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# Thermal and Mineralogical Investigation of Copper Converter Slag

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***Abstract*— In recent years, secondary resources (slags, scraps, etc.) have become a very important source for all valuable metals like copper or zinc due to the depletion of high grade ores and increasing the demand of these metals. Copper is lost to slag between 4 and 8 wt. % during the copper converting process stage. Beside its theoretical consideration, characterization of the slag should be investigated to maximize the copper recovery via selection of suitable metallurgical process. Therefore, in this study, physical, chemical, mineralogical and thermal properties of the converter slag supplied from Eti Copper Co. was determined in detail by using several common techniques.**

***Keywords—Converter Slag; Characterization; Thermal Analysis.***

## I. INTRODUCTION

In copper production, pyrometallurgical route mainly including concentration, smelting, converting and refining steps is widespread used for sulfidic type copper ores. Smelting and converting stages are metallurgical thermal processes operated in a large hearth-type furnace at 1200 - 1300 °C. The converting stage is a substantial unit process to transform into molten blister copper by insufflate to the matte, mixture of copper-iron sulphide. There are two main steps in converting; the first step is slag making and the second one is blister copper making. In the first blowing step, when air blows to matte in order to form slag phase, silica is being widely used as a fluxing agent. The overall reaction in converting stage was demonstrated by Davenport et al. [1] as follow (Rx.1);

Cu-Fe-S (Molten Matte) + $O_2$ (Air Blast) + $SiO_2$ (Flux) → $Cu^o$ (Blister) + ($2FeO{:}SiO_2$)-($Fe_3O_4$) (Molten Slag with Magnetite) + $SO_2$ (1)

However, excessive silica usage results in high viscosity and strong acidity, which causes the loss of valuable metals. In the world, copper losses to the slag at both stages (smelting and converting) in the pyrometallurgical copper production constitute a major problem. The researches [2-4] on this problem indicated that mainly there are two types of copper losses to slag in both stages. These are namely mechanical and physico-chemical losses. The mechanical copper losses arise from mechanically entrapped particles or floating unstable droplets of matte which do not find enough time to reach to the matte layer. The mechanical losses are mainly related to the viscosity of the slag. When the slag viscosity increases, mechanical copper losses also increase. The physico-chemical losses are directly associated with the solubility of copper in sulphide and oxide forms in slag. In other words, the copper losses are present in the slag melt as copper ions [4].

Several authors [1-5] have reported that the industrial smelting and converting slags frequently based on fayalite type slags which of the principle components are silica and iron oxide (FeOx and magnetite) apart from minor amounts of CaO, $Al_2O_3$, and alkali oxides (ZnO, PbO, MgO and so on). These slags also contain important amount of valuable metals (especially copper). Since the converter slag includes considerable amount of copper metal, it should be characterized in detail before applying any recovery process. Up to date lots of studies [2-10] have been revealed different types of copper slag (smelting, converting, fire refining or flotation slag), but a few of them [5,11] includes thermal investigation of the slag. This is a first parameter to be carried out just before developing a pyrometallurgical recovery process. Therefore, in this study, characterization of the converter slag was carried out by using several analysis devices or techniques in terms of chemical, mineralogical and especially thermal analysis. By this way, determination of the possible process that can be applied to copper converter slags was promoted. Also, both a negative effect of these wastes on the environment and financial losses are prevented.

## II. MATERIAL AND METHOD

Representative converter slag (CS) sample was supplied by Eti Copper Inc. in powder form (-100 micron) so it was ready to use for its characterization. In order to check homogeneity of the CS five samples of CS were taken from different points of their 10-kg containers. The results showed that CS was well mixed homogenous powder sample.

