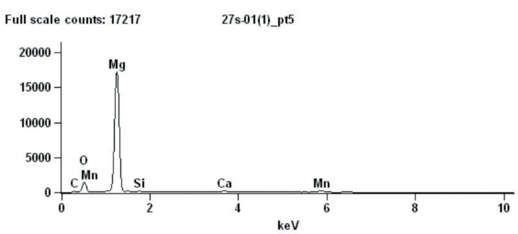

Point 3



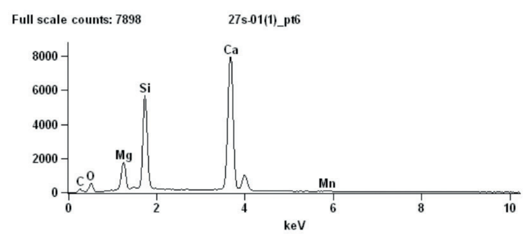

Point 4



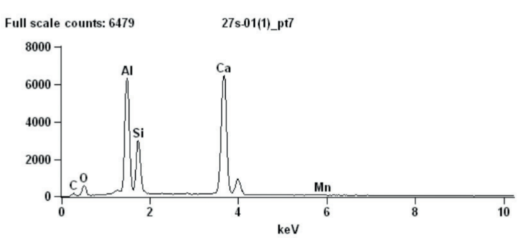

Point 5



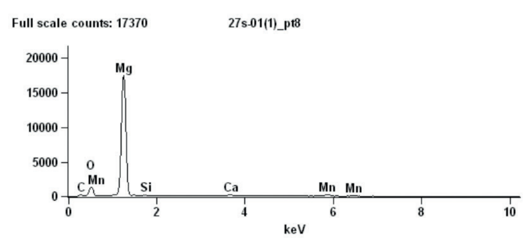

Point 6



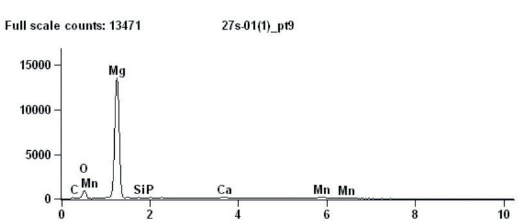

Point 7



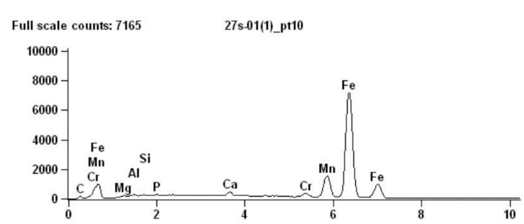

Point 8




Point 9




Point 10




Point 11

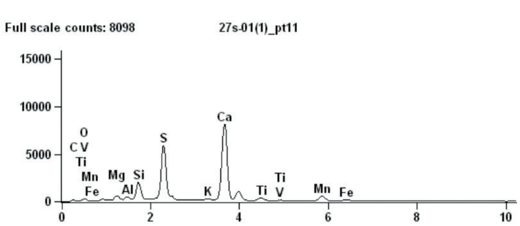


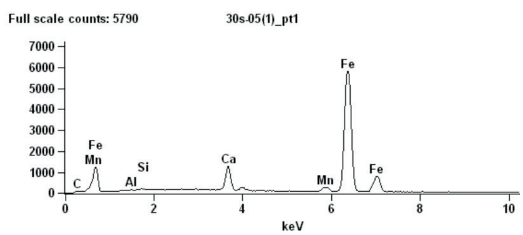
**Table 4:** *Chemical composition of slag phases according to Figure 6*

| Point of analysis | Oxides [$w$/%] | | | | | | | | | Σ |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | FeO | MnO | MgO | CaO | $Cr_2O_3$ | $P_2O_5$ | |
| 1 | 0.35 | - | 0.19 | 61.69 | 19.58 | - | 18.19 | - | - | 100.00 |
| 2 | 0.70 | 1.69 | 5.60 | 9.15 | 2.90 | - | 79.96 | - | - | 100.00 |
| 3 | - | - | - | 22.46 | 64.89 | 5.80 | 2.51 | 4.34 | - | 100.00 |
| 4 | 19.64 | - | - | - | - | - | 78.66 | - | 1.70 | 100.00 |

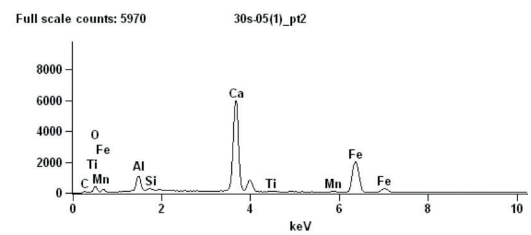
Explanations:
Points: 1 – solid solution of FeO-MnO-CaO, 2 – calcium oxide, 3 – solid solution of FeO-MnO, 4 – dicalcium silicate

**Table 5:** *EDS spectrums (Scanning Microscopy) according to Figure 6*

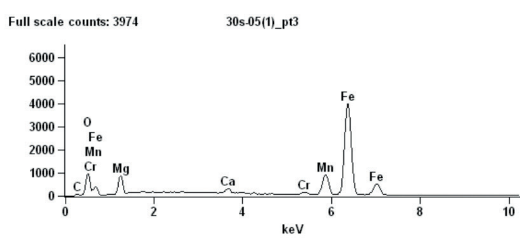
Point 1



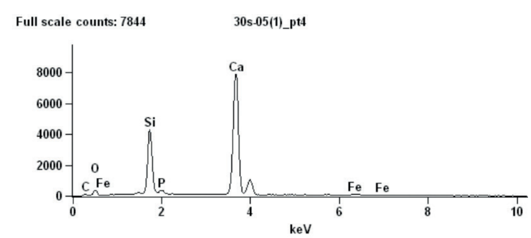

Point 2




Point 3




Point 4




## Conclusions

Studied slags after steel production are characterized by diverse mineral and chemical composition. Among their components there can be distinguished: glaze, which is usually a dominant compound, metallic precipitations and non-metallic phases – oxides (mainly solid solutions of FeO, MnO, MgO and CaO) and silicates, represented by a large group of calcium silicates. In internal structures of silicates phases the presence of different elements substitutions, which are not present in nature, have been observed. Silicates which do not contain any substitutions are rare. Similar components may also be distinguished in slags from other steelmaking processes, but their quantitative participation and the content of admixtures in them are usually different. That is why, an individual approach to each type of studied slags is very important.

Metals may occur in metallurgical slags as fine drops not separated from slag during a metallurgical process, may form polymetallic aggregates, inclusions and its own phases (especially oxide ones), they can also hide in structures of silicate phases. Metals are also dispersed in glaze and amorphous substance.

It is very important to do mineralogical and chemical researches of slags to get to know what forms of metals occurrence there are, what the minerals resistance to weathering processes is and in which conditions metals are liberated from their components. This knowledge will be useful in economic activities connected with using metallurgical slag as a secondary material.

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