INTRODUCTION

Large quantities of industrial by-products are being generated continuously by metallurgical industries. Generally these by-products such as slags and fly ashes are landfilled or dumped into the sea. But landfilling or dumping is not the most correct option in environmental management due to environmental problems, high costs and lack of wide lands especially in the industrial areas and copper plants, respectively. So, popular options of management of these wastes are recycling and reuse.

Copper slag, which is produced during pyro-metallurgical production of copper from copper ores contains materials like iron, alumina, calcium oxide, silica etc. It has been estimated that approximately 2.2-3.0 tons copper slag is generated for every ton of copper as a by-product material in each year and approximately 24.6 million ton of slag is generated from world copper industry. Dumping or disposal of such huge quantities of slag cause environmental and space problems. During the past two decades attempts have been made by several investigators and copper producing units all over the world to explore the possible utilization of copper slag [1,2]. Due to the ever strict environmental regulations, waste treatment costs and limited availability of disposal sites, the development of new and cost-effective waste management practices has become increasingly significant in recent years. In this regard, recovery of the contained metal values recycling and utilization of copper slag as substitute for natural recourses for the production of value-added products appear to be the propitious options for management of these wastes [3]. The ceramics sector can incorporate large amounts of waste materials without relevant process modifications, while taking advantage of the calorific value from waste combustion or incorporating the residue in the internal structure of materials, such that the residue forms part of these materials’ matrix and becomes an inert element [4]. As stated in the literature [5-12], the use of ecologic products has become important aspect in the ceramic sector. Copper slag can be utilized in the ceramic glazes to prevent pollution and to recycle these wastes.

The element iron usually exists in nature in the form of oxides although it can also be found as hydroxides, silicates, carbonates and sulfides in small events and even in native form, in small proportions [13]. Iron oxide is also unavoidable in solid wastes, especially in copper slags. Most of the effects from iron oxide addition result from the presence of the crystalline groups of hematite (α-Fe₂O₃) under oxidizing conditions [14]. Glaze containing Li₂O may show different crystallization behaviour since Li₂O is a strong flux and can influence changes in the oxidation state of Fe₂O₃ in the glaze. It has been reported that lithium metasilicate easily crystallized at low temperature in a Li₂O–Fe₂O₃–SiO₂ glass. LiFeSiO₄, LiFeO₃ and LiFeO₂ crystalline phases were formed during crystallization in CaO–MgO–Li₂O–Fe₂O₃ glasses. In the LiO₂–ZnO–SiO₂ system, it was thought that Li₂ZnSiO₄ phase developed due to the reaction of ZnO with Li₂SiO₃. A small addition of Li₂O changes the crystallization path by precipitation of β-quartz.
solid solution and Willemite at low temperature (800-900 °C). Doping of Li2O also stimulated the formation of Franklinite in Fe2O3-ZnO solid–solid interaction. However, it is still not clear which phases will form when Fe2O3 is added to glazes containing Li2O and ZnO [14].

In this study, ceramic glazes containing Li2O-ZnO system were studied as a function of copper slag content from Eti Bakir Kastamonu Küre Plant, Turkey. Furthermore, copper slag was used as raw material in order to produce colourful artistic glazes.

### EXPERIMENTAL

Six copper smelting slag containing artistic glaze compositions were formulated using the Seger method and prepared by traditional glaze processing. These glaze compositions labelled as CS1, CS2, CS3, CS4, CS5 and CS6, respectively. Copper slag (15 % ) was added into the glaze compositions. Glazes were applied onto commercial porcelain bodies and fired at 1200 °C for 3 h in oxidizing atmosphere. The differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the copper slag was performed in a thermal analyzer in a synthetic air atmosphere and a heating rate of 10 °C/min, from 20 °C to 1200 °C. The crystalline phases in copper slag was identified by X-ray diffraction (XRD-Bruker AXS D8 Advance series) using CuKα radiation (λ = 1,5406 Å) from 1.5° to 70° 2θ interval, 40 kV and 40 mA of accelerating voltage scanning with a step of 0.02° and step time of 1 s. Glazes were coated with a thin film of gold palladium and studied by scanning electron microscopy (SEM-Leo 440, at 20 kV) coupled with energy dispersive X-ray (EDX) spectroscopy.

### RESULTS AND DISCUSSION

The result of the XRD analysis of the copper slag is shown in Fig. 1. Copper slag consists of quartz (SiO2-ICDD 085-0335) pyrite (FeS2-ICDD71-1680) and chamosite (Mg5.036Fe4.964Al2.724(Si5.70Al2.30O20)(OH)16-ICDD 085-2163) (Fig. 1).

The copper slag is characterized by differential thermal analysis as shown in Fig. 2.

The DTA curve showed that, dehydration, the release of OH (dehydroxylation reactions) and decarbonization reactions are endothermic processes, with peaks centered at about 105, 240, 405, 460, 505 and 550 °C, respectively (Fig. 2). Decomposition of organic matter is an exothermic reaction with peaks centered at about 650-870 °C. After about 900 °C, various exothermic effects appeared probably due to the crystallization in high temperatures. The thermogram shows that between 100-550 °C the copper slag undergoes a mass loss of 55 % corresponding to endothermic peaks.