Characterization of the slag sample was realized by using several analysis devices or techniques in terms of chemical, mineralogical and thermal analysis. Initially, their chemical compositions were analyzed by using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and X-Ray Fluorescence (XRF) from Central Laboratory of Middle East Technical University (METU). In addition, magnetite content of the sample was determined by SATMAGAN S135 (Saturation Magnetization Analyzer). Then, the mineralogical characterization of CS sample was done by X-Ray Diffractometer (XRD; Bruker D8 Advance model available in the Central Laboratory of Karamanoglu

Mehmetbey University) and Scanning Electron Microscopy (SEM; Zeiss Evo LS10 model available in the Metallurgical and Materials Engineering Department of Karadeniz Technical University). Finally, the thermal behavior of the sample was investigated by thermogravimetric and differential thermal analysis (TGA-DTA).

## III. RESULTS AND DISCUSSIONS

Firstly, the particle size distributions of the supplied converter slag were analyzed by using Malvern Mastersizer 3000. By means of the data obtained from the Malvern Application Ver.5.60 software, d(0.1), d(0.5) and d(0.9) were determined as 1.137 µm, 13.022 µm and 43.148 µm, respectively. As a result of the measurements, the surface mean diameter and volume weighted mean diameter were calculated as D[3,2]= 3.694 µm and D[4,3]= 18.281 µm, respectively. In addition, moisture of the slag sample was determined as 0.8%.

### A. *Chemical Analysis*

Chemical analysis of the sample was carried out by different techniques; ICP-MS, SATMAGAN and XRF. Cu, S, $Fe_{total}$ as well as $SiO_2$ in the slag were obtained by ICP-MS analyses. XRF (Bruker S8 Tiger) was especially used to analyze the other elements (Ca, Al, Zn, Pb) in the slag sample.

SATMAGAN S135 with a maximum error of ±0.5% of the measured values was used to measure the magnetite content of each sample. Initially, it was calibrated with standards, supplied by Outokumpu Company. A calibration curve was drawn by using the standard samples with 3.75%, 17.75%, 30.95% and 44.75% $Fe_3O_4$. Then, the percentage of magnetite in the CS sample was determined by using the calibration curve. Table 1 summarizes the chemical analyses of CS sample obtained by the three different techniques mentioned above. All results were in accordance with each other especially in terms of the copper content of slag.

TABLE I. CHEMICAL ANALYSIS OF CONVERTER SLAG

| Element/Comp. | % | Element/Comp. | % |
|---|---|---|---|
| Cu | 4.45 | PbO | 0.5 |
| $SiO_2$ | 23.8 | $Al_2O_3$ | 1.6 |
| FeO | 38.4 | CaO | 0.9 |
| $Fe_3O_4$ | 20.0 | $Na_2O$ | 0.7 |
| S | 1.1 | $K_2O$ | 0.7 |
| ZnO | 4.2 | MgO | 1.1 |
| Total | 97.45 (%) | | |

As seen from Table 1, the converter slag has 4.45% Cu which was a typical copper loss to the actual industrial converter slag. This copper value belonged to the minimum copper content in CS among the three parallel chemical analyses. Comparing to smelting slag characterized previously [4], magnetite content in the CS is relatively high, but silica content is relatively low.

### B. *XRD Analysis*

In order to do the mineralogical characterization of slag sample, a Bruker Advance D8 model XRD instrument was used. The peaks of diffraction were recorded and plotted against a horizontal scale between 5 and 85 in degrees of 2θ, which was the angle of the detector rotation using intervals of 0.02° with CuKα radiation. The X-ray patterns which belong to CS sample is given in Figure 1.