Copper slag is rich in iron oxide (57.40 %) and silicon oxide (28.63 %), lower amounts of other metal oxides (less than 10 %) are also present (Table-1). The most important hazardous oxides in the copper slag are CuO, ZnO and MnO.

As the copper slag contains a large amount of iron oxide its potential for use as replacement for iron ore in the ceramic products was considered.

Table-2 shows the molecular formulations of glazes which formulated using the Seger method and were prepared by mixing SiO2, Al2O3, Na2O, Li2O, ZnO, CaO, B2O3 and copper slag.

After the gloss firing at 1200 °C, all of the glazes have greenish to brown colour and dark brown colour depending on the iron oxide content from slag and the glaze compositions. Iron oxide acted as a flux and accelerator of phase separation on the iron oxide content from slag. The aesthetic appearance of the glazes is significant (Fig. 3).

<table>
<thead>
<tr>
<th>Oxides (wt. %)</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
<th>CuO</th>
<th>MnO</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28.63</td>
<td>6.77</td>
<td>57.40</td>
<td>0.30</td>
<td>1.24</td>
<td>0.32</td>
<td>0.81</td>
<td>0.96</td>
<td>0.08</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffraction patterns of copper slag

![Fig. 1. X-ray diffraction patterns of copper slag](image-url)

![Fig. 2. Thermal analysis (DTA-TG) of the copper slag](image-url)

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It could be seen that, large number of irregular shaped crystals disorderly distributed in glass matrix. The chemical compositions of crystals were analyzed by EDX. The crystals were rich in Si, Na, Ca, Fe and Zn. Heterogeneous microstructures and larger crystals were observed on the surfaces of the all glazes because of higher content of ZnO. CS3 and CS6 glazes were needed to be gloss fired in the high temperature range of 1300-1350 °C. Their surfaces were unmatured related to the high levels of Al2O3. Crystalline effects were found depending on chemical composition in all glazes in which the copper slag contents were 15 wt. % after firing at 1200 °C.

**Conclusion**

Copper slag wastes are often characterized as hazardous materials exposing environmental and storage space problems for disposal. The utilization of copper slag waste as raw material in the production of ceramic glazes was investigated. In this study, the aesthetic and technical characteristics of glazes containing 15 % wt. copper slag were examined. Phase separation occurred in all glaze composition when the glass melt separates into two or more liquids of slightly different chemistry. Fine fibrous growths were developed in some glazes. Presence of iron oxide in the Li2O-B2O3-SiO2 glazes stimulates the crystallization of the glazes. The recycling of industrial waste into artistic glazes can be a technological solution both from ecological and economic point of view. In this way, possible pollution and public health problems can be prevented. As a result, copper slag behaves as a colouring agent for artistic glazes without any treatment. Thus it can be used in ceramic glazes for decorative applications.

**TABLE-2**

<table>
<thead>
<tr>
<th>Code</th>
<th>Basic Oxides</th>
<th>Neutral oxides</th>
<th>Acid oxides</th>
<th>Waste material</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS1</td>
<td>0.40 Na2O, 0.20 Li2O, 0.40 ZnO</td>
<td>0.20 Al2O3, 2.00 SiO2, 0.75 B2O3</td>
<td>15 % copper slag</td>
<td></td>
</tr>
<tr>
<td>CS2</td>
<td>0.50 Li2O, 0.50 ZnO</td>
<td>0.30 Al2O3, 1.0 SiO2, 1.0 B2O3</td>
<td>15 % copper slag</td>
<td></td>
</tr>
<tr>
<td>CS3</td>
<td>0.40 Li2O, 0.30 CaO, 0.30 ZnO</td>
<td>0.25 Al2O3, 1.20 SiO2, 0.75 B2O3</td>
<td>15 % copper slag</td>
<td></td>
</tr>
<tr>
<td>CS4</td>
<td>0.40 Na2O, 0.30 Li2O, 0.30 ZnO</td>
<td>0.15 Al2O3, 2.00 SiO2, 0.75 B2O3, 2.00 TiO2</td>
<td>15 % copper slag</td>
<td></td>
</tr>
<tr>
<td>CS5</td>
<td>0.45 Na2O, 0.25 Li2O, 0.30 ZnO</td>
<td>0.20 Al2O3, 1.2 SiO2, 1.0 B2O3</td>
<td>15 % copper slag</td>
<td></td>
</tr>
<tr>
<td>CS6</td>
<td>0.70 Li2O, 0.30 ZnO</td>
<td>0.30 Al2O3, 1.80 SiO2, 0.75 B2O3</td>
<td>15 % copper slag</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Surface appearance and colour of the glazes prepared by copper slag fired at 1200 °C; CS1, CS2, CS3, CS4, CS5 and CS6.

Fig. 4. SEM micrograph of the CS1 glaze and EDX pattern taken from the crystal occurrence.
Fig. 5. SEM micrograph of the CS2 glaze and EDX pattern taken from the crystal occurrence

Fig. 6. SEM micrograph of the CS3 glaze and EDX pattern taken from the crystal occurrence

Fig. 7. SEM micrograph of the CS4 glaze and EDX pattern taken from the crystal occurrence
Fig. 8. SEM micrograph of the CS5 glaze and EDX pattern taken from the crystal occurrence

Fig. 9. SEM micrograph of the CS6 glaze and EDX pattern taken from the crystal occurrence

ACKNOWLEDGEMENTS

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REFERENCES