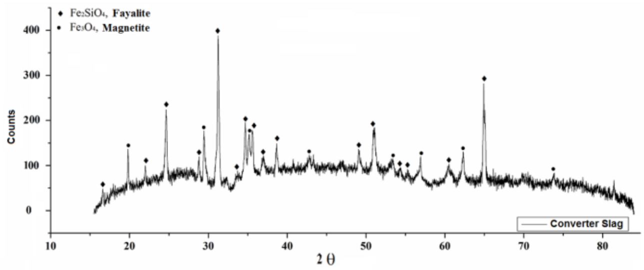


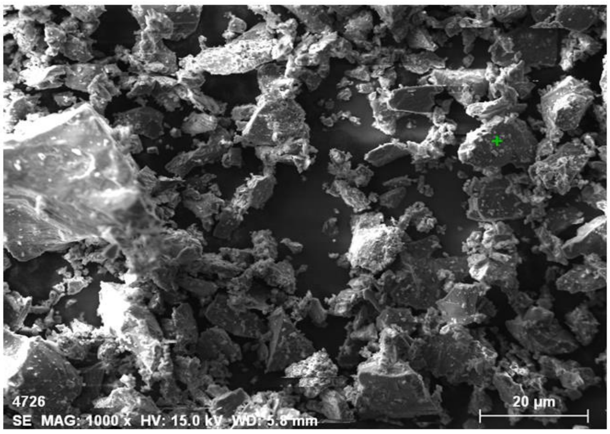

Fig. 1. *X-Ray diffraction patterns of EBİ converter slag*

According to the researchers [5,8], fayalite and magnetite were the main phases of copper converter slags. It is seen from the Figure 1 that XRD pattern of CS exhibits the same results with the previous studies. In here, despite the presence of Zn and Cu determined by the chemical analysis of the slag, Cu and Zn bearing phases could not be detected in the XRD pattern due to the density of the magnetite and fayalite phases in the slag.

### C. *SEM Analysis*

Scanning Electron Microscope (SEM) was used to identify the minor or trace phases in the slag. SEM analyses were carried out on gold coated CS sample by using Zeiss Evo LS10 model equipped with Energy Dispersive X-Ray Spectroscopy (EDS). The results of SEM studies on CS with the EDS results for the selected points are shown in Figures 2 to 7.

When SEM images are examined, it has been determined that the converter slag is not a homogeneous structure in both shape and size. The presence of different structures in the converter slag has been revealed by means of EDS analysis. According to the EDS analysis results, the converter slag composed of magnetite, matte, metallic copper and complex (Cu-Fe-Zn) sulfides besides the main iron silicate (Fayalit) matrix. In addition, previous studies on the fayalite type copper converter slag stated that different particles or inclusions carbon rich particles or oxide (CaO, $Al_2O_3$) particles could be observed [3,8,10].




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| Fe | 26 | K-series | 164.44 | 96.98 | 92.42 | 6.5 |
| Si | 14 | K-series | 2.94 | 1.73 | 3.29 | 0.4 |
| O | 8 | K-series | 2.19 | 1.29 | 4.29 | 0.9 |
| | | Total: | 169.57 | 100.00 | 100.00 | |

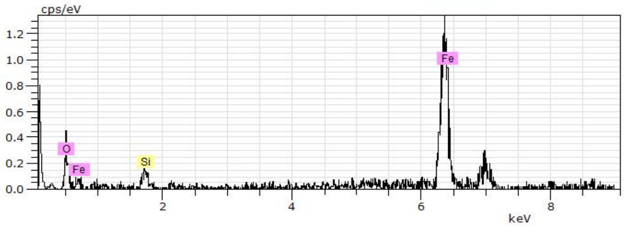
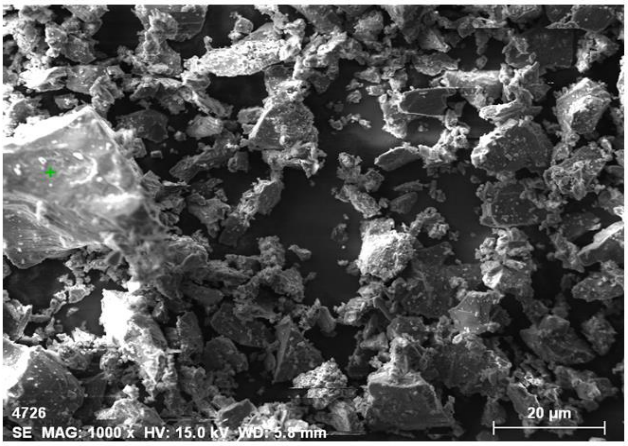



Fig. 2. *Magnetite in converter slag*




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| O | 8 | K-series | 25.17 | 37.21 | 60.04 | 4.8 |
| Fe | 26 | K-series | 19.17 | 28.33 | 13.09 | 0.8 |
| Si | 14 | K-series | 14.00 | 20.69 | 19.01 | 0.7 |
| Zn | 30 | K-series | 4.82 | 7.13 | 2.81 | 0.5 |
| K | 19 | K-series | 1.56 | 2.31 | 1.52 | 0.1 |
| Al | 13 | K-series | 1.55 | 2.29 | 2.19 | 0.1 |
| Ca | 20 | K-series | 1.39 | 2.05 | 1.32 | 0.1 |
| | | Total: | 67.66 | 100.00 | 100.00 | |

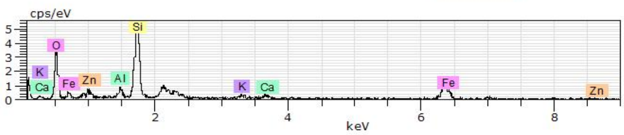
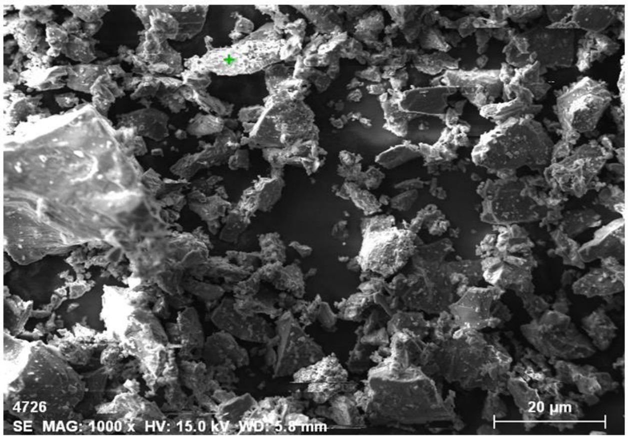



Fig. 3. *Fayalite with other oxides in converter slag*




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| Cu | 29 | K-series | 45.77 | 62.55 | 45.25 | 1.9 |
| S | 16 | K-series | 16.89 | 23.08 | 33.09 | 0.7 |
| Fe | 26 | K-series | 6.21 | 8.49 | 6.99 | 0.4 |
| O | 8 | K-series | 2.99 | 4.09 | 11.75 | 1.0 |
| Si | 14 | K-series | 1.31 | 1.79 | 2.92 | 0.1 |
| | | Total: | 73.17 | 100.00 | 100.00 | |

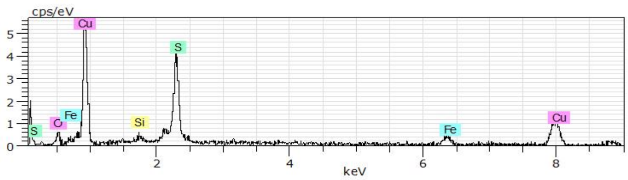
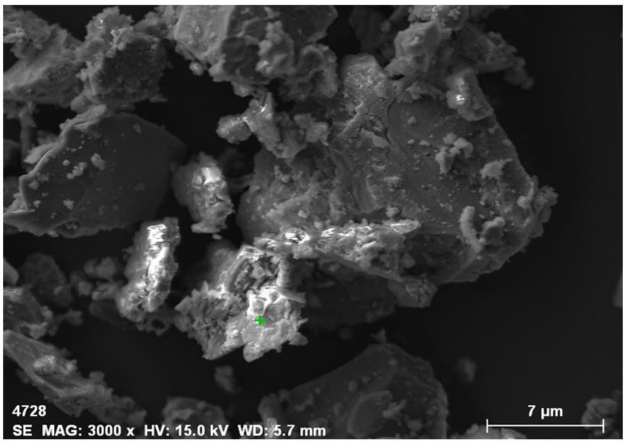



Fig. 4. *Matte inclusions in converter slag*




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| Fe | 26 | K-series | 47.75 | 51.75 | 29.21 | 1.8 |
| O | 8 | K-series | 23.89 | 25.89 | 51.01 | 4.0 |
| Si | 14 | K-series | 10.21 | 11.07 | 12.42 | 0.5 |
| Cu | 29 | K-series | 7.11 | 7.71 | 3.82 | 0.6 |
| S | 16 | K-series | 3.31 | 3.59 | 3.53 | 0.2 |
| | | Total: | 92.28 | 100.00 | 100.00 | |

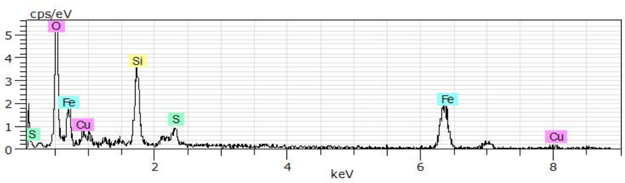
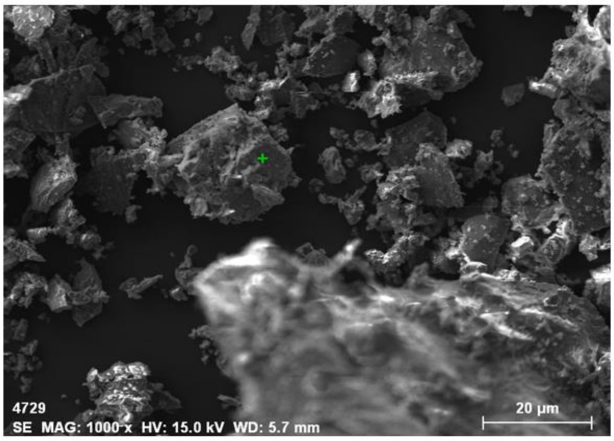



Fig. 5. *Fayalite with matte inclusions in converter slag*




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| Cu | 29 | K-series | 64.56 | 58.65 | 51.00 | 3.0 |
| Fe | 26 | K-series | 38.84 | 35.29 | 34.91 | 2.1 |
| Si | 14 | K-series | 5.05 | 4.59 | 9.03 | 0.6 |
| O | 8 | K-series | 1.61 | 1.46 | 5.06 | 0.7 |
| | | Total: | 110.07 | 100.00 | 100.00 | |

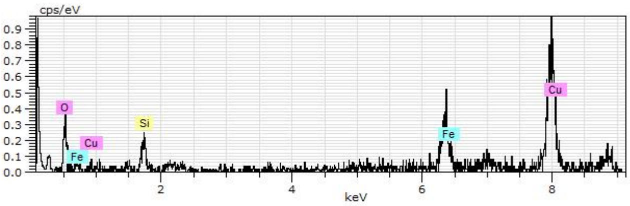
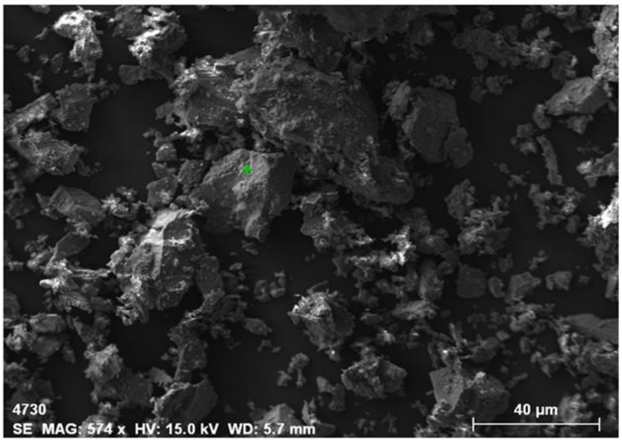



Fig. 6. *Fayalite with metallic copper in converter slag*




| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|---|---|---|---|---|---|---|
| Fe | 26 | K-series | 28.81 | 33.86 | 24.13 | 1.1 |
| Cu | 29 | K-series | 24.18 | 28.42 | 17.80 | 1.3 |
| O | 8 | K-series | 9.88 | 11.61 | 28.87 | 2.2 |
| S | 16 | K-series | 9.35 | 11.00 | 13.65 | 0.4 |
| Si | 14 | K-series | 6.69 | 7.87 | 11.14 | 0.4 |
| Zn | 30 | K-series | 6.17 | 7.25 | 4.41 | 0.6 |
| | | Total: | 85.08 | 100.00 | 100.00 | |

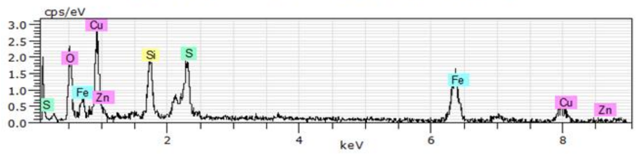



Fig. 7. *Complex (Cu-Fe-Zn) sulfides in converter slag*

The color mapping method, which is obtained by using SEM and EDS data, is a widely used method by researchers to determine the possible phases in their sample and to observe the elemental distribution in it. In this study, a color mapping method was applied to converter slag. Thus, the distribution of the main elements (Cu, Fe, Si, O and S) in the slag was determined (Figure 8). In the color mapping; Copper (Cu) is represented by green, Iron (Fe) by red, Silicon (Si) by turquoise, Sulfur (S) by purple and Oxygen (O) by yellow. Black regions in the Figure 8 indicate that the corresponding element is not (or trace amount) in that region. As can be seen from Figure 8, Fe, O and Si are the most commonly obtained elements. These three elements are scattered throughout the slag, which proves that Fayalite with $2FeO.SiO_2$ structure is the main phase. Despite the presence of iron and oxygen, the absence of silicon in some regions asserts to the magnetite ($Fe_3O_4$). The existence of the Matte ($Cu_2S.FeS$) phase reveals the presence of the same sulphide in the regions where the copper is concentrated. On the other hand, the presence of some points that do not overlap with Copper and Sulfur indicate the presence of metallic Copper or the presence of dissolved copper.

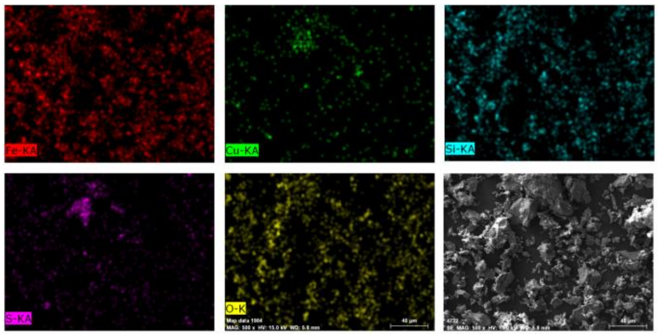



Fig. 8. *SEM elemental color mapping with EDS spectra for the selected area of converter slag*

## D. *Thermal Analysis*

In order to determine the thermal properties of the converter slag, Thermogravimetric analysis (TGA-DTA) was carried out in an oxygen atmosphere at a heating rate of 25 $^{o}C$/min from room temperature to 1200 $^{o}C$. The thermal analysis curve given in Figure 9 was carried out at Central Laboratory of Karamanoğlu Mehmetbey University.

Thermal analysis graph in Figure 9 showed that no mass loss from the sample was observed at low temperatures (<200 $^{o}C$) because converter slag contains very low moisture (0.8%) and any chemically bonded water. The increase in mass between 300 and 500 $^{o}C$ is thought to be an increase in the graph due to the oxidation of some elements, such as metallic copper which presents in the sample. As seen in DTA curve, an endothermic peak appeared at the same temperatures may be attributed to oxidation reaction of metallic copper or matte inclusions. Rapid mass loss at high temperatures (> 900 $^{o}C$) can be explained by the deterioration of the sulfur structures in the converter slag and the removal of $SO_2$ gases from the sample. According to the DTA graph, the slag started to melt with an endothermic peak at about 1180 ºC due to effects of other oxides. Thermal analysis results obtained this study are in general agreement with the results of thermal behavior of copper converter slags studied by several researchers [5,11].

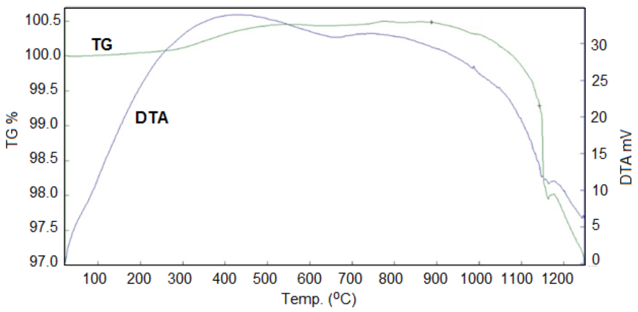



Fig. 9. *Thermal analysis of copper converter slag*

## IV. Conclusion

In this study, chemical, mineralogical and thermal characterization of a copper converter slag was investigated to reveal its thermal behavior and its existing phases, especially in Cu. Chemical analysis results of the sample showed that converter slag was mainly composed of 4.45% Cu, 23.8% $SiO_2$, 38.4% FeO, 20.0% $Fe_3O_4$, and 4.2% ZnO. XRD pattern reveals that the main phases in the slag were identified as fayalite and magnetite. According to SEM analysis, Cu was found in the slag as metallic, matte inclusions and complex (Cu-Fe-Zn) sulfide form. In addition, the distribution of the main elements (Cu, Fe, Si, O and S) in the slag was determined by applying a color mapping method. Characterization of slag was completed by revealing its thermal properties that the melting point of the slag was about 1080 ºC. Results of the characterization showed that after the recovery of copper with different forms (matte inclusion, complex sulfide or metallic form) from the slag by applying hydro or pyrometallurgical process, secondary wastes (byproduct of recovery process) can be used in several applications instead of accumulation of disposal areas.

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## References

[1] Schlesinger, M. E., King, M.J., Davenport, A.W., Sole, K.C., Extractive Metallurgy of Copper, Elsevier, Fourth ed. 2002, Pergamon.

[2] Imris, I., Sanchez, M. and Achurra, G., Copper losses to slags obtained from the El Teniente process, Trans. Inst. Min. Metal. C, 2005, 114C, pp. 135–140.

[3] Jalkanen H., Vehviläinen J., and Poijärvi J., Copper in solidified copper smelter slags. Scandinavian Journal of Metallurgy, 2003. 32, pp. 65–70.

[4] Ruşen, A., Geveci, A., Topkaya, Y. A., and Derin, B. (2012). Investigation of effect of colemanite addition on copper losses in matte smelting slag. Canadian Metallurgical Quarterly, 51(2), pp. 157-169.

[5] Gorai B., and Jana R.K., Characteristics and utilisation of copper slag—a review. Resources, Conservation and Recycling, 2003. 39(4), pp. 299–313.

[6] Das B., Mishra B.K., Angadi S., Pradhan SK, Prakash S., Mohanty J., Characterization and recovery of copper values from discarded slag. Waste Management & Research, 2010, 28(6), pp. 561–567.

[7] Gbor P.K., Mokri V., and Jia C.Q., Characterization of smelter slags. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 2000. 35(2): pp. 147–167.

[8] I. Mihailova, D. Mehandjiev, Characterization of Fayalite from Copper Slags, Journal of the University of Chemical Technology and Metallurgy, 2010, 45, pp. 317-326.

[9] Wang X., Geysen D., Padilla T. S.V., D'Hoker N., Van Gerven T., Blanpain B. (2013) Characterization of Copper Slag. In: Kvithyld A. et al. (eds) REWAS 2013. Springer, Cham.

[10] D. S. Rao, S. Angadi, P. S. R. Reddy. Characterization of Precious Metal Resources in Copper Slag and Their Implications in Beneficiation Journal of The Institution of Engineers (India): Series D, April 2015, Volume 96, Issue 1, pp. 7–13.

[11] Gyurov, S., Kostova, Y., Klitcheva, G., Ilinkina, A., Thermal decomposition of pyrometallurgical copper slag by oxidation in synthetic air, Waste Management Resources, 2011 29(2), pp.157-64